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Carbonate Formation from Oxiranes and Carbon Dioxide Catalyzed by Organotin Halide-Tetraalkylphosphonium Halide Complexes

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Synopsis. Cycloaddition of carbon dioxide to oxiranes was excellently promoted by the complexes of organotin halides and tetraalkylonium halides, while either components of the complexes had no catalytic activity individually. Particularly, the complex composed of Bu_3SnI-Bu_4PI was the most favorable catalyst, yielding a variety of five-membered cyclic carbonates under neutral and mild conditions.

Among many studies on carbon dioxide (CO_2) fixation, the reaction of oxiranes with CO_2 has received attention, yielding poly- or cyclic carbonates in the presence of many kinds of catalysts.[1] In particular, the synthesis of five-membered cyclic carbonates has been ardently investigated, and for example, a devised catalytic reactions using γ-butyrolactones and oxiranes was recently reported.[2] However, some inactive or acid sensitive oxiranes were hardly converted to the corresponding cyclic carbonates by these methods. We recently reported that the complexes composed of organotin halides and Lewis bases showed a catalytic activity toward the addition of CO_2 to oxiranes.[3] In this system, it was proposed that the coordinated Lewis bases activated the tin-halogen bond. It is well known that onium haides also readily complexate with organotin halides in a different mode to form a salt complex.[4] Its synthetic use, however, has been scarcely reported.

We wish to report herein a method using a 1 : 1 complex of Bu_3SnI and Bu_4PI as a catalyst(**3**),[5] which permitted inactive or acid sensitive oxiranes to react with CO_2 to produce the corresponding carbonates in good yields. This is probably due to the neutrality and high activity of the catalyst **3**.

The effects of combinations of organotin halides with onium halides on the product yield of the addition of CO_2 to 2-ethyloxirane were shown in Table 1, which shows the following notable features. (1) Tetrabutylphosphonium iodide was more suitable than Bu_4NI (Entries 1, 12). (2) The activity order of Bu_4PX (X=halogen) is X=I>Br>Cl (Entries 1—3). (3) The activities of organotin halides decrease as the following orders; Bu_3SnI, Me_3SnI, Ph_3SnI (Entries 1, 4, 5), Bu_3SnI, Bu_3SnBr, Bu_3SnCl (Entries 1, 6, 7), and Me_3SnI, Me_2SnI_2 (Entries 4, 8). All these orders were reverse to the order of acidity of organotin halides.[6] Thus, the lowest acidic complex **3** was the most efficient catalyst among the complexes examined. This was an interesting result, since even acid sensitive oxiranes were hoped to be beautifully converted to the corresponding carbonates by this almost neutral catalyst.[7] (4) The formation of 1 : 1 complex was strongly suggested by the comparison of the results of Entries 1, 10, and 11. In addition, the complex formation was also confirmed by ^{119}Sn NMR. The upfield shift values by complexations suggest that a five coordinated tin complex is formed,[8] although a six coordinated one, [Me_3SnBr-Et_4NBr], is proposed by Seyferth et al.[4b]

The above tendencies (1)—(4) were distinctly different from the case of ZnX_2-Bu_4NI systems reported quite recently by Kisch et al.,[9] in which $ZnCl_2$ being a stronger acid is more active than ZnI_2, and an ammonium halide is preferred to a phosphonium halide. Furthermore, use of excess amounts of Bu_4NI (4 equiv) is required for the formation of carbonates in high yields.

In the complex Bu_3SnI-Bu_4PI, the iodide anion in Bu_4PI is thought to be transfered on the tin atom,[4] and this iodide anion may play an effective role for a nucleophilic cleavage of oxirane rings, although a detailed mechanism can not be proposed because of the indefinite configuration of the complex.

Table 2 exemplifies the results of the synthesis of

Table 1. Reaction of **1b** with CO_2 (Atmospheric Pressure)[a]

Entry	Sn compd	Onium halide	Yield/% of **2b**[b]		
			2 h	3 h	5 h
1	n-Bu_3SnI	n-Bu_4PI	60	84	100
2	n-Bu_3SnI	n-Bu_4PBr	18	41	87
3	n-Bu_3SnI	n-Bu_4PCl	13	34	65
4	Me_3SnI	n-Bu_4PI	42	75	91
5	Ph_3SnI	n-Bu_4PI	39	58	84
6	n-Bu_3SnBr	n-Bu_4PI	41	58	84
7	n-Bu_3SnCl	n-Bu_4PI	31	53	77
8	Me_2SnI_2	n-Bu_4PI	11	39	75
9	n-Bu_3SnCl	n-Bu_4PCl	13	18	30
10[c]	n-Bu_3SnI	n-Bu_4PI	19	50	75
11[d]	n-Bu_3SnI	n-Bu_4PI	74	87	100
12	n-Bu_3SnI	n-Bu_4NI	16	50	93

a) 2-Ethyloxirane/Sn compd/onium halide=50/1/1 mmol, 60 °C. b) Monitored by GC. c) n-Bu_4PI 0.5 mmol. d) n-Bu_4PI 2 mmol.

Table 2. Reaction of Oxiranes with CO_2 by n-Bu_3SnI-n-Bu_4PI[a)]

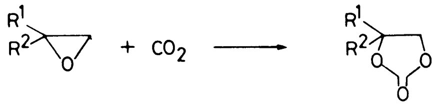
Entry	Oxirane	Temp/°C	Time/h	Carbonate	Yield of $\mathbf{2}$[b)]/%
i	**1a**	40	1	**2a**	100
ii	**1b**	40	1	**2b**	95 (76)[c)]
iii[d)]	**1b**	40	1	**2b**	16
iv	**1c**	40	1	**2c**	83
v	**1d**	40	3	**2d**	88
vi	**1e**	40	3	**2e**	97
vii	**1f**	40	3	**2f**	86
viii	**1g**	40	1	**2g**	80
ix[e]	**1h**	100	5	**2h**	85

a) Oxirane/n-Bu_3SnI/n-Bu_4PI=50/1/1 mmol, CO_2=50 kg cm^{-2}. b) Determined by GC.. c) Benzene (5 cm^3) solvent, 3 h. d) SnI_2 was used instead of n-Bu_3SnI. e) n-Bu_3SnI-n-Bu_4PI 0.1 eq mol.

various carbonates **2** in the presence of the catalyst **3**. The complexation was essential, since neither Bu_3SnI nor Bu_4PI individually showed any catalytic activity, giving **2b** less than 2% yields under similar conditions. This catalyst was very effective for the reaction of monosubstituted oxiranes. For example, 2-methyloxirane gave propylene carbonate quantitatively at 40 °C for 1 h. Moreover, even in the reaction of acid sensitive monosubstituted oxiranes such as allyl glycidyl ether and glycidyl methacrylate, the corresponding carbonates could be isolated in high yields without polymerization or decomposition (Entries vi, vii). Although the reactivity of oxiranes bearing electron-withdrawing substituents was somewhat lower, satisfactory yields of **2** were effected by the prolonged reaction times. Some vigorous conditions, 100 °C, 5h, were required for the addition of CO_2 to 2,2-dimethyloxirane (85% yield, Entry ix).

An additional advantage of the complex **3** was its high solubility in organic solvents, thus carbonate **2b** was easily obtained from the reaction using benzene as a solvent as well as without solvent (Entry ii). On the contrary, the SnI_2-Bu_4PI system was inefficient probably due to a poor solubility of SnI_2, giving **2b** in only 16% yield (Entry iii).

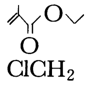
The complex catalyst, Bu_3SnI-Bu_4PI, provides a method for carboxylation of unreative or acid sensitive oxiranes, extending the scope of a carbonate synthesis under mild conditions.



1a—h

	R^1	R^2
a	CH_3	H
b	CH_3CH_2	H
c	C_6H_5	H
d	CH_3OCH_2	H
e		H

2a—h

	R^1	R^2
f		H
g	$ClCH_2$	H
h	CH_3	CH_3

Experimental

The following instruments were used: Melting points, Yanagimoto micro melting point apparatus; IR spectra, Hitachi 260-10; Mass spectra, Hitachi RMU-6E; GC, Shimadzu 8A (FID, 5% FFAP or 2% OV-17 on Chromosorb WAW); ^{1}H NMR and ^{13}C NMR spectra, Hitachi R-90H.

Tin compounds[10)] and onium halides[11)] were prepared according to the known methods. All oxiranes were available commercially, and were used after distillation on CaH_2.

Values of the boiling points of the compounds are given as °C/mmHg (1 mmHg=133.322Pa).

Reaction of 2-Ethyloxirane and CO_2 under Atmospheric Pressure (Table 1). In a typical procedure, a mixture of organotin compound (1 mmol) and onium halide (1 mmol) and 2-ethyloxirane (50 mmol) was placed in a 30 cm^3 three necked flask, and was heated at 60 °C under the slow stream of CO_2 gas. The amounts of 4-ethyl-1,3-dioxolan-2-one (**2b**) were monitored by GC.

Reaction of Oxiranes and CO_2 under Pressurized Conditions (Table 2). An oxirane (50 mmol), Bu_3SnI (1 mmol), Bu_4PI (1 mmol) and a magnetic bar were placed in a 50 cm^3 stainless steel autoclave, then CO_2 gas was pressurized up to 50 kg cm^{-2}. The vessel was heated with stirring at an appropriate temperature. After cooling, the yields of carbonates were determined by GC. All carbonates were isolated by distillation or recrystalization, and **2a**, **2b**, **2c**, **2d**, and **2g** were characterized by spectral data and bps.[2)]

4-Allyoxymethyl-1,3-dioxolan-2-one (2e): Bp 108 °C/2 mmHg (lit,[2)] 92—94 °C/0.1 mmHg); IR (neat) 1800 (C=O), 1645 cm^{-1} (C=C); MS m/z 158 (M^+); ^{1}H NMR ($CDCl_3$) δ=3.4—4.1 (4H, m), 4.1—4.6 (2H, m), 4.7—5.0 (1H, m), 5.1—5.4 (2H, m), 5.7—6.1 (1H, m).

4-Methacryloyloxymethyl-1,3-dioxolan-2-one (2f): Bp 123 °C/2 mmHg (lit,[2)] 72—73 °C/0.1 mmHg); IR (neat) 1800 (C=O), 1735 (C=O), 1640 cm^{-1} (C=C); MS m/z 186 (M^+); ^{1}H NMR ($CDCl_3$) δ=2.0—2.2 (3H, s), 4.3—4.9 (4H, m), 4.9—5.4 (1H, m), 5.7 (1H, s), 6.2 (1H, s); ^{13}C NMR ($CDCl_3$) δ=17.6, 63.2, 65.9, 73.8, 126.3, 134.9, 154.4, 166.0.

4,4-Dimethyl-1,3-dioxolan-2-one (2h): Bp 57 °C/2 mmHg (lit,[12)] 224 °C/760 mmHg); IR (neat) 1800 cm^{-1} (C=O); MS m/z 116 (M^+); ^{1}H NMR ($CDCl_3$) δ=2.2 (6H, s), 4.8 (2H, s).

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