Organometallics 1987, *6*, 137–140

Reaction of Carbon Dioxide with Oxetane Catalyzed by Organotin Halide Complexes: Control of Reaction by Ligands

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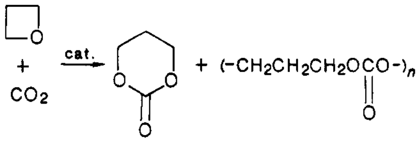
Received May 20, 1986

Complexes of organotin iodides with phosphines or phosphine oxides catalyze the addition of carbon dioxide to oxetane, giving trimethylene carbonate and polycarbonate. The choice of a ligand is crucial. All the complexes with Bu_3P gave polycarbonate, but the combination of Bu_3SnI with $Bu_3P{=}O$ yielded trimethylene carbonate exclusively in good yields. The complex $Bu_2SnI_2{\cdot}Bu_3P{=}O$ had no catalytic activity in the formation of either polycarbonate or trimethylene carbonate. The coordination mode of ligands and the stability of the complexes seem to be important. The function of ligands is suggested not only to involve activation of the tin–halogen bond but also to decrease the acidity of tin compounds, thus suppressing polymerizations.

Although complexes of organotin halides with ligands such as amines, phosphines, and phosphine oxides have been investigated with respect to their structures and stability,[1] their applications in organic syntheses have received little attention. We recently reported that organotin halide–base complexes cleave oxirane rings regioselectively[2] and act as excellent catalysts in cycloadditions of oxiranes with heterocumulenes such as isocyanates, carbodiimides, and isothiocyanates.[3] In these reactions, the complexation is very significant, and free organotin halides have no catalytic activity. The coordination of bases to the tin atom might be considered to activate the tin–halogen bond.

On the other hand, of the many studies of carbon dioxide (CO_2) fixation, reactions of CO_2 with oxiranes have been ardently investigated. These give polycarbonates[4] and five-membered cyclic carbonates[5] in the presence of various metal catalysts. In contrast, oxetanes, four-membered cyclic ethers, have considerably lower reactivity.[6] Therefore, activation by strong acids such as BF_3 and H_2SO_4 is indispensable for many synthetic uses of oxetanes.[7] The reaction of oxetane with CO_2 which is also important due to resources and environmental problems has been scarcely discussed until quite recently. Koinuma[8] reported the copolymerization of CO_2 with oxetane; the degrees of CO_2 fixation, however, were relatively low because of incorporation of polyoxetane units. We recently pointed out that CO_2 readily reacts with oxetanes in the presence of organotin halide complexes[9] or tetraphenylstibonium halides,[10] yielding polycarbonates and trimethylene carbonate, respectively.

Scheme I



1   2

cat.	main product
$Bu_3SnI{\cdot}$phosphine	2
$Bu_2SnI_2{\cdot}$phosphine	2
$Bu_3SnI{\cdot}$phosphine oxide	1
$Bu_2SnI_2{\cdot}$phosphine oxide	

Table I. Copolymerization of Oxetane with CO_2[a]

entry	Sn compd	additive	conditns temp, °C	conditns time, h	yield, % 1	yield, % 2
1	Bu_3SnI		100	24	0	0
2	Bu_2SnI_2		100	24	0	0^b
3	Bu_3SnI	PBu_3	100	24	0	99
4	Bu_3SnI	PBu_3	100	4	25	19
5	Bu_2SnI_2	PBu_3	100	24	0	91^c
6	Bu_2SnI_2	PBu_3	100	4	3	79
7	Bu_2SnI_2	PBu_3	80	4	5	47
8	Bu_2SnI_2	Et_3N	100	24	0	51
9	Bu_3SnBr	PBu_3	100	24	9	20
10	Bu_2SnBr_2	PBu_3	100	24	0	98

[a] Oxetane:Sn compd.:additive = 20:0.4:0.4 mmol, CO_2 = 50 kg/cm^2. [b] Homopolymer of oxetane was obtained. [c] Oxetane was consumed completely, and 9% of homopolymer was obtained.

In this paper we wish to report that the choice of compounds which complex with organotin iodides Bu_3SnI and Bu_2SnI_2 affects the catalytic activity and the kinds of products formed as shown in Scheme I. The role of these ligands and a plausible reaction path are discussed.

Results and Discussion

It was briefly reported that an alternating copolymeric carbonate of CO_2 and oxetane was readily produced in the presence of organotin halide–base complexes such as $Bu_3SnI{\cdot}$phosphine and $Bu_2SnI_2{\cdot}$phosphine.[9] In this reaction, the use of a complex is essential, or otherwise, no fixation of CO_2 is observed, and only the slow polymeri-

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Table II. Polymerization of Trimethylene Carbonate[a]

entry	cat.	yield of 2, %	M_r[b]
1		0	
2	Bu_2SnI_2	98	4250
3	$Bu_2SnI_2 \cdot Bu_3P$	89	2100
4	Bu_3SnI	82	
5	$Bu_3SnI \cdot Bu_3P{=}O$[c]	0	
6	$Bu_3SnI \cdot Bu_3P$[c]	63	

[a] 1:cat. = 20:0.4 mmol, 100 °C, 4 h, CO_2 = 50 kg/cm^2. [b] Determined by vapor pressure method. [c] Sn:additive = 0.4:4 mmol.

Table III. Cycloaddition of CO_2 with Oxetane Catalyzed by Organotin Halide Complexes[a]

entry	Sn compd	additive	time, h	yield, % 1	yield, % 2
1	Bu_3SnI	Bu_3P	1	10	7
2	Bu_3SnI	$Bu_3P{=}O$	4	41	0
3	Bu_3SnI	$Bu_3P{=}O$	15	0	93
4	Bu_3SnI	$Bu_3P{=}O$[b]	15	74	6
5	Bu_3SnI	HMPA	4	26	0
6	Bu_3SnI	HMPA[b]	4	57	0
7	Bu_3SnI	HMPA[b]	24	100	0
8	Bu_3SnI	DMF[b]	4	25	0
9	Bu_2SnI_2	$Bu_3P{=}O$	4	trace	0
10[c]	Bu_3SnI	HMPA[b]	10[d]	37	5

[a] Oxetane:Sn compd:additive = 20:0.4:0.4 mmol, 100 °C, CO_2 = 50 kg/cm^2. [b] Additive = 4 mmol. [c] 2-Methyloxetane was used instead of oxetane. [d] 110 °C.

zation of oxetane is observed. In the course of our studies of this reaction, the formation of trimethylene carbonate (1) was recognized when heating was stopped for 4 h (Table I, entry 4), and, therefore, polycarbonate (2) was thought to be produced by the polymerization of 1. However, attempts aimed at selective formation of 1 failed in these catalytic systems as summarized in Table I. The orders of catalytic activity were follows: $Bu_2SnX_2 > Bu_3SnX$ (X; halogen), I > Br, and phosphine > amine. The ratios of 1 and 2 produced were determined by ^1H NMR spectroscopy.

In next stage, the polymerization of 1 was investigated. Compound 1 was not polymerized merely by heating at 100 °C under a pressure of CO_2. Although polymerization was accelerated by either Bu_2SnI_2 or $Bu_2SnI_2 \cdot Bu_3P$ catalyst, yielding polycarbonate in 98% and 89% yields, respectively, the molecular weight of complex-catalyzed polymer was lower than that of the Bu_2SnI_2 catalyzed one, 2100 vs. 4250, respectively, as shown in Table II. The polymerization activity of Bu_2SnI_2 apparently is depressed on complexation with Bu_3P, and thus selective formation of 1 may be possible by using appropriate organotin complexes.

Accordingly, various complexes of butyltin halides were explored, and the results are summarized in Table III. As already reported, amines such as triethylamine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) have lower activity.[9] Moreover, disproportionation of the complexes is apt to occur.[11] The complex $Bu_3SnI \cdot Bu_3P$ did not give 1 selectively even in very short reaction times (entry 1). In turn, phosphine oxides, which coordinate to the tin atom via oxygen, were used as ligands.[12] The complex of Bu_3SnI and $Bu_3P{=}O$ produced 1 exclusively in 41% yield (entry 2). Hexamethylphosphoric triamide (HMPA), which also coordinates via oxygen, yielded 1 in rather lower yield without polymerization (entry 5). However, in a prolonged reaction 1 was converted quantitatively to 2 even by the $Bu_3SnI \cdot Bu_3P{=}O$ catalyst system (entry 3). This problem has been resolved by performing the reaction in the presence of a large excess of $Bu_3P{=}O$ (entry 4). In particular, no polymerization proceeded in the presence of a large excess of HMPA, and only 1 was produced quantitatively (entry 7). Addition of an excess of HMPA did not depress the activity of the complex (entries 5 and 6). Dimethylformamide (DMF) was also a suitable ligand although the catalytic activity was rather low. These results observed with Bu_3SnI systems contrast with those of $Bu_2SnI_2 \cdot Bu_3P{=}O$ complex where neither 1 nor 2 were formed at all. Recovery of the oxetane was almost quantitative (entry 9). This fact is noteworthy since Bu_2SnI_2 was more active than Bu_3SnI in combination with Bu_3P (Table I, entries 4 and 6). Consequently, the choice of combinations of organotin halides with ligands is very important for the reaction of oxetane with CO_2. For the production of polycarbonate, the Bu_2SnI_2·phosphine system is the most active catalyst. On the other hand, trimethylene carbonate can be obtained without polymers with the Bu_3SnI·phosphine oxide catalyst system. This reaction system is considered to be almost neutral in contrast to the already reported reactions using oxetanes, in which strong Lewis acids are required.[7]

Scheme II

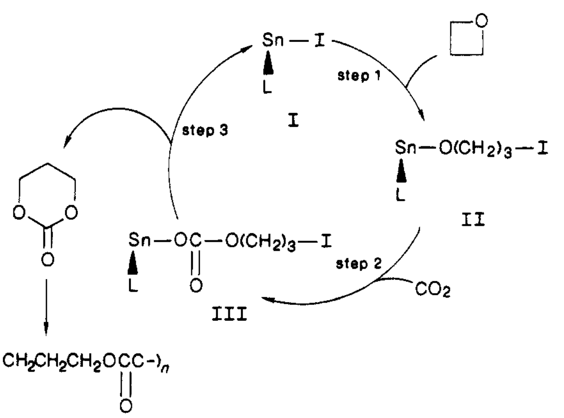

Table IV. Oxetane Ring Cleavage by Organotin Halide Complexes[a]

entry	Sn compd	additive	oxetane convn, %
1			0
2	Bu_3SnI		8
3	Bu_3SnI	Bu_3P	22
4	Bu_3SnI	$Bu_3P{=}O$	24
5	Bu_2SnI_2		26
6	Bu_2SnI_2	Bu_3P	98
7	Bu_2SnI_2	$Bu_3P{=}O$	90

[a] Oxetane:Sn compd:additive = 10:10:10 mmol, 45 °C, 2 h.

Reaction Mechanism

A reaction path catalyzed by organotin halides is proposed as illustrated in Scheme II. Thus, in step 1 oxetane is cleaved by the tin halide complex to give an organotin iodopropoxide (II). Then the insertion of CO_2 into the resulting Sn–O bond in II forms the adduct III in step 2. In step 3, trimethylene carbonate is produced and the tin halide complex is regenerated by an intramolecular nucleophilic reaction of terminal iodide. Polycarbonate (2) is obtained by polymerization of 1 in the presence of the organotin iodide.

With Bu_3P and $Bu_3P{=}O$, the effects of added ligands were investigated in each step. At first, equimolar reac-

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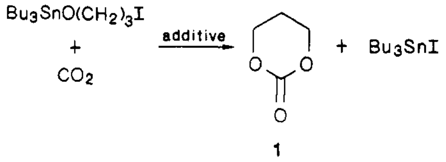
Scheme III



1

additive[a]	yield of 1, %
	0
Bu_3P	12
$Bu_3P{=}O$	68

[a] Sn alkoxide:additive = 10:10 mmol, CO_2 = 50 kg/cm^2, 100 °C, 2 h.

tions of oxetane with organotin halides were performed at 45 °C for 2 h. In the absence of ligands, 8% and 26% of the oxetane was consumed by Bu_3SnI and Bu_2SnI_2, respectively. The conversions of oxetane were increased by addition of Bu_3P or $Bu_3P{=}O$ as summarized in Table IV. From these results, it is apparent that the complexation with these ligands facilitates the cleavage of oxetane ring. The Sn–iodide bond may be activated by such coordination, and this may allow the adduct to form. This hypothesis may be justified by the fact that, according to Allen,[12] an apical Sn–halogen bond is lengthened by the coordination of a phosphine oxide. Moreover, the occurrence of II was suggested by the fact that $CH_3COO(CH_2)_3I$ was obtained by addition of acetyl chloride after the reaction of oxetane with $Bu_2SnI_2 \cdot Bu_3P{=}O$ or with $Bu_3SnI \cdot Bu_3P{=}O$ (see Experimental Section). However, the results shown in Table IV are not compatible with the formation of 1 and 2 in Tables I and III. In particular, it must be pointed out that the $Bu_2SnI_2 \cdot Bu_3P{=}O$ complex, having no activity in the addition of oxetane with CO_2, had readily cleaved the oxetane ring.

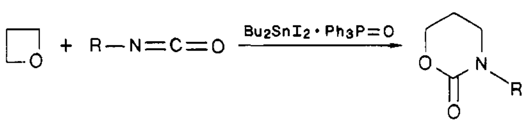
The facile insertion of CO_2 into the Sn–O bond is well-known.[13] Actually, CO_2 readily reacted at room temperature with $Bu_3SnO(CH_2)_3I$ (which was synthesized by the reported method[14]), giving $Bu_3SnOCOO(CH_2)_3I$. This adduct showed an absorption band at 1620 cm^{-1} (C=O) in the IR spectrum, but CO_2 was gradually released in the absence of CO_2 gas. From these results, it may be considered that coordination does not play an important role in this step (step 2). The role of ligands in the step 3 was examined in terms of the reaction of $Bu_3SnO(CH_2)_3I$ and CO_2 (Scheme III). As shown in Scheme III, no carbonate was obtained in the absence of an additive. Trimethylene carbonate was obtained in 68% yield when $Bu_3P{=}O$ was added, while the addition of Bu_3P gave 1 in 12% yield with a small amount of polycarbonate. The addition of Bu_3P or $Bu_3P{=}O$ apparently stimulates the intramolecular cyclization (step 3) because the insertion of CO_2 is thought to proceed smoothly as noted above. Further, these results are consistent with the results as listed in Table III. From these facts, ligands such as phosphines and phosphine oxides are considered to play important roles in the formation of 1, especially in steps 1 and 3 in Scheme II.

Farhangi reported that Bu_2SnCl_2 forms a 1/1 complex with Bu_3P in solution,[11] while formation of 1/2 complex of Me_2SnCl_2 with $Ph_3P{=}O$ was described.[15] Also in our system, the formation of a 1/2 complex of Bu_2SnI_2 with

Scheme IV

$Ph_3P{=}O$ was confirmed by elemental analysis. In addition, the coordination of $Bu_3P{=}O$ was suggested by the shift of the P=O stretching absorption band in the IR from 1160 to 1120 cm^{-1} by complexation. Moreover, both of the complexes $Bu_3SnI \cdot Bu_3P{=}O$ and $Bu_3SnI \cdot Bu_3P$ are thought to be 1/1 adducts. As exemplified in Scheme IV, coordination numbers around the tin atom in 1/1 and 1/2 complexes are five and six, respectively.

The distinct difference in the catalytic activity between $Bu_2SnI_2 \cdot Bu_3P{=}O$ and the other complexes can be explained by assuming that a stable six-coordinate tin compound is coordinatively saturated, thus having lower activity. Moreover, the activity may be ascribable to the apical Sn–I bond in Scheme IV.[15,16] However, Bu_2SnI_2·phosphine oxide complex could cleave the oxetane ring under mild conditions. Moreover, the cycloaddition of oxetane with isocyanates, more highly active isoelectric analogues of CO_2, is promoted by an equimolar amount of this complex, as already reported (eq 1).[17] Therefore,



(1)

it must be taken into consideration that the regeneration of the active species in step 3 may be difficult in the reaction of CO_2 and that the reactivity of CO_2 is much lower than that of isocyanates.

The polymerization of 1 can be assumed to occur as follows; organotin halide complexes have no ability in polymerization because the acidity is decreased by coordination. Polymerization probably is caused by free organotin halides. This assumption was supported by the fact that a large excess of $Bu_3P{=}O$ suppressed the dissociation of Bu_3SnI, so there was no polymerization (Table II, entry 5). On the other hand, the complexes of Bu_3P are perhaps too unstable to suppress polymerization completely even in the presence of an excess of Bu_3P (Table II, entry 6).

This novel catalyst system, organotin halide complexes, has some advantages; the coordination to tin enhances the nucleophilicity of the halogen to cleave an oxetane ring, and further the acidity of tin is decreased by coordination, and this reduces side reactions such as homopolymerization of oxetane[18] and polymerization of 1. Consequently, the fixation of CO_2 with oxetane has become feasible under neutral conditions; either trimethylene carbonate or polycarbonate was selectively obtained by using appropriate organotin halide complexes.

Experimental Section

General Comments. The following instruments were used: melting points, Yanagimoto micro melting point apparatus; IR, Hitachi 260-10; mass spectra, Hitachi RMU-6E; GC, Shimadzu

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8A (FID, 5% FFAP on Chromosorb WAW, and Porapak N); ^{1}H NMR and ^{13}C NMR, Hitachi R-90H; number average molecular weight, KORONA-114 (vapor pressure method).

Oxetanes[19] and tin compounds[20] were produced according to already known methods. Carbon dioxide and tri-*n*-butylphosphine oxide were purchased from commercial sources and used without further purification. Freshly distilled tri-*n*-butylphosphine was used. *N*,*N*-Dimethylformamide (DMF) and hexamethylphosphoric triamide (HMPA) were distilled after being dried over CaH_2. The compound $Bu_3SnO(CH_2)_3I$ was produced from Bu_3SnOMe and $AcO(CH_2)_3I$ as reported.[14]

Reaction of Oxetane with Carbon Dioxide. Oxetane (20 mmol), tin halide (0.4 mmol), and ligand (0.4 mmol) were placed in a 30-mL stainless steel autoclave, and then CO_2 gas was introduced up to 50 kg/cm^2. The vessel was heated with stirring with a magnetic stirrer. After cooling, the reaction mixture was dissolved in $CHCl_3$. The amount of trimethylene caronate (1) was determined by GC and/or ^{1}H NMR. The yields of polymers were determined on the basis of amount of 1 and the residual weight after evaporation (20 mmHg for 10 h). In those cases where no 1 was formed, the content of CO_2 and the number average molecular weight of the polymer were determined by ^{1}H NMR and vapor pressure osmometry, respectively. In many cases, the ratio of 1 ($CH_2CH_2CH_2{}^aOCOO$), 2 ($-CH_2CH_2CH_2{}^bOCOO-$), and oxetane polymer ($-CH_2CH_2CH_2{}^cO-$) could be calculated on the basis of the ratio of H^a (δ 4.49 (t)), H^b (δ 4.21 (t)), and H^c (δ 3.40 (t)) in ^{1}H NMR ($CDCl_3$).

Copolymer of CO_2 with oxetane: white waxlike; IR (neat) 1740 (C=O), 1260 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.0 (quint, 2 H), 4.21 (t, 4 H).

1,3-Dioxan-2-one (trimethylene carbonate) (1): mp 47–48 °C (lit.[21] 47–48 °C); IR (KBr) 1740 cm^{-1} (C=O); MS, *m/e* 102 (M$^+$); ^{1}H NMR ($CDCl_3$) δ 2.17 (quint, 2 H), 4.49 (t, 4 H).

4-Methyl-1,3-dioxan-2-one (4-methyltrimethylene carbonate): bp 116–118 °C (2 mmHg) (lit.[21] 100–110 °C) (0.8 mmHg); IR 1745 cm^{-1} (C=O); MS, *m/e* 116 (M$^+$); ^{1}H NMR ($CDCl_3$) δ 1.44 (d, 3 H), 1.7–2.3 (m, 2 H), 4.3–4.5 (m, 2 H), 4.5–4.8 (m, 1 H).

Polymerization of 1. Catalyst (0.4 mmol), 1 (20 mmol), and an additive (amount shown in Table II) were placed in a 30-mL stainless-steel autoclave, and then the mixture was allowed to react with stirring at 100 °C for 4 h under a pressure of CO_2 (50 kg/cm^2). The conversion of 1 and the formation of 2 were confirmed by GC and ^{1}H NMR.

Reaction of $Bu_3SnO(CH_2)_3I$ with CO_2. (A) Without Ligands. $Bu_3SnO(CH_2)_3I$ (5 mmol) was heated at 100 °C for 2 h under a pressure of CO_2 (50 kg/cm^2) in a 30-mL stainless-steel autoclave. The IR spectrum of the reaction mixture showed a C=O absorption band at 1620 cm^{-1}, but this absorption quickly disappeared. Finally, no CO_2 fixation was observed.

(B) With Ligands. Except of addition of Bu_3P or $Bu_3P{=}O$, similar reactions as above were conducted. In the case of Bu_3P, the production of polycarbonate was characterized by ^{1}H NMR, but the exact amount could not be determined because of accompanying impurities.

Cleavage of Oxetane Ring by Organotin Halide Complexes. Representative procedure: oxetane (10 mmol), Bu_2SnI_2 (10 mmol), and $Bu_3P{=}O$ (10 mmol) were heated at 45 °C for 2 h in a 30-mL two-necked flask under nitrogen. After the conversion of oxetane was confirmed by GC (90%) (Porapak N, 150 °C), the unreacted oxetane was removed in vacuo, and then a benzene solution (10 mL) of acetyl chloride (10 mmol) was added. Immediate reaction occurred, and 6.5 mmol of $CH_3COO(CH_2)_3I$ was obtained (72% yield based on consumed oxetane). When $Bu_3SnI{\cdot}Bu_3P{=}O$ was used, 1.1 mmol was obtained (46% yield): bp 58 °C (3 mmHg); IR (neat) 1740, 1230 cm^{-1}. This compound was characterized by the comparison with an authentic sample produced from $HO(CH_2)_3I$ and acetyl chloride.

Complexes of Bu_2SnI_2 with Phosphine Oxides. The mixture of Bu_2SnI_2 (13 mmol) and $Ph_3P{=}O$ (10 mmol) was stirred until it had solidified (about 2 h). Unreacted Bu_2SnI_2 was washed out with dry hexane, and the residual complex was isolated by filtration, yielding $Bu_2SnI_2{\cdot}2Ph_3P{=}O$ quantitatively, mp 107–109 °C. Further purification was not performed. All procedures were conducted under a dry nitrogen atmosphere. IR (KBr); 1145 cm^{-1} (P=O) (cf. free $Ph_3P{=}O$, 1195 cm^{-1}). Anal. Calcd for $C_{44}H_{48}O_2P_2I_2Sn$: C, 50.65; H, 4.64. Found: C, 50.29; H, 5.07.

The complex with $Bu_3P{=}O$ could be obtained in a similar manner. However it is a liquid and could not be purified completely. IR (neat); 1120 cm^{-1} (P=O) (cf. free $Bu_3P{=}O$, 1160 cm^{-1}).

Acknowledgment. This research was supported by a grant from the Asahi Glass Foundation for Industrial Technology.

Registry No. 1, 2453-03-4; 1 (4-methyl derivative), 17361-58-9; 2, 50862-75-4; HMPA, 680-31-9; DMF, 68-12-2; CO_2, 124-38-9; Bu_3SnI, 7342-47-4; Bu_2SnI_2, 2865-19-2; Bu_3SnBr, 1461-23-0; Bu_2SnBr_2, 996-08-7; PBu_3, 998-40-3; Et_3N, 121-44-8; $Bu_3P{=}O$, 814-29-9; $(-OCH(CH_3)CH_2CH_2OCO-)_n$, 105018-61-9; $Bu_3SnO(CH_2)_3I$, 93912-82-4; $CH_3COO(CH_2)_3I$, 62116-24-9; $Bu_2SnI_2{\cdot}2Ph_3P{=}O$, 105018-57-3; $Bu_2SnI_2{\cdot}Bu_3P$, 105018-58-4; $Bu_3SnI{\cdot}Bu_3P$, 105018-59-5; $Bu_3SnI{\cdot}Bu_3P{=}O$, 105018-60-8; oxetane, 503-30-0; 2-methyloxetane, 2167-39-7.

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