404 *Bull. Korean Chem. Soc., Vol. 13, No. 4, 1992*

Ok-Sang Jung et al.

sonable choice for the input to model calculations to illustrate the possible effects of an gating mode in the transient kinetics.

Figure 1 shows that the transient time before reaching the steady state is shorter in general for gated reactions when compared with the ungated reactions. In particular, as the ratio of the gate-opening rate to the gate-closing rate decreases down to a factor of 1/10, the steady state is established within 100 ps. The value of k_c was fixed at 1.0 ns^{-1}.

In Figure 2, we fixed the ratio of k_o/k_c to unity, and instead changed the magnitudes of both rate constants. As the gating mode fluctuates more rapidly, the transiency in the dynamical variation of the bimolecular kinetics becomes less prominent.

References

1. B. Otto, J. Schroeder, and J. Troe, *J. Chem. Phys.*, **81**, 202 (1984).
2. E. M. Eyring, in *Physical Chemistry*, ed. by H. Eyring (Academic, New York, 1970), Vol. IXB, Chap. 8.
3. D. P. Millar, R. J. Robbins, and A. H. Zeweil, *J. Chem. Phys.*, **75**, 3649 (1981).
4. S. Lee, M. Yang, K. J. Shin, K. Y. Choo, and D. Lee, *Chem. Phys.*, **156**, 339 (1991).
5. K. Chou and G. Zhou, *J. Am. Chem. Soc.*, **104**, 1409 (1982).
6. S. A. Rice and M. J. Pilling, *Prog. React. Kinet.*, **9**, 93 (1979).
7. M. Smoluchowski, *Ann. Phys.*, **48**, 1103 (1915); *Z. Phys. Chem. (Leipzig)*, **92**, 129 (1917).
8. S. A. Rice, *Comprehensive Chemical Kinetics 25, Diffusion-Limited Reactions* (Elsevier, Amsterdam, 1985).
9. F. C. Collins and G. E. Kimball, *J. Colloid Sci.*, **4**, 425 (1949).
10. G. Wilemski and M. Fixman, *J. Chem. Phys.*, **58**, 4009 (1973).
11. R. Kapral, *Adv. Chem. Phys.*, **48**, 71 (1981).
12. S. Lee and M. Karplus, *J. Chem. Phys.*, **86**, 1883 (1987).
13. E. W. Montroll, *J. Chem. Phys.*, **14**, 202 (1946).
14. H. L. Friedman, *J. Phys. Chem.*, **70**, 3931 (1966).
15. K. Solc and W. H. Stockmayer, *J. Chem. Phys.*, **54**, 2981 (1971).
16. S. Lee and M. Karplus, *J. Chem. Phys.*, **86**, 1904 (1987).
17. J. A. McCammon and S. H. Northrup, *Nature* **293**, 316 (1981).
18. S. H. Northrup, F. Zarrin, and J. A. McCammon, *J. Phys. Chem.*, **86**, 2314 (1982).
19. A. Szabo, D. Shoup, S. H. Northrup, and J. A. McCammon, *J. Chem. Phys.*, **77**, 4484 (1982).
20. S. H. Lin, K. P. Li, and H. Eyring, in *Physical Chemistry*, ed. by H. Eyring (Academic, New York, 1975), Vol. VII, Chap. 1.
21. L. Monchick, J. L. Magee, and A. H. Samuel, *J. Chem. Phys.*, **26**, 935 (1957).
22. T. R. Waite, *Phys. Rev.*, **107**, 463 (1957); *J. Chem. Phys.*, **28**, 103 (1958); *Ibid.*, **32**, 21 (1960).
23. H. L. Frisch and F. C. Collins, *J. Chem. Phys.*, **20**, 1797 (1952).
24. O. G. Berg, *Chem. Phys.*, **31**, 47 (1978).
25. J. T. Hynes and J. M. Deutch, in *Physical Chemistry*, ed. by D. Henderson (Academic, New York, 1976), Vol. XIB, Chap. 8.
26. I. N. Sneddon, *The Use of Integral Transforms* (McGraw-Hill, New York, 1972).
27. *IMSL Library Reference Manual*, 9th ed. (International Mathematical and Statistical Libraries, Inc., Houston, Texas, 1982).
28. J. Sines, S. A. Allison, A. Wierzbicki, and J. A. McCammon, *J. Phys. Chem.*, **94**, 959 (1990).
29. S. A. Allison, J. A. McCammon, and J. Sines, *J. Phys. Chem.*, **94**, 7133 (1990).

Preparation and Structure of $\overline{CH_2CH_2OOCCHCH_2SnCl_3}$

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A new estertin, $\overline{CH_2CH_2OOCCHCH_2SnCl_3}$, was prepared and its structure was determined by X-ray crystallography ($P2_12_12_1$; $a=9.439(1)$, $b=9.601(1)$, $c=10.779(1)$ Å, $Z=4$) and refined to $R=0.0356$. The coordination geometry around the tin atom approximates to a trigonal bipyramid with the intramolecularly coordinated oxygen O(1), (Sn-O(1), 2.482(6) Å) and Cl(2) occupying mutually *trans* positions (O(1)-Sn-Cl(2), 176.4(2)°).

Introduction

Since a novel synthetic route to "estertin" was reported[1], a large number of estertin compounds and their derivatives have been investigated because of their interesting bonding mode and industrial applicability[2-8].

In continuing efforts to extend the estertin chemistry[9], this paper reports the preparation and structure of the title compound.

Preparation and Structure of CH₂CH₂OOCCHCH₂SnCl₃

Bull. Korean Chem. Soc., Vol. 13, No. 4, 1992 405

Experimental

The title compound was prepared according to the same method for $CH_3OOCCH_2CH(COOCH_3)SnCl_3$[9] : $SnCl_2$ (4.91 g, 50 mmol) and α-methylene-γ-butyrolactone (9.48 g, 50 mmol) in 40 m*l* of diethyl ether were placed in a 250 m*l* two neck flask equipped with a reflux condenser and a gas inlet tube. Through the stirred suspension was bubbled for 1 h anhydrous hydrogen chloride (1.83 g, 50 mmol) at 20°C. After the solvent was removed at reduced pressure, the residue was recrystallized from a dichloromethane-petroleum ether mixture (1 : 1) to give colorless crystals (mp. 149-152°C) suitable for X-ray crystalloraphy. Anal. found (calcd for $C_5H_7O_2$-Cl_3Sn) : C, 18.70 (18.53); H, 2.12 (2.18). IR (KBr pellet, cm⁻¹) : ν (C=O), 1690.

All the crystallographic data were obtained on an Enraf-Nonius CAD4 automatic diffractometer with graphite-monochromated molybdenum radiation (λ (Kα1)=0.70930 Å, λ(Kα2)=0.71359 Å) at an ambient temperature of 23(2)°C. A single crystal was mounted inside of a sealed, thin-walled glass capillary. From the systematic absences the space group, $P2_12_12_1$, was uniquely determined. The cell constants were determined by the least-squares refinement of the diffraction geometry for 25 intense reflections having $7° < θ < 13°$. The three intensity standards were monitored during intensity data collection, and did not reveal any systematic variation. The data were collected in ω/2θ scan mode using variable rates up to $θ_{max} = 25°$ for the range of $0 ≤ h ≤ 10$, $-11 ≤ k ≤ 0$, and $0 ≤ l ≤ 12$ and corrected for Lorentz-polarization effects. The structure was solved by the conventional heavy atom method and difference Fourier techniques and refined by means of full-matrix least-squares procedures. The nonhydrogen atoms were refined anisotropically. The positions of hydrogen atoms were found on the difference Fourier map and refined isotropically using a riding model (C-H, 0.95 Å). All calculations were performed by using SHELX-76, a system of computer programs for X-ray structure determination by G. M. Sheldrick[10]. The crystal parameters and procedural information on data collection and structure refinement are given in Table 1.

Results and Discussion

The reaction of $SnCl_2$ with a rigid cyclic *s-cis* α,β-unsaturated ester, α-methylene-γ-butyrolactone, under anhydrous hydrogen chloride proceeded affording the title compound (Eq. (1)) in the same way as the corresponding reaction[1]
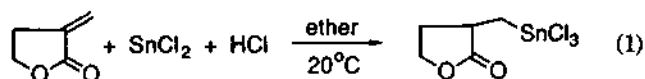
with simple α,β-unsaturated ester. The product is obtained as fairly air-stable crystalline solid with sharp melting point, and is soluble in polar organic solvents.

The ORTEP drawing with the atomic labeling scheme of the compound is presented in Figure 1. The final atomic coordinates and thermal parameters are shown in Table 2 and the bond distances and angles in Table 3. The compound is a discrete molecule with no close intermolecular contacts. The geometry around the tin atom is a distorted trigonal bipyramid with C(1), Cl(1), and Cl(3) in the equatorial posi-

Table 1. Crystal Parameters and Procedural Information

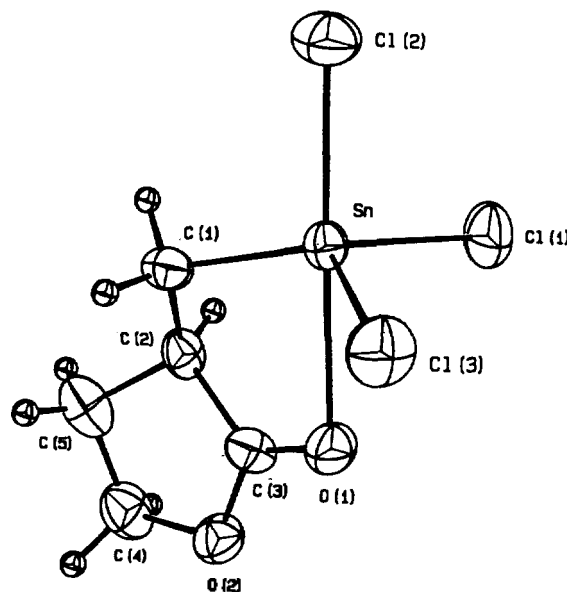| Formula	$C_5H_7O_2Cl_3Sn$
f_w	324.16
Space group	$P2_12_12_1$
a, Å	9.439(1)
b, Å	9.601(1)
c, Å	10.779(1)
V, Å³	976.8(2)
Z	4
d_{calcd}, gcm⁻³	2.204
Crystal size, mm	0.32×0.40×0.42
μ, cm⁻¹	31.45
Scan method	ω/2θ
Data collected	*h,k,l* 3<2θ<44
No. total observation	1028
No. unique data>3σ(I)	971
No. parameters refind	106
gof	0.576
$R = (\sum |F_o - F_c|)/\sum |F_o|$	0.0356
$R_w = (\sum |F_o - F_c|w^{1/2})/\sum |F_o|w^{1/2}$	0.0375

$^a w = 1.00/(σ^2(F) + 0.010333\ F^2)$

Figure 1. ORTEP drawing of $CH_2CH_2OOCCHCH_2SnCl_3$ showing 50% probability thermal ellipsoids and numbering scheme.

tions and Cl(2) and O(1) in the apical positions *via* intramolecular carbonyl oxygen-to-tin coordination. The distortion appears to be caused by the small bite angle of O(1)-Sn-C(1) (75.7(3)°) with the concomitant splaying of the C(1)-Sn-Cl2) (106.9(2)°), but the axial bond (O(1)-Sn-Cl(2), 176.4(2)°) is almost linear. The axial Sn-Cl(2) distance (2.342(2) Å) is slightly longer compared with the equatorial bonds (Sn-Cl(1), 2.324(2) Å; Sn-Cl(3), 2.333(2) Å). The Sn-O(1) distance (2.482 (6) Å) in the present compound is longer than that (2.347(5) Å) in $CH_3OOCCH_2CH_2SnCl_3$[3]. This indicates a weaker coordination of the carbonyl group in a cyclic ester than in a simple ester due to the rigid heterocyclic system which shows a

406 *Bull. Korean Chem. Soc., Vol. 13, No. 4, 1992*

Ok-Sang Jung et al.

Table 2. Positional and Equivalent Isotropic Thermal Parameters[a]

Atom	X/A	Y/B	Z/C	U_{eq}
Sn	0.2201(<1)	0.0632(<1)	0.5095(1)	0.031(<1)
Cl(1)	0.4591(2)	0.0083(3)	0.4929(2)	0.051(1)
Cl(2)	0.1306(3)	−0.1641(2)	0.5188(3)	0.054(1)
Cl(3)	0.1373(2)	0.1119(3)	0.3102(2)	0.046(1)
O(1)	0.3111(7)	0.3042(6)	0.4855(5)	0.043(4)
O(2)	0.3031(6)	0.4943(6)	0.6022(6)	0.041(3)
C(1)	0.1437(8)	0.1690(8)	0.6671(7)	0.034(4)
C(2)	0.2416(8)	0.2887(8)	0.7023(7)	0.034(4)
C(3)	0.2907(8)	0.3620(7)	0.5872(7)	0.034(4)
C(4)	0.2610(11)	0.5300(10)	0.7318(9)	0.050(5)
C(5)	0.1816(10)	0.4065(10)	0.7790(11)	0.053(6)

[a] Equivalent isotropic U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Bond Distances (Å) and Angles (°)

Sn-Cl(1)	2.324(2)	O(2)-C(3)	1.286(10)
Sn-Cl(2)	2.342(2)	O(2)-C(4)	1.492(11)
Sn-Cl(3)	2.333(2)	C(1)-C(2)	1.523(10)
Sn-O(1)	2.482(6)	C(2)-C(3)	1.500(11)
Sn-C(1)	2.107(8)	C(2)-C(5)	1.511(12)
O(1)-C(3)	1.243(9)	C(4)-C(5)	1.492(12)
Cl(2)-Sn-Cl(1)	98.2(1)	C(4)-O(2)-C(3)	108.7(7)
Cl(3)-Sn-Cl(1)	107.5(1)	C(2)-C(1)-Sn	110.9(4)
Cl(3)-Sn-Cl(2)	96.1(1)	C(3)-C(2)-C(1)	109.6(6)
O(1)-Sn-Cl(1)	82.4(2)	C(5)-C(2)-C(1)	118.3(7)
O(1)-Sn-Cl(2)	176.4(2)	C(5)-C(2)-C(3)	102.5(7)
O(1)-Sn-Cl(3)	80.4(2)	O(2)-C(3)-O(1)	122.6(7)
C(1)-Sn-Cl(1)	120.3(2)	C(2)-C(3)-O(1)	124.6(6)
C(1)-Sn-Cl(2)	106.9(2)	C(2)-C(3)-O(2)	112.8(7)
C(1)-Sn-Cl(3)	122.1(2)	C(5)-C(4)-O(2)	105.6(7)
C(1)-Sn-O(1)	75.7(3)	C(4)-C(5)-C(2)	102.8(8)
C(3)-O(1)-Sn	105.7(5)		

comparatively smaller tendency to donate electron[11]. The bond distances of Sn-Cl and Sn-C are comparable to those in $CH_3OOCCH_2CH_2SnCl_3$[3] or $CH_3OOCCH_2CH(COOCH_3)CH_2$-$SnCl_3$[9].

In conclusion, the title compound is prepared by the reaction of $SnCl_2$ with a *s-cis* α,β-unsaturated ester, α-methylene-γ-butyrolactone, in the presence of anhydrous hydrogen chloride, which is unprecedented although the reactions with simple α,β-unsaturated ester have been well evaluated. The Sn-O distance of intramolecular carbonyl oxygen-to-tin coordination is weaker than the corresponding bonds in simple estertin compounds.

References

1. R. E. Hutton and V. Oakes, Organotin Compounds : New Chemistry and Applications, ACS 157, Am. Chem. Soc. Washington DC, 176, p. 123; J. W. Burley, R. E. Hutton and V. Oakes, *J. Chem. Soc., Chem. Commun.*, 803 (1976).
2. R. E. Hutton, J. W. Burley, and V. Okaes, *J. Organomet. Chem.*, **156**, 369 (1978).
3. P. G. Harrison, T. J. King, and M. A. Healy, *J. Organomet. Chem.*, **182**, 17 (1979).
4. R. A. Howie, E. S. Paterson, J. L. Wardell, and J. W. Burley, *J. Organomet. Chem.*, **259**, 71 (1983).
5. R. A. Howie, E. S. Paterson, J. L. Wardell, and J. W. Burley, *J. Organomet. Chem.*, **304**, 301 (1986).
6. B. K. Deb and A. K. Ghosh, *Polyhedron*, **5**, 863 (1986).
7. B. K. Deb and A. K. Ghosh, *Can. J. Chem.*, **65**, 1241 (1987).
8. S. W. Ng, C. Wei, V. G. Kumar Das, J. P. Charland, and F. E. Smith, *J. Organomet. Chem.*, **364**, 343 (1989).
9. Our previous paper : O. S. Jung, J. H. Jeong, and Y. S. Sohn, *J. Organomet. Chem.*, **397**, 17 (1990).
10. G. M. Sheldrick, SHELX 76 : Program for Crystal Structure Determination, Univ. of Cambridge, U. K., 1976.
11. G. Marcotrigiano, G. C. Pellacani, Copreti, and G. Toshi, *Bull. Chem. Soc. Jpn.*, **48**, 1018 (1975).