

## Structure of a Bicyclic Organostannane Resulting from a Trimethyltin Hydride Addition–Cyclization Reaction

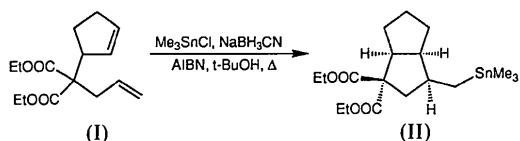
BY FRANCINE BÉLANGER-GARIÉPY, ROGER LÉGER AND STEPHEN HANESSIAN\*

Département de Chimie, Université de Montréal, CP 6128, Succ. A, Montréal, Québec, Canada H3C 3J7

(Received 18 June 1991; accepted 19 November 1991)

**Abstract.** ( $\pm$ )-*cis*-Diethyl 4-(trimethylstannylmethyl)-bicyclo[3.3.0]octane-2,2-dicarboxylate,  $C_{18}H_{32}O_4Sn$ ,  $M_r = 431.14$ , triclinic,  $P\bar{1}$ ,  $a = 7.674(2)$ ,  $b = 11.113(3)$ ,  $c = 13.346(4)$  Å,  $\alpha = 71.64(2)$ ,  $\beta = 79.49(2)$ ,  $\gamma = 86.62(2)^\circ$ ,  $V = 1062.1(5)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.348$  Mg m<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 1.22$  mm<sup>-1</sup>,  $F(000) = 444$ ,  $T = 293$  K,  $R = 0.055$  and  $wR = 0.063$  for 2526 observed reflections. Trimethyltin hydride adds to the terminal double bond of 1,6-dienes and the resulting radical leads to *exo*-trigonal ring closure. The major product was analyzed by X-ray crystallography to determine the relative configuration of the ring junction which could not be established unambiguously by <sup>1</sup>H NMR studies. The *cis*-fused bicyclo[3.3.0] system contains a trimethylstannylmethyl side arm which is in the concave face of the molecule.

**Experimental.** The intramolecular free radical ring closure of diene (I) in the presence of  $Me_3SnH$ , led to the formation of a crystalline bicyclic compound (II) in 45% yield. The orientation of the substituents was deduced from a single-crystal X-ray diffraction structure determination.



Crystal of  $C_{18}H_{32}O_4Sn$  bounded by  $\{011\}$ ,  $\{010\}$  and  $\{100\}$ , dimensions  $0.11 \times 0.33 \times 0.38$  mm. Unit-cell dimensions from 25 well centred reflections in the range  $18.0 \leq \theta \leq 20.2^\circ$ . Nonius CAD-4 diffractometer, Mo  $K\alpha$  radiation,  $\omega$  scan,  $\Delta\omega = (0.80 + 0.35 \tan \theta)^\circ$ ,  $2\theta_{max} = 50.0^\circ$ . A total of 7449 reflections ( $-9 \leq h \leq 9$ ,  $-13 \leq k \leq 13$ ,  $-15 \leq l \leq 15$ ) were measured at 293 K; a set of 3725 unique reflections were retained after averaging equivalent reflections in Laue  $\bar{1}$  symmetry ( $R_{int} = 0.05$ ), of which 2526 with  $I \geq 3.00\sigma(I)$  were retained for structure determination

\* To whom correspondence should be addressed.

and refinement. Orientation monitored every 200 measurements, intensity checked every hour using seven standard reflections, largest intensity fluctuations 2.2%. The Lorentz, polarization and absorption corrections were performed using a Gaussian integration technique (grid  $10 \times 10 \times 10$ ); transmission coefficients range 0.65–0.88.†

The Sn atom was located from a Patterson map, other atoms from difference Fourier synthesis. The structure was refined on  $F$  isotropically by full-matrix least squares, then anisotropically by block-diagonal least squares. The C(13) and C(14) atoms appeared disordered. The peaks around these C atoms were grouped into two sets with reasonable angles and distances. The refinement of the splitting of C(13) and C(14) into C(131), C(141) and C(132), C(142) converged to an occupancy factor of 0.50 respectively. All H atoms were found from difference Fourier synthesis and/or calculated, then fixed at idealized positions [ $C-H = 0.95$  Å,  $B_{(H-methyls)} = 8.0$  and  $B_{(H-C)} = 5.0$  Å<sup>2</sup>].

† The programs used here are modified versions of: *NRC-3* (Lp absorption correction), *NRC-2* (data reduction), *NRC-10* (bond distances and angles) and *NRC-22* (mean planes) (Ahmed, Hall, Pippy & Huber, 1973); Fourier and Patterson maps (Zalkin, unpublished); *NUCLS* (least-squares refinement) (Doedens & Ibers, 1967); and *ORTEP* (stereodrawings) (Johnson, 1965).

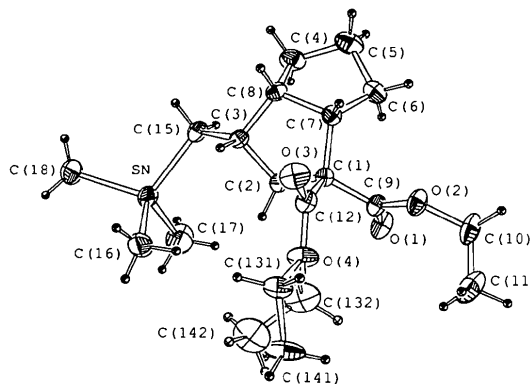


Fig. 1. An *ORTEP* drawing showing the atomic numbering. Ellipsoids are drawn at the 40% probability level. The H atoms are represented by spheres of arbitrary size.

Table 1. Final atomic coordinates with *e.s.d.*'s in parentheses ( $\times 10^5$  for Sn;  $\times 10^4$  for O,C) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ )

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}$
Sn	28289 (8)	125178 (4)	11247 (4)	75
O(1)	1279 (6)	7673 (5)	4702 (4)	82
O(2)	3397 (6)	6215 (4)	4611 (4)	76
O(3)	6628 (5)	7854 (5)	2555 (4)	84
O(4)	5600 (5)	8671 (5)	3851 (4)	78
C(1)	3464 (7)	8003 (5)	3104 (4)	46
C(2)	2648 (7)	9312 (5)	2654 (5)	49
C(3)	3259 (8)	9646 (6)	1452 (5)	52
C(4)	1237 (10)	8165 (8)	1004 (7)	85
C(5)	947 (11)	6774 (8)	1518 (8)	99
C(6)	1562 (11)	6518 (7)	2565 (7)	88
C(7)	3233 (8)	7330 (6)	2286 (5)	58
C(8)	3044 (8)	8395 (6)	1236 (5)	58
C(9)	2577 (8)	7320 (6)	4224 (5)	58
C(10)	2693 (12)	5441 (8)	5700 (6)	99
C(11)	3533 (16)	5786 (10)	6453 (7)	131
C(12)	5417 (8)	8149 (6)	3118 (5)	58
C(131)	7502 (13)	8955 (12)	3833 (10)	72
C(132)	7216 (25)	8603 (27)	4276 (20)	112
C(141)	7398 (18)	9398 (18)	4795 (14)	116
C(142)	7630 (29)	9908 (28)	4182 (25)	135
C(15)	2352 (9)	10817 (6)	800 (5)	66
C(16)	5260 (13)	12356 (9)	1694 (8)	110
C(17)	760 (18)	12840 (11)	2281 (10)	147
C(18)	3022 (13)	14094 (8)	-308 (7)	101

Function minimized:  $\sum w(|F_o| - |F_c|)^2$ . Final  $R = 0.055$ ,  $wR = 0.063$  {weight derived from the counting statistics,  $w = 1/[\sigma^2(F) + 0.0025(F)^2]$ } and  $S = 1.646$  for 228 parameters. Maximum  $(\Delta/\sigma) = 0.22$ , average  $(\Delta/\sigma) = 0.03$ . Residual electron density fluctuations on final difference Fourier synthesis: general background  $\pm 0.36 e \text{\AA}^{-3}$ , five peaks from 0.95 to 0.49  $e \text{\AA}^{-3}$  near the Sn atom.

The scattering curves for the non-H atoms were taken from Cromer & Mann (1968) and those for the H atoms from Stewart, Davidson & Simpson (1965). Real and imaginary parts of anomalous dispersion of Sn were taken from Cromer & Liberman (1970). The final atomic coordinates are given in Table 1.\* Fig. 1 shows the molecular conformation. Bond distances, bond angles and torsion angles are given in Table 2.

**Related literature.** For the preparation of some related compounds *via* an Sn-mediated radical cyclization reaction, see Fish, Kuivila & Tyminsky (1967) and also Hanessian, Bennani & Léger (1990).

We thank the Natural Sciences and Engineering Research Council of Canada and Le Ministère de l'Éducation du Québec for financial support.

\* Lists of anisotropic temperature factors, H-atom coordinates, least-squares-planes data and structure factors, and a stereoview of the molecule have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54872 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD0062]

Table 2. Bond distances ( $\text{\AA}$ ), bond angles ( $^\circ$ ) and torsion angles ( $^\circ$ ) with *e.s.d.*'s in parentheses

Sn—C(15)	2.133 (7)	C(7)—C(8)	1.547 (9)
Sn—C(16)	2.117 (10)	C(1)—C(9)	1.500 (8)
Sn—C(17)	2.102 (13)	O(1)—C(9)	1.197 (8)
Sn—C(18)	2.136 (9)	O(2)—C(9)	1.341 (8)
C(3)—C(15)	1.528 (9)	O(2)—C(10)	1.458 (9)
C(1)—C(2)	1.532 (8)	C(10)—C(11)	1.442 (14)
C(2)—C(1)	1.517 (8)	C(1)—C(12)	1.521 (8)
C(3)—C(8)	1.530 (10)	O(3)—C(12)	1.183 (8)
C(8)—C(4)	1.527 (10)	C(12)—O(4)	1.316 (8)
C(4)—C(5)	1.492 (13)	O(4)—C(131)	1.506 (12)
C(5)—C(6)	1.494 (13)	O(4)—C(132)	1.444 (21)
C(6)—C(7)	1.532 (11)	C(131)—C(141)	1.501 (23)
C(7)—C(1)	1.544 (9)	C(132)—C(142)	1.465 (44)
C(15)—Sn—C(16)	109.4 (3)	C(4)—C(8)—C(7)	104.7 (6)
C(15)—Sn—C(17)	110.1 (4)	C(6)—C(7)—C(8)	105.4 (6)
C(15)—Sn—C(18)	110.2 (3)	C(7)—C(1)—C(9)	113.1 (5)
C(16)—Sn—C(18)	108.1 (4)	C(7)—C(1)—C(12)	110.8 (5)
C(17)—Sn—C(18)	109.4 (4)	C(2)—C(1)—C(12)	109.5 (5)
C(16)—Sn—C(17)	109.6 (4)	C(2)—C(1)—C(9)	112.3 (5)
Sn—C(15)—C(3)	114.0 (4)	C(9)—C(1)—C(12)	108.2 (5)
C(15)—C(3)—C(2)	114.0 (5)	C(1)—C(9)—O(1)	125.6 (6)
C(15)—C(3)—C(8)	117.3 (5)	C(1)—C(9)—O(2)	116.5 (5)
C(1)—C(2)—C(3)	104.0 (5)	O(1)—C(9)—O(2)	123.9 (6)
C(2)—C(3)—C(8)	102.9 (5)	O(2)—C(10)—C(11)	109.8 (7)
C(3)—C(8)—C(4)	116.2 (6)	C(1)—C(12)—O(3)	126.2 (6)
C(8)—C(4)—C(5)	104.1 (7)	C(1)—C(12)—O(4)	110.4 (5)
C(4)—C(5)—C(6)	103.4 (7)	O(3)—C(12)—O(4)	123.4 (6)
C(5)—C(6)—C(7)	104.1 (7)	C(9)—O(2)—C(10)	117.0 (5)
C(6)—C(7)—C(1)	115.8 (6)	C(12)—O(4)—C(131)	112.9 (7)
C(7)—C(1)—C(2)	102.8 (5)	C(12)—O(4)—C(132)	123.3 (11)
C(3)—C(8)—C(7)	106.2 (5)	O(4)—C(131)—C(141)	103.2 (10)
C(8)—C(7)—C(1)	106.1 (5)	O(4)—C(132)—C(142)	106.1 (20)
Sn—C(15)—C(3)—C(2)	61.9 (6)	C(8)—C(7)—C(1)—C(12)	-94.5 (6)
Sn—C(15)—C(3)—C(8)	-177.7 (4)	C(2)—C(1)—C(9)—O(1)	6.5 (9)
C(15)—C(3)—C(2)—C(1)	169.9 (5)	C(7)—C(1)—C(9)—O(1)	-109.7 (4)
C(15)—C(3)—C(8)—C(7)	-153.1 (5)	C(2)—C(1)—C(9)—O(2)	-176.3 (5)
C(15)—C(3)—C(8)—C(4)	-37.2 (8)	C(7)—C(1)—C(9)—O(2)	67.9 (7)
C(1)—C(2)—C(3)—C(8)	41.8 (6)	C(2)—C(1)—C(12)—O(3)	-109.3 (7)
C(2)—C(3)—C(8)—C(7)	-27.1 (6)	C(7)—C(1)—C(12)—O(3)	3.4 (9)
C(3)—C(8)—C(7)—C(1)	2.7 (6)	C(2)—C(1)—C(12)—O(4)	70.1 (6)
C(8)—C(7)—C(1)—C(2)	22.5 (6)	C(7)—C(1)—C(12)—O(4)	-177.2 (5)
C(7)—C(1)—C(2)—C(3)	-39.9 (6)	C(1)—C(9)—O(2)—C(10)	179.6 (6)
C(4)—C(5)—C(6)—C(7)	-40.5 (8)	O(1)—C(9)—O(2)—C(10)	-3.1 (10)
C(5)—C(6)—C(7)—C(8)	23.0 (8)	C(9)—O(2)—C(10)—C(11)	-89.1 (8)
C(6)—C(7)—C(8)—C(4)	2.5 (7)	C(1)—C(12)—O(4)—C(131)	-174.5 (7)
C(7)—C(8)—C(4)—C(5)	-27.2 (8)	O(3)—C(12)—O(4)—C(131)	4.9 (10)
C(8)—C(4)—C(5)—C(6)	42.3 (8)	C(12)—O(4)—C(131)—C(141)	-174.0 (9)
C(1)—C(7)—C(6)—C(5)	139.9 (6)	C(1)—C(12)—O(4)—C(132)	161.4 (13)
C(1)—C(7)—C(8)—C(4)	-120.8 (6)	O(3)—C(12)—O(4)—C(132)	-19.2 (15)
C(2)—C(3)—C(8)—C(4)	88.8 (7)	C(12)—O(4)—C(132)—C(142)	128.9 (17)
C(2)—C(1)—C(7)—C(6)	-94.0 (6)	O(2)—C(9)—C(1)—C(12)	-55.2 (6)
C(3)—C(8)—C(4)—C(5)	-144.0 (6)	O(1)—C(9)—C(1)—C(12)	127.5 (7)
C(3)—C(8)—C(7)—C(6)	126.0 (6)	O(3)—C(12)—C(1)—C(9)	128.0 (7)
C(3)—C(2)—C(1)—C(9)	-161.8 (5)	O(4)—C(12)—C(1)—C(9)	-52.6 (7)
C(3)—C(2)—C(1)—C(12)	78.0 (6)	C(3)—C(15)—Sn—C(16)	25.7 (6)
C(6)—C(7)—C(1)—C(9)	27.4 (8)	C(3)—C(15)—Sn—C(17)	-94.9 (6)
C(6)—C(7)—C(1)—C(12)	149.0 (6)	C(3)—C(15)—Sn—C(18)	144.4 (5)
C(8)—C(7)—C(1)—C(9)	143.9 (5)		

## References

- AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1973). *NRC Crystallographic Programs for the IBM 360 System*. Accession Nos. 133-147. *J. Appl. Cryst.* **6**, 309-346.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891-1898.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321-324.
- DOEDENS, R. J. & IBERS, J. A. (1967). *Inorg. Chem.* **6**, 204-210.
- FISH, R. H., KUIVILA, H. G. & TYMINSKY, I. J. (1967). *J. Am. Chem. Soc.* **89**, 5861-5868.
- HANESSIAN, S., BENNANI, Y. L. & LÉGER, R. (1990). *Acta Cryst.* **C46**, 701-703.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175-3187.