9 and azobenzenes **1**, **2**, and **4** suggests that isomerization of either olefin or azobenzene chromophore by a rotational path depends strongly on a solvent and resonance assisted lowering of the bond orders to reach transition states very close to **7b** or **8**,**9b**, respectively.

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Synthesis and Crystal Structure of the First Stannacyclopropene Derivative

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Recent interest in the chemistry of the Main Group carbene analogues, R_2M: (M = Si, Ge, Sn), has centered on the reactions of these species with carbon-carbon multiple bonds.[1] Herein, we describe the reaction of a diorganostannylene (R_2Sn:), **1** [R = bis(trimethylsilyl)methyl],[2] with an acetylene **2**[3] to provide the first known example of a stannacyclopropene **3** (Scheme I). Full characterization of **3**, including the crystal structure and ^{119}Sn NMR, reveals an unique thermal equilibrium among **1**, **2**, and **3** which occurs in solution above −16 °C, with **1** and **2** being favored at higher temperatures (Scheme I).

Synthesis of **3** (Scheme I). Silylenes (R_2Si:) and germylenes (R_2Ge:) have previously been shown to react with the cyclic acetylene **2** to form the corresponding silacyclopropenes and germacyclopropenes, respectively.[1e,f] Analogously, titration of a deep red equilibrium mixture of **1** and the distannene **4** in methylcyclohexane with 1.2 equiv of **2** at room temperature results in complete decolorization of the solution. Removal of the solvent and excess acetylene under reduced pressure quantitatively provides **3** as a pale yellow crystalline material which is subsequently recrystallized twice from methylcyclohexane at −40 °C.

Compound **3** exhibits physical properties that are fully consistent with the stannacyclopropene structure.[4] A $^{13}C\{^1H\}$ NMR (75 MHz, −25 °C, methylcyclohexane-d_{14}) δ (ppm from solvent reference peak at 34.6 ppm) displays a resonance at 163.9 ppm [$^1J(^{117/119}Sn-^{13}C) = 9.2$ Hz] which is assigned to the stannacyclopropene carbon atoms.[4] In addition, a $^{119}Sn\{^1H\}$ NMR (112 MHz, −25 °C, methylcyclohexane-d_{14}) δ (ppm from Me_4Sn, negative for upfield) shows a single resonance at −536.8 ppm which is more than 100 ppm upfield from the chemical shifts of the highly strained cyclotristannanes.[5] IR (Nujol) and Raman (solid, −60 °C) data show $\nu_{C=C}$ at 1587 cm^{-1} which first decreases in the IR and then disappears within 5 min after exposure to air.

Crystallographic Analysis of **3**.[4] As shown in Figure 1, the stannacyclopropene ring system of **3** forms an isosceles triangle with $Sn-C_{sp^2}$ bond lengths of 2.136 (5) and 2.134 (4) Å, respectively, which are comparable in length to $Sn-C_{sp^2}$ bond distances found in acyclic systems.[6] The C_1-C_2 bond length of 1.340 (6) Å is in agreement with the value found for the $C_{sp^2}-C_{sp^2}$ bond length in the analogous germacyclopropene derivative,[1c] while the exocyclic Sn-C bond lengths of 2.172 (4) Å and 2.181 (3) Å, respectively, are shorter than those found in tetrakis[bis(trimethylsilyl)methyl]distannene, **4** [2.207 (5) − 2.225 (6) Å].[2] Due to the absence of any close intermolecular distances between tin and sulfur, the difference in bond lengths between $S-C_4$ (1.849 (8) Å) and $S-C_5$ (1.776 (7) Å) may arise from crystal packing interactions.

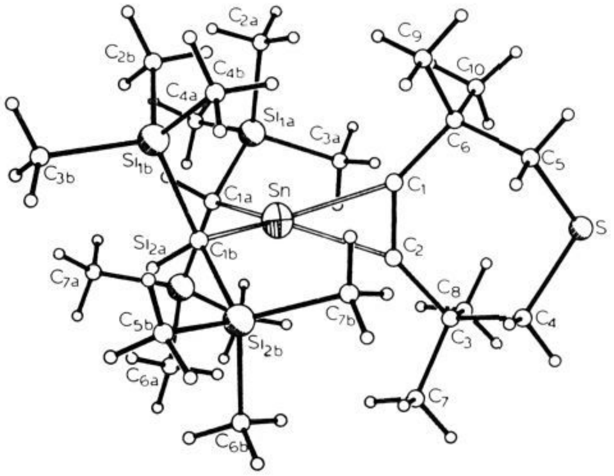
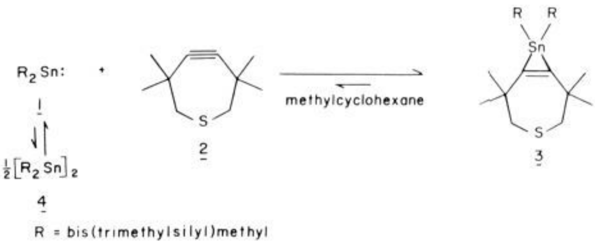


Figure 1. Crystal structure of **3**: bond lengths (Å) $Sn-C_1$ 2.136 (5), $Sn-C_2$ 2.134 (4), $Sn-C_{1a}$ 2.172 (4), $Sn-C_{1b}$ 2.181 (3), C_1-C_2 1.340 (6), C_4-S 1.849 (8), C_5-S 1.776 (7); bond angles (deg) C_1SnC_2 36.6 (2), SnC_1C_2 71.6 (3), SnC_2C_1 71.8 (3), C_1SnC_{1a} 124.0 (1), C_1SnC_{1b} 121.8 (2), C_2SnC_{1a} 121.6 (1), C_2SnC_{1b} 124.6 (1), $C_{1a}SnC_{1b}$ 110.1 (2).

Scheme I



An essential feature of the structure of **3** is the 355.9° and 356.3° sums for two sets of angles ($C_{1b}-Sn-C_{1a}$, C_1-Sn-C_{1b}, C_1-Sn-C_{1a} and $C_{1b}-Sn-C_{1a}$, C_2-Sn-C_{1b}, C_2-Sn-C_{1a}, respectively) at tin. Compared to the 328.5° value expected for an idealized tetrahedral configuration, the arrangement of C_{1a}, C_{1b}, and the midpoint of C_1-C_2 can best be considered nearly trigonal coplanar about the tin atom (the Sn atom and these other three atoms or points are coplanar to within 0.005 Å) which undoubtedly helps to minimize steric interactions between the bulky substituents. In addition, C_3 and C_6 are not coplanar with the plane of the stannacyclopropene ring but rather lie 0.024 Å below and 0.058 Å above it, respectively.

Properties of **3**. Besides being air- and moisture-sensitive in the solid state, **3**, in solution, is in rapid equilibrium above −16 °C with **1** (and presumably, to some extent, with **4**) and the free acetylene **2**.[7] Both the $^{119}Sn\{^1H\}$ NMR and $^{13}C\{^1H\}$ NMR of **3** show temperature dependency, with no resonance for the C_{sp^2} atoms being observed at 20 °C in the latter. Upon the addition of 1.3 equiv of **2** to a solution of **3** (c = 0.069 M, methylcyclohexane), a dynamic exchange between free and complexed acetylene is observed by ^{1}H NMR at 20 °C (the coalescence

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[1] (a) Seyferth, D.; Annarelli, D. C.; Duncan, D. P. *Organometallics* **1982**, *1*, 1288. (b) Schriewer, M.; Neumann, W. P. *J. Am. Chem. Soc.* **1983**, *105*, 897. (c) Marx, R.; Neumann, W. P.; Hillner, K. *Tetrahedron Lett.* **1984**, *25*, 625. (d) Ando, W.; Fujita, M.; Yoshida, H.; Sekiguchi, A. *J. Am. Chem. Soc.* **1988**, *110*, 3310. (e) Egorov, M. P.; Kolesnikov, S. P.; Struchkov, Yu. T.; Antipin, M. Yu.; Sereda, S. V.; Nefedov, O. M. *J. Organomet. Chem.* **1985**, *290*, C27. (f) Krebs, A.; Berndt, J. *Tetrahedron Lett.* **1983**, *24*, 4083.

[2] Goldberg, D. E.; Hitchcock, P. B.; Lappert, M. F.; Thomas, K. M.; Thorne, A. J.; Fjeldberg, T.; Haaland, A.; Schilling, B. E. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2387 and earlier work cited therein.

[3] Krebs, A.; Wilke, J. *Top. Curr. Chem.* **1983**, *109*, 189.

[4] Detailed information is supplied in the Supplementary Material.

[5] Cf. (a) δ −416.5 for hexakis(2,6-diethylphenyl)cyclotristannane [Masamune, S.; Sita, L. R.; Williams, D. J. *J. Am. Chem. Soc.* **1983**, *105*, 630] and (b) δ −378.9 for hexakis(2,4,6-triisopropylphenyl)cyclotristannane [Masamune, S.; Sita, L. R. *J. Am. Chem. Soc.* **1985**, *107*, 6390].

[6] Cf. (a) 2.15 (4) Å for triphenylvinyltin [Theobald, F.; Trimaille, B. *J. Organomet. Chem.* **1984**, *267*, 143] and (b) 2.08 (3) Å for 1,1,1-trichloroacetatotrivinyltin [Calogero, S.; Clmente, D. A.; Peruzzo, V.; Tagliavini, G. *J. Chem. Soc., Dalton Trans.* **1979**, *7*, 1172].

[7] This behavior is reminiscent of the thermal equilibrium reported between a cyclotristannane and a distannene, see ref 5b.

temperature) by a broad resonance at 2.65 ppm, which separates into two resonances (2.69 ppm and 2.55 ppm) at −16 °C and sharpens to a single resonance (2.64 ppm) at 40 °C. Photolysis of **3** in methylcyclohexane at −196 °C (glass matrix) and −78 °C to 25 °C (solution) using a Hanovia high-pressure lamp (quartz) produced no apparent change as monitored by ^{1}H NMR at the corresponding temperatures (−78 °C and 25 °C, respectively).

We believe the model that best describes bonding interactions in **3** is, at least at −25 °C, that of a π-complex, a formulation which has been developed for three-membered ring Main Group heterocycles.[8,9] Further experimental and theoretical investigations are currently underway to probe this model for stannacyclopropenes.

Acknowledgment. We thank Kimberly Orsborn for her assistance in preparing **2**, Dr. Robert Donohoe for collection of the Raman data, Dr. Cynthia Day of Crystalytics Co. for the structural analysis of **3**, and CMU for a Faculty Development Grant.

Supplementary Material Available: Detailed information concerning the spectral data and crystallographic analysis of **3**, including listings of atomic coordinates and temperature factors, bond lengths, bond angles, anisotropic temperature factors, and an ORTEP representation of **3** (11 pages). Ordering information is given on any current masthead page.

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[8] (a) Dewar, M. J. S. *Bull. Soc. Chim.* **1951**, *18*, C71. (b) Hoffmann, R.; Fujimoto, H.; Swenson, J. R.; Wan, C.-C. *J. Am. Chem. Soc.* **1973**, *95*, 7044. (c) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 783. (d) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800.

[9] This model is, in essence, identical with that for the Dewar–Chatt–Duncanson description of transition-metal olefin and acetylene complexes, see: (a) Dewar, M. J. S. *Bull. Soc. Chim.* **1951**, *18*, C79. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.

A New Strategy for 1,4- and 1,4,7-Polycarbonyl Compounds

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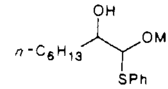
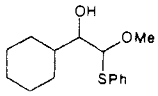
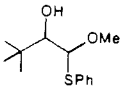
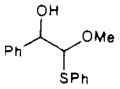
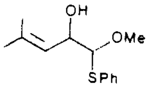
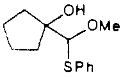
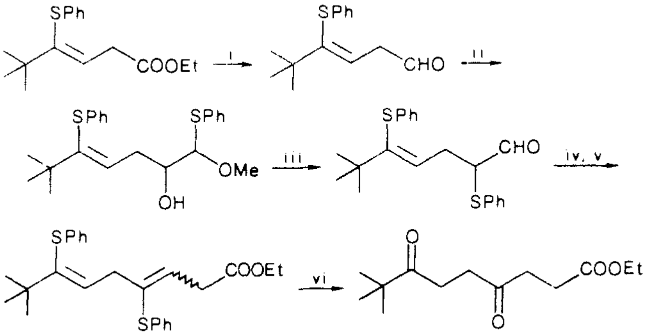
1,4-Dicarbonyl compounds constitute key intermediates in various natural product syntheses, and a number of methodologies for their syntheses have appeared.[1] Now we report a conceptually new strategy based on the successive C_1 and C_2 homologation of an aldehyde which can be extended to the synthesis of 1,4,7-tricarbonyl compounds.

Table I. Synthesis of α-Phenylthioaldehydes **3**[a]

entry	**2**	$MeSO_2Cl$ (equiv)	Et_3N (equiv)	reactn time, h	**3** yield,[b] %
1		1.5	1.5	12	83
2		1.3	1.3	12	79
3		1.8	1.8	12	88
4		1.3	1.3	0.25[c]	77
5		1.3	1.3	1[c]	71
6		3.3	3.3	24	88

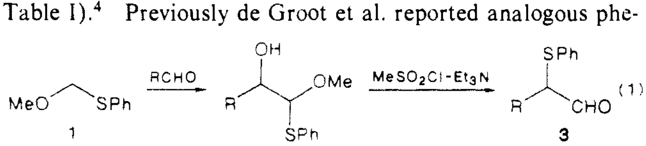
[a] Reaction conditions: in benzene at 20 °C unless otherwise noted. [b] Isolated yields after column chromatography. All compounds gave satisfactory NMR, IR, and HRMS spectral data. [c] In benzene–hexane (4:1) at 0 °C.

Scheme I[a]



[a] (i) DIBAH (1.0 equiv), toluene, −78 °C, 15 min; (ii) MeO(PhS)-CHLi (3 equiv), THF, −78 to −40 °C, 1 h, 51% through i and ii; (iii) $MeSO_2Cl$ (1.5 equiv)–Et_3N (1.5 equiv), benzene, 0 °C, 1 h, 68%; (iv) **6a** (2.0 equiv), THF, 50 °C, 12 h; (v) *t*-BuOK (1.6 equiv), THF, −78 °C, 30 min, 75% through iv and v; (vi) CF_3COOH–H_2O (4:1), 20 °C, 10 h, 100%.

In the course of the studies on synthetic applications of methoxy(phenylthio)methane (**1**),[2] we have found that exposure of the carbonyl adducts **2**[3] to methanesulfonyl chloride–triethylamine provides α-sulfenyl aldehydes **3** in good yields (eq 1, Table I).[4] Previously de Groot et al. reported analogous phenylthio migration reaction with thionyl chloride–pyridine which,



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[1] Reviews: Ellison, R. A. *Synthesis* **1973**, 397. Ho, T.-L. *Synth. Commun.* **1974**, *4*, 265. Rio, G.; Lecas-Nawracka, A. *Bull. Soc. Chim. Fr.* **1976**, 317. 1,4-Addition of acyl anion or its equivalent to α,β-unsaturated systems: Corey, E. J.; Hegedus, L. S. *J. Am. Chem. Soc.* **1969**, *91*, 4926. Seyferth, D.; Hui, R. C. *J. Am. Chem. Soc.* **1985**, *107*, 4551. Shono, T.; Nishiguchi, I.; Ohmizu, H. *J. Am. Chem. Soc.* **1977**, *99*, 7396. Scheffold, R.; Orlinski, R. *J. Am. Chem. Soc.* **1983**, *105*, 7200. Mukaiyama, T.; Narasaka, K.; Furusato, M. *J. Am. Chem. Soc.* **1972**, *94*, 8641. Stork, G.; Maldonado, L. *J. Am. Chem. Soc.* **1974**, *96*, 5272. Albright, J. D. *Tetrahedron* **1983**, *39*, 3207. Groebel, B.-T.; Seebach, D. *Synthesis* **1977**, 357. Stetter, H. *Angew. Chem.* **1976**, *88*, 695. Krief, A. *Tetrahedron* **1980**, *36*, 2531. Acylation of homoenolate anions: Kondo, K.; Tunemoto, D. *Tetrahedron Lett.* **1975**, 1397. Ponaras, A. A. *Tetrahedron Lett.* **1976**, 3015. Hosomi, A.; Hashimoto, H.; Sakurai, H. *J. Org. Chem.* **1978**, *43*, 2551. Ryu, I.; Matsumoto, K.; Ando, M.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1980**, *21*, 4283. Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1984**, *106*, 3368. Coupling of acyl and β-oxo radicals: Wehrli, P.; Chu, V. *J. Org. Chem.* **1973**, *38*, 3436. Cerfontain, H.; van Noort, P. C. M. *Synthesis* **1980**, 490. Coupling of enolates: Crombie, L.; Harper, S. H. *J. Chem. Soc.* **1952**, 869. Miyashita, M.; Yanami, T.; Yoshikoshi, A. *J. Am. Chem. Soc.* **1976**, *98*, 4679. Kosugi, M.; Takano, I.; Sakurai, M.; Sano, H.; Migita, T. *Chem. Lett.* **1984**, 1221. Rathke, M. W.; Lindert, A. *J. Am. Chem. Soc.* **1971**, *93*, 4605. Ito, Y.; Konoike, T.; Harada, T.; Saegusa, T. *J. Am. Chem. Soc.* **1977**, *99*, 1487. For other methods: Werstiuk, N. H. *Tetrahedron* **1983**, *39*, 205.

[2] For the previous study of this series: Sato, T.; Okura, S.; Otera, J.; Nozaki, H. *Tetrahedron Lett.* **1987**, *28*, 6299. For a review: Otera, J. *Synthesis* **1988**, 95.

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