Desilylative Chlorostannation of Silylmethyl-Substituted Cyclopropanes by SnCl₄ To Give 3-Butenyltrichlorostannanes. An Entry to Homoallylmetal Compounds

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Summary: Electrophilic ring opening of silylmethyl-substituted cyclopropanes **2** with SnCl₄ takes place in a highly regioselective manner to afford good yields of homoallyltrichlorostannanes **4**.

The notable nucleophilic reactivity of oxy-substituted cyclopropanes 1 toward electrophiles, which results in ring opening,[1] may be contrasted with that of the parent cyclopropanes with alkyl substituents which show relatively low reactivity toward electrofiles.[2] During the course of our studies on the reactions of 1 with metal salts,[3] we have observed that the cyclopropane ring opening by metal salts is markedly affected by the substitution of a silyl group as R in 1 for the usual alkyl (methyl or ethyl) group.[4] This observation led us to expect that silylmethyl-substituted cyclopropanes 2[5] should be susceptible to electrophilic ring opening by metal salts. If such a reaction does proceed, it would serve as a new and useful entry to homoallylmetal compounds 3.[5] Herein we report a first example of such a reaction sequence leading to a homoallylic trichlorostannane, 3 (M = SnCl₃), which involves the reaction of 2 with SnCl₄.[6]
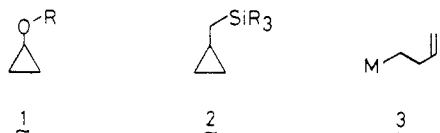
In a typical procedure, to ((trimethylsilyl)methyl)-cyclopropane (2a) (3 mmol) in dichloromethane (3 mL) was added tin tetrachloride (3 mmol) at 0 °C under an atmosphere of dry nitrogen. On the addition of SnCl₄, a slightly exothermic reaction took place. The solution was stirred at 15 °C for 1 h. After removal of the solvent and Me₃SiCl, the residual colorless oil was purified by bulb-to-bulb

Table I. Conversion of (Silylmethyl)cyclopropanes 2 to 3-Butenylstannanes 4[a]

substrate 2[b]	temp, time (°C, h)	product 4 yield (%)	bp (°C (mmHg)) ¹H NMR(Sn–CHₙ–)[c]
△_/SiMe₃ **2a**	15, 1	Cl₃Sn⌒∖∖ **4a**[d] (87)	98 (3) 2.47(2H, t, J = 6 Hz) J_{H–Sn} = 84 Hz
△⟨_/SiMe₃ **2b**	15, 1	Cl₃Sn⌒∖⟨ **4b** (90)	100 (2) 2.59(2H, br s) J_{H–Sn} = 82 Hz
∖△_/SiMe₃ **2c**[e]	15, 1	Cl₃Sn⌒⟨∖ **4c**[f] (84)	56 (0.7)[g] 2.49(2H, d, J = 6.5 Hz) J_{H–Sn} = 80 Hz
⬡△_/SiMe₃ **2d**	15, 4	Cl₃Sn⌒⬡∖ **4d** (84)	150–155 (2)[g] 2.59(2H, s) J_{H–Sn} = 82 Hz
C₇H₁₅∖△_/SiMe₃ **2e**[h]	25, 6	Cl₃Sn⌒⟨∖ C₇H₁₅ **4e** (91)	150–155 (2) 2.46(1H, dd, J = 10,12 Hz)[i] 2.53(1H, dd, J = 5,12 Hz) J_{H–Sn} = 83 Hz
Me₃Si∖△_/SiMe₃ **2f**[j]	25, 6	Cl₃Sn⌒⟨∖ SiMe₃ **4f**[k] (87)	110–120 (3)[g] 2.28(1H, dd, J = 7,10 Hz) [l]
Me₂PhSi∖△_/SiMe₃ **2g**[j]	25, 16	Cl₃Sn⌒⟨∖ SiPhMe₂ **4g** (89)	150–156 (2)[g] 2.38(1H, dd, J = 7,7 Hz) [l]

[a] Reactions were carried out on 1–3 mmol scale (see text). [b] **2a–g** were prepared from allylic silanes and zinc carbenoid reagents (CH₂I₂–Zn(Cu) and/or CH₂I₂–ZnEt₂). See supplementary material. [c] δ values (reference, Me₄Si; solvent, CDCl₃) obtained from 100-MHz NMR spectra. Values of J_{H–Sn} coupling constants are obtained from measured average for ¹¹⁹Sn and ¹¹⁷Sn. [d] Anal. Calcd for C₄H₇SnCl₃: C, 17.15; H, 2.52. Found: C, 17.16; H, 2.39. [e] A mixture of E and Z isomers (E/Z = 8/2, by GLC). [f] Anal. Calcd for C₅H₉SnCl₃: C, 20.41; H, 3.08. Found: C, 20.51; H, 3.17. [g] Bath temperatures. [h] A mixture of E and Z isomers (E/Z = 85/15, by GLC). [i] Resolved by using 360 MHz (CDCl₃). [j] E isomer. [k] Anal. Calcd for C₇H₁₅SiSnCl₃: C, 23.86; H, 4.29. Found: C, 23.82; H, 4.33. [l] Satellites due to H–Sn were not well-recognized.

distillation to give 3-butenyltrichlorostannane (4a) (bath temperature 98 °C (3 mmHg)) in 87% yield.
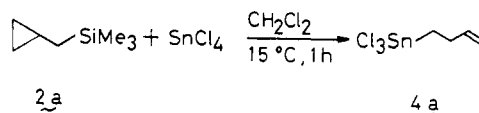
Substituted cyclopropanes required prolonged reaction times (see Table I). The reactions were clean, and yields were generally high. Further reaction of 4a with 2a leading to bishomoallylic products did not take place on prolonged reaction times (25 °C, 1 day).

Interestingly, ring cleavage occurred with complete selectivity at the methylene carbon in the case of alkyl-substituted cyclopropanes 2b–e to produce homoallyltrichlorostannanes 4b–e, respectively. This reaction course may be understood in terms of site-selective attack by SnCl₄ at the sterically less hindered site (as depicted 5), followed by formation of a cation stabilized by hyperconjugative interaction with the adjacent carbon–silicon bond. Ring opening then leads to 4 and Me₃SiCl.

A noteworthy feature of this stannylation reaction is the unexpected mode of site selectivity observed in the

(1) For reviews, see: (a) Gibson, D. H.; DePuy, C. H. *Chem. Rev.* **1974**, *74*, 605. (b) Wenkert, E. *Acc. Chem. Res.* **1980**, *13*, 27. (c) Murai, S.; Ryu, I.; Sonoda, N. *J. Organomet. Chem.* **1983**, *250*, 121.

(2) Recent reports of electrophilic cyclopropane ring opening. For mercuration: (a) Collum, D. B.; Mohamadi, F.; Hallock, J. S. *J. Am. Chem. Soc.* **1983**, *105*, 6882. (b) Bloodworth, A. J.; Chan, K. H.; Cooksey, C. J. *J. Org. Chem.* **1986**, *51*, 2110. For bromination: (c) Lambert, J. B.; Shulz, W. J., Jr.; Mueller, P. H.; Kobayashi, K. *J. Am. Chem. Soc.* **1984**, *106*, 792.

(3) Electrophilic ring opening of 1 (R = Me₃Si) with metal salts provides a useful entry to β-metallo ketones, see a review: Ryu, I.; Sonoda, N. *J. Synth. Chem. Jpn.* **1985**, *43*, 112; *Chem. Abstr.* **1985**, *102*, 166796p.

(4) Ryu, I.; Murai, S.; Sonoda, N. *Chem. Lett.* **1976**, 1049.

(5) Behavior of 2 toward some electrophiles. Sulfonation and acylation, see: (a) Dubois, M. G.; Pillot, J.-P.; Dunoguès, J.; Duffaut, N.; Calas, R. *J. Organomet. Chem.* **1977**, *124*, 135. (b) Dubois, M. G.; Dunoguès, J.; Calas, R. *Can. J. Chem.* **1981**, *59*, 802. (c) Dubois, M. G.; Dunoguès, J. *J. Organomet. Chem.* **1986**, *309*, 35. Halogenation, see: (d) Dubois, M. G.; Dunoguès, J.; Calas, R. *J. Chem. Res., Synop.* **1979**, 6; *J. Chem. Res. Miniprint* **1979**, 379. Protonation, see: (e) Fleming, I. unpublished results. (Noted in a review: p 783 in Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761.)

(6) Related β-stannyl ketone synthesis via 1 (R = Me₃Si) and SnCl₄, see: Ryu, I.; Murai, S.; Sonoda, N. *J. Org. Chem.* **1986**, *51*, 2389.

cleavage of silyl-substituted cyclopropanes 2f and 2g.[7] These reactions afforded 4f and 4g, respectively, in which the trichlorostannyl group was introduced onto the carbon atom bearing the silyl group.[8] Apparently, the silicon atom attached directly to the ring carbon seems to have enhanced the partial rate of electrophilic displacement at the carbon relative to that at the methylene carbon. Such an α effect of silicon has not been reported so far, to the best of our knowledge.[9]

The reactivity of the thus obtained homoallyltrichlorostannanes 4 was studied. Treatment of 4a and 4f with MeMgI/THF afforded trimethylstannyl homoallylic derivatives 6a (92%) and 6f (90%).[10] The latter was easily converted to (1-silyl-3-butenyl)lithium upon treatment with *n*-BuLi/THF. Bromination of 4a afforded the dibromo adduct 7, in which the C–Sn bond remained intact.[11]

5   6a (R = H)   7
         6f (R = SiMe3)
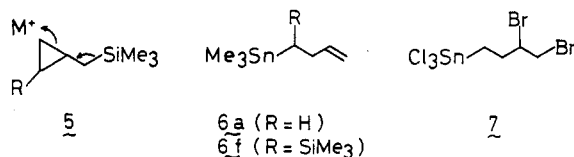
In summary, a new and facile ring opening reaction of the (silylmethyl)cyclopropane 2 by SnCl$_4$ has been discovered. Two distinct activating roles of the organosilicon moiety, i.e., the promotion of the ring cleavage of cyclopropanes toward electrophilic attack (β effect) and the control of the regiochemistry of the cleavage (α effect), also were demonstrated. Further extentions to other homoallylmetal synthesis are now underway.[12]

Supplementary Material Available: A listing of IR (ν(C= C)) ^{1}H and ^{13}C NMR spectral data for the products 4a–g (4 pages). Ordering information is given on any current masthead page.

(7) Cf. Acylation and sulfonation of 2f, see: ref 5a and 5c.

(8) The regioisomeric purity of each product (for 4c–g) is ~100% by ^{13}C NMR criteria. See supplementary material.

(9) Although mechanistically not related, a formally similar type of α cleavage has been observed in the nucleophilic ring opening of α,β-epoxysilanes, see: Colvin, E. *Silicon in Organic Synthesis*; Butterworth: London, 1981; Chapter 8.

(10) 6a has been previously prepared by the reaction of 3-butenylmagnesium chloride with trimethylstannyl chloride. Facile destannylative cyclization of 6a has been observed in the reaction with some electrophiles, see: Peterson, D. J.; Robbins, M. D. *Tetrahedron Lett.* 1972, 2135. Peterson, D. J.; Robbins, M. D.; Hansen, J. R. *J. Organomet. Chem.* 1974, 73, 237.

(11) Cyclopropylmethyl bromide was not formed. Cf. ref 10.

(12) This simple stratagem for homoallylic compounds proved eminently successful for some other Lewis acids. For instance, 2a reacted with SbCl$_3$ in CH$_2$Cl$_2$ relatively slowly (15 °C, 1 day) to give 1-butenyldichlorostibine. 2a also reacted with haloboranes immediately at the ambient temperature. Details will be published in the due course.

Book Reviews

Supported Metal Complexes, a New Generation of Catalysts. By F. R. Hartley. D. Reidel, Boston. 1985. 318 pp. $59.00.

Catalysis is traditionally classified into homogeneous catalysis (molecular catalysis in solution) and heterogeneous catalysis (usually occurring on the surface of a solid). Some important examples defy this simple classification, such as catalysis by enzymes and by molecular structures chemically anchored to solids. The latter is the subject of this book. Transition-metal complex catalysts bonded to solid polymers and metal oxides are isolated in a separate phase, simplifying their separation from fluid-phase products of the catalytic reaction and minimizing corrosion. These supported molecular catalysts have been tailor made to incorporate, for example, coordinatively unsaturated metal centers, chiral complexes, and multicenter catalytic sites. Ultimately, they may rival the enzymes in their subtlety and efficiency, and they offer tantalizing prospects of industrial application. So far, however, the only significant applications are of metal oxide supported complexes of Ti, Zr, and Cr for α-olefin polymerization.

This book is a valuable, thoroughly referenced account and a useful introduction to the field, including summaries of catalyst preparation and characterization and detailed descriptions categorized by catalytic reaction types. The differences between soluble catalysts and their anchored analogues are well-recognized. The writing reflects an organometallic chemist's view and does not strongly represent the surface chemistry of oxide supports. Structures on oxides are too often taken uncritically from the literature; organometallic chemistry on these surfaces is more subtle and less well-defined than the book suggests. This reviewer would also have liked to see more depth in the assessment of the polymerization catalysts and a more critical evaluation of the barriers to applications of supported metal complex catalysts,

involving such issues as catalyst stability and deactivation.
B. C. Gates, *University of Delaware*

Inorganic Syntheses. Volume 24. Jean'ne M. Shreeve, Editor-in-Chief. Wiley, New York. 1986. xxii + 391 pages.

The newest volume of this tried and true series brings many synthetic procedures that will be of interest and utility to readers of this journal: (CF$_3$)$_2$Hg, (CF$_3$)$_2$Cd·DME, Ph$_3$PF$_2$, EtB(OH)$_2$, (Et$_2$B)$_2$O and (Et$_3$BO)$_3$, (Me$_3$SiCH$_2$)$_3$In, (Me$_3$SiCH$_2$)$_3$Al, (Me$_3$SiCH$_2$)$_2$AlBr, Me$_3$SiCH$_2$Li, CpTl, Si(NCO)$_4$, Ph$_3$P=CCl$_2$, Ph(Me$_3$Si)C=PCl, Ph$_3$P=C=PPh$_3$ (Me$_3$Si)$_2$C=P(Cl)=C-(SiMe$_3$)$_2$, (Me$_3$SiNMe)$_2$CO, (H$_3$Si)$_2$Se, CH$_3$HgY (Y = NO$_3$, O$_2$C-CF$_3$, I), Cp$_2$M(CO)$_2$ (M = Ti, Zr, Hf) (and the C$_5$Me$_5$ analogues), Na$_2$[Fe(CO)$_4$], Na$_2$[Fe$_2$(CO)$_8$], and Na$_3$[Fe$_3$(CO)$_{11}$], [CpFe(CO)$_3$] [CF$_3$SO$_3$], CpFe(CO)$_2$(CH=CMe$_2$), Et$_4$N [HRu$_3$(CO)$_{11}$], CpFe-(diphos)Br and CpFe(diphos)MgBr, {(1,5-COD)(C$_5$H$_5$N)[(c-C$_6$H$_{11}$)$_3$P]Ir}PF$_6$, Ru(η^2-CH$_2$=CHCO$_2$Me)(CO)$_4$, MoCl$_3$·3THF, Pt(η^2-C$_2$H$_4$)(PR$_3$)$_2$, and Au(CO)Cl. The book, of course, contains much more: syntheses of many fluorine-containing compounds (not unexpected, in view of the editor's research area), a section on organic superconducting solids, diverse transition-metal compounds and complexes including TiCl$_2$, phenylimido complexes of tungsten and rhenium, lithium insertion compounds of vanadium and rhenium, and dinitrogen complexes of Fe(II). Finally, there is a long chapter on trifluoromethanesulfonates (triflates).

There really is not much that one can say about a new *Inorganic Syntheses* volume. These books always are welcome additions to our bookshelves. The syntheses, which are described in detail, have been checked, so one may expect that they are repeatable. One can only hope that these volumes will keep coming and that inorganic chemists will continue to take part in this labor of love: