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Cyclopropanation and epoxidation of 1,2-distannylalkenes and 1-silyl-2-stannylalkenes

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Abstract

Cyclopropanation of the title compounds is possible under certain conditions (CH_2I_2–Sm (Hg)) in special cases, but epoxidation is apparently a general reaction which occurs readily in a stereospecific manner when they are treated with *m*-chloroperbenzoic acid.

Keywords: Tin; Silicon; Cyclopropanation; Epoxidation

1. Introduction

Palladium-catalysed addition reactions between hexamethylditin or trimethyl (trimethylsilyl) stannane lead to the corresponding *Z*-distannylalkenes and *Z*-1-silyl-2-stannylalkenes [1]:

$$Me_3SnEMe_3 + R'C\equiv CH \xrightarrow{[Pd]} Z\text{-}Me_3SnCR'{=}CHER_3$$

(where E = Si or Sn)

The presence of two functional groups with different reactivities offers various possibilities for functionalization by replacement of the stannyl and silyl groups by organic residues. In addition, the double bond itself can undergo modification, e.g. by hydrogenation with diimine [2]. We felt that it would be of interest to look at further typical reactions of double bonds in these compounds, and this paper reports our initial results on cyclopropanation and epoxidation.

2. Results and discussion

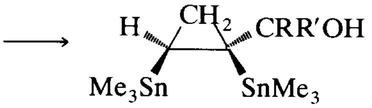
2.1. Cyclopropanation

While the Hine method of cyclopropanation (chloroform plus a strong base) is not suitable for application to vinyltins, a number of alternatives have been described in the literature. In our hands, the Seyferth et al. [3] method using $PhHgCBr_3$, the diazoester method (N_2CHCO_2Et–Cu) [4] and the Simmons–Smith method (CH_2I_2–(Zn–Cu)) [5] did not lead to the formation of cyclopropanes.

The Molander–Etter method [6] in which the zinc-copper couple is replaced by amalgamated samarium is only applicable to allylic alcohols, and has been used by Lautens and Delanghe [7] for the cyclopropanation of vinylsilanes and vinylstannanes; the diastereoselectivity was found to be very high. We thus attempted to apply this method to appropriate distannylalkenes and silylstannylalkenes:

$$Z\text{-}Me_3SnCH{=}C(SnMe_3)CRR'OH + CH_2I_2\text{–}Sm(Hg)$$

1a, R = R′ = H
1b, R = H, R′ = Me
1c, R = R′ = Me



2a
2b

$$Z\text{-}Me_3SiCH{=}C(SnMe_3)CRR'OH + CH_2I_2\text{–}Sm(Hg)$$

3a, R = R′ = H
3b, R = H, R′ = Me
3c, R = R′ = Me

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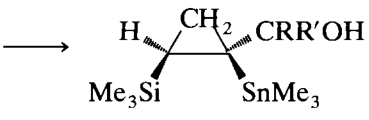


4a
4b

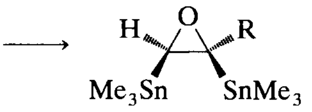
While compounds **1a** and **3a** were completely consumed and the novel cyclopropanes **2a** and **4a** thus formed isolated with yields of 64% and 68% respectively, the consumption of **1b** and **3b** was only 26% and 40% respectively (only one diastereomer was detected) Compounds **1c** and **3c** did not react under the conditions used. The products **2a**, **2b** and **4a**, **4b** were identified by multinuclear NMR spectroscopy, spectral data are reported in Table 1. In **2a** and **2b** the tin-tin coupling constants (the sum of three- and four-bond components) were 281 Hz and 289 Hz respectively, while in **4a** and **4b** the corresponding tin-silicon coupling constants were 26 Hz and 28 Hz respectively. The proton and carbon data were as expected for three-membered rings; in the case of the tin-carbon coupling constants we have labelled the long-range constants as if there were only a single-path coupling present, although this is not strictly correct.

2.2. Epoxidation

Since the use of *m*-chloroperbenzoic acid (*m*-CPBA) for the epoxidation of vinyltins has already been described [8], we attempted to extend its use to include 1,2-distannylalkenes and 1-silyl-2-stannylalkenes:

Z-Me$_3$SnCH=C(SnMe$_3$)R + *m*-CPBA

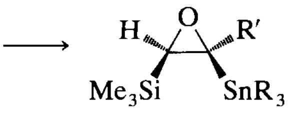
1a, R = CH$_2$OH
1b, R = CHMeOH
1c, R = CMe$_2$OH
1d, R = H
1e, R = Ph
1f, R = CH$_2$OMe



5a
5b
5c
5d
5e
5f

Z-Me$_3$SiCH=C(SnR$_3$)R′ + *m*-CPBA

3d, R = Me, R′ = Ph
3e, R = Me, R′ = CMe$_2$OH
3f, R = Bu, R′ = Ph
3g, R = Bu, R′ = CH$_2$OMe



6d
6e
6f
6g

Use of an excess (1.5–2.5 equivalents) of the peracid led to a very clean reaction in all cases studied; KF was used to remove excess peracid as well as the *m*-chlorobenzoic acid formed. The presence of tributylstannyl residues **3f** rather than trimethylstannyl residues **3g** provided no problems. Only one isomer was formed in each case (except for the reaction of **1b** to give **5b**, which led to a 1 : 1 mixture of diastereomers because of the chiral centre already present in the starting material) and to check the stereochemistry of the reaction three E-1,2-distannylalkenes (R = H (**7a**); Ph (**7b**); CH$_2$OMe (**7e**)) obtained by UV-catalysed isomerization of the *Z*-alkenes [1] were also allowed to react. Again the reaction was stereospecific, and multinuclear

Table 1
Selected NMR data for distannylcyclopropanes **2a,2b** and Silylstannylcyclopropanes **4a,4b** of the type Me$_3$MC^{1}H$_X$C^{2}C(SnMe$_3$)-(C^{4}HROH)C^{3}H$_A$H$_B$ (M = Sn (**2a,2b**) or Si (**4a,4b**))

Compound	δ(Sn) (ppm) [*J*(Sn,Sn) (Hz)]	δ(Si) (ppm) [*J*(Si,Sn) (Hz)]	δ(C(1)) (ppm) [^1J(M,C(1)) (Hz); ^2J(Sn,C(1)) (Hz)]	δ(C(2)) (ppm) [^1J(Sn,C(2)) (Hz); ^2J(M,C(2)) (Hz)]	δ(C(3)) (ppm) [^2J(Sn,C(3)) (Hz); ^2J(M,C(3)) (Hz)]	δ(C(4)) (ppm) [^2J(Sn,C(4)) (Hz)]	δ(H$_A$) (ppm) [^2J(H$_A$H$_B$) (Hz)]	δ(H$_B$)	δ(H$_X$) [^3J(H$_A$H$_X$) (Hz); ^3J(H$_B$H$_X$) (Hz)]
2a	1.0, 12.6 [281]		7.6 [503; 14]	17.5 [519; ND]	11.3 [20; 10]	76.4 [20]	0.53 [3.6]	0.61	−0.14 [6.9; 9.8]
2b	−1.0, 6.3 [289]		8.3 [498; 13]	23.1 [519; ND]	11.1 [20; 10]	80.7 [22]	0.50 [3.9]	0.68	−0.08 [6.9; 10.1]
4a	9.7	1.2 [26]	11.0 [69; 13]	17.9 [509; ND]	10.7 [10; ND]	76.5 [18]	0.44 [3.6]	0.54	−0.47 [6.9; 10.2]
4b	3.1	1.2 [28]	8.3 [ND; 9]	23.1 [ND; ND]	10.4 [12; ND]	76.8 [33]	0.39 [3.6]	0.70	−0.29 [7.2; 10.2]

ND, not determined.

NMR spectroscopy as well as mass spectra confirmed the structure of all the epoxides prepared. NMR data are reported in Table 2. The tin–tin coupling constant was found to vary between 33 Hz (R = Ph) and 75 Hz (R = H) in compounds **5e–5f** but was much lower in the products **8a** derived from **7a** (25 Hz), **8b** from **7b** (18 Hz) and **8c** from **7c** (16 Hz) thus confirming the stereospecificity of the epoxidation reaction and the geometry of the products. The tin–silicon coupling is as expected about an order of magnitude smaller. In the case of the tin–carbon coupling constants we have as above labelled the long-range constants as if there were only a single-path coupling present. The "three-bond" couplings appear to be extremely insensitive to the dihedral angle (0° or 180°)

3. Experimental details

All manipulations involving organotin compounds were carried out in an argon atmosphere. NMR measurements were carried out at room temperature in the PFT mode using a Bruker AM-300 spectrometer operating at 300 MHz for ^{1}H, 75.43 MHz for ^{13}C, 59.60 MHz for ^{29}Si and 111.93 MHz for ^{119}Sn. $CDCl_3$ was used as solvent (solute concentration about 30% by volume for heteronuclei; maximum 5% for ^{1}H) and internal lock (for ^{13}C in addition as internal standard set at 77.0 ppm) Me_4Si and Me_4Sn were employed as external standards for ^{1}H, ^{29}Si and ^{119}Sn respectively.

3.1. Cyclopropanation

Samarium powder (3.0 g, 20 mmol) was dried using the flame of a Bunsen burner and treated with $HgCl_2$ (0.54 g, 2 mmol) and dry tetrahydrofuran (THF) (8.5 ml); the mixture was stirred for 10 min at room temperature. The alkene (2 mmol) in THF (8.5 ml) was added and the mixture cooled to −78°C. Methylene iodide (5.3 g, 20 mmol) was added dropwise within 10 min, the solution turning deep blue-green (SmI_2) After 4 h the reaction mixture was allowed to warm to

Table 2

Selected NMR data for distannyloxiranes **5a–5f**, **7a–7c** and silylstannyloxiranes **6d–6g** of the type $Me_3MC^1HOC^2CR(SnMe_3)$ (M≡Sn (**5a–5f**,**7a–7c**), Si (**6d–6g**))

Compound	δ(Sn) (ppm) [J(Sn,Sn) (Hz)]	δ(Si) (ppm) [J(Si,Sn) (Hz)]	δ(C(1)) (ppm) [^1J(M,C(1)) (Hz); ^2J(Sn,C(1)) (Hz)]	δ(C(2)) (ppm) [^1J(Sn,C(2)) (Hz); ^2J(M,C(2)) (Hz)]	δ(C^R [a]) (ppm) [^2J(Sn,C^R) (Hz)]	δ(H) (ppm) [^2J(Sn,H) (Hz); ^3J(Sn,H) (Hz)]
5a	−11.6, −20.6 [53]		55.1 [483; 20]	62.7 [509, ND]	71.3 [64]	2.74 [26.8; 103.6]
5b^{I} [b]	−14.8, −21.4 [57]		55.2 [483; 20]	68.2 [512; ND]	79.6 [46]	2.42 [27.0; ND]
5b^{II} [b]	−9.2, −20.7 [55]		52.8 [484; 20]	64.5 [502; ND]	69.9 [76]	2.86 [27; ND]
5c	−11.5, −22.2 [61]		54.4 [483; 23]	69.3 [532; ND]	73.9 [58]	2.79 [28.0; ND]
5d	−18.5 [75]		51.2 [506; ND]	51.2 [506; ND]		2.73 [ND]
5e	−3.9, −24.3 [33]		63.0 [470; 22]	62.5 [519; ND]	147.6 [53]	2.62 [24.2; 108.2]
5f	−10.6, −21.5 [49]		55.6 [491; 20]	60.9 [521; ND]	82.7 [51]	2.54 [24.2; 97.8]
7a	−8.0 [25]		48.7 [477; 14]	48.7 [477; 14]		2.58 [34.0; 124.0]
7b	5.5, −18.5 [18]		58.8 [473; ND]	61.1 [481; 15]	145.1 [51]	2.96 [23.6; 117.4]
7c	−5.4, −17.1 [16]		52.4 [465; ND]	60.9 [491; 18]	79.6 [53]	2.64 [27.8; 109.0]
6d	−7.4	−1.0 [4.4]	67.8 [67; 15]	70.6 [504]	155.1 [50]	2.18 [20.4]
6e	−18.3	−1.0 [7.2]	52.7 [69; 18]	70.2 [521]	73.8 [58]	2.40 [23.6]
6f	−26.1	−1.1 [3.3]	60.3 [69; 14]	64.0 [409]	148.8 [46]	2.11 [19.0]
6g	−29.7	−1.0 [4.4]	54.6 [69; 13]	61.4 [417]	83.2 [46]	1.97 [17.8]

ND, not determined.

[a] C^R denotes the carbon atom of the group R which is closest to tin.

[b] **5b** contains a chiral centre, so that two stereoisomers are formed.

room temperature and poured onto 20 ml of a saturated solution of potassium carbonate; it turned brown and vigorous gas evolution was observed. After extraction with ether (3 × 20 ml) and separation the combined organic phases were washed with saturated brine and dried over $MgSO_4$. Ether and THF were removed at the water pump and the residue subjected to Kugelrohr distillation in vacuo.

Compound **2a** (boiling point (b.p.) 100°C at 0.001 Torr) was obtained as a clear liquid with a 64% yield. Mass spectroscopy (MS) (80 eV): *m/e* 383 (8%, $M^+ -$ Me); 345 (29%); 329 (7%, $Me_6Sn_2^+$); 219 (10%); 203 (41%, $C_3H_3SnMe_3^+$); 165 (100%, $SnMe_3^+$); 150 (47%, $SnMe_2^+$); 135 (62%, $SnMe^+$); 120 (7%, Sn^+); 53 (11%, $C_4H_5^+$)

Compound **2b** was present to the extent of 26% in the distillate (b.p., 120°C at 0.001 Torr) together with 74% of the starting material **1b**.

Compound **4a** (b.p., 85°C at 0.001 Torr) was obtained after two Kugelrohr distillations as a clear liquid with a 68% yield.

Compound **4b** was present to the extent of 40% in the light-yellow distillate (b.p., 100°C at 0.01 Torr) together with 60% of the starting material **3b**.

3.2. Epoxidation

A solution of the alkene (7.5 mmol) in $CHCl_3$ (3 ml) was cooled to −20°C and treated within 20 min with an excess (1.5–2.5 equivalents) of *m*-CPBA dissolved in $CHCl_3$ (15–25 ml) After 2 h the mixture was treated with an excess (2.5–4.5 equivalents) of KF and stirred for 2 h at room temperature. The KF complexes were removed by filtration using a bed of $MgSO_4$; the filter cake was washed with a large amount of $CHCl_3$. The solvent was subsequently removed in vacuo, leaving the products as colourless or light-yellow viscous oils which were characterized by elemental analysis, multinuclear NMR spectroscopy and additionally in the following cases by mass spectrometry.

The relative amounts of alkene : *m*-CPBA: KF used were as follows: **5a**, 1 : 1.5 : 2.5; **5b**, 1 : 2 : 3.5; **5c**, 1 : 1.5 : 2.5; **5d**, 1 : 2 : 3.5; **5e**, 1 : 2.5 : 4.5; **5f**, 1 : 1.5 : 2.5; **6d**, 1 : 2 : 3.5; **6e**, 1 : 2.5 : 4.5; **6f**, 1 : 2.5 : 4.5; **6g**, 1 : 1.8 : 3.4; **7a**, 1 : 2 : 3.5; **7b**, 1 : 2.5 : 4.5; **7c**, 1 : 2 : 3.5.

5a: MS: *m/e* 355 (11%, $M^+ -$ Me); 329 (7%, $Me_6Sn_2^+$); 299 (17%, $Me_4Sn_2^+$); 191 (11%, C_2H_2-$SnMe_3^+$); 165 (100%, $SnMe_3^+$); 150 (23%, $SnMe_2^+$); 135 (51%, $SnMe^+$); 120 (12%, Sn^+)

5b: MS: *m/e* 399 (1%, $M^+ -$ Me); 369 (1%, $M^+ -$ Me); 369 (1%, $M^+ -$ CHMeOH); 345 (29%); 329 (9%, Me_6Sn2^+); 219 (10%); 203 (41%, $C_3H_3SnMe_3^+$); 165 (100%, $SnMe_3^+$); 150 (34%, $SnMe_2^+$); 135 (53%, $SnMe^+$); 120 (15%, Sn^+)

5c: MS: *m/e* 397 (3%, $M^+ - 2$ Me); 329 (9%, $Me_6Sn_2^+$); 165 (100%, $SnMe_3^+$); 150 (41%, $SnMe_2^+$); 135 (27%, $SnMe^+$); 120 (4%, Sn^+)

6d: MS: *m/e* 356 (11%, M^+); 341 (12%, $M^+ -$ Me); 239 (80%, Me_6SiSn^+); 165 (75%, $SnMe_3^+$); 135 (28%, $SnMe^+$); 120 (8%, Sn^+); 91 (14%, C_7H_7); 84 (100%); 73 (71%, $SiMe_3^+$); 59 (7%, $SiMe_2^+$)

6e: MS: 323 (0.3%, M^+); 305 (3%, $M^+ -$ Me − H_2O); 239 (46%, Me_6SiSn^+); 165 (86%, $SnMe_3^+$); 135 (40%, $SnMe^+$); 73 (100%, $SiMe_3^+$); 59 (92%, $SiMe_2^+$); 45 (60%, $SiMe^+$)

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References

[1] T.N. Mitchell, A. Amamria, H. Killing and D. Rutschow, *J. Organomet. Chem., 304* (1986) 257; T.N. Mitchell, R. Wickenkamp, A. Amamria, R. Dicke and U. Schneider, *J. Org. Chem., 52* (1987) 4868; L. Chenard, E.D. Laganis, F. Davidson and T.V. Rajan Babu, *J. Org. Chem., 50* (1985) 366; L. Chenard and C.M. Van Zyl, *J. Org. Chem., 51* (1986) 3561.

[2] T.N. Mitchell and B. Kowall, *J. Organomet. Chem., 481* (1994) 137.

[3] D. Seyferth, J.M. Burlitch, R.J. Minasz, J.Y.-P.Mui, H.D. Simmons, A.J.H. Treiber and S.R. Dowd, *J. Am. Chem. Soc., 87* (1965) 4259.

[4] F. Ebel, R. Brunner and P. Mangelli, *Helv. Chim. Acta, 12* (1929) 19.

[5] E. LeGoff, *J. Org. Chem., 29* (1964) 2048.

[6] G.A. Molander and J.B. Etter, *J. Org. Chem., 52* (1987) 3942; G.A. Molander and L.S. Harring, *J. Org. Chem., 54* (1989) 3525.

[7] M. Lautens and P.H.M. Delanghe, *J. Org. Chem., 57* (1992) 798.

[8] G. Ayrey, J.R. Parsonage and R.C. Poller, *J. Organomet. Chem., 56* (1973) 193; J.M. Chong and E.K. Mar, *J. Org. Chem., 57* (1992) 46.