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Note

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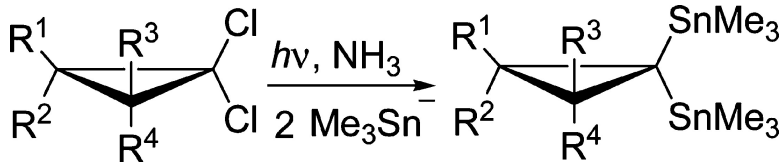

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Synthesis of 1,1-Bis(trimethylstannyl)cyclopropanes by the $S_{RN}1$ Mechanism

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Summary: The reactions of readily available 1,1-dichlorocyclopropanes, obtained by addition of dichlorocarbene to alkenes, with Me_3Sn^- anions are reported. The process is described in terms of a photoinduced $S_{RN}1$ substitution. The 1,1-bis(trimethylstannyl)cyclopropanes were obtained in good to excellent isolated yield (71−90%); 7,7-dichloro-2-oxa-bicyclo[4.1.0]heptane gave the 1,1-bis(trimethylstannyl) product in only 40% yield.

The preparation of substituted cyclopropyl rings has been a subject of considerable efforts in the last 40 years. Due to their easy conversion to useful reactive intermediates, tin-substituted cyclopropanes are an important family of compounds of established application in organic synthesis. Even though 1,2-bis(trialkylstannyl)cyclopropanes are known,[1] their 1,1-analogues are less explored with regard to their preparation, properties, and applications in organic synthesis.[2]

The unimolecular radical nucleophilic substitution, or $S_{RN}1$, reaction is an alternate process by which a nucleophilic substitution is achieved. Since the scope of this process has been increased considerably over the last decades, nowadays it serves as an important synthetic strategy.[3] The wide variety of nucleophiles that can be used, the great functional group tolerance, and the fact that many carbon−carbon and carbon−heteroatom bonds can be formed make the $S_{RN}1$ reaction a powerful synthetic tool.

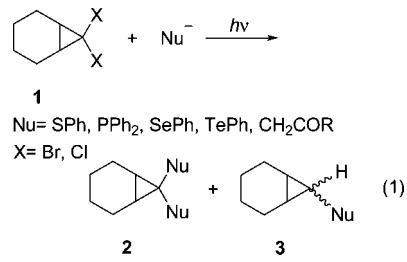
We have described the photostimulated reactions of Me_3SnNa, prepared in liquid ammonia through the reaction of chlorotrimethylstannane with Na metal,[4] with several substrates, such as chloroarenes[5] and haloadamantanes[6] that afford stannanes in very good to excellent yields, in reactions that occur by the $S_{RN}1$ mechanism, an alternative to the usual Grignard or organolithium route to stannanes.

Table 1. Photoinduced Reactions of 1,1-Dichloro-2,2-diphenylcyclopropane (4) with Me_3Sn^- Anion

entry[a]	reaction time (min)	Cl^- (%)[b]	substrate **4** recovered	products (yield, %)[c]
1	60	90	11%	**5** (58%), **6** (8%), **7** (trace)
2	120	97	2%	**5** (86%), **6** (11%), **7** (trace)
3[d]	60	9	74%	**5** (trace), **6** (trace), **7** (20%)
4[e]	60	52	trace	**5** (20%), **6** (trace), **7** (75%)
5[f]	60	36	65%	**5** (25%)

[a] All experiments were performed in liquid ammonia using 2.2 equiv of Me_3Sn^- anions with irradiation with two HPI-T 400 W lamps (cooled with air and water). [b] Chloride ions were determined potentiometrically considering two chlorines per mole of substrate. [c] Yields were determined by ^1H NMR with the internal standard method. [d] Reaction performed in the dark. [e] 20 mol % of 1,4-dinitrobenzene was added. [f] One equiv of Me_3Sn^- anion was used.

A few examples of the reactions of 1,1-dihalocyclopropanes, mainly of 1,1-dihalonorcarane **1**, with sulfur, phosphorus, and ketone enolate anions have been studied previously. Of interest were their mechanistic aspects as well as their applications in the preparation of substituted cyclopropanes. These reactions afforded low to moderate yields of disubstituted products **2** together with monosubstituted reduced compound **3** (eq 1).[3a] Such reactions have not been carried out with Me_3Sn^- anions.



The reaction of alkenes with dihalocarbenes by the phase transfer catalysis route serves excellently for the synthesis of 1,1-dichlorocyclopropanes.[7] This led us to study their reactions with Me_3Sn^- anions as a route for the preparation of new 1,1-bis(trimethylstannyl)cyclopropanes by the $S_{RN}1$ mechanism.

The reaction of 1,1-dichloro-2,2-diphenylcyclopropane (**4**) with Me_3SnNa under photostimulation in liquid ammonia for 1 h afforded the disubstituted product 1,1-bis(trimethylstannyl)-2,2-diphenylcyclopropane (**5**) in 58% yield together with unreacted substrate (11%) and the monosubstituted reduced compound **6** (8%) and a trace amount of the monoreduced product **7** (entry 1 in Table 1). When the reaction time

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(1) For a review of the synthesis and applications of cyclopropylstannanes, see: Rubina, M.; Gevorgyan, V. *Tetrahedron* **2004**, *60*, 3129, and references therein.

(2) As far as we know there is only one report of the synthesis of their 1,1-analogues, such as 7,7-bis(trimethylstannyl)norcarane; see: Seyferth, D.; Lambert, R. L., Jr. *J. Organomet. Chem.* **1975**, *88*, 287.

(3) For reviews, see: (a) Rossi, R. A.; Pierini, A. B.; Peñéñory, A. B. *Chem. Rev.* **2003**, *103*, 71–167. (b) Rossi, R. A.; Pierini, A. B.; Santiago, A. N. In *Organic Reactions*; Paquette, L. A., Bittman, R., Eds.; Wiley & Sons: New York, 1999; pp 1−271. (c) Rossi, R. A. In *Synthetic Organic Photochemistry*; Griesberck, A. G., Mattay, J., Eds.; Marcel Dekker: New York, 2005; Vol. 12, Chapter 15, pp 495−527.

(4) Kraus, C. A.; Sessions, W. *J. Am. Chem. Soc.* **1925**, *47*, 2361.

(5) (a) Yammal, C. C.; Podestá, J. C.; Rossi, R. A. *J. Org. Chem.* **1992**, *57*, 5720. (b) Córsico, E. F.; Rossi, R. A. *Synlett* **2000**, 227. (c) Santiago, A. N.; Basso, S. M.; Montañez, J. P.; Rossi, R. A. *J. Phys. Org. Chem.* **2006**, *19*, 829. (d) Bardagi, J. I.; Rossi, R. A. *J. Org. Chem.* **2008**, *73*, 4491.

(6) (a) Santiago, A. N.; Stahl, A. E.; Rodriguez, G. L.; Rossi, R. A. *J. Org. Chem.* **1997**, *62*, 4406. (b) Santiago, A. N.; Toledo, C. A.; Rossi, R. A. *J. Org. Chem.* **2002**, *67*, 2494.

(7) For reviews on the preparation and synthetic applications of dihalogenocyclopropanes, see: (a) Halton, B.; Harvey. J. *Synlett* **2006**, 1975. (b) Banwell, M. G.; Beck, D. A. S.; Stanislawski, P. C.; Sydnes, M. O.; Taylor, R. M. *Curr. Org. Chem.* **2005**, *9*, 1589. (c) Fedorynski, M. *Chem. Rev.* **2003**, *103*, 1099, and references therein.

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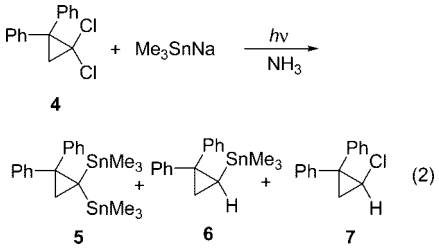
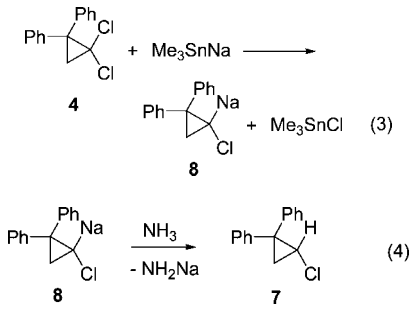
doubled to 2 h, a high yield of **5** (86%) was obtained (entry 2 in Table 1) (eq 2). In a preparative scale reaction carried out under identical conditions product **5** was isolated in 72% yield. The reaction proceeded in the dark only sluggishly, yielding the reduced compound **7** as the main product (20%, entry 3 in Table 1).



A photoinduced reaction performed in the presence 20 mol % of 1,4-dinitrobenzene, a good inhibitor of the $S_{RN}1$ reaction, gave a high yield of **7** and the disubstituted product **5** in only 20% yield (entry 4 in Table 1). The fact that **5** is not produced under dark conditions confirms that it is formed by the $S_{RN}1$ mechanism. Product **7** is formed by halogen−metal exchange reaction of the substrate with Me_3SnNa (eq 3).[8] The compound **8** formed is protonated very fast by liquid ammonia (eq 4). This is supported by the fact that compound **7** is the main product when the reaction conditions do not favor the $S_{RN}1$ process (absence of light or in the presence of an inhibitor, entries 3 and 4 in Table 1).

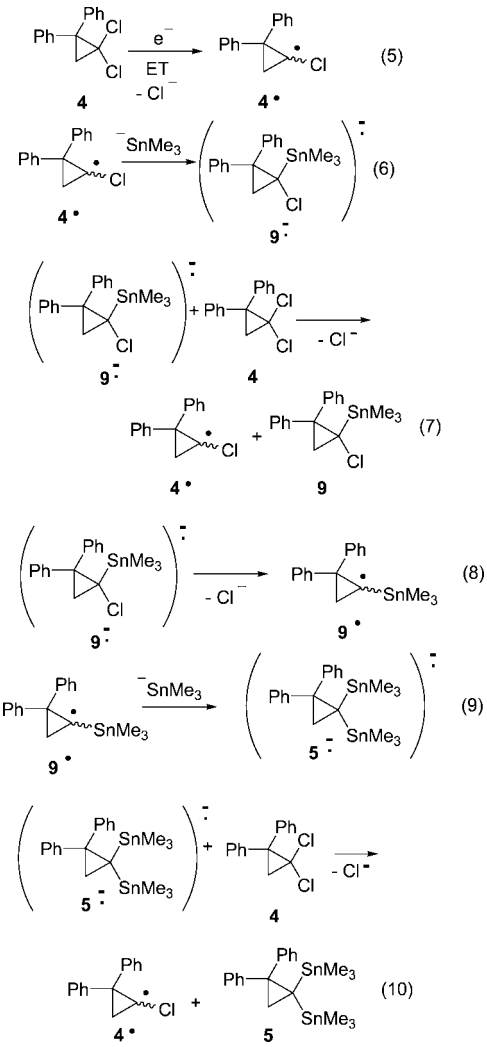


In the reactions of **4** with 1 equiv of the nucleophile, **5** was the only product formed (entry 5 in Table 1), and 65% of unreacted **4** was recovered. This result shows that the monosubstitution product with retention of chlorine **9** is not an intermediate in the formation of disubstitution product **5** because it is not formed in these experimental conditions.

In the experiments we noted that disubstituted product **5** is formed in higher yields if the neat substrate **4** is added to the reaction flask under irradiation while the system is being irradiated. When **4** is added neat prior to irradiation or as a solution in dry ether, the main product of the reactions was the monosubstituted reduced compound **6**. These observations suggested the operation of a very fast halogen−metal exchange mechanism (eqs 3 and 4) in conditions that do not favor the ET mechanism.

In view of the results discussed above the mechanism sketched in eqs 5−10 can be proposed.

Photoinduced ET to the substrate forms radical **4**• and Cl^- ions by an electron transfer (ET) reaction and fragmentation of the C−Cl bond, which is the first step of the chain propagation cycle (eq 5). After stannyl anion addition to radical **4**• the



generated radical anion **9**•− (eq 6) is unstable and fragments into the corresponding tertiary radical **9**• and chloride anion (eq 8). The fact that compound **9** is not formed even when 1 equiv of the nucleophile was employed suggests that the fragmentation of the radical anion **9**•− is faster than the intermolecular electron transfer to dichloride **4** (eq 7).

Radical **9**• couples with the nucleophile, yielding the disubstituted product radical anion **5**•− (eq 9), which by electron transfer to **4** closes the propagation steps of the chain reaction.

To test the scope of the reaction, 1,1-dichlorocyclopropanes **10-S**−**17-S**, prepared from the corresponding alkenes, were used as substrates in the photoinduced $S_{RN}1$ reaction with Me_3Sn^- anions as nucleophile (Table 2).

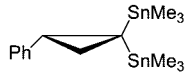
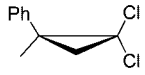
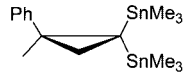
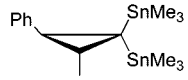
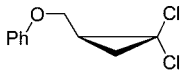
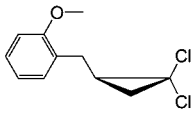
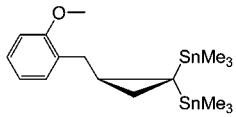
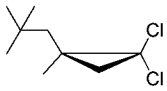
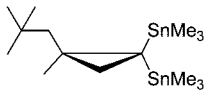
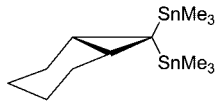
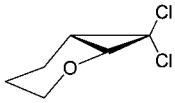
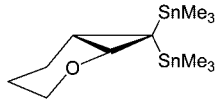
In summary, we have demonstrated that 1,1-dichlorocyclopropanes react under irradiation with Me_3Sn^- anions in liquid ammonia to give 1,1-bis(trimethylstannyl)cyclopropanes in good to excellent isolated yield.

Experimental Section

Photostimulated Reactions of 1,1-Dichlorociclopropanes with $^-SnMe_3$ Anions in Liquid Ammonia. The following procedure is representative of all these reactions. Ammonia (150 mL), previously dried over Na metal, was distilled into a 250 mL three-neck round-bottomed flask equipped with a coldfinger condenser at −78 °C and a magnetic stirrer under a nitrogen atmosphere. To ammonia was added Me_3SnCl (2.2 equiv, 219 mg) and then Na metal in small pieces. The addition of Na metal continued until the blue solution from solvated electrons in excess remained for 10 min.

(8) It has been demonstrated before that when the halogen−metal exchange is faster than the $S_{RN}1$ mechanism, the anion formed is protonated very rapidly by liquid ammonia; see ref 5a.

Table 2. Reactions of Me_3Sn^- Anions with 1,1-Dichlorocyclopropanes[a]

Entry	Substrate	Product (% yield) [b]	(Cl^-) [c]
1	**4**	**5** (72)	96
2	 **10-S**	 **10-P** (71)	90
3	 **11-S**	 **11-P** (82)	98
4	 **12-S**	 **12-P** (83)	**95**
5	 **13-S**	 **13-P** (72)	100
6	 **14-S**	 **14-P** (78) (94)[d]	100
7	 **15-S**	 **15-P** (78)	93
8	 **16-S**	 **16-P** (90)	100
9	 **17-S**	 **17-P** (40)	100

[a] The reactions were performed in 150 mL of liquid ammonia with 1 equiv of substrates and 2.2 equiv of the nucleophile and irradiated with two HPI-T 400 W lamps (cooled with air and water) during 2 h. [b] Isolated product yields. [c] Chloride ions were determined potentiometrically considering two chlorines per mol of substrate. [d] Yield was determined by ^{1}H NMR with the internal standard method.

After the last addition, when no more solid was present, Me_3Sn^- anions were ready for use. The neat substrate 1,1-dichloro-2-phenylcyclopropane **10-S** (1 equiv, 93.5 mg) was added to the solution when the reaction flask was already being irradiated. The irradiation was continued for 2 h. The reaction was quenched with ammonium nitrate, and the ammonia was allowed to evaporate. Water was added to the residue and the mixture was extracted with CH_2Cl_2 (3 × 20 mL) and diethyl ether (2 × 20 mL) The organic extract was dried over anhydrous $MgSO_4$ and filtered, and the solvent was removed to leave the crude product as a light colored oil. The 1,1-bis(trimethylstannyl)cyclopropane (**10-P**) (158 mg, 71%) was isolated by radial thin-layer chromatography on silica gel (stabilized with 5% triethylamine) eluting with petroleum ether as a colorless oil. ^{1}H NMR (Cl_3CD): −0.25 (9H, s, $^2J_{HSn}$ = 52.16, 50.4 Hz, CH_3Sn), 0.15 (9H, s, $^2J_{HSn}$ = 51, 49.3 Hz, CH_3Sn), 1.23 (1H, dd, J_{HH} = 6.8, 4.3 Hz, CH_2), 1.40 (1H, t, J_{HH} = 4.3 Hz, CH_2), 2.36 (1H, dd, J = 6.8, 4.3 Hz, CH), 7.21 (5H, m, CH). ^{13}C NMR (Cl_3CD): −9.78 ($^1J_{CSn}$ = 324.6, 310.2 Hz, CH_3Sn), −8.49 ($^1J_{CSn}$ = 329.3, 315.3 Hz, CH_3Sn), 2.8 (C), 12.56 ($^2J_{CSn}$ = 27.1, 21.8 Hz, CH_2), 24.79 ($^2J_{CSn}$ = 20.8 Hz, CH),125.94 (CH), 128.15 (CH), 128.9 (CH), 143.5 (C). ^{119}Sn NMR (Cl_3CD): δ 20.3, 38,6. HR-MS (EI): calcd for $C_{14}H_{23}\,^{118}Sn^{120}Sn$ 428.9838, found $[M - CH_3]^+$ 428.9854. Anal. Calcd for $C_{15}H_{26}Sn_2$: C, 40.60; H, 5.91; Sn, 53.50. Found: C, 40.75; H, 5.95.

1,1-Bis(trimethylstannyl)-2,2-diphenylcyclopropane (5). Compound **5** was obtained according to the general procedure and recrystallized from ethanol as white crystals and isolated in 72% yield (155 mg). ^{1}H NMR (Cl_3CD): −0.22 (18H, s, $^2J_{HSn}$ = 50.9 Hz, CH_3Sn), 1.79 (2H, s, $^3J_{HSn}$ = 83.9, 56.8 Hz, CH_2), 7.13 (2H, m, CH), 7.23 (4H, t, J_{HH} = 7.5 Hz, CH), 7.48 (4H, d, J_{HH} = 7.5 Hz, CH). ^{13}C NMR (Cl_3CD): −7.84 ($^1J_{CSn}$ = 326.7, 312.8 Hz, CH_3Sn), 11.15 (C), 19.99 ($^2J_{CSn}$ = 26.3 Hz, CH_2), 40.85 (C), 126.31 (CH), 128.43 (CH), 129.54 (CH), 147.36 (C). ^{119}Sn NMR (Cl_3CD): 16. Mp: 128.4−129.9 °C. HR-MS (EI): calcd for $C_{20}H_{27}\,^{120}Sn_2$ 507.0151, found $[M - CH_3]^+$ 507.0146. Anal. Calcd for $C_{21}H_{30}Sn_2$: C, 48.52; H, 5.82; Sn, 45.67. Found: C, 48.35; H, 5.83.

1-Trimethylstannyl-2,2-diphenylcyclopropane (6). Compound **6** was obtained from the photoinduced reaction for 120 min (entry 2 in Table 1) and purified by radial thin-layer chromatography on silica gel eluting with petroleum ether as a colorless oil. ^{1}H NMR (Cl_3CD): −0.21 (9H, s, $^2J_{HSn}$ = 54.2, 51.9 Hz, CH_3Sn), 1.06 (1H, dd, J_{HH} = 10.4, 7.8 Hz, CH), 1.42 (1H, dd, J_{HH} = 10.4, 3.9 Hz, CH_2), 1.51 (1H, J_{HH} = 7.8, 3.9, Hz, CH_2), 7.21 (10H, m, CH). ^{13}C NMR (Cl_3CD): −9.96 ($^1J_{CSn}$ = 346.8, 331.6 Hz, CH_3Sn), 15.13 (CH), 19.64 ($^2J_{CSn}$ = 20.9 Hz, CH_2), 33.85 (C), 125.36 (CH), 126.38 (CH), 127.10 (CH), 128.03 (CH), 128.32 (CH), 130.34 (CH), 145.01 (C), 148.04 (C). ^{119}Sn NMR (Cl_3CD): 0.1. HR-MS (EI): calcd for $C_{17}H_{19}\,^{120}Sn_2$ 343.0503, found $[M - CH_3]^+$ 343.0508.

1,1-Bis(trimethylstannyl)-2-methyl-2-phenylcyclopropane (11-P). The compound **11-P** (166 mg, 82%) was obtained according to the general procedure and isolated by radial thin-layer chromatography on silica gel eluting with petroleum ether as a colorless oil. ^{1}H NMR (Cl_3CD): −0.37 (9H, s, $^2J_{HSn}$ = 51.6, 49.5 Hz, CH_3Sn), 0.17 (9H, s, $^2J_{HSn}$ = 51.2, 48.6 Hz, CH_3Sn), 1.12 (1H, d, J_{HH} = 3.8, $^3J_{HSn}$ = 82.7, 56.8 Hz, CH_2), 1.42 (1H, d, J_{HH} = 3.8, $^3J_{HSn}$ = 83.4, 56.7 Hz, CH_2), 1.44 (3H, s, CH_3), 7.15 (1H, m, CH), 7.25 (4H, m, CH). ^{13}C NMR (Cl_3CD): −8.31($^1J_{CSn}$ = 325.9, 311.4 Hz, CH_3Sn), −6.74 ($^1J_{CSn}$ = 321.3, 306.1 Hz, CH_3Sn), 10.09 (C), 21.4 ($^2J_{CSn}$ = 29, 25.9 Hz, CH_2), 30.98 (C), 31.39 ($^3J_{CSn}$ = 45.2, 16.3 Hz, CH_3), 126.0 (CH), 128.41 (CH), 128.98 (CH), 148.59 (C). ^{119}Sn NMR (Cl3CD): δ 15.7, 17.1. HR-MS (EI): calcd for $C_{15}H_{25}\,^{120}Sn_2$ 444.9995, found $[M - CH_3]^+$ 445.0006. Anal. Calcd for $C_{16}H_{28}Sn_2$: C, 41.98; H, 6.16; Sn, 51.86. Found: C, 42.22; H, 6.14.

***trans*-1,1-Bis(trimethylstannyl)-2-methyl-3-phenylcyclopropane (12-P).** Compound **12-P** was obtained according to the general procedure and purified by radial thin-layer chromatography on silica gel eluting with petroleum ether as a colorless oil in 83% yield (234 mg). ^{1}H NMR (Cl_3CD): −0.26 (9H, s, $^2J_{HSn}$ = 51.7, 49.7 Hz, CH_3Sn), 0.15 (9H, s, $^2J_{HSn}$ = 51, 49 Hz, CH_3Sn), 1.30 (3H, d, J_{HH} = 5.9 Hz, CH_3), 1.76 (1H, dq, J_{HH} = 5.9 Hz, $^{trans}J_{HH}$ = 4.3 Hz, CH), 2.17 (1H, d, $^{trans}J$ = 4.3 Hz, $^3J_{HSn}$ = 76.5, 54.1 Hz, CH), 7.13 (3H, m, CH), 7.22 (2H, m, CH). ^{13}C NMR (Cl_3CD): −7.91 ($^1J_{CSn}$ = 326.4, 312.5 Hz, CH_3Sn), −7.12 ($^1J_{CSn}$ = 322.1, 308.1 Hz, CH_3Sn), 14.79 (C), 20.87 ($^2J_{CSn}$ = 26.9, 17.2 Hz, CH), 21.1 ($^3J_{CSn}$ = 22.9 Hz, CH_3), 33.69 ($^2J_{CSn}$ = 26.3, 20.2 Hz, CH), 125.83 (CH), 128.08 (CH), 128.62 (CH), 143.77 (C). ^{119}Sn NMR (Cl_3CD): 17, 20.3. HR-MS (EI): calcd for $C_{15}H_{25}\,^{120}Sn_2$ 444.9995, found [M −

$CH_3]^+$ 445.0005. Anal. Calcd for $C_{16}H_{28}Sn_2$: C, 41.98; H, 6.16; Sn, 51.86. Found: C, 41.90; H, 6.17.

1,1-Bis(trimethylstannyl)-2-(phenyloxymethyl)cyclopropane (13-P). Compound **13-P** was obtained according to the general procedure. The crude product was distilled under reduced pressure using a Kügelrohr apparatus and was isolated in 72% yield (95.1 mg) as a light colored oil. ^{1}H NMR (Cl_3CD): 0.07 (9H, s, $^2J_{HSn}$ = 51.4, 49.5 Hz, CH_3Sn), 0.1 (9H, s, $^2J_{HSn}$ = 52, 50 Hz, CH_3Sn), 0.82 (1H, t, J_{HH} = 4.0, $^3J_{HSn}$ = 79.5, 61.2 Hz, CH_2), 1.05 (1H, dd, J_{HH} = 6.8, 4.0 Hz, $^3J_{HSn}$ = 71.8, 52.5 Hz, CH_2), 1.6 (1H, qd, J_{HH} = 6.9, 3.7 Hz, CH), 3.72 (1H, dd, J_{HH} = 9.7, 7.3 Hz, CH_2), 4.01 (1H, ddt, J_{HH} = 9.7, 6.6, 2.2 Hz, CH_2), 6.89 (2H, m, CH), 6.95 (1H, m, CH), 7.29 (2H, m, CH). ^{13}C NMR (Cl_3CD): −9.81 ($^1J_{CSn}$ = 327.5, 314.1 Hz, CH_3Sn), −7.63 ($^1J_{CSn}$ = 327.5, 314.1 Hz, CH_3Sn), −4.56 (C), 12.87 ($^2J_{CSn}$ = 24.3 Hz, CH_2), 19.49 (CH), 73.36 ($^3J_{CSn}$ = 47.22, 24.3 Hz, CH_2), 114.5 (CH), 120.53 (CH), 129.42 (CH), 158.85 (C). ^{119}Sn NMR (Cl_3CD): 24.8, 39.8. HR-MS (EI): calcd for $C_{15}H_{25}{}^{120}Sn_2$ 460.9944, found $[M - CH_3]^+$ 460.9949.

1,1-Bis(trimethylstannyl)-2-(2-methoxybenzyl)cyclopropane (14-P). The compound **14-P** was obtained according to the general procedure. It was separated and isolated by radial thin-layer chromatography on silica gel eluting with petroleum ether as a colorless oil in 78% yield (39.4 mg). ^{1}H NMR (Cl_3CD): 0.03 (9H, s, $^2J_{HSn}$ = 51.4, 48.9 Hz, CH_3Sn), 0.06 (9H, s, $^2J_{HSn}$ = 51.4, 49.5 Hz, CH_3Sn), 0.75 (1H, t, J_{HH} = 3.8 Hz, $^3J_{HSn}$ = 79.2, 60.6 Hz, CH_2), 0.91 (1H, dd, J_{HH} = 6.9, 3.8 Hz, CH_2), 1.38 (1H, m, CH), 2.37 (1H, dd, $^{gem}J_{HH}$ = 15.1, J_{HH} = 8.3 Hz, CH_2), 2.88 (1H, dd, $^{gem}J_{HH}$ = 15.1, J_{HH} = 5.6 Hz, CH_2), 3.83 (3H, s, CH_3), 6.86 (1H, d, J_{HH} = 7.9 Hz, CH), 6.93 (1H, td, J_{HH} = 7.4, 0.9 Hz, CH) 7.20 (1H, td J_{HH} = 7.8, 1.6 Hz, CH), 7.31 (1H, dd, J_{HH} = 7.4, 1.4 Hz, CH). ^{13}C NMR (Cl_3CD): −9.8 ($^1J_{CSn}$ = 322.5, 307.7 Hz, CH_3Sn), −7.67 ($^1J_{CSn}$ = 322.8, 309.6 Hz, CH_3Sn), −1.82, 14.08 ($^2J_{CSn}$ = 26.9, 24.4 Hz, CH_2), 20.32 ($^2J_{CSn}$ = 23.5, 18.9 Hz, CH), 35.88 ($^3J_{CSn}$ = 45.5, 23.4 Hz, CH_2), 55.22 (CH_3), 110.03 (CH), 120.35 (CH), 126.95 (CH), 129.21 (CH), 130.67 (C), 157.23 (C). ^{119}Sn NMR (Cl_3CD): 22.6, 36.5. HR-MS (EI): calcd for $C_{16}H_{27}{}^{120}Sn_2$ 475.0100, found $[M - CH_3]^+$ 475.0110.

1,1-Bis(trimethylstannyl)-2-methyl-2-neopentylcyclopropane (15-P). Compound **15-P** was obtained according to the general procedure and purified by radial thin-layer chromatography on silica gel eluting with petroleum ether as a colorless oil in 78% yield (80.5 mg). ^{1}H NMR (Cl_3CD): 0.08 (18H, s, $^2J_{HSn}$ = 49,5 Hz, CH_3Sn), 0.83 (2H, m, CH_2), 0.97 (9H, s, CH_3), 1.18 (1H, d, J_{HH} = 13.9 Hz, CH_2), 1,23 (3H, s, CH_3), 1.54 (1H, d, J_{HH} = 13,9 Hz, CH_2). ^{13}C NMR (Cl_3CD): −6.25 ($^1J_{CSn}$ = 316.8, 302.4 Hz, CH_3Sn), −5.92 ($^1J_{CSn}$ = 318.5, 304.2 Hz, CH_3Sn), 11.63 (C), 23.85 ($^2J_{CSn}$ = 21 Hz, C), 24.28 ($^3J_{CSn}$ = 29 Hz, CH_2), 27.95 ($^3J_{CSn}$ = 47.7, 16.9 Hz, CH_3), 31.05 (CH_3), 32.56 (C), 55.62 ($^2J_{CSn}$ = 42.62, 14.6 Hz, CH_2). ^{119}Sn NMR (Cl_3CD): 10.9, 15.4. HR-MS (EI): calcd for $C_{14}H_{31}{}^{120}Sn_2$ 439.0464, found $[M - CH_3]^+$ 439.0471. Anal. Calcd for $C_{15}H_{34}Sn_2$: C, 39.87; H, 7.58; Sn, 52.54. Found: C, 40.02; H, 7.59.

7,7-Bis(trimethylstannyl)norcarane (16-P).[2,9] Compound **16-P** was obtained according to the general procedure and was purified by column chromatography on silica gel eluting with petroleum as a colorless oil and isolated in 90% (181 mg). ^{1}H NMR (Cl_3CD): 0 (9H, s, $^2J_{HSn}$ = 50.2, 48.2 Hz, CH_3Sn), 0.17 (9H, s, $^2J_{HSn}$ = 50.9, 48.6 Hz, CH_3Sn), 1.19 (2H, m, CH), 1.30 (4H, m, CH_2), 1.55 (2H, m, CH_2), 1.98 (2H, m, CH_2). ^{13}C NMR (Cl_3CD): −9.2 ($^1J_{CSn}$ = 316.6, 303.1 Hz, CH_3Sn), −5.85 ($^1J_{CSn}$ = 319.3, 304.4 Hz, CH_3Sn), 7.61 (C), 17.54 ($^2J_{CSn}$ = 24.2 Hz, CH), 21.13 (CH_2), 25.63 ($^3J_{CSn}$= 41.9, 32.5 Hz, CH_2). ^{119}Sn NMR (Cl_3CD): δ −1, 38.

7,7-Bis(trimethylstannyl)-2-oxa-bicyclo[4.1.0]heptane (17-P). Compound **17-P** was obtained according to the general procedure. The crude product was distilled under reduced pressure using a Kügelrohr apparatus, and the compound (**17-P**) was isolated in 40% yield (48.6 mg) as a light colored oil. ^{1}H NMR (Cl_3CD): 0 (9H, s, $^2J_{HSn}$ = 51.7, 49.6 Hz, CH_3Sn), 0.15 (9H, s, $^2J_{HSn}$ = 52.9, 50.7 Hz, CH_3Sn), 1.17 (1H, m, CH), 1.56 (3H, m, CH_2), 2.1 (1H, m, CH_2), 3.6 (3H, m, CH_2, CH). ^{13}C NMR (Cl_3CD): −9.49 ($^1J_{CSn}$ = 327.98, 313.16 Hz, CH_3Sn), −6.17 ($^1J_{CSn}$ = 333.33, 317.5 Hz, CH_3Sn), 8.73 (C), 17.94 ($^2J_{CSn}$ = 24.3 Hz, CH), 21.35 (CH_2), 22.59 ($^3J_{CSn}$ = 46.37, 36.02 Hz, CH_2), 57.52 ($^2J_{CSn}$ = 29.6 Hz, CH), 63.89 (CH_2). ^{119}Sn NMR (Cl3CD): −2.3, 26.4. HR-MS (EI): calcd for $C_{11}H_{23}O^{120}Sn_2$ 410.9787, found $[M - CH_3]^+$ 410.9796.

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Supporting Information Available: Experimental details, references for known compounds, complete characterization data of the compounds, and ^{1}H NMR and ^{13}C NMR spectra of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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