(8.3 g) was crystallized from boiling nitroethane to give 4.6 g of red crystals, mp 210–212 °C. TL chromatography on silica (toluene) showed a single spot. The 2,4-DNP (4.5 g) was treated with 120 mL of 20% aqueous $TiCl_3$ in 600 mL of 1,2-dimethoxyethane at reflux for 45 min under nitrogen.[10] The reaction mixture was cooled, diluted with water, and extracted with ether. The ether extract was washed with water, dried ($MgSO_4$), filtered, and concentrated to give 2.5 g of a dark yellow oil, which was placed on a column of silica gel (1 in. diameter × 6 in.) and eluted with a 1:1 mixture of ether/hexane. Concentration gave 1.5 g of nearly colorless **9a** (GC retention time 24.64 min): ^{13}C NMR ($CDCl_3$) δ 198.8, 148.5, 133.6, 131.5, 129.0, 127.2, 126.4, 40.4, 39.7, 33.6, 30.0, 25.2, 20.8.

Chromic Acid Oxidation of 3a and 3b to 9a and *trans*-1,2,3,4,4a,9,10,10a-Octahydrophenanthren-3-one (9b). A 2.5-g sample of $AlCl_3$-isomerized mixture prepared from **3a**/**3b** (96:4, Scheme I) and containing **3a**/**3b** (1:2.65) was oxidized with chromic acid as described above. The crude reaction product was Kugelrohr distilled to give 1.5 g of yellow oil, bp 110–140 °C (1.5 mm). This partially solidified on standing. The GC ratio of **9a**/**9b** was 1:2.3 at 24.69 and 25.82-min retention times. Two crystallizations from petroleum ether gave colorless crystals of **9b**: mp 92.5–93.5 °C (lit.[14] mp 95–96 °C); ^{13}C NMR ($CDCl_3$) δ 198.0, 147.1, 133.4, 132.4, 127.0, 126.2, 125.0, 46.5, 42.6, 40.5, 33.5, 29.6, 26.1, 25.4.

Pd/C Hydrogenation of 9b to 3b. A 1-g sample of **9b** in 50 mL of acetic acid containing 0.2 g of 10% Pd/C was hydrogenated at 50 psi and 40–45 °C. The filtered solution was concentrated, and the residue was dissolved in ether and washed with 10% $NaHCO_3$ and then water. The ether extract was dried ($MgSO_4$), filtered, and concentrated to a yellow oil, whih was distilled (Kugelrohr) to give 0.6 g of **3b** as a colorless oil: ^{13}C NMR $CDCl_3$) δ 140.1, 136.5, 128.7, 125.2, 125.1, 125.0, 43.6, 40.4, 34.2, 30.7, 30.5, 29.7, 26.8, 26.1.

Acknowledgment. The Oklahoma State University authors thank the National Institute for Petroleum and Energy Research, Bartlesville, OK 74005, and the Oklahoma State University Center for Energy Research for financial support.

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[14] Cook, J. W.; Hewett, C. L.; Lawrence, C. A. *J. Chem Soc.* **1936**, 71.

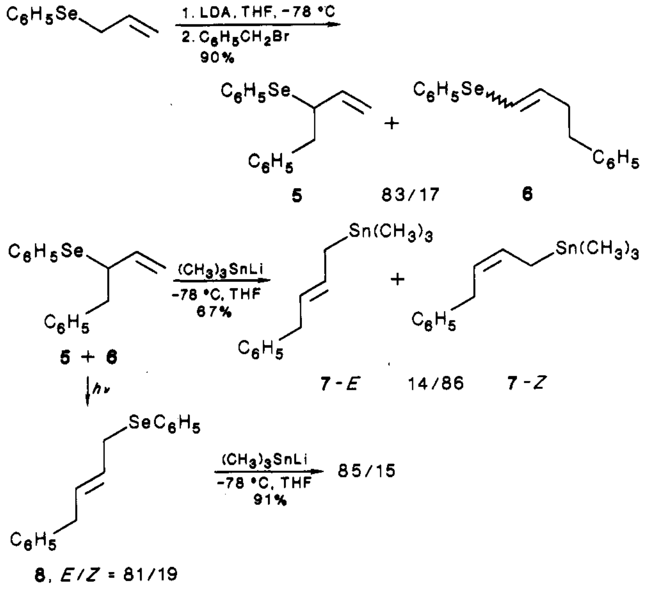
Communications

Organoselenium Chemistry.[1] Preparation of Allyl, Allenyl, and Propargyl Stannanes by Substitution of Phenylseleno with Trimethylstannyl

Summary: Allyl and otherwise activated phenylseleno groups are replaced by trimethylstannyl on reaction with (trimethylstannyl)lithium.

Sir: Organotin compounds have many applications in organic synthesis as mild anion equivalents.[2a] Important uses have been found in Lewis acid[2b] or palladium[2c] catalyzed condensations with electrophiles, free radical coupling reactions,[2d] and conversion to organolithium reagents by Li/Sn exchange.[3] While traditional methods for the formation of carbon–tin bonds such as the reaction of triorganostannyl lithium, magnesium, or copper reagents with alkyl halides and the reaction of lithium and Grignard reagents with triorganostannyl halides have served well for the preparation of simple tin compounds, they are not always effective for more complex systems.

Scheme I



We report here that allyl, benzyl, allenyl, and propargyl selenides, as well as selenoacetals and selenoketals, react with (trimethylstannyl)lithium at -78 °C to give trimethylstannyl compounds (Table I).[1b,4] The advantage of this procedure over most others is that the chemistry of α-lithioallyl (**1a,b**),[1a–d,7a] -benzyl (**2**)[1e,7b] -allenyl (**3**),[1f] and

---

[1] For previous papers on this series, see: (a) Reich, H. J.; Schroeder, M. C.; Reich, I. L. *Isr. J. Chem.* **1984**, *24*, 157. (b) Reich, H. J. *J. Org. Chem.* **1975**, *40*, 2570. (c) Reich, H. J.; Willis, W. W., Jr. *J. Org. Chem.* **1980**, *45*, 5227. (d) Reich, H. J.; Clark, M. C.; Willis, W. W., Jr. *J. Org. Chem.* **1982**, *47*, 1618. (e) Reich, H. J.; Chow, F.; Shah, S. K. *J. Am. Chem. Soc.* **1979**, *101*, 6638. (f) Reich, H. J.; Shah, S. K.; Gold, P. M.; Olson, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 3112. (g) Reich, H. J.; Yelm, K. E.; Reich, I. L. *J. Org. Chem.* **1984**, *49*, 3438.

[2] (a) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworth: London, 1987. (b) Naruta, Y. *J. Am. Chem. Soc.* **1980**, *102*, 3774. Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 555. Yamamoto, Y.; Marayuma, K. *Heterocycles* **1982**, *18*, 357. (c) Sheffy, F. K.; Godschalx, J. P.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4833. Keinan, E.; Peretz, M. *J. Org. Chem.* **1983**, *48*, 5302. (d) Keck, G. E.; Enholm, E. J.; Kachensky, D. F. *Tetrahedron Lett.* **1984**, *25*(18), 1867.

[3] Seyferth, D.; Weiner, M. A. *J. Org. Chem.* **1959**, *24*, 1395. Seyferth, D.; Weiner, M. A.; Vaughan, L. G.; Raab, G.; Welch, D. E.; Cohen, H. M.; Alleston, D. L. *Bull. Soc. Chim. Fr.* **1963**, 1364.

[4] There have been reports of the substitution of sulfides, sulfoxides, and sulfones with organometallic reagents[5] and under free-radical[6] conditions. An analogue to the present reaction is the formation of allylsilanes from allyl sulfides with an organomanganese reagent.[5a]

[5] (a) Fugami, K.; Oshima, K.; Utimoto, K.; Nozaki, H. *Tetrahedron Lett.* **1986**, *27*(19), 2161. (b) Masaki, Y.; Sakuma, K.; Kaji, K. *J. Chem. Soc., Chem. Commun.* **1980**, 434. Barsanti, P.; Calō, V.; Lopez, L.; Marchese, G.; Naso, F.; Pesce, G. *J. Chem. Soc., Chem. Commun.* **1978**, 1085. Gendreau, Y.; Normant, J. F.; Villieras, J. *J. Organomet. Chem.* **1977**, *142*, 1.

[6] (a) Ueno, Y.; Okawara, M. *J. Am. Chem. Soc.* **1979**, *101*, 1893. Ueno, Y.; Aoki, S.; Okawara, M. *J. Am. Chem. Soc.* **1979**, *101*, 5414. Osakada, K.; Chiba, T.; Nakamura, Y.; Yamamoto, T.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1589. (b) Sano, H.; Okawara, M.; Ueno, Y. *Synthesis* **1984**, 933.

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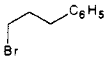
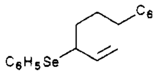
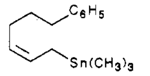
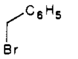
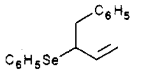
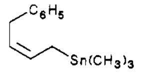
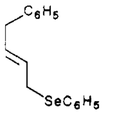
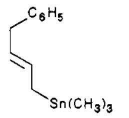
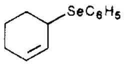
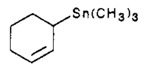
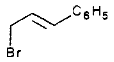
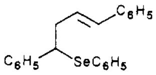
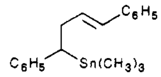
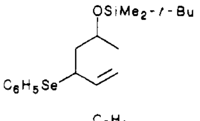
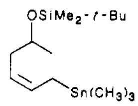
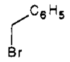
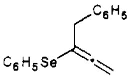
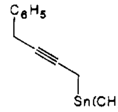
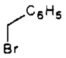
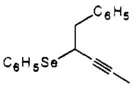
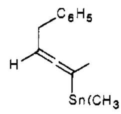
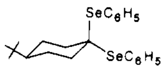
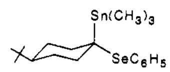
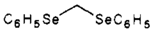
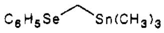
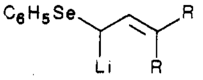
Table I. Preparation of Selenides and Reaction with (Trimethylstannyl)lithium

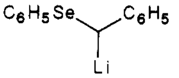
lithium reagent	electrophile	selenide	yield, %	stannane	yield, %	E/Z
1a[a]			99		92[b] 90[c]	15/85 8/92
1a[d]			90		67[b] 62[c]	20/80 23/77
e			87		91	85/15
f			96		80	
2			93		90	
1a	1.  2 TBSCl		88		90	13/87
3			89		73	
4	1.  2 CH_3I		86		92	
g			77		81	
			–		78	

[a] Approximately 4% of γ-alkylation product was formed. [b] A 2/1 ratio of $(CH_3)_3SnLi$ to selenide was used. [c] A 1.1/1 ratio of $(CH_3)_3SnLi$ to selenide was used. [d] Approximately 17% of γ-alkylation product was formed. [e] Selenide 8 was prepared by photochemical isomerization of 5. [f] Selenide prepared from 3-bromo-1-cyclohexene. This reaction required 2 equiv of $(CH_3)_3SnLi$. [g] Selenide was prepared by reaction of ketone with benzeneselenol.

-propargyl (4) selenides[1f] can be used for assembly of the carbon frameworks from simple precursors.[8]



1a, R = H
b, R = CH_3



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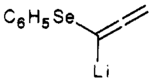

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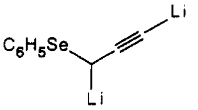

4

The procedure we have worked out is illustrated in Scheme I. The product obtained from benzylation of α-lithioallyl phenyl selenide (an 83/17 mixture of 5 and 6)[9,10a] gave a 14/86 E/Z ratio of only the terminal isomer 7 on treatment with (trimethylstannyl)lithium at −78 °C.[10b] The 1,3-transposed selenide 8 (81/19 E/Z), prepared by photochemical isomerization of 5 gave the same regioisomer, but in an 85/15 E/Z ratio. Furthermore, the 14/86

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[7] (a) Jones, D. N.; Peel, M. R. *J. Chem. Soc., Chem. Commun.* **1986**, 216. Yamamoto, Y.; Yatagai, H.; Saito, Y.; Maruyama, K. *J. Org. Chem.* **1984**, *49*, 1096. (b) Mitchell, R. H. *J. Chem. Soc., Chem. Commun.* **1974**, 990.

[8] The process resembles the displacement of allyl sulfonyl groups with tributyltin hydride under free-radical conditions,[6a] which is, however, limited to terminally unsubstituted allyl sulfones. As with the present process, metalated allyl sulfones can be used to form carbon-carbon bonds prior to replacement by the tin group.

[9] The alkylation of α-lithioallyl selenides gives small amounts of γ-alkylated products.

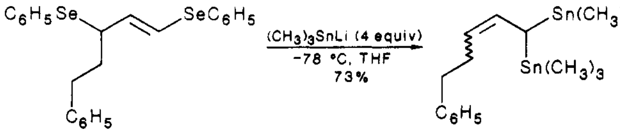
[10] (a) Typical experimental procedure: 6-Phenyl-3-(phenylseleno)-1-hexene. To phenyl allyl selenide (1.58 g, 8.0 mmol), in 10 mL of THF at −78 °C, was added 7.8 mL of 1.13 M LDA in THF. After 20 min at −78 °C, 1-bromo-3-phenylpropane (1.59 g, 8.0 mmol) was added, and the solution was warmed to room temperature for 30 min. The reaction mixture was quenched with water and extracted with pentane. The combined organic portions were washed with dilute HCl, 7% $NaHCO_3$, and brine and dried (Na_2SO_4). Purification by column chromatography (10/1 hexane/ether) yielded 2.51 g, 99%, of selenide containing ≈4% of γ-alkylated product. ^1H NMR (200 MHz, $CDCl_3$): δ 1.80 (m, 4 H), 2.70 (t, 8 Hz, 2 H), 3.80 (br q, 8 Hz, 1 H), 4.75 (d, 17.5 Hz, 1 H), 4.88 (d, 10 Hz, 1 H), 5.88 (dt, 17.5, 9 Hz, 1 H), 7.2–7.4 (m, 10 H). IR: 2930, 1580, 1500, 990, 920, 750, 710 cm^{-1}. MS: M$^+$ 316.0730 (calcd for $C_{18}H_{20}Se$, 316.0725). (b) (*Z*)-6-Phenyl-1-(trimethylstannyl)-2-hexene. To a solution of $LiSnMe_3$ (0.28 M, 20.2 mL, 5.65 mmol), in 50 mL of THF at −78 °C, was added 3-(phenylseleno)-6-phenyl-1-hexene (1.62 g, 5.14 mmol) in 25 mL of THF. The solution was stirred for 10 min at −78 °C and transferred to a separatory funnel containing water, pentane, and some dry ice (to retard air oxidation of PhSeM). The aqueous layer was extracted with pentane, and the organic portions were washed with brine and dried (Na_2SO_4). The product was purified by Kugelrohr distillation, 140–150 °C at 0.1 mm, to give 1.50 g, 90%, of stannane (E/Z, 8/92). ^1H NMR (500 MHz, $CDCl_3$): δ 0.11 (s, $^2J_{^{119}Sn-H}$ = 52 Hz, $^2J_{^{117}Sn-H}$ = 50 Hz, 9 H), 1.72 (tt, 7.5, 7.2 Hz, 2 H), 1.76 (d, 9 Hz, $^2J_{Sn-H}$ = 66 Hz, 2 H), 2.08 (q, 7.2 Hz, 2 H), 2.67 (t, 7.5 Hz, 2 H), 5.19 (dtt, 10.5, 7.2, 1.2 Hz, 1 H), 5.60 (dtt, 10.5, 9.0, 1.6 Hz, 1 H), 7.3 (m, 5 H). IR: 2920, 1610, 1500, 1450, 1260, 1100, 1030, 780, 700 cm^{-1}. ^{13}C NMR (125.76 MHz, $CDCl_3$): δ −9.8 (q, $^1J_{Sn-C}$ = 319 Hz), 12.5 (t, $^1J_{Sn-C}$ = 296 Hz), 26.7 (t), 31.6 (t), 35.8 (t), 124.4 (d, $^2J_{Sn-C}$ = 43 Hz), 125.6 (d), 128.2 (d), 128.2 (d), 128.5 (d), 142.6 (s). MS: M$^+$ 322.0891 (calcd for $C_{15}H_{24}Sn$, 322.0893). Anal. Calcd for $C_{15}H_{24}Sn$: C, 55.77; H, 7.49. Found: C, 55.44; H, 7.69.

ratio obtained in the first reaction was equilibrated to a 75/25 mixture on treatment with (trimethylstannyl)lithium at 25 °C, indicating that the *E* isomer was the more stable product.

In the above example, and in all other cases we have examined, the *regiochemical* preference was for the isomer with the tin at the less substituted end of the allyl or allenyl–propargyl fragment largely independent of the starting position of the phenylseleno group. The *stereochemistry* was kinetically controlled, provided that the reaction was quenched at low temperature.

We have not determined whether the regiochemistry observed at low temperature is the result of kinetic or thermodynamic factors, since in no case was the less stable regioisomer obtained. We have seen no indications of an induction period for the reaction (it is usually over within minutes at –78 °C). Single-electron transfer as well as S_N2 mechanisms has been proposed for the reaction of stannyllithium reagents with allyl halides and tosylates.[11]

Allyl selenides containing acetoxy and benzoyloxy groups did not react cleanly, but compounds containing cyano, *tert*-butyldimethylsiloxy, amino,[1a] and nonactivated phenylseleno groups gave the desired products. The alkylated 1,3-bis(phenylseleno)propene[1d] **9** gave bisstannylated product **10** when excess lithium reagent was used. Apparently the first substitution proceeded as usual to give a trimethylstannylated allyl selenide, which then reacted a second time.



9

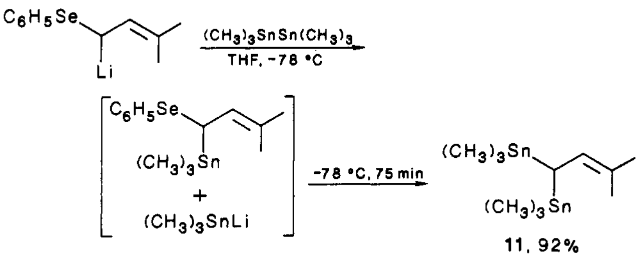
10, *E*/*Z* = 3/2

Allenyl and propargyl selenides work well in the reaction, giving the less substituted of the two possible isomers.

Two 1,1-bis(phenylseleno)alkanes were treated with (trimethylstannyl)lithium. Each gave cleanly the product of monosubstitution. Even under forcing conditions no 1,1-bis(trimethylstannyl) product was detected in any of these cases. In the 4-*tert*-butylcyclohexane system only the axial trimethylstannyl compound was formed. Stereochemistry was determined from the characteristic ^{77}Se chemical shifts of axial and equatorial seleno groups.

Sulfides[12] and sulfones will also react with tin lithium reagents, but much slower than do the selenides. Thus benzyl phenyl sulfide and sulfone reacted slowly with (trimethylstannyl)lithium at room temperature (≈40% reaction after several hours at 25 °C), and (phenylseleno)(phenylthio)methane gave exclusively the product of selenium substitution (<0.3% of $PhSeCH_2SnMe_3$ was formed).

Hexamethyldistannane is reactive toward nucleophiles.[13] We have taken advantage of this reactivity to achieve the preparation of 1,1-bis(trimethylstannyl) compounds using selenides as starting materials. The lithioallyl selenide **1b**, prepared by using lithium diisopropylamide, was treated with hexamethyldistannane to give a 92% yield of **11**.[14] The course of the reaction probably involves the "counterattacking" sequence shown.[15]



11, 92%

The procedures described here make available a variety of trimethylstannyl compounds from conveniently available precursors.

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Registry No. **1a**, 74472-76-7; **1b**, 56529-39-6; **2**, 56253-58-8; **3**, 112042-24-7; **4**, 61713-47-1; **5**, 112042-06-5; **7**-(*E*), 112042-12-3; **7**-(Z), 112042-19-0; **8**, 17417-78-6; **9**, 112042-21-4; **10**-(*E*), 112042-22-5; **10**-(*Z*), 112042-23-6; **11**, 86309-32-2; $BrCH_2CH_2CH_2C_6H_5$, 637-59-2; $BrCH_2C_6H_5$, 100-39-0; $BrCH_2CH{=}CHC_6H_5$, 4392-24-9; $H_2C(O)$, 50-00-0; $C_6H_5SeCH(CH{=}CH_2)(CH_2CH_2CH_2C_6H_5)$, 112042-05-4; $C_6H_5CH(SeC_6H_5)(CH_2CH{=}CHC_6H_5)$, 112042-07-6; $C_6H_5SeCH(CH{=}CH_2)[(CH_2CH(CH_3)(OSiMe_2\text{-}t\text{-}Bu)]$, 112042-08-7; $C_6H_5SeC(CH_2C_6H_5){=}C{=}CH_2$, 112042-09-8; $C_6H_5SeCH(C{\equiv}CCH_3)(CH_2C_6H_5)$, 112042-10-1; $C_6H_5SeCH_2SeC_6H_5$, 20343-90-2; (*E*)-$C_6H_5CH_2CH_2CH_2CH{=}CHCH_2Sn(CH_3)_3$, 112042-11-2; (*Z*)-$C_6H_5CH_2CH_2CH_2CH{=}CHCH_2Sn(CH_3)_3$, 112042-18-9; $C_6H_5CH{=}CHCH_2CH(C_6H_5)[Sn(CH_3)_3]$, 112042-13-4; (*E*)-$(CH_3)_3SnCH_2CH{=}CHCH_2CH(CH_3)(OSiMe_2\text{-}t\text{-}Bu)$, 112042-14-5; (*Z*)-$(CH_3)_3SnCH_2CH{=}CHCH_2CH(CH_3)(OSiMe_2\text{-}t\text{-}Bu)$, 112042-20-3; $C_6H_5CH_2C{\equiv}CCH_2Sn(CH_3)_3$, 112042-15-6; $C_6H_5CH_2CH{=}C{=}C(CH_3)[(Sn(CH_3)_3]$, 112042-16-7; $C_6H_5SeCH_2Sn(CH_3)_3$, 103596-69-6; $(CH_3)_3SnSn(CH_3)_3$, 661-69-8; benzeneselenol, 645-96-5; 3-bromo-1-cyclohexene, 1521-51-3; methyloxirane, 75-56-9; 4-*tert*-butylcyclohexanone, 98-53-3; 3-phenylselenylcyclohexene, 83442-20-0; 1,1-bis(phenylselenyl)-4-*tert*-butylcyclohexane, 71518-68-8; 3-(trimethylstannyl)cyclohexene, 17314-43-1; *cis*-1-(phenylselenyl)-4-*tert*-butyl-1-(trimethylstannyl)cyclohexane, 112042-17-8.

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Hans J. Reich,* James W. Ringer
Department of Chemistry
University of Wisconsin
Madison, Wisconsin 53706

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A Novel One-Flask Cyclopropanation and Vinylcyclopropanation Method for α-Enones. Copper(I)-Induced γ-Thiophenoxide Removal from Conjugate Adducts

Summary: A novel concept for performing a one-flask cyclopropanation of conjugated enones consists of conjugate addition of an appropriate phenylthio-stabilized organolithium compound followed by treatment of the resulting enolate anion with cuprous trifluoromethanesulfonate. The cyclopropanes generated by this procedure can be simple ones, substituted for example by silyl- and

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