

(2c) (11.7 g, 50 mmol), Me_3SiCN (10 mL, 75 mmol), $\text{Pd}(\text{PPh}_3)_4$ (580 mg, 0.5 mmol), and 50 mL of Et_3N was stirred for 30 min under reflux in a 100-mL round-bottom flask under a nitrogen atmosphere. The reaction mixture was diluted with hexane and filtered. Solvent was then removed in vacuo. The residue was chromatographed (silica gel, hexane/ EtOAc = 9/1) to give 4.84 g (73 %) of 4-methoxybenzocyanide (3c): mp 58–59 °C (lit.¹² mp 61–62 °C); $^1\text{H NMR}$ (CDCl_3) δ 3.80 (s, 3 H, CH_3O), 6.85 (d, J = 9 Hz, 2 H, Ph), 7.50 (d, J = 9 Hz, 2 H, Ph); IR (Nujol) 2220 (CN), 1605 (Ph) cm^{-1} ; MS, m/e 133 (M^+).

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Registry No. 1, 7677-24-9; 2a, 591-50-4; 2b, 615-37-2; 2c, 696-62-8; 2d, 637-87-6; 2e, 589-87-7; 2f, 624-38-4; 2g, 619-44-3; 3a, 100-47-0; 3b, 529-19-1; 3c, 874-90-8; 3d, 623-03-0; 3e, 623-00-7; 3f, 623-26-7; 3g, 1129-35-7; $\text{Pd}(\text{PPh}_3)_4$, 14221-01-3.

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New Synthetic Reactions with $(\text{Ph}_3\text{Sn})_2\text{Zn} \cdot \text{TMEDA}$ Complex. Regio- and Stereoselective Synthesis of Vinylstannanes

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We have developed various new reactions with a reagent which is believed to have a Zn–Sn single bond.² This paper deals with the results of the study of the synthetic reactions with the isolable complex $(\text{Ph}_3\text{Sn})_2\text{Zn} \cdot \text{TMEDA}$.³ Two methods for vinylstannane synthesis with this complex have been examined: (1) addition to acetylenic bonds in the presence of transition-metal catalysts to give vinylstannanes⁴ and (2) transformation of alkenyl halides and enol triflates into vinylstannanes.^{5,6} The complex has behaved in the same way as the compounds that are generated from Ph_3SnLi and ZnBr_2 in situ in these reactions and has proved to be effective for synthetic use.

Reactions of $(\text{Ph}_3\text{Sn})_2\text{Zn} \cdot \text{TMEDA}$ with Terminal Alkynes. Previously we have reported that the reaction of $(\text{Bu}_3\text{Sn})_2\text{Zn}$ prepared in situ with carbon–carbon triple

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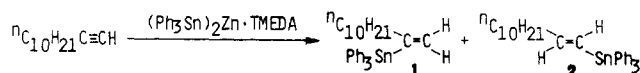
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Scheme I



Scheme II

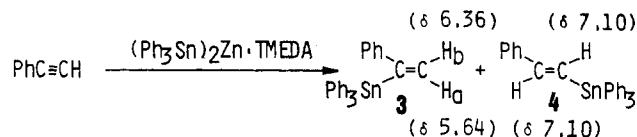
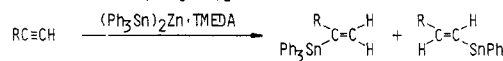
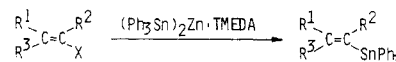


Table I. Reaction of Acetylenic Compounds with $(\text{Ph}_3\text{Sn})_2\text{Zn} \cdot \text{TMEDA}$



acetylene	catalyst	yield, %	ratio of I/II
$n\text{-C}_{10}\text{H}_{21}$	CuCN	87	83/17
	$\text{PdCl}_2(\text{PPh}_3)_2$	59	62/38
	$\text{Pd}(\text{PPh}_3)_4$	50	50/50
	$\text{RhCl}(\text{PPh}_3)_3$	30	40/60
$\text{PhCH}_2\text{OCH}_2\text{CH}_2$	CuCN	80	78/22
	Ph	CuCN	70

Table II. Reaction of Alkenyl Halides and Enol Triflates with $(\text{Ph}_3\text{Sn})_2\text{Zn} \cdot \text{TMEDA}$ ^a



substrate				product	
R ¹	R ²	R ³	X	yield, %	E/Z
$n\text{-C}_6\text{H}_{13}$	H	H	I	75	100/0
H	H	$n\text{-C}_{10}\text{H}_{21}$	I	67	25/75
H	$n\text{-C}_{10}\text{H}_{21}$	H	I	63	
H	$n\text{-C}_{10}\text{H}_{21}$	H	OSO_2CF_3	78	
H	$n\text{-C}_5\text{H}_{11}$	H	OSO_2CF_3	70	
H	CH_3	H	Br^b	82	
H	Ph	H	OSO_2CF_3	50	
Ph	H	H	Br	65	100/0
H	H	Ph	Br	62	50/50

^a The reactions were performed at 25 °C for alkenyl iodides and enol triflates and 60 °C for alkenyl bromides. Substrate (1.0 mmol), the complex (2.0 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (0.05 mmol) were employed. ^b Bromide (3.0 mmol) and the complex (1.0 mmol) were employed.

bonds proceeds easily in the presence of various kind of transition-metal catalysts to give vinylstannanes after aqueous workup.² Here we wish to report that $(\text{Ph}_3\text{Sn})_2\text{Zn} \cdot \text{TMEDA}$ adds to acetylenic bonds in the same manner as $(\text{Ph}_3\text{Sn})_2\text{Zn}$ derived from Ph_3SnLi and ZnBr_2 in situ.

Treatment of 1-dodecyne with $(\text{Ph}_3\text{Sn})_2\text{Zn} \cdot \text{TMEDA}$ in THF in the presence of CuCN catalyst gave a mixture of 2-(triphenylstannyl)-1-dodecene (1) and the (*E*)-1-triphenylstannyl isomer (2) (83:17) in 87% combined yield (Scheme I). The regiochemistry of the reaction depends on the nature of the transition-metal catalysts. Representative results are summarized in Table I. In general, 2-stannyl-1-alkenes were obtained as major products. As shown in Scheme II, the reaction proceeded in *cis* fashion. The reaction of phenylacetylene with the complex in the presence of CuCN provided a mixture of 1-phenyl-1-(triphenylstannyl)ethene (3) and the 2-triphenylstannyl isomer (4). The product 3 showed $^1\text{H NMR}$ (CDCl_3 , 200 MHz) signals at δ 5.64 (d, $J(\text{H}_a\text{---}\text{H}_b)$ = 1.8 Hz, $J(\text{Sn}\text{---}\text{H}_a)$ = 77 Hz, H_a) and 6.36 (d, $J(\text{H}_a\text{---}\text{H}_b)$ = 1.8 Hz, $J(\text{Sn}\text{---}\text{H}_b)$ = 165 Hz, H_b). The other isomer 4 having $^1\text{H NMR}$ ab-

Table III. ^{119}Sn NMR Spectral Data of (Triphenylstannyl)alkenes

R	$\text{Ph}_3\text{Sn}-\text{C}(\text{H})=\text{C}(\text{H})-\text{R}$	$\text{H}-\text{C}(\text{H})=\text{C}(\text{H})-\text{SnPh}_3$	$\text{R}-\text{C}(\text{H})=\text{C}(\text{H})-\text{SnPh}_3$
$n\text{-C}_{10}\text{H}_{21}$	-133.3	-136.7	-150.4
CH_3	-133.6		
$n\text{-C}_5\text{H}_{11}$	-133.5		
$n\text{-C}_6\text{H}_{13}$		-136.4	-150.2
Ph	-130.3	-131.6	-149.8
$\text{PhCH}_2\text{OCH}_2\text{CH}_2$	-132.8	-137.6	

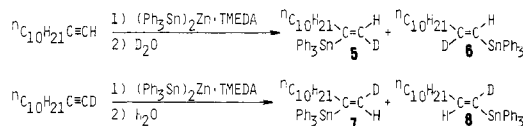
sorption at δ 7.10 (s, 2 H, H_c and H_d) was identical with the sample derived from (*E*)- $\text{PhCH}=\text{CHMgBr}$ and Ph_3SnCl . Assignment of the stereochemistry of H_a and H_b was based on the magnitude of the coupling constants of the olefinic proton with ^{117}Sn and ^{119}Sn isotopes.⁷ Quenching the reaction mixture with D_2O gave a mixture of vinylstannanes whose ^1H NMR spectrum showed only two signals in the olefinic region at δ 6.36 and 7.10. The disappearance of the higher field signal at δ 5.64 in the spectrum is consistent with a cis addition process.⁸

The reaction of 1-dodecyne with $(\text{Ph}_3\text{Sn})_2\text{Zn}$ generated from Ph_3SnLi^9 and ZnBr_2 in situ also proceeded very easily at 25 °C in the presence of CuCN catalyst and gave an isomeric mixture (1/2 = 76:24) whose ratio was similar to that with $(\text{Ph}_3\text{Sn})_2\text{Zn}\cdot\text{TMEDA}$.¹⁰

Conversion of Alkenyl Halides and Enol Triflates into (Triphenylstannyl)alkene with $(\text{Ph}_3\text{Sn})_2\text{Zn}\cdot\text{TMEDA}$ Complex. Treatment of alkenyl iodides¹¹ or enol triflates¹² with the complex in the presence of $\text{Pd}(\text{PPh}_3)_4$ catalyst at 25 °C gave vinylstannanes by the cross-coupling reaction. Copper(I) cyanide is less effective than Pd catalyst. For instance, the reaction of 2-[(trifluoromethyl)sulfonyloxy]-1-dodecene with the complex in the presence of CuCN catalyst (0.1 equiv) gave the desired vinylstannane in 16% yield under the same reaction conditions as the Pd catalysis. In contrast to alkenyl iodides, alkenyl bromides were less reactive, and heating the reaction mixture at 60 °C was essential for the complete conversion into vinylstannanes. As shown in Table II, the stereochemical outcome depends on the nature of the substrates. Whereas (*E*)-1-iodo-1-octene gave (*E*)-1-(tri-

(7) According to the literature, $J(\text{Sn}-\text{H}_{\text{trans}})$ is about two times as large as $J(\text{Sn}-\text{H}_{\text{cis}})$. Leusink, A. J.; Budding, H. A.; Marsman, J. W. *J. Organomet. Chem.* 1967, 9, 285.

(8) The cis addition process was also supported by the following results. Treatment of a mixture of 1-dodecyne and $(\text{Ph}_3\text{Sn})_2\text{Zn}\cdot\text{TMEDA}$ in the presence of CuCN catalyst gave (*Z*)-1-deuterio-2-(triphenylstannyl)-1-dodecene (5) as a major product along with the regio isomer 6 after quenching with D_2O . The ^{119}Sn NMR spectrum of the compound



5 showed triplet at -133 ppm ($J(\text{Sn}-\text{D}_{\text{cis}}) = 11.1$ Hz). Meanwhile, the compound 7 derived from $\text{C}_{10}\text{H}_{21}\text{C}\equiv\text{CD}$ showed triplet at -133 ppm ($J(\text{Sn}-\text{D}_{\text{trans}}) = 27.0$ Hz). These results confirm that Ph_3Sn and Zn add to triple bonds in cis fashion. Quintard, J.-P.; Degueil-Castaing, M.; Dumartin, G.; Rahm, A.; Pereyre, M. *J. Chem. Soc., Chem. Commun.* 1980, 1004.

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(11) For the cross-coupling reactions of alkenyl halides with organometallic compounds, see: Noyori, R. *Transition Metal Organometallics in Organic Synthesis*; Academic: New York, 1976; Vol. 1, pp 83-187. Tamao, K.; Sumitani, K.; Kiso, Y.; Zembayashi, M.; Fujioka, A.; Kodama, S.; Nakajima, I.; Minato, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* 1976, 49, 1958. Negishi, E. *Acc. Chem. Res.* 1982, 15, 340.

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phenylstannyl)-1-octene exclusively, the (*Z*)-1-iodo-1-dodecene provided a mixture of (*Z*)-1-(triphenylstannyl)-1-dodecene and *E* isomer (75:25).

The ^{119}Sn NMR spectra are very useful for the determination of the stereochemistry (Table III).^{13,14}

Experimental Section

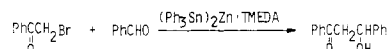
Distillation of the products was performed by use of Kugelrohr (Büchi), and boiling points are indicated by an air bath temperature without correction. All melting points were obtained on a Yanaco MP-50929 melting points apparatus and are uncorrected. The IR spectra were determined on a JASCO IR-810 spectrometer, the mass spectra on a Hitachi M-80 machine, the proton NMR spectra on Varian EM-390 and Varian XL-200 spectrometers, and the ^{119}Sn NMR spectra on a JEOL JNM-FX 90Q spectrometer. The chemical shifts of the proton NMR are given in δ with Me_4Si as an internal standard, and those of the ^{119}Sn NMR are given in δ with tetramethylstannane as an internal standard. The analyses were carried out by the staff at the Elemental Analyses Center of Kyoto University. Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl. Purification of products was performed by column chromatography on silica gel or preparative thin-layer chromatography (TLC).

Preparation of $(\text{Ph}_3\text{Sn})_2\text{Zn}\cdot\text{TMEDA}$ Complex. The complex was prepared following the method^{3a} described for the preparation of $\text{Ph}_3\text{SnZnCl}\cdot\text{TMEDA}$ which has been made from Ph_3SnH and EtZnCl .¹⁵ A hexane solution of Et_2Zn (1.5 M, 6.7 mL, 10 mmol) and TMEDA (1.28 g, 11 mmol) were combined in THF (10 mL) under an argon atmosphere. The reaction mixture was cooled to -78 °C, and a solution of triphenyltin hydride (7.7 g, 22 mmol) in THF (10 mL) was added dropwise. The resulting mixture was warmed to 0 °C and kept there for 2 h. After being stirred for another 5 h at 25 °C, the mixture was cooled in ice, and pentane (20 mL) was added. The precipitated white solid was filtered off, washed with a THF/pentane (1/2) mixture (10 mL \times 2), and dried in vacuo to give the complex (7.2 g, 82% yield) with mp 172-175 °C, which gave satisfactory analytical data. All attempts for recrystallization failed because of the partial decomposition of the complex. Anal. Calcd for $\text{C}_{42}\text{H}_{46}\text{NSn}_2\text{Zn}$: C, 57.21; H, 5.22; N, 3.18. Found: C, 57.12; H, 5.40; N, 2.96.

General Procedure for the Stannylation of Acetylenes. The reaction of 1-dodecyne with $(\text{Ph}_3\text{Sn})_2\text{Zn}\cdot\text{TMEDA}$ in the presence of CuCN catalyst is representative. A solution of 1-dodecyne (0.16 g, 1.0 mmol) in THF (2 mL) was added to a suspension of $(\text{Ph}_3\text{Sn})_2\text{Zn}\cdot\text{TMEDA}$ (1.76 g, 2.0 mmol) in THF (10 mL) at 0 °C under an argon atmosphere. A catalytic amount of CuCN (9 mg, 0.1 mmol) was added, and the resulting mixture was stirred at 0 °C for 30 min and then at 25 °C for 4 h. The reaction mixture was poured into ice-cooled water and extracted with ethyl acetate. The combined organic layers were washed with a saturated aqueous NaCl solution and dried with Na_2SO_4 . Evaporation of the solvent afforded a crude oil, which was chromatographed over silica gel (hexane) to give a mixture of 2-(triphenylstannyl)-1-dodecene (1) and (*E*)-1-(triphenylstannyl)-1-dodecene (2) (0.39 g, 83:17) in 87% combined yield: bp 200 °C (bath temperature, 0.08 torr); IR (neat) 2922, 1428, 1074, 726, 697 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.88 (br t, $J = 3.5$ Hz, 3 H), 1.0-1.5 (m, 19 H), 2.10-2.40 (m, 0.34 H), 2.42 (t, $J = 7$ Hz, 1.66 H), 5.4 (br s, 0.17 H), 5.97 (br s, 0.17 H), 6.22 (m, 1.66 H),

(13) Quintard, J.-P.; Degueil-Castaing, M.; Dumartin, G.; Barbe, B.; Petraud, M. *J. Organomet. Chem.* 1982, 234, 27.

(14) The complex was also effective for the Reformatsky-type reactions as $\text{Bu}_3\text{SnAlEt}_2$ reagent (Matsubara, S.; Tsuboniwa, N.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* 1984, 57, 3242). For instance, treatment of β -bromoacetophenone with $(\text{Ph}_3\text{Sn})_2\text{Zn}\cdot\text{TMEDA}$ afforded enolate which reacted with benzaldehyde to give β -hydroxy carbonyl compound in 88% yield.



(15) They also mentioned about the preparation of $(\text{Ph}_3\text{Sn})_2\text{Zn}\cdot\text{TMEDA}$ in the table of their report briefly. We chose this complex because Et_2Zn is more readily accessible than EtZnCl .

(16) We thank Toyo Stauffer Chemical Company for the gift of Et_2Zn .

7.3-7.8 (m, 15 H). Physical data of pure compounds **1** and **2** are described below.

4-(Benzyloxy)-2-(triphenylstannyl)-1-butene and 4-(benzyloxy)-1-(triphenylstannyl)-1-butene. The reaction of 4-(benzyloxy)-1-butyne with $(\text{Ph}_3\text{Sn})_2\text{Zn-TMEDA}$ in the presence of CuCN catalyst according to the general procedure gave a mixture of the title compounds. Isomeric ratio 4-(benzyloxy)-2-(triphenylstannyl)-1-butene/the 1-(triphenylstannyl) isomer = 79/21 was determined by ^1H NMR and ^{119}Sn NMR spectra. Each isomer was purified by preparative TLC on silica gel (10:1 hexane/ethyl acetate). 4-(Benzyloxy)-2-(triphenylstannyl)-1-butene: bp 220-225 °C (0.08 torr, bath temperature); IR (neat) 3062, 2900, 2854, 1481, 1429, 1099, 1075, 997, 929, 728, 698 cm^{-1} ; NMR (200 MHz, CDCl_3) δ 2.73 (t, $J = 6.4$ Hz, 2 H), 3.48 (t, $J = 6.4$ Hz, 2 H), 4.13 (s, 2 H), 5.46 (br s, 1 H), 6.06 (br s, 1 H), 7.10-7.75 (m, 20 H). Anal. Calcd for $\text{C}_{29}\text{H}_{28}\text{OSn}$: C, 68.13; H, 5.52. Found: C, 68.41; H, 5.57. 4-(Benzyloxy)-1-(triphenylstannyl)-1-butene (semisolid): IR (neat) 3060, 2922, 2852, 1428, 1100, 1074, 1024, 998, 726, 696 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 2.50-2.70 (m, 2 H), 3.59 (t, $J = 6.7$ Hz, 2 H), 4.52 (s, 2 H), 6.29 (m, 2 H), 7.10-7.78 (m, 20 H).

1-Phenyl-1-(triphenylstannyl)ethene and (E)-1-Phenyl-2-(triphenylstannyl)ethene. A solution of phenylacetylene in THF was treated with $(\text{Ph}_3\text{Sn})_2\text{Zn-TMEDA}$ to give a mixture of title compounds. Each isomer was prepared in a pure form from 1-[(trifluoromethyl)sulfonyl]oxy-1-phenylethene or (E)- β -bromostyrene (see below).

General Procedure for the Reaction of Acetylenic Compound with $(\text{Ph}_3\text{Sn})_2\text{Zn}$ Generated in Situ. Phenyllithium (1.81 M, cyclohexane/ether (70/30) solution, 6.6 mL, 12 mmol) was added to a suspension of SnCl_2 (0.76 g, 4.0 mmol) in THF (10 mL) at 0 °C under an argon atmosphere. After being stirred for 30 min at 0 °C, the resulting solution of Ph_3SnLi ⁸ was treated with ZnBr_2 (0.45 g, 2.0 mmol). The mixture was stirred for another 15 min, and a solution of 1-dodecyne (0.17 g, 1.0 mmol) in THF (2.0 mL) was added. A catalytic amount of CuCN (9 mg, 0.1 mmol) was added, and the whole was stirred at 0 °C for 15 min and then at 25 °C for 2 h. Workup followed by purification as described above gave a mixture of **1** and **2** (76:24) in 68% combined yield. (Triphenylstannyl)lithium prepared from Ph_3SnH and lithium diisopropylamide could also be used for the reaction.

2-[(Trifluoromethyl)sulfonyl]oxy-1-heptene. This compound was produced from 1-heptyne and trifluoromethanesulfonic acid according to the reported procedure.¹⁷ 2-[(Trifluoromethyl)sulfonyl]oxy-1-dodecene and 1-phenyl-1-[(trifluoromethyl)sulfonyl]oxy]ethene were produced in the same manner.

General Procedure for the Transformation of Alkenyl Iodides and Enol Triflate into Vinylstannanes. Conversion of 2-[(trifluoromethyl)sulfonyl]oxy-1-dodecene into 2-(triphenylstannyl)-1-dodecene is representative. A solution of 2-[(trifluoromethyl)sulfonyl]oxy-1-dodecene (0.32 g, 1.0 mmol) in THF (2.0 mL) was added to a suspension of $(\text{Ph}_3\text{Sn})_2\text{Zn-TMEDA}$ (1.76 g, 2.0 mmol) in THF (10 mL). A catalytic amount of $\text{Pd}(\text{PPh}_3)_4$ (58 mg, 0.05 mmol) was added, and the resulting mixture was stirred at 25 °C for 3 h. Ice-cooled 1 N HCl was added, and the mixture was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated. The resulting residue was purified by preparative TLC on silica gel (hexane) to give 2-(triphenylstannyl)-1-dodecene (0.40 g) in 78% yield: bp 175 °C (0.08 torr, bath temperature); IR (neat) 3062, 2922, 1429, 1074, 922, 726, 698 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 0.88 (t, $J = 6.5$ Hz, 3 H), 1.0-1.55 (m, 16 H), 2.42 (t, $J = 7.5$ Hz, 2 H), 5.38 (s, 1 H), 5.95 (s, 1 H), 7.3-7.8 (m, 15 H). Anal. Calcd for $\text{C}_{30}\text{H}_{38}\text{Sn}$: C, 69.65; H, 7.40. Found: C, 69.65; H, 7.67.

(E)-1-(Triphenylstannyl)-1-octene: bp 160 °C (0.1 torr, bath temperature); IR (neat) 3062, 2924, 2852, 1598, 1429, 1075, 997, 726, 697 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 0.80-0.95 (m, 3 H), 1.05-1.55 (m, 8 H), 2.15-2.35 (m, 2 H), 6.21 (m, 2 H), 7.30-7.70 (m, 15 H). Anal. Calcd for $\text{C}_{26}\text{H}_{30}\text{Sn}$: C, 67.71; H, 6.56. Found: C, 67.52; H, 6.60.

A mixture of (E)- and (Z)-1-(triphenylstannyl)-1-dodecene: bp 170 °C (0.08 torr, bath temperature); IR (neat) 3060, 2922,

1598, 1429, 1075, 726, 697 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 0.80-0.95 (m, 3 H), 0.95-1.50 (m, 16 H), 2.00-2.10 (m, 1.5 H), 2.13-2.30 (m, 0.5 H), 6.10 (d, $J = 12$ Hz, 0.75 H), 6.20 (m, 0.5 H), 6.80 (dt, $J = 12$ and 7.0 Hz, 0.75 H), 7.25-7.78 (m, 15 H). Anal. Calcd for $\text{C}_{30}\text{H}_{38}\text{Sn}$: C, 69.65; H, 7.40. Found: C, 69.76; H, 7.62.

2-(Triphenylstannyl)-1-heptene: bp 150 °C (0.08 torr, bath temperature); IR (neat) 3062, 2926, 1429, 1075, 726, 698 cm^{-1} ; NMR (200 MHz, CDCl_3) δ 0.73 (br t, $J = 6.0$ Hz, 3 H), 0.95-1.70 (m, 9 H), 2.4 (t, $J = 7.0$ Hz, 2 H), 5.37 (br s, 1 H), 5.93 (br s, 1 H), 7.1-7.9 (m, 15 H). Anal. Calcd for $\text{C}_{25}\text{H}_{28}\text{Sn}$: C, 67.15; H, 6.31. Found: C, 67.13; H, 6.39.

2-(Triphenylstannyl)-2-propene: mp 77-79 °C (from hexane/ CH_2Cl_2); IR (KBr) 3058, 2926, 1427, 1078, 728, 697 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 2.15 (t, $J = 1.6$ Hz, 3 H), 5.37 (br s, 1 H), 5.98 (br s, 1 H), 7.25-7.75 (m, 15 H). Anal. Calcd for $\text{C}_{21}\text{H}_{20}\text{Sn}$: C, 64.50; H, 5.16. Found: C, 64.46; H, 5.02.

1-Phenyl-1-(triphenylstannyl)ethene: bp 180-185 °C (0.1 torr, bath temperature); IR (neat) 3060, 2925, 1480, 1428, 1075, 1023, 998, 727, 697 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 5.64 (d, $J = 1.8$ Hz, 1 H), 6.36 (d, $J = 1.8$ Hz, 1 H), 7.10-7.75 (m, 20 H). Anal. Calcd for $\text{C}_{26}\text{H}_{22}\text{Sn}$: C, 68.91; H, 4.89. Found: C, 68.66; H, 4.86.

(E)-1-Phenyl-2-(triphenylstannyl)ethene. According to the literature,¹⁸ the Grignard reagent derived from (E)- β -bromostyrene was treated with Ph_3SnCl to give the title compound: mp 120-121 °C (hexane); IR (KBr) 3060, 1428, 1075, 1000, 990, 728, 698 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.10 (s, 2 H), 7.23-7.80 (m, 20 H).

(Z)-1-Phenyl-2-(triphenylstannyl)ethene. The compound was prepared from (Z)- β -bromostyrene in similar fashion as the E isomer: bp 190 °C (0.08 torr, bath temperature); IR (neat) 3060, 2986, 1567, 1481, 1429, 1074, 1022, 997, 727, 697 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 6.48 (d, $J = 13$ Hz, 1 H), 7.06-7.75 (m, 20 H), 7.86 (d, $J = 13$ Hz, 1 H). Anal. Calcd for $\text{C}_{26}\text{H}_{22}\text{Sn}$: C, 68.91; H, 4.89. Found: C, 68.96; H, 4.96.

Registry No. 1, 104849-57-2; 2, 104849-58-3; 5, 104849-59-4; 6, 104849-60-7; 7, 104849-61-8; 8, 104849-62-9; I (R = $\text{PhCH}_2\text{OCH}_2\text{CH}_2$), 104849-63-0; I (R = Ph), 104849-65-2; II (R = $\text{PhCH}_2\text{OCH}_2\text{CH}_2$), 104849-64-1; II (R = Ph), 57682-80-1; $(\text{Ph}_3\text{Sn})_2\text{Zn-TMEDA}$, 39587-92-3; $\text{PdCl}_2(\text{PPh}_3)_2$, 13965-03-2; $\text{Pd}(\text{PPh}_3)_4$, 14221-01-3; $\text{RhCl}(\text{PPh}_3)_3$, 40237-23-8; $(\text{Ph}_3\text{Sn})_2\text{Zn}$, 104849-66-3; Et_2Zn , 557-20-0; CuCN, 544-92-3; $n\text{-C}_{10}\text{H}_{21}\text{C}\equiv\text{CH}$, 765-03-7; $\text{PhCH}_2\text{OCH}_2\text{CH}_2\text{C}\equiv\text{CH}$, 22273-77-4; $\text{PhC}\equiv\text{CH}$, 536-74-3; $n\text{-C}_{10}\text{H}_{21}\text{C}\equiv\text{CD}$, 86014-19-9; Ph_3SnH , 892-20-6; SnCl_2 , 7772-99-8; ZnBr_2 , 7699-45-8; (E)-1-iodo-1-octene, 42599-17-7; (Z)-1-iodo-1-dodecene, 66553-45-5; 2-iodo-1-dodecene, 104849-67-4; 2-[(trifluoromethyl)sulfonyl]oxy-1-dodecene, 103885-03-6; 2-[(trifluoromethyl)sulfonyl]oxy-1-heptene, 104849-68-5; 2-bromo-1-propene, 557-93-7; 1-phenyl-1-[(trifluoromethyl)sulfonyl]oxy]ethene, 28143-79-5; (E)-1-bromo-2-phenylethene, 588-72-7; (Z)-1-bromo-2-phenylethene, 588-73-8; (E)-1-(triphenylstannyl)-1-octene, 104849-72-1; 2-(triphenylstannyl)-1-heptene, 104849-69-6; 2-(triphenylstannyl)-2-propene, 104849-70-9; (Z)-1-(triphenylstannyl)-1-dodecene, 104849-71-0; (Z)-1-phenyl-2-(triphenylstannyl)ethene, 17421-59-9.

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Regioselective Alkylation of 3-Substituted 3-Sulfolenes

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The deprotonation/alkylation of 2,5-dihydrothiophene 1,1-dioxide (3-sulfolene), in conjunction with the cheletropic extrusion of SO_2 , has recently been shown to be a

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