830 *Organometallics* 1982, *1*, 830–833

Pure, Unsolvated (α-Methoxyvinyl)lithium and Related Acyl Anion Equivalents via the Transmetalation of Organotin Compounds

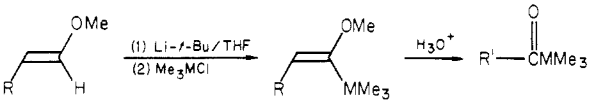
John A. Soderquist* and Grace Ji-Ho Hsu[1]

Department of Chemistry, University of San Francisco, San Francisco, California 94117

Received December 7, 1981

A detailed study of the deprotonation of simple vinyl ethers is reported. The major α-deprotonation reaction is accompanied by a temperature-dependent β-deprotonation process. Pure, unsolvated (α-methoxyvinyl)lithium and related acyl anion equivalents can be prepared quantitatively from the transmetalation of (α-methoxyvinyl)tin compounds using *n*-butyllithium in hexane solution. These lithiated compounds are useful intermediates for the preparation of α-deuterated and silylated vinyl ethers, the latter providing an efficient route to acetylsilanes. A comparison of the relative efficiency of the transmetalation of (α-methoxyvinyl)- and vinyltin compounds is reported.

Our interest in the development of new routes to acyl derivatives of group 4 metalloids led us to investigate the application of deprotonated vinyl ethers to give metalated adducts which are conveniently hydrolyzed to give the desired metalloidal ketones.[2]



M = Si, Ge, Sn

With an excess of the lithiated vinyl ether relative to the amount of the metalloidal halide, good yields of desired vinylmetalloids could be routinely obtained. Examination of the deprotonation reaction mixtures revealed that for representative vinylic and aromatic vinyl ethers, side reactions invariably accompanied the formation of the desired metalloidal adduct.

Several earlier studies have shown that this methodology can also be used to prepare simple acetylsilanes from unsubstituted vinyl ethers.[3] However, one of these studies revealed tha, under stoichiometric conditions, no intermediate metalloidal vinyl ether was produced but rather only a low yield of the acetylsilane.[3a] This result suggested that the deprotonation of even unsubstituted vinyl ethers was neither clean nor stoichiometric under the best conditions reported. Further, the high solubility of the lithium compound under the conditions of its generation in coordinating solvents precluded purification prior to its use as a synthetic reagent.

To overcome these apparent difficulties in the preparation of lithiated vinyl ethers, we chose to investigate the transmetalation[4,5] of (α-methoxyvinyl)tin compounds as a potential route to pure, unsolvated acyl anion equivalents.

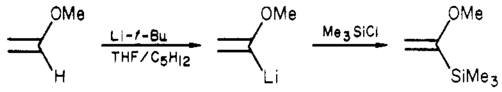
Table I. Yield[a] of 2 under Various Reaction Conditions

mole ratio MVE:Li-*t*-Bu:Me_3SiCl	temp, °C (time)[b]	% yield
1:1:1	$-78 \rightarrow 0$ (20 min)[c]	68
1.5:1:1	$-78 \rightarrow 0$ (20 min)	66
1:1:1	$-78 \rightarrow 0$ (120 min)[d]	88
1.5:1.5:1	$-78 \rightarrow 0$ (20 min)	99
2:2:1	$-78 \rightarrow 0$ (20 min)	100
1:1:1	0	43
2:2:1	0	69
2:2:1	−78	5

[a] Yields based on Me_3SiCl used and determined by GC analysis using $C_{10}H_{22}$ as an internal standard (6 ft × 1/8 in. 30% SE-30 on DCDMS-treated Chrom W column). [b] Time required to warm from −78 to 0 °C. [c] Also observed were 3 (trace), 9 (7%), 10 (7.4%), and MVE (20%). [d] Also observed were 3 (2%), 9 (1%), 10 (1.5%), and MVE (9%).

Results and Discussion

We determined the efficiency of the deprotonation of methyl vinyl ether (MVE) under various reaction conditions by conversion of the lithium compound (1) to the corresponding volatile silylated derivative (2) with subsequent GC analysis. These results are summarized in Table I.



1 2

We also investigated bases other than *tert*-butyllithium (e.g., *n*-butyllithium) and cosolvents other than THF (e.g., 1,2-dimethoxyethane, diethyl ether, hexanes-*N,N,N′,N′*-tetramethylethylenediamine) but found the *tert*-butyllithium–THF system reported by Baldwin and co-workers[6] to give superior results.

From the data in Table I, it was clear that the best conditions involved the low-temperature addition of excess *tert*-butyllithium solution to an excess of MVE in THF solution followed by a slow warmup to 0 °C to give 1 which gives a quantitative yield of 2.

The synthetic utility of this approach is exemplified by the conversion of chlorotrimethylsilane to acetyltrimethylsilane (3) in 66% overall isolated yield, a superior

---

[1] Supported by a William and Flora Hewlett Foundation Grant of Research Corp.

[2] (a) Soderquist, J. A.; Hassner, A. *J. Am. Chem. Soc.* **1980**, *102*, 1577; (b) *J. Org. Chem.* **1980**, *45*, 541. (c) Hassner, A.; Soderquist, J. A. *J. Organomet. Chem.* **1977**, *131*, Cl. (d) Soderquist, J. A.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 3571.

[3] (a) Dexheimer, E. M.; Spialter, L. *J. Organomet. Chem.* **1976**, *107*, 229. (b) Soderquist, J. A.; Hassner, A. *Ibid.* **1978**, *156*, C12. (c) Brook, A. G.; Harris, J. W.; Lennon, J.; Sheikh, M. E. *J. Am. Chem. Soc.* **1979**, *101*, 83.

[4] (a) Seyferth, D.; Weiner, M. A. *J. Am. Chem. Soc.* **1961**, *83*, 3583; (b) *Chem. Ind.* (*London*). **1959**, 402.

[5] For applications of the transmetalation reaction to sulfur-substituted acyl anion equivalents see: (a) Grobel, B.-T.; Seebach, D. *Synthesis* **1977**, 357; (b) *Chem. Ber.* **1977**, *110*, 867.

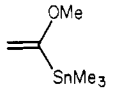
[6] (a) Baldwin, J. E.; Hofle, G.; Lever, O. W., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 7125. (b) Lever, O. W. Jr. *Tetrahedron* **1976**, *32*, 1943.

0276-7333/82/2301-0830$01.25/0 © 1982 American Chemical Society

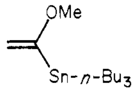
result to other routes previously reported to this compound.[3a,7]

$$\mathrm{Me_3SiCl} \xrightarrow[84\%]{1} \mathbf{2} \xrightarrow[\mathrm{H^+},\,78\%]{\mathrm{H_2O}} \underset{\mathbf{3}}{\mathrm{CH_3C({=}O)SiMe_3}}$$

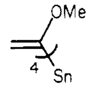
Using these conditions, we also prepared several (α-methoxyvinyl)tin compounds in good isolated yield from the corresponding tin chlorides.



4 (85%)

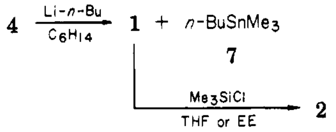


5 (92%)



6 (72%)

Vinyltin compounds[4] are known to undergo smooth transmetallation reaction in ether solvent to give the corresponding vinyllithium compounds. Unsolvated vinyllithium can be prepared by using alkane reaction solvents, but the reaction does not proceed to completion. We examined the reaction of **4** with *n*-butyllithium in hexane and found it to give a white solid which dissolves freely in either diethyl ether (EE) or THF to give, after silylation, quantitative yields of both **2** and *n*-butyltrimethyltin (**7**).



Filtration after transmetalation of the supernatant liquid removes the dissolved **7**, leaving the pure lithium compound (**1**) which after washing with pentane is converted to **2** in 97% yield free of impurities.

Isolation of the pyrophoric **1** in 95% yield can be easily accomplished by washing the precipitated material several times with pentane followed by drying in vacuo. We attempted to prepare the lithium compound by deprotonation of MVE in THF using *tert*-butyllithium followed by solvent removal in vacuo but invariably obtained a glassy solid which gave ca. 60% of **2** after silylation and which also contained minor alkane impurities as well as THF which corresponded to 50 mol % of the amount of **2**. This suggested that the lithium product was complexed to THF, and this ligand could not be easily removed without decomposition of **1**.

As a more economical source of **1** we carried out the transmetalation of **6** with 4 equiv of *n*-butyllithium which gave **2** (73%) and **5** (83%).

We found that pure **5** undergoes smooth transmetalation in 2 h at 25 °C to give, after silylation, **2** in 95% yield and a 94% yield of tetra-*n*-butyltin (**8**).

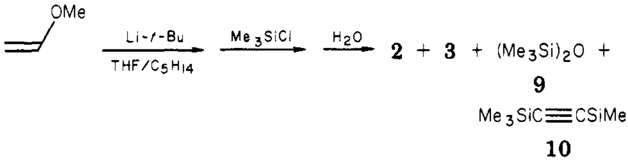
Employing these reaction conditions gives, after silylation, a 90% yield of **2** from **6** and 4 equiv of *n*-butyllithium, making this a highly efficient and economical route to the pure unsolvated reagent (**1**).

$$\mathbf{6} \xrightarrow[\mathrm{C_6H_{14}}]{4\mathrm{Li}\text{-}n\text{-}\mathrm{Bu}} \mathbf{1} + \underset{\mathbf{8}}{n\text{-}\mathrm{Bu_4Sn}} \xrightarrow{-\mathbf{8}} \xrightarrow{\mathrm{Me_3SiCl}} \mathbf{2}$$

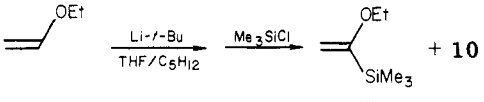
From the results given in Table I, it was clear that the actual warmup process in the deprotonation of methyl vinyl ether was critical in the case of the 1:1:1 stoichiometry, where minor amounts of byproducts were found to accompany the formation of **2** (see Table I).

The presence of **9** and **3** could be easily understood from the hydrolysis of chlorotrimethylsilane and **2**, respectively.

The presence of **10** in these reaction mixtures was more puzzling. Acetylenic products had not been reported by using the *tert*-butyllithium–THF system although an *n*-butyllithium–THF medium at ambient temperature was reported to give acetylenic products.[7b] Lever proposes a β metalation process to account for such products. Additionally, **10** was not observed in reaction mixture where in apparent excess of **1** was used.



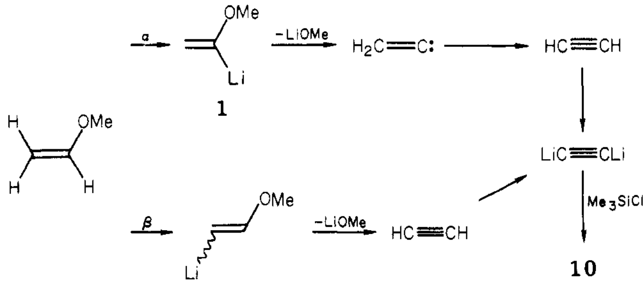
Analysis of the starting vinyl ether ruled out an acetylene impurity[8] as the precursor of **10**. Further, we used ethyl vinyl ether (purity >99.7%) and found that **5** was also formed in 3.4% yield together with the desired (α-ethoxyvinyl)trimethylsilane (**11**) in 59% yield under the 20-min warmup and 1:1:1 stoichiometric conditions.



11

With use of the conditions reported by Oakes and Sebastian,[9] which utilized excess *tert*-butyllithium to deprotonate the ether, the yield of **6** increased to 90% while **10** diminished to 1.4%. Thus, the acetylenic silane (**10**) appears to form from the metalation reaction rather than from the deprotonation of acetylene in the starting vinyl ether.

At least two pathways could result in the formation of **10**.



While we did not observe products derived from the vinylidene intermediate in path α, we chose to test the stability of **1** in regard to such a decomposition reaction. To do this, we prepared pure **1** by the transmetalation procedure, dissolved it in a 50:50 THF/pentane mixture at −78 °C, and allowed it to warm to 0 °C over ca. 20 min. After treatment with chlorotrimethylsilane, only **2** was observed in 95% yield without the formation of **10**. Thus, it appears likely that β-deprotonation of MVE rather than decomposition of **1** is responsible for the formation of **10** in our original reaction mixtures.

Still unanswered was the question as to why no **5** was found in reaction mixtures using an excess of **1** relative to chlorotrimethylsilane. To better understand this phenomenon, we treated pure **1** in THF solvent with **10**.

$$\mathbf{1} + \underset{\mathbf{10}}{\mathrm{Me_3SiC{\equiv}CSiMe_3}} \xrightarrow[\text{(2) }\mathrm{H_2O}]{\text{(1) THF}\ \ 0\ ^\circ\mathrm{C}} \mathbf{2} + \mathrm{HC{\equiv}CSiMe_3} + \mathrm{HC{\equiv}CH}$$

---

(7) Brook, A. G. *Adv. Organomet. Chem.* **1968**, *7*, 95.

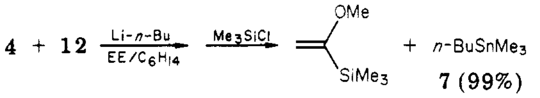
(8) Varying amounts of acetylene have been observed in commercial cylinders of MVE. DePuy, C. H., private communication.

(9) Oakes, F. T.; Sebastian, J. F. *J. Org. Chem.* **1980**, *45*, 4959.

After 1 h, 2 formed quantitatively, indicating that if minor amounts of dilithioacetylene were formed in deprotonation mixtures which, after silylation, gave 10, this compound underwent smooth transmetalation with the excess 1 in the mixtures to give back dilithioacetylene and form the desired product, 2.

We also examined the base strength of 1 in THF by adding equal molar amounts of either triphenylmethane or diisopropylamine and found, after silylation, only MVE but no detectable amount of 2, indicating that 1 was sufficiently basic to deprotonate these weak acids.

The relative efficiency of the transmetalation of vinyltrimethyltin (12) was compared to (*α*-methoxyvinyl)trimethyltin (4). Whereas 4 gives an essentially quantitative reaction with *n*-butyllithium in hexane to give solid 1 in 2 h at 0 °C, these conditions do not provide any detectable amount of solid vinyllithium from 12. However, in diethyl ether, 12 gives, after silylation, vinyltrimethylsilane in 90% yield accompanied by *n*-butyltrimethyltin (7) in 99% yield consistent with Seyferth's findings that ether solvents enhance this reaction.[4] An equal molar mixture of 4 and 12 and *n*-butyllithium, after silylation, gives only products derived from the transmetalation of the *α*-methoxyvinyl compound (4) with recovered 12 observed in 92%. For a demonstration that this result was not merely a kinetic phenomenon, prior treatment of 12 in ether with *n*-butyllithium, followed by the addition of 4, followed by silylation gave only recovered 12 (100%), 2 (90%), and 7 (99%), indicating that vinyllithium undergoes smooth transmetallation with the (*α*-methoxyvinyl)tin derivative (4) to give 1 and the vinyltin compound (12).

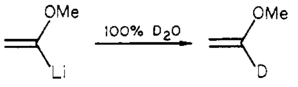


2 (99%)

In ether solution, we also found that methylithium undergoes smooth transmetalation with (*α*-methoxyvinyl)tin compounds such as 6 to give, after silylation, 2 (80%) and tetramethyltin in essentially quantitative yield.

Pure 1 dissolved in THF-d_8 gives NMR signals at δ 3.34 (s, 3 H), 3.93 (s, 1 H), 4.84 (s, 1 H). However, at probe temperatures (ca. 33 °C), decomposition of 1 occurs with the formation of peaks centered at 3.64 ppm. However, in C_6D_6 containing 1 and THF in equal molar amounts, the reagent is stable to these conditions and gives the corresponding NMR signals at 3.59, 4.56, and 5.39 ppm, respectively. Thus, the proton magnetic environments are dramatically solvent dependent as is the reagent stability.

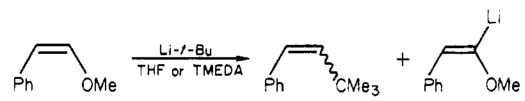
In order to demonstrate the utility of the transmetalation procedure, we carried out the preparation of *α*-deuteriovinyl methyl ether (13) in 82% isolated yield in >99% chemical purity with no NMR or MS evidence for non-*α*-deuteration.



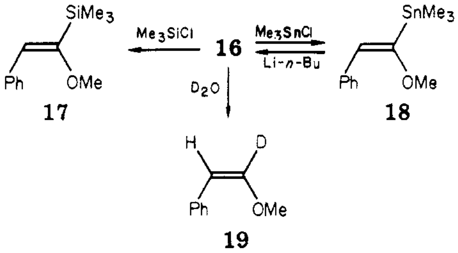
1 13

Our studies[2a] on the deprotonation of *cis*-*β*-methoxystyrene (14) with *tert*-butyllithium had revealed that this reaction gave unreacted starting material, addition–elimination products (15) as well as the desired *Z*-lithiated product (16).

This prevented preparation of a cleanly deuterated product but allowed the isolation of pure silylated and stannylated derivatives by distillative purification. In hexane solution, 18 underwent smooth transmetallation to give pure, unsolvated 16 as a pale tan solid which either can be silylated to give 17 in 76% GC yield or deuterated to give (*Z*)-*β*-deuterio-*β*-methoxystyrene (19) in 40% isolated yield.



14 15 16



17 18 19

Conclusion

In this study we have examined the deprotonation of vinyl ethers with *tert*-butyllithium using THF solvent and found that minor amounts of *β* deprotonation can accompany the major *α*-deprotonation process. The preparation of pure silylated or stannylated products requires an excess of the lithiated vinyl ethers with respect to the chlorometalloids used. Silylated vinyl ethers provide a highly efficient route to acetylsilanes. Stannylated vinyl ethers undergo smooth, efficient transmetalation with *n*-butyllithium in hexane to give pure, unsolvated (*α*-methoxyvinyl)lithium and related compounds which are easily freed from impurities for use in subsequent preparations.

Experimental Section

All experiments were carried out by using predried glassware (4 h at 110 °C) under either a nitrogen or argon atmosphere. Standard handling techniques for air-sensitive compounds were employed throughout this study.[10]

Organolithium reagents were obtained from Aldrich Chemical Co. and were standarized by using the method of Lipton, Sorenson, Sadler, and Shapiro.[11] Methyl vinyl ether was obtained from Union Carbide and was directly distilled into reaction solvents. Other ethers and hydrocarbon solvents were distilled from lithium aluminum hydride prior to use. Chlorotrimethylsilane was distilled from calcium hydride. All other organosilicon and organotin compounds not prepared in this study were obtained from commercial sources or prepared as previously described[2] and were used directly without additional purification.

NMR data were obtained by using either a Varian E360 or FT80A spectrometer. MS data[12,13] were obtained by using a Finnigan 4000 GC-MS. IR data were obtained by using a Perkin-Elmer Model 457 spectrophotometer (TF = thin film). All gas chromatographic measurements were obtained by using a Perkin-Elmer Model Sigma 1B instrument using 5% SE-30 on silylated Chrom W (6 ft × $^1/_8$ in.).

General Procedure for the Deprotonation of MVE. A standard (1.0 M) solution of methyl vinyl ether was prepared in THF, and appropriate quantities of the reagent were treated dropwise with standardized *tert*-butyllithium in pentane at the appropriate temperature. For reactions at −78 → 0 °C, the mixtures were allowed to warm to 0 °C and subsequently recooled to −78 °C, treated with chlorotrimethylsilane, allowed to reach ambient temperature, and, after addition of decane as an internal

---

[10] Brown, H. C.; Midland, M. M.; Levy, A. B.; Kramer, G. W. "Organic Synthesis via Boranes"; Wiley Interscience: New York, 1975; Chapter 9.

[11] Lipton, M. F.; Sorensen, C. M.; Sadler, A. C.; Shapiro, R. H. *J. Organomet. Chem.* **1980**, *186*, 155.

[12] Soderquist, J. A.; Hassner, A. *J. Organomet. Chem.* **1981**, *217*, 151.

[13] Unless otherwise noted (asterisk), ms peaks for organotin compounds are reported only for the tin-120 isotope (32.85%).

standard, quenched with saturated ammonium chloride solution. A portion of the organic layer was dried over anhydrous potassium carbonate and subsequently analyzed by gas chromatography. A similar procedure was used for the study of ethyl vinyl ether. A glassy solid resulted after attempted removal at 0.10 torr in the MVE deprotonation reaction which gave, after silylation in ethereal solution, a 60% yield of **2** together with THF (50 mol % of **2**) as well as minor amounts of alkane impurities.

(α-Methoxyvinyl)trimethylsilane (2). Methyl vinyl ether (72 g, 1.24 mol) was dissolved in THF (450 mL) at −78 °C and transferred to a 2-L round-bottomed flask using a double-ended needle. While reaction temperature of <−70 °C was maintained, *tert*-butyllithium solution (500 mL, 2.0 M, 1.0 mol) was added dropwise over ca. 90 min. The mixture was allowed to slowly warm to 0 °C over 3 h and subsequently recooled to −78 °C. Chlorotrimethylsilane (84.6 g, 0.78 mol) was added dropwise, and the mixture was allowed to warm to room temperature and stirred for an additional 1 h. The mixture was quenched with saturated NH_4Cl solution, extracted with water (12 × 250 mL), dried over anhydrous K_2CO_3, and distilled to give 85 g (84%) of **2**: bp 102–104 °C (760 torr); NMR ($CDCl_3$) δ 0.09 (s, 9 H), 3.50 (s, 3H), 4.28 (d, 1 H, J = 2.0 Hz), 4.50 (d, 1 H), J = 2.0 Hz); MS, m/z 130 (6), 115 (20), 89 (47), 73 (100), 59 (29, 44 (11), 42 (15); IR (TF) 1590 cm^{-1} (C=C). Calcd for $C_6H_{14}OSi$: C, 55.32; H, 10.83. Found: C, 55.58; H, 10.92.

Acetyltrimethylsilane (3). To **2** (65 g, 0.50 mol) was added 300 mL of a 4:1 acetone–1 M HCl mixture. After 1 h at 25 °C, the pale yellow-green solution was treated with ether (150 mL) and water (150 mL). The aqueous layer was extracted with ether (2 × 50 mL), and the combined ether extracts were washed with water (3 × 100 mL), dried over anhydrous $MgSO_4$, and distilled to give 45 g (78%) of **3**: bp 112 °C (760 torr) [lit.[7] 112 °C (760 torr)]. NMR (CCl_4) δ 0.09 (s, 9 H), 2.16 (s, 3 H); MS, m/z 116 (13), 101 (11), 73 (100), 59 (6), 44 (34), 42 (15); IR (TF) 1645 cm^{-1} (C=O). Calcd. for $C_5H_{12}OSi$: C, 51.66; H, 10.41. Found: C, 51.75; H, 10.42.

(α-Methoxyvinyl)trimethyltin (4). To a cold solution (−78 °C) of (α-methoxyvinyl)lithium prepared as for **2** from MVE (11.5 g, 200 mmol) and *tert*-butyllithium (83 mL, 1.8 M, 150 mmol) was added chlorotrimethyltin (20.0 g, 100 mmol) in THF (20 mL) to give after workup 18.7 g (85%) of **4**: bp 51 °C (19 torr); NMR ($CDCl_3$) δ 0.26 (s, 9 H), 3.57 (s, 3 H), 4.15 (d, 1 H, J = 2 Hz), 4.71 (d, 1 H, J = 2 Hz); MS, m/z 222 (4), 207 (61), 181 (47), 165 (100), 151 (60), 135 (42), 120 (18); IR (TF) 1575 cm^{-1} (C=C). Calcd for $C_6H_{11}OSn$: C, 32.63; H, 6.39. Found: C, 32.82; H, 6.42.

(α-Methoxyvinyl)tri-*n*-butyltin (5). As for **4**, from MVE (100 mmol), *tert*-butyllithium (75 mmol), and chlorotri-*n*-butyltin (16.3 g 50 mmol), 16.0 g (92%) of **5**, bp 85–86 °C (0.10 torr), was obtained: NMR ($CDCl_3$) δ 0.6–1.8 (m, 21 H), 3.62 (s, 3 H), 4.34 (d, 1 H, J = 2 Hz), 4.97 (d, 1 H, J = 2 Hz); MS, m/z 291 (87), 265 (21), 235 (100), 209 (13), 175 (69), 145 (34), 121 (75); IR (TF): 1575 cm^{-1} (C=C). Calcd for $C_{15}H_{32}OSn$: C, 51.90; H, 9.29. Found: C, 52.03; H, 9.32.

Tetrakis(α-methoxyvinyl)tin (6). To a cold (−78 °C) solution of (α-methoxyvinyl)lithium prepared as for **2** from methyl vinyl ether (67 g, 1.16 mol) in THF (300 mL) and *tert*-butyllithium (400 mL, 2.0 M, 0.80 mol) was added tin tetrachloride (39.2 g, 0.15 mol) in pentane (300 mL) dropwise. After being quenched with saturated NH_4Cl solution, the dried (K_2CO_3) solution was concentrated and distilled to give 37.4 g (72%) of **6**, bp 116–120 °C (0.2 torr). Recrystallization from 95% ethanol gives a crystalline material: mp 25–27 °C; NMR ($CDCl_3$) δ 3.60 (s, 12 H), 4.47 (d, 4 H, J = 2.5 Hz, $J_{\text{Sn-H}}$ = 43 Hz), 4.90 (d, 4 H, J = 2.5 Hz, $J_{\text{Sn-H}}$ = 139, 133 Hz) MS, m/z 291 (19), 209 (11), 177 (12), 151 (47), 114 (100)*; IR (CCl_4) 1578 cm^{-1} (C=C). Calcd for $C_{12}H_{20}OSn$: C, 41.53; H, 5.81. Found: C, 41.80; H, 5.83.

(α-Ethoxyvinyl)trimethylsilane (11). To ethyl vinyl ether (10.8 g, 150 mmol) in THF (75 mL) at −78 °C was added *tert*-butyllithium solution (75 mL, 2.0 M, 150 mmol) dropwise. After the addition was completed, the mixture was allowed to warm to 0 °C over ca. 1 h, recooled to −78 °C and treated with chlorotrimethylsilane (10.9 g, 100 mmol), and allowed to reach ambient temperature. After 1 h, the mixture was quenched with saturated ammonium chloride solution, dried over anhydrous potassium carbonate, filtered, and distilled to give 9.8 g (68%) of **11**: bp 117–119 °C (760 torr); NMR ($CDCl_3$) δ 0.10 (s, 9 H), 1.22 (t, 3 H, J = 8 Hz), 3.70 (q, 2 H, J = 8 Hz), 4.27 (d, 1 H, J = 2 Hz), 4.57 (d, 1 H, J = 2 Hz); MS; m/z 144 (30), 129 (40), 89 (87), 73 (100), 59 (98), 45 (82), 73 (76).

General Procedure for the Transmetalation of (α-Methoxyvinyl)tin Compounds. A solution of the appropriate (α-methoxyvinyl)tin compound in hexanes (1 M) at 0 °C was treated with 1 equiv of *n*-butyllithium solution, and the mixture was stirred for an additional 2 h unless otherwise noted. The precipitate was dissolved directly with added THF (ca. 20% v/v), treated with chlorotrimethylsilane, decane standard, and quenched with saturated ammonium chloride solution. The organic portion was dried over anhydrous potassium carbonate prior to GC analysis. Alternatively, the preciptated lithium compound was filtered by using a fritted side-arm filter, washed with several portions of pentane, and either dried in vacuo or dissolved in an appropriate solvent for subsequent reactions. A similar method was used to carry out a comparative study of **4** and **12** in ether solution as described in the Results and Discussion.

General Procedure for the Reaction of 1 with 10. A solution of **1** in THF at −78 °C was treated with 0.50 mol equiv of *bis*-(trimethylsilyl)acetylene (**10**). After being warmed to 0 °C, the mixtures were quenched at appropriate time intervals with saturated ammonium chloride solution, decane standard was added, and, after the mixture was dried over anhydrous potassium carbonate, the organic layer was analyzed by GC. Initially, at 15 min and at 1 h, the yield of **2** increased regularly from 22 → 48 → 100%. At these intervals, mono(trimethylsilyl)acetylene gave values of 36, 71, and 0%. The recovered **10** diminished (60, 17, and 0%) consistent with the formation of **2**. MVE was also observed at the intermediate reactions times. The volatile acetylene was observed only in minor amounts in each run.

α-Deuteriovinyl Methyl Ether (13). A 50-mL round-bottomed flask equipped with a septum inlet, fritted-glass filter, and empty Dewar condenser was charged with tetrakis(α-methoxyvinyl)tin (**6**) (2.67 g, 7.7 mmol) in hexanes (15 mL). While a reaction temperature of 0 °C was maintained with an ice bath, *n*-butyllithium solution (22 mmol) was added and the mixture was allowed to stir for 2 h. The white precipitate was filtered and washed with hexanes (3 × 5 mL) and decane (6 × 5 mL). Dry-ice/acetone coolant was placed in the condenser, and the lithium compound in a decane (10 mL) slurry was treated with 100% D_2O (1.0 mL) dropwise. After 15 min, the mixture was frozen with a Dry-ice/acetone bath, and the condenser was replaced with a distillation apparatus. Distillation gave 1.06 g (82%) of **13**: bp ca. 14 °C (99+% pure by GC); MS, m/z 59 (100), 44 (87), 42 (27), 32 (22), 31 (62), 30 (59); NMR (CCl_4) δ 3.50 (s, 3 H), 3.93 (m, 1 H), 4.05 (dd, 1 H, J = 2 Hz).

(*Z*)-β-Deuterio-β-methoxystyrene (19). To a solution of **18** (0.98 g, 4.0 mmol) in pentane (4 mL) was added *n*-butyllithium (2.66 mL, 1.5 M, 4.0 mmol) dropwise. After 2 h at 0 °C, the mixture was filtered, washed with pentane (4 × 5 mL), and quenched with D_2O (1.5 mL). After separation, the dried (K_2CO_3) organic material was concentrated and distilled to give 0.21 g (40%) of **19**: bp ca. 55 °C (0.6 torr); NMR (CCl_4) δ 3.70 (s, 3 H), 5.10 (b s, 1 H), 7.20 (m, 5 H); MS m/z 135 (66), 92 (100), 66 (40), 51 (23), 39 (30).

Acknowledgment. The support of the William and Flora Hewlett Foundation Grant of Research Corp. and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We also thank Mr. Demitrios Dalietos for his valuable help with the mass spectrometry.