Synthesis of 2,3-Disubstituted 1,3-Butadienes from Organotin Precursors and Butadienyllithium Reagents. Diels–Alder Reactivity[1]

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Abstract: 1,4-Bis(trimethylstannyl)-2-butyne (**1**) and 2,3-bis(trimethylstannyl)-1,3-butadiene (**2**), versatile synthons for the 2,3-dianion of 1,3-butadiene, have been prepared from either 1,4-dichloro-2-butyne or 2,3-dichloro-1,3-butadiene by reaction with 2 equiv of (trimethylstannyl)lithium. At –78 °C, the kinetic product from either dichloro precursor is **1** which can be isomerized to **2**. The monolithium species formed from **1** and **2** have been characterized by ^{13}C NMR. One equivalent of methyllithium added to **1** at –78 °C forms 2-lithio-1-(trimethylstannyl)-2,3-butadiene (**5**), while **2** forms 2-lithio-3-(trimethylstannyl)-1,3-butadiene (**6**). A second equivalent of methyllithium converts **5** to a dilithio species, **7**, whose ^{13}C NMR spectrum is consistent with $(LiCH_2C{\equiv}CCH_2Li)_n$. The reagent **6** slowly isomerizes to **5** at –50 °C and also forms **7** at this temperature when excess methyllithium is present. 2-Lithio diene **6** (and the cuprate and Grignard reagent prepared from it) is a convenient starting material for the preparation of numerous 2-x-3-(trimethylstannyl)-1,3-butadienes by reaction with electrophiles such as halosilanes, disulfides, selenium, alkyl halides, positive halogen sources, aldehydes, and ketones. Many of the trimethylstannyl-substituted dienes prepared in this way can be lithiated a second time and quenched to give 2-x-3-y-1,3-butadienes (x, y = Me_3Si, Me_3Si (**4**); n-C_6H_{13}–, n-C_6H_{13}– (**22**); –$SiMe_2CH_2CH_2Me_2Si$– (**12**); –$SeCH_2Se$– (**15**); $PhCH_2Se$–, n-$C_{12}H_{25}$– (**24**); –$SeCH_2Me_2Si$– (**14**); n-C_6H_{13}–, HO_2C– (**23**); and Me_3Si–, PhS– (**19**)). Direct electrophilic substitution of trimethylstannyl in **2** (acylation) and **1** (iodination, aminomethylation) was also successful. One of the goals of this research was to develop a reactive equivalent of 2,3-dichloro-1,3-butadiene. To this end, we have compared the Diels–Alder reactivity of *N*-methylmaleimide with **2** and many of the compounds prepared from it. Surprisingly, **2** is a less reactive diene than its parent dichloride. However, 2-chloro-3-(trimethylstannyl)-1,3-butadiene (**17**) is an effective alternative to **2**.

Introduction

Conjugated dienes are important intermediates in organic syntheses, in part for their utility in the Diels–Alder reaction.[2] In connection with our interest in the preparation of polychlorinated biphenyl arene oxides,[1f] we examined 2,3-dichloro-1,3-butadiene as a Diels–Alder diene and found, like others previously,[3] that it has very low reactivity, dimerizes and polymerizes readily, and is thus usable only with very reactive dienophiles. We therefore undertook the examination of trialkylstannyl or trialkylsilyl substituted dienes as synthons for 2,3-dichlorobutadiene and report here the preparation of 1,4-bis(trimethylstannyl)-2-butyne (**1**) and 2,3-bis(trimethylstannyl)-1,3-butadiene (**2**) and their conversion to a variety of 2,3-substituted conjugated butadienes. These two isomeric tin compounds are versatile synthons for the 2,3-dianion of 1,3-butadiene[4–6] and can be used to prepare numerous substituted dienes difficult to prepare by other methods. We also report on the Diels–Alder reactivity of several of these dienes.

The Li/Sn exchange was first used by Seyferth and Weiner for the preparation of vinyllithium from tetravinyltin[7] and has been extended to the production of a great number of interesting organolithium compounds. Bis(trialkylstannyl) compounds of various types have been used for the sequential or simultaneous introduction of electrophiles, either directly or by prior conversion of C–Sn to C–Li or other C–M bonds (Chart I). These include several 1,1-,[8] 1,2-,[9] 2,3-,[10] or 3,3-bis(stannyl) olefins[1b,11] as well

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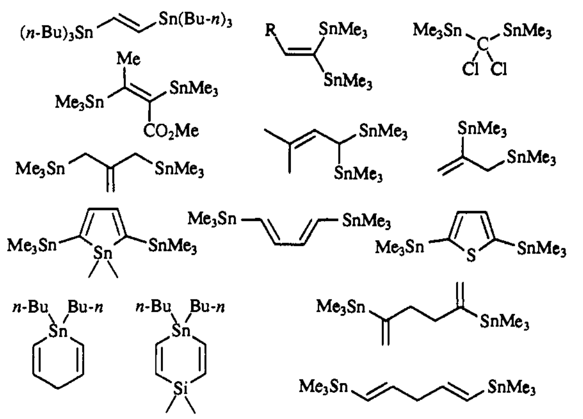
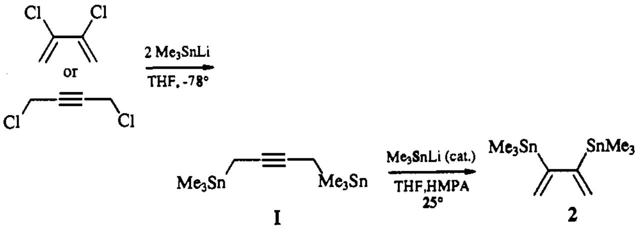
Chart I



as stannacyclohexadienes,[12] stannacyclopentadienes,[6a] 1,4-bis(stannyl)-1,3-butadienes,[6a,6b] 1,5-bis(stannyl)-1,4-pentadienes,[13] 2,5-bis(stannyl)-1,5-hexadienes,[6b] bis(stannyl) aromatic compounds,[14] and bis(stannyl)methanes.[15] Compounds **1** and **2** are new additions to this group.

Results and Discussion

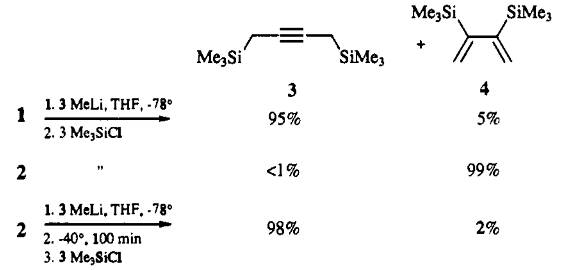
Preparation of 1,4-Bis(trimethylstannyl)-2-butyne (1) and 2,3-Bis(trimethylstannyl)-1,3-butadiene (2). Both of the title compounds have been previously made by Zimmerman and Linder.[16] They treated the ditosylate of 1,4-dihydroxy-2-butyne[17] with (trimethylstannyl)lithium[11,18] and isolated 1,4-bis(trimethylstannyl)-2-butyne (**1**) as well as some 2,3-bis(trimethylstannyl)-1,3-butadiene (**2**). Butyne **1** was subsequently converted to the mono- and disilyl derivatives by treatment with *n*-butyllithium and trimethylchlorosilane.



1 2

We found that treatment of either 2,3-dichloro-1,3-butadiene[19] or the commercially available 1,4-dichloro-2-butyne with 2 equiv of (trimethylstannyl)lithium in THF gave the somewhat air-sensitive bis(trimethylstannyl)acetylene (**1**). If this reaction was done carefully at −78 °C with no excess (trimethylstannyl)lithium and quenched at that temperature, less than 0.5% of the more stable isomer, butadiene **2**, was formed. Under more vigorous conditions, partial isomerization to butadiene **2** occurred. The extent of isomerization depended on details of reaction conditions and the batch of (trimethylstannyl)lithium used. If only 1 equiv of the stannyllithium was used, 50% of the dichloro compound was converted to **1** and no half-reacted chloro–tin compounds (allene, butadiene, or acetylene) could be detected. Both 2-(trimethylstannyl)-[20] and 1,4-bis(trimethylstannyl)butadiene[6a] have been prepared by reaction of 2-chloro- or 1,4-dichlorobutadiene with trimethylstannyl anion.

Scheme I



The equilibration of propargyl- and allenyltin compounds[21] and of allylstannanes[22] is known to occur under the influence of Lewis acids or polar nucleophilic solvents. Attempts to isomerize **1** to **2** by similar methodology (e.g., use of $MgBr_2$ on heating in methanol or dimethyl sulfoxide) met with little success. Compound **1**, however, could be reliably isomerized to **2** by treatment with a catalytic amount of (trimethylstannyl)lithium or methyllithium in THF/HMPA (2 equiv) at 25 °C for 30 min.[23] A similar equilibration of *cis*- and *trans*-crotylstannanes in ether using catalytic amounts of *n*-butyl- or methyllithium has been reported.[24] Minimum conditions needed for the isomerization varied with the batch of (trimethylstannyl)lithium. One-pot conversion of 1,4-dichloro-2-butyne to **2** could be accomplished in 70% yield. Butadiene **2** is a distillable liquid which solidifies in the freezer (−20 °C) and can be stored under nitrogen indefinitely as a low-melting solid. Acetylene **1** is much less stable and slowly decomposes (several months) even at freezer temperatures.

The analogous reaction between 2,3-dichloro-1,3-butadiene and (tributylstannyl)lithium (prepared from tributyltin hydride and lithium diisopropylamide)[25] was also attempted. In this case, the reaction was not very clean and even in the presence of HMPA, only a trace of the stannylated butadiene was formed along with 2-tributylstannyl-1-buten-3-yne.

Lithium Reagents Prepared by Li/Sn Exchange of 1 and 2. Treatment of **1** or **2** with excess (>2 equiv) methyllithium and trimethylchlorosilane at −78 °C in THF cleanly gave bis(trimethylsilyl)acetylene (**3**) or -butadiene **4**, independent of whether the lithium reagent or the silyl chloride was added first (Scheme I). However, if **2** was treated with 2 equiv of methyllithium and the solution warmed to above −50 °C for varying amounts of time and trimethylsilylated, the product mixture slowly changed from **4** to essentially pure **3**. These striking results suggest some interesting possibilities. For example,

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(17) (a) 1,4-Dihydroxy-2-butyne has been used as a precursor of 2,3-disubstituted butadienes. See: Fleming, I.; Taddei, M. *Synthesis* **1985**, 899. For sulfenate [2,3] sigmatropic rearrangement, see: Jeganathan, S.; Okamura, W. H. *Tetrahedron Lett.* **1982**, *23*, 4763. For Claisen rearrangement, see: Ishino, Y.; Nishiguchi, I.; Kim, M.; Hirashima, T. *Synthesis* **1982**, 740. (b) 1,4-Dichlorobutyne has been used to prepare a variety of 2- and/or 3-substituted 1,3-butadienes. See: Bridges, A. J.; Fischer, J. W. *Tetrahedron Lett.* **1983**, *24*, 445. Zhu, L.; Rieke, R. D. *Tetrahedron Lett.* **1991**, *32*, 2865. (c) Batt, D. G.; Ganem, B. *Tetrahedron Lett.* **1978**, 3323.

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(23) No allene intermediates were detected. 1-Stanna-2,3-butadienes apparently rearrange easily.[22b]

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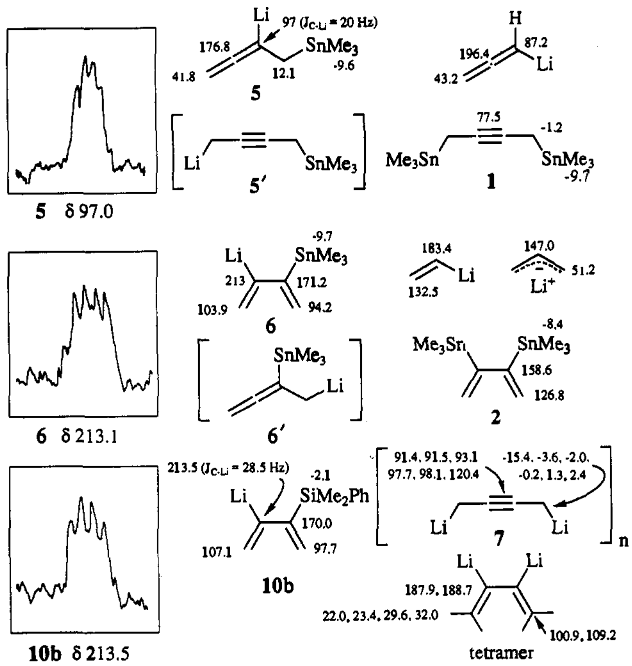
Chart II. ^{13}C NMR Shifts of **5**, **6**, **7**, **10b**, and Model Compounds



there might be two isomeric dilithium reagents or perhaps two isomeric tin ate complexes in solution[1d,6b] which interconvert only above -50 °C. We therefore undertook a study of the transmetalation reactions of **1** and **2**.

Spectroscopic Characterization of Lithium Reagents from 1 and 2. Low-temperature NMR spectra of the lithium reagents prepared from **1** and **2** provided valuable information about their structure in solution. ^{13}C NMR shifts are shown in Chart II, together with some model compounds to aid in the interpretation.[26a,b,27] Treatment of **1** with 1 equiv of methyllithium produced a lithium reagent which clearly had an allenic structure, **5**, rather than an alternative formulation, **5′**, since ^{13}C–^{7}Li coupling to a single lithium was observed for one of the quarternary carbons (97 ppm), the central allenic carbon was characteristically downfield (176.8 ppm), and the terminal $=$CH$_2$ group at δ 41.8 had a J_{C-H} of 158.3 Hz, as expected for an sp^2 carbon. There does, however, appear to be extensive charge delocalization to the terminal carbon, as judged by the upfield shift (41.8 ppm) similar to that of allenyllithium (43.2 ppm)[26a] and allyllithium (51.2 ppm).[26a,b] It is therefore not surprising that some reactions of **5** occur at the terminal carbon to give acetylenic products.

Treatment of a solution of **5** with a second equivalent of methyllithium resulted in the disappearance of the signals of **5**, the appearance of six peaks at 90–120 ppm, and a poorly resolved set of six broad (unresolved Li–C coupling?) peaks between -15 and 3 ppm in the ^{13}C NMR spectrum at -100 °C. The ^{7}Li NMR spectrum was similarly complicated. The chemical shifts (Chart II) are consistent with a formulation of dianion **7** as (LiCH$_2$C$\equiv$CCH$_2$Li)$_n$,[27a,28] where the aggregate structure provides for a number of different environments for both the CH$_2$ and alkyne signals. When samples of **7** in THF were warmed in an attempt to coalesce the multiple signals, an orange precipitate formed at approximately -20 °C and the ^{13}C NMR signals disappeared. The solid did not dissolve on cooling. The reagent had not decomposed, since quenching with trimethylchlorosilane produced a 95% yield of **3**. Apparently, the solution obtained at low temperature is metastable and converts to an insoluble, perhaps polymeric, form of **7** on warming. The structure of **7** was not investigated further. It is interesting that a methylated analog of **7**, 2,5-dimethyl-3,4-dilithio-2,4-hexadiene, has a dilithiobutadiene rather than a dilithiobutyne structure in solid state and in solution.[27c]

A low-yield synthesis of **7** by the Shapiro reaction has been reported.[27b] The metalation of 2-butyne does not produce **7** but rather a trilithium reagent in which all three metalations have occurred on a terminal carbon (i.e., formally the formation of a 1,1,1-trilithiobutyne).[27d] Several known dilithium reagents related to **7** are 2,5-dimethyl-3,4-dilithio-2,4-hexadiene,[27c] 1,4-dilithiobutadiene[6a] and substituted derivatives,[1c,6b,c] *o,o′*-dilithiobiphenyl,[29] and 2,3-bis(lithiomethyl)-1,3-butadiene.[30]

Similar treatment of **2** with methyllithium produced a lithium reagent best formulated as **6** and not **6′**. A well-resolved ^{13}C–^{7}Li coupling (J = 27 Hz) was observed for the C–Li carbon, whose chemical shift (213.1 ppm) was downfield of that of vinyllithium[26a] at 183.4 ppm, perhaps indicative of some allenic character. The trimethyl- and phenyldimethylsilyl analogs of **6**, lithium reagents **10a** and **10b**, were similar, with ^{7}Li–C coupling of 26 Hz for **10a** and 28.5 Hz for **10b**. The four vinyl protons of **10b** have different chemical shifts up to -30 °C (δ 5.4 and 4.6, d, J = 9 Hz; δ 4.2 and 3.8, J = 5.4 Hz). This defines some limitations on the rate of interconversion between **10b** and its allylic isomer **10b′**. Charge delocalization in both **6** and **10** is indicated by the downfield shift of the C–Li carbons (possible development of allenic character[31]) and the upfield shift of the terminal CH$_2$ groups (δ 94.2). When a solution of **6** was warmed to -50 °C, the spectrum slowly changed to that of **5**.

Derivatization of Lithium Reagents from 1 and 2. Key information which helped to explain the unusual results presented in Scheme I was provided by a series of quenching studies. Even though NMR studies showed that compound **1** was quantitatively converted to monolithium reagent **5** on treatment with 1 equiv of methyllithium, it could not be cleanly monosilylated to **8** under any conditions; mixtures of **1**, **3**, and **8** were always obtained (Scheme II). Under conditions of inverse addition, some isomerization of **1** to **2** occurred, probably due to warming during the transfer. When ≥2 equiv of methyllithium was used, predominant formation of **3** was observed under all conditions. The ~5% of **4** formed from **1** may arise because the mono- (**5**) and/or dilithium (**7**) reagents silylate to a small extent to give allene intermediates, which proceed to diene rather than acetylene products during the second step (e.g., monosilylation of **7** at an allenyl position gives **10**, which is known to give butadiene **4** on silylation). In fact, 1–2% of 1,2-bis(trimethylsilyl)-2,3-butadiene (not shown in Scheme II) was usually formed during the reactions of **1** with methyllithium–trimethylchlorosilane. Apparently, the rates of mono- and ditransmetalation of **1** are close and competitive with silylation of either lithium reagent so that *in situ* exchanges of monosilyl compound **8** cannot be avoided at -78 °C.[32]

Butadiene **2** behaved quite differently than did **1**. Treatment of **2** with 1 equiv of methyllithium in THF at -78 °C followed

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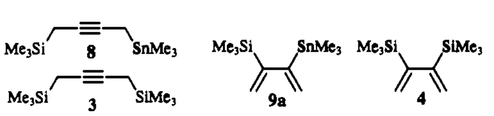
(31) We prepared **10b** with the goal of examining the chirality of the lithium reagent. Allenic delocalization requires a skew conformation (analogous to **37b**), and in this structure, the SiMe$_2$ groups would be diastereotopic. The SiMe$_2$ remained a singlet in the ^{13}C and ^{1}H NMR spectra down to -142 °C. Thus, either there is insufficient chemical-shift difference to detect decoalescence or, more likely, the rotation barrier is below ≈7 kcal/mol.

(32) Barfield, M.; Bates, R. B.; Beavers, W. A.; Blacksberg, I. R.; Brenner, S.; Mayall, B. I.; McCulloch, C. S. *J. Am. Chem. Soc.* **1975**, *97*, 900.

Scheme II



1 $\xrightarrow[2.\ Me_3SiCl]{1.\ MeLi,\ THF,\ -78°}$	**1**	**8**	**3**	**2**	**9a**	**4**
Addition of Me$_3$SiCl to RLi (normal):						
3.2 MeLi, 3.7 Me$_3$SiCl, THF	-	-	91	-	1	6
1.2 MeLi, 2.6 Me$_3$SiCl, THF	7	38	40	4	2	-
Addition of RLi to Me$_3$SiCl (inverse):						
1 MeLi, 3.6 Me$_3$SiCl, THF	2	56	11	27	1	-
2 $\xrightarrow[2.\ Me_3SiCl]{1.\ MeLi,\ THF,\ -78°}$	**1**	**8**	**3**	**2**	**9a**	**4**
Addition of Me$_3$SiCl to RLi (normal):						
4 MeLi, 6 Me$_3$SiCl, THF	-	-	-	-	-	>99
Addition of RLi to Me$_3$SiCl (inverse):						
2.2 MeLi, 2.6 Me$_3$SiCl, THF	-	-	5	-	65	30
2.2 MeLi, 8.1 Me$_3$SiCl, THF	-	-	6	-	82	12
1.1 MeLi, 1.2 Me$_3$SiCl, pentane	-	-	2	1	95	2

by silylation or reaction with other electrophiles gave generally clean monoderivatization of **6**. Under optimal preparative conditions (inverse addition of **6** to trimethylchlorosilane in pentane), 95% of monosubstitution product **9a** was obtained. When the monolithium reagent **6** formed from **2** at -78 °C was treated with excess methyllithium, the behavior was more complex. Treatment with ≥2 equiv of trimethylchlorosilane (normal addition) gave only disilylbutadiene **4**. If the lithium reagent solution was added to a solution of trimethylchlorosilane (inverse addition), then the ratio of monosilylation to disilylation (**9a**/**4**) was a direct function of the excess of trimethylchlorosilane used (Scheme II, the small amounts of **3** formed are the result of warming during the inverse addition). Apparently, the silylation of **6**, the silylation of excess methyllithium, and the Li/Sn exchange of **9a** by excess methyllithium are competitive. Confirmation was provided by quenching with a much more reactive electrophile, pivaldehyde, which gave clean monosubstitution even when excess methyllithium was used. Control experiments have shown that the reaction of methyllithium with pivaldehyde is faster than the Li/Sn exchange of **2**.

Seyferth has observed a similar phenomenon in the silylation of the monolithium reagent from 1,2-bis(tributylstannyl)ethene.[9a] In this case, the use of inverse addition gives monosilylated product, whereas in our case, the exchanges were more rapid so that even inverse addition gave substantial bis substitution.

When a solution of **6** and excess methyllithium was warmed to -50 °C, the product distribution changed from pure disilylbutadiene **4** to mostly disilylacetylene **3** over a period of several hours. This signals the formation of the dilithium reagent **7**, either by a second metalation of **6** or a rearrangement of **6** to **5** (as shown by NMR studies) followed by a rapid second metalation of **5**.

On the basis of these chemical studies and spectroscopic work, we have concluded that the processes outlined in Scheme III are at work. Both **1** and **2** are converted to monolithium reagents **5** and **6**, respectively, on treatment with methyllithium in THF at -78 °C, but only **1** is converted to a dilithium reagent, **7**, with more than 1 equiv of methyllithium under these conditions. The monolithium reagent **6** prepared from **2** is converted to the same dilithium reagent **7** only at temperatures above -50 °C. In either case, the formation of **3** (from **1** at low temperature or **2** at higher temperature) results from silylation of dilithium reagent **7**. Compound **3** can also be formed by the stepwise process **1** to **5** to **8** to **3**. The exclusive formation of **4** from **2** is the result of a stepwise *in situ* Li/Sn exchange–silylation sequence (**2** to **6** to **9a** to **4**).

This system shows interesting and complex behavior because of strikingly divergent thermodynamic and kinetic control. Compound **1** is the kinetic product from the reaction of 1,4-dichloro-2-butyne *or* 2,3-dichlorobutadiene with (trimethylstannyl)lithium, but diene **2** is *more* stable than **1** so *either* dihalide can serve as a precursor to *either* of the stannanes. In the monolithium reagents, the dienyl structure **6** is *less* stable than the isomeric structure **5** and the common dilithium reagent **7** seems to be propargylic in nature and gives acetylenic products. Thus, **2** can give *either* diene or acetylene products depending on whether the lithium reagents are used under kinetic control or allow to equilibrate. Finally, **2** can be prepared from **1** by equilibration, and **1** can be prepared from **2** by the sequence of >2 equiv of methyllithium at -50 °C (**2** to **7**) and stannylation with (trimethylstannyl)bromide (**7** to **1**).

Scheme III

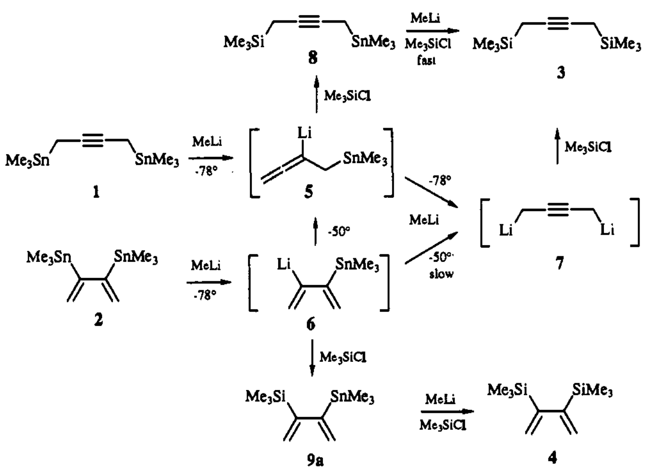
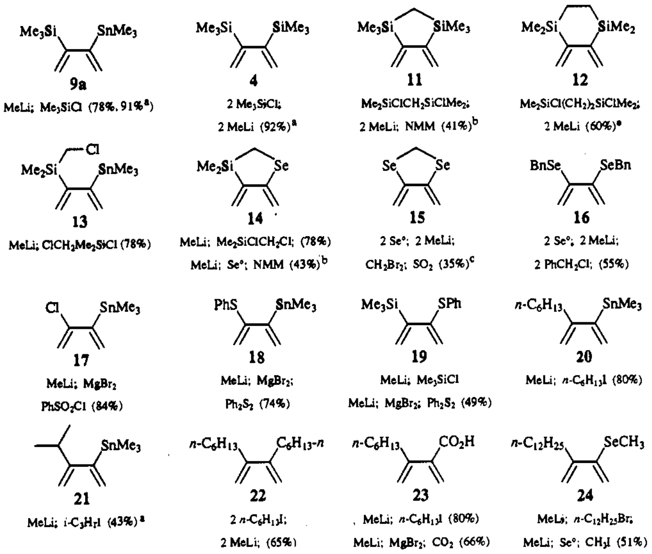


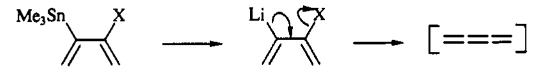
Chart III[a]



[a] (a) Yield determined by NMR integration. (b) Yield is for the Diels–Alder adduct with *N*-methylmaleimide (NMM). (c) Yield is for cycloadduct with SO$_2$.

Monosubstitution Reactions of 2,3-Bis(trimethylstannyl)-1,3-butadiene. Chart III summarizes the 2,3-disubstituted butadienes we have prepared from **2**. In a typical procedure, a solution of monolithium reagent **6** was prepared by adding methyllithium to a solution of **2** in THF. An electrophile was then added to the solution, or the solution was transferred by using a cooled (-78 °C), jacketed syringe or cannula to a solution of the electrophile in THF, ether, or pentane at -78 °C. The reaction was quenched at either -78 or 25 °C depending on the reactivity of the electrophile. The inverse addition procedure generally provided the cleanest products and highest yields, although care has to be taken to keep the solution of **6** below -50 °C.

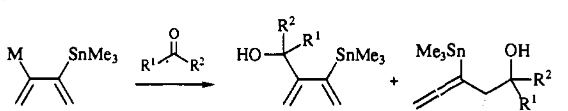
Attempts to form **6** in diethyl ether or 40:1 ether/THF gave very little silylated product after trimethylchlorosilane quenching, even when the anionic solutions were allowed to warm to room temperature. The use of *n*-butyllithium instead of methyllithium suffered from the fact that butyl groups exchange with tin methyl groups and become incorporated into the products. For several electrophiles (chlorination, **17**, sulfenylation, **18**, **19**, and carboxylation, **23**), it was advantageous to first convert lithio diene **6** to the Grignard reagent[4c] by treatment with magnesium bromide etherate in ether/benzene. It appears that the utilization of the Grignard reagent, as well as inverse quenches into less polar solvents like ether and pentane, improves the yields by eliminating Li/Sn exchanges that could occur during quenches in THF. This was particularly important in the cases of chlorination and sulfenylation where the Li/Sn exchange of the product was favored by the presence of an electronegative substituent and could lead to an intermediate (**25**) capable of LiX elimination to butatriene. Such elimination apparently prevents any further derivatization of chloro–tin compound **17**, but *in situ* treatment of tin sulfide **18** and trimethylchlorosilane with methyllithium produced **19** in 55% NMR yield, comparable to that obtained by first introducing the silyl group (**9**) followed by sulfenylation. The elimination of **25** (X = SPh) was, therefore, slower than reaction with the chlorosilane. It was also possible to obtain bis-sulfenylated products from both **1** and **2** by similar *in situ* reactions, but mixtures of diene, allene, and acetylene products were formed. Of all the entries in Chart III, the synthesis of 2-chloro-3-(trimethylstannyl)-1,3-butadiene (**17**) was the only one that was optimized since this diene was used in a synthesis of 3,4,3′,4′-tetrachlorobiphenyl 2,3-oxide.[1f]



25

The monolithium reagent **6** can be alkylated with primary (**20**, **22**, **23**, and **24**) and some secondary halides (**21**). The reaction between **6** and 1-iodobutane occurs within 20 min at −78 °C in THF. In most of the alkylation reactions, the THF solutions were slowly warmed to room temperature. The alkylation, however, must occur at low temperature since **6** has been shown to disproportionate at higher temperatures. Only minor amounts of allenes were detected in the reactions of the compounds in Chart III.

The reactions of **6** and the Grignard and cuprate reagents prepared from it with several carbonyl compounds were also examined. The lithium reagent **6** produced mostly diene products **26**, but some allenic reactivity was seen with acetone and 3-heptanone **27**. (Yields in parentheses were determined by NMR integration.)



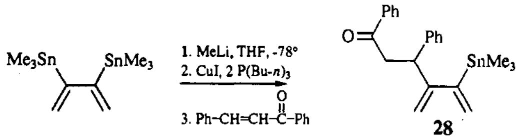
26 **27**

M	R¹	R²	products, yield	
Li	Me	Me	**26a**, 59 (69)	**27a** (18)
MgBr	Me	Me	**26a**	**27a** (82)
Li	CH_2CH_2Ph	H	**26b**, 42 (52)	**27b**
MgBr	CH_2CH_2Ph	H	**26b** (14)	**27b** (80)
Li	*n*-Pr	*n*-Pr	**26c**, 61 (63)	**27c** (<2)

The formation of allenes has also been noted for 2-lithio-1,3-butadiene.[4a] Like those reactions with heteroatom electrophiles discussed above, employing an inverse quench into a solution of the carbonyl compound in ether seemed to generally improve yields and minimize unreacted starting material **2**.[33] Benzaldehyde and conjugated ketones (benzophenone and chalcone) failed to produce useful amounts of the corresponding dienes **26**. Benzophenone gave some allene **27** together with recovered starting material. A royal blue solution was produced upon mixing **6** and benzophenone, indicating the production of lithium benzophenone ketyl.

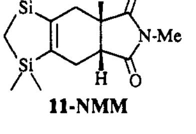
The Grignard reagent prepared from the reaction of **6** with magnesium bromide gave allenes as the major or only products upon reaction with carbonyl compounds. This parallels the reactivity of the known 1,3-butadien-2-ylmagnesium chloride,[26c,34] although the preference for allene formation appears to be greater for our reagent.

The conversion of **6** to organocopper reagents was also studied. Using the 1,4-addition to chalcone to give **28** for comparison of several types of copper reagents ($CuI{\cdot}2P(Bu\text{-}n)_3$ (64%),[35a] $^1/_2$ $CuBr{\cdot}SMe_2$ (55%),[35b] $i\text{-}Pr_2NCu$ (33%),[35c] and CuCN (0%),[35d]), the highest yield obtained was with the tributylphosphine organocopper complex. In the case of the Gilman reagent (R_2CuLi), the yield was based upon chalcone and required 2 equiv of **6**. No allene products were seen in these reactions. Only diene products are reported for the 1,4-addition to enones using 1,3-butadien-2-ylmagnesium chloride in the presence of catalytic cuprous bromide–dimethyl sulfide.[36] A similar attempt to employ the Grignard reagent and catalytic cuprous iodide–tributylphosphine in the addition to chalcone led only to the allene product (37% yield).

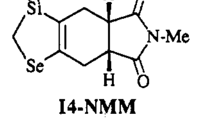


28

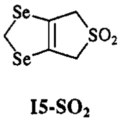
Disubstitution Reactions of 2,3-Bis(trimethylstannyl)-1,3-butadiene. Since the Li/Sn exchange of **2** and the monoderivatized butadienes such as **9**, **18**, or **20** appeared to be faster than the reaction of methyllithium with many electrophiles, some double derivatizations (formation of compounds **4**, **11**, **12**, **15**, **16**, and **22**) could be carried out *in situ* by simply adding 2–3 equiv of methyllithium to a solution of **2** and 2 equiv of the electrophile in THF at −78 °C. Such reactions were successful with silyl halides, elemental selenium, and *n*-hexyl iodide as the electrophile. Alternatively, two different groups can be introduced sequentially, provided the first group is stable to strong bases. Chart III shows a variety of 2,3-disubstituted butadienes which have been prepared by one or the other of these methods. In the examples employing elemental selenium, a dienyl bis(selenolate) was probably formed since all of the otherwise insoluble elemental selenium disappeared from the solution. This intermediate was then alkylated to give **15** and **16**. Cyclic five-membered ring dienes **11**, **14**, and **15** were very reactive Diels–Alder dienes which easily polymerized, even at −20 °C. They were best isolated and characterized as the *N*-methylmaleimide (**11-NMM** and **14-NMM**) or sulfur dioxide (**15-SO₂**) adducts.



11-NMM



14-NMM



15-SO$_2$

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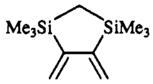
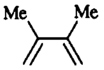
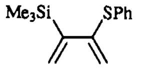
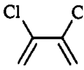
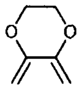
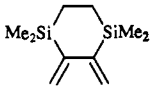
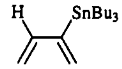
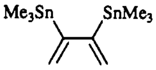
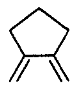
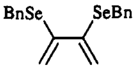
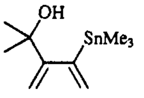
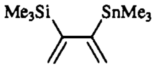
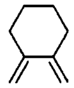
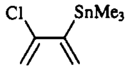
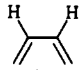
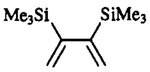
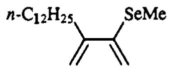
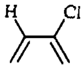
(33) Compound **2** was formed by a Li/Sn exchange between **6** and its reaction product with the electrophile.

(34) Kondo, K.; Dobashi, S.; Matsumoto, M. *Chem. Lett.* **1976**, 1077. Nunomoto, S.; Yamashita, Y. *J. Org. Chem.* **1979**, *44*, 4788.

(35) (a) Tanaka, T.; Toru, T.; Okamura, N.; Hazato, A.; Sugiura, S.; Manabe, K.; Kurozumi, S. *Tetrahedron Lett.* **1983**, *24*, 4103. (b) House, H. O.; Chu, C.-Y.; Wilkins, J. M.; Umen, M. J. *J. Org. Chem.* **1975**, *40*, 1460. Marfat, A.; McGuirk, P. R.; Helquist, P. *J. Org. Chem.* **1979**, *44*, 3888. (c) Bertz, S. H.; Dabbagh, G.; Villacorta, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 5824. (d) Marino, J. P.; Jaén, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 3165. Gorlier, J.-P.; Hamon, L.; Levisalles, J.; Wagnon, J. *Chem. Commun.* **1973**, 88.

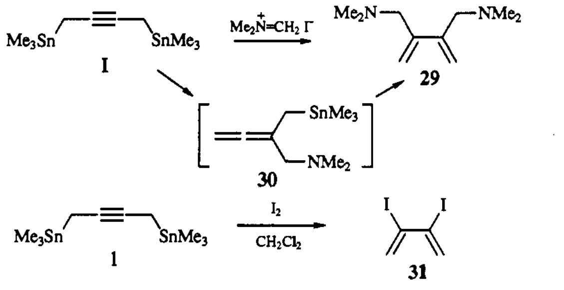
(36) Shea, K. J.; Pham, P. Q. *Tetrahedron Lett.* **1983**, *24*, 1003.

Table I. Relative Rates for the Reaction of Dienes with *N*-Methylmaleimide at 80 °C in Benzene-d_6

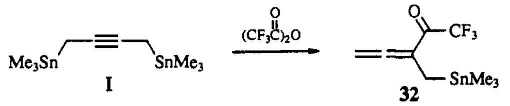
compound			compound			compound			compound		
no.	structure	k_{rel}	no.	structure	k_{rel}	no.	structure	k_{rel}	no.	structure	k_{rel}
11		70000[a]			290	**19**		80[c]	**35**		5
		4000[b]	**12**		175	**36**		80	**2**		1
		3200[b]	**16**		110[c]	**26a**		70	**9a**		0.4
		1350[b]	**17**		100			20[d]	**4**		0.06
		400						16			

[a] This value was estimated from rates measured at 25 °C with benzoquinone as the dienophile. [b] Extrapolated from data in ref 40a, measured at 30 °C in dioxane using maleic anhydride as the dienophile (maleic anhydride is 1.4 times as reactive as *N*-methylmaleimide toward cyclopentadiene.[2d] [c] This value was extrapolated from rates measured at 25 °C in $CDCl_3$ using a value of −33 eu for $\Delta S^{\ddagger}$. [d] Estimated from data in ref 2c, comparing 2,3-dimethylbutadiene and butadiene at 30 °C in dioxane.

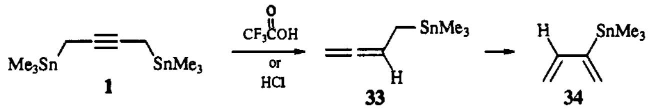
Electrophilic Substitution of 1,4-Bis(trimethylstannyl)-2-butyne. Propargylstannanes and silanes generally undergo electrophilic substitution with the formation of allenes.[37] Two sequential reactions of bis(stannyl)acetylene **1** should thus lead to butadienes.[38] Overman and co-workers have employed Mannich reagents as intramolecular electrophiles for the cyclization of vinylsilanes,[39] and Reich et al. have shown that allylstannanes react with Mannich reagents to give aminomethylated products.[1e] Treatment of **1** with 2 equiv of Eschenmoser's salt in chloroform or methylene chloride led to 2,3-bis((dimethylamino)methyl)-1,3-butadiene (**29**). When this reaction was carried out in $CDCl_3$ and examined by NMR before all of the essentially insoluble salt was consumed, only **1**, **29**, and trimethyliodostannane were observed. The presumed intermediate allene **30** thus reacted more rapidly with Eschenmoser's salt than did acetylene **1**. A similar, double substitution with I_2 led to the easily polymerizable 2,3-diiodobutadiene (**31**). Reactions with acid chlorides or isobutyraldehyde in the presence of Lewis acids ($SnCl_4$, $EtAlCl_2$, $AlCl_3$, or $BF_3{\cdot}OEt_2$) failed.



An electrophilic substitution reaction of **1** that stopped at the allene (monoaddition) stage was seen with trifluoroacetic anhydride. In this case, further addition of anhydride to **32** was probably not favored due to the destabilizing effect of the α-trifluoroacetyl group on the intermediate cation.



Protodestannylation of **1** in the presence of trifluoroacetic acid gave approximately equal amounts of allene **33** and the more stable diene **34** after 10 min at room temperature. Fourteen hours later, isomerization to the diene was complete. Evidently, the trimethylstannyl trifluoroacetate formed was a sufficiently active Lewis acid to effect the allene to diene isomerization. This could be avoided when protodestannylation was performed using HCl generated *in situ* by the reaction of acetyl chloride and methanol in $CDCl_3$.



Electrophilic Substitution of 2,3-Bis(trimethylstannyl)-1,3-butadiene. Several electrophilic substitution reactions of **2** were attempted (protodestannylation, peracid oxidation, and acylation). We found poor selectivity between mono- and disubstitution, such that mixtures of allenes and dienes were often formed. Compound **2** was much less reactive than **1** with electrophiles. For example, reaction of **1** with trifluoroacetic anhydride was complete in 15 min at room temperature; a similar reaction with **2** gave no detectable product after 12 h. We found no useful reactivity in our brief survey.

Diels–Alder Reactivity of 2,3-Disubstituted-1,3-butadienes. Our original purpose in preparing diene **2** was for use in Diels–Alder reactions as a more reactive equivalent of 2,3-dichlorobutadiene (**35**), which is known to be a very poor Diels–Alder diene.[3] Unfortunately, **2** is even less reactive than **35** and quite unsuitable for our purpose. Table I reports a comparison of **2** with several dienes in their reactivity toward *N*-methylmaleimide.[40] Most of the reactions were carried out at 80 °C in benzene and followed by NMR in sealed tubes containing a small amount of methylene blue as a radical inhibitor. The table also includes some relevant literature rates, extrapolated to our reaction conditions.

The relatively high reactivity of chloro stannyl diene **17** makes it an effective alternative to **2** as an equivalent to 2,3-dichlo-

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(37) Kitching, W.; Fong, C. W.; Smith, A. J. *J. Am. Chem. Soc.* **1969**, *91*, 767.

(38) Pornet, J.; Kolani, N. *Tetrahedron Lett.* **1981**, *22*, 3609.

(39) Overman, L. E.; Malone, T. C.; Meier, G. P. *J. Am. Chem. Soc.* **1983**, *105*, 6993.

(40) For reactivity studies of a variety of 2,3-disubstituted butadienes, see: (a) Scharf, H.-D.; Plum, H.; Fleischhauer, J.; Schleker, W. *Chem. Ber.* **1979**, *112*, 862. (b) Sustmann, R.; Böhm, M.; Sauer, J. *Chem. Ber.* **1979**, *112*, 883.

robutadiene for Diels–Alder reactions. The thermal stability of **17** has not been carefully studied. Although it can be used up to 150 °C, it does decompose to give trimethylchlorostannane at that temperature.

In the absence of special effects, 1-silyl-1,3-butadienes are significantly deactivated (factor of 10–1000) compared to butadiene itself.[41] 2-Silyl or 2-stannyl substitution seems to deactivate butadienes less or perhaps even activate them toward cycloaddition,[17c,42] as shown by the high reactivity of cyclic bis(silanes) **11** and **12** and monostannylbutadiene **36**. The reason for the exceptionally poor reactivity of acyclic bis(trimethylstannyl)- and bis(trimethylsilyl)-substituted dienes **2**, **4**,[43] and **9a** may be in part steric repulsion between the groups which disfavors the s-*cis* conformation. However, a strictly steric explanation seems weak because of the relatively small effective size of trimethylstannyl groups (e.g., the *A* value is 1.0 kcal/mol).[44a] The relatively small difference between **2** and **9a** also argues against large steric interactions between the 2,3-substituents since trimethylsilyl (A = 2.5 kcal/mol[44b]) is much larger than trimethylstannyl, as does the relatively high reactivity of compound **26a** in which a bulky alkyl group replaces one of the trimethylstannyl groups. It is possible, of course, that **26a** is a special case because the s-*cis* conformation may be favored by attractive interactions resulting from coordination between the trimethylstannyl group and the hydroxyl. The interactions between vicinal C–Sn bonds can be compared to that between adjacent lone pairs in hydrazines.[45] We therefore propose that there may also be an electronic component resulting from unfavorable repulsive interactions between the two electron-rich syn- (or anti-) periplanar C–Sn bonds in the s-*cis* (or s-*trans*) conformation. The relatively high reactivity of chloro stannyl diene **17** could then be from a related stabilizing interaction (anomeric effect) between the electron-deficient C–Cl and electron-rich C–Sn bonds which favors planar structures.

We have not been able to clearly define the conformation of **2**. The UV spectrum (Figure 1, λ_{max} 200, sh, 228 nm) does not seem to clearly define a skew geometry, as does that of 2,3-di-*tert*-butylbutadiene (λ_{max} 185, sh, 209 nm),[46] but the characteristic diene absorption at ca. 230 nm is weaker than that in **17** and a "normal" diene, 2,4-hexadiene. However, this absorption is almost absent in **26a**, which is a reactive Diels–Alder diene. Unfortunately, the tin substituents will perturb the spectra of both planar and skew conformations in an unpredictable way.

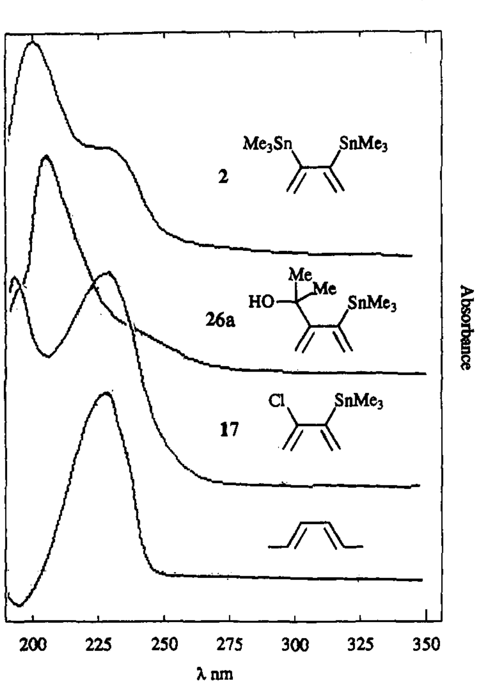
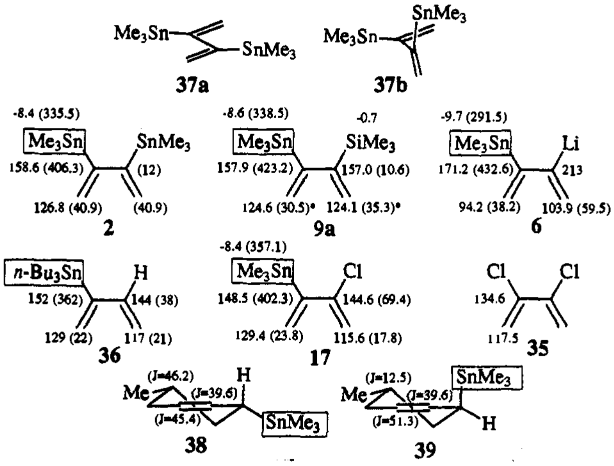


Figure 1. UV spectra in hexane.

Chart IV. ^{13}C NMR Chemical Shifts, δ(^{119}Sn–^{13}C Couplings, Hz)



Three-bond carbon–tin couplings in saturated systems follow a Karplus-like relationship[47a] and might be expected to be sensitive to diene conformation (i.e., **37a** or **37b**). Chart IV shows the J_{C-Sn} values in **2**, **6**, and **9a**, which might have a tendency to adopt conformations such as **37b**, as well as two others, **17** and **36**, where one would expect a planar or near planar conformation. All couplings are reported for ^{119}Sn, where these are resolved from ^{117}Sn. There are, in fact, systematic differences between the two types: **17** and **36** have larger single-bond $^{2}J_{C-Sn}$ (69.4 and 38 Hz) and smaller $^{3}J_{C-Sn}$ (17.8 and 21 Hz) than do **2**, **6**, and **9a**. However, the ^{3}J value is in the opposite direction from that predicted by a naive Karplus argument. The allylic stannane model compounds **38** and **39** help to clarify the situation: the ^{3}J through the sp^{3} carbons is much larger (46.2 Hz) for *cis* isomer **38**, in which the Sn and carbon are anti, than in the *trans* isomer (12.5 Hz), in which they are gauche, as predicted by a Karplus relationship. It is interesting, however, that the magnitudes are in the opposite direction for the allylic ^{3}J coupling (45.4 for *cis*, 51.3 for *trans*). The ^{2}J values are very similar in the two isomers.[47b] We can thus make a weak argument based on these coupling trends that **2**, **6**, and **9a** adopt perpendicular conformations, but it seems likely that there are strong electronic effects on these C–Sn couplings. We would need more definitive information to arrive at a clear decision on the origins of the low Diels–Alder reactivity of **2**, **4**, and **9a**.

Summary. Short syntheses of 1,4-bis(trimethylstannyl)-2-butyne (**1**) and 2,3-bis(trimethylstannyl)-1,3-butadiene (**2**) have been developed. The Li/Sn exchange of **1** and **2** gives mono- (**5** and **6**) and dilithium (**7**) reagents which have been spectroscopically characterized. A wide variety of both symmetric and unsymmetric 2,3-disubstituted 1,3-butadienes can be prepared from them. Some electrophilic substitutions of **1** and **2** have also been investigated and provided access to a number of interesting allenes and dienes.

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Experimental Section

General. Nuclear magnetic resonance (NMR) spectra were obtained on an IBM FX-200, Bruker WP-200, WP-270, AM-360, or AM-500 spectrometer. Unless otherwise specified, the spectra were measured in $CDCl_3$ using tetramethylsilane (δ 0) or $CHCl_3$ (δ 7.24) as reference for the ^{1}H NMR spectra, $CDCl_3$ triplet (δ 77.0) in the ^{13}C spectra, and tetramethylstannane (δ 0) for ^{119}Sn spectra. Couplings (J_{Sn-H} and J_{Sn-C}) are reported for ^{119}Sn, where these were resolved from ^{117}Sn signals; otherwise, the reported values represent an average. Infrared (IR) spectra were recorded on a Beckman 4230, Beckman Acculab 7, or Mattson Polaris spectrophotometer. An AEI MS-902 or Kratos MS-80 spectrometer was employed to obtain mass spectra (MS). Elemental analyses were done by Galbraith Laboratories. Bath temperatures are reported for Kugelrohr distillations. Reported melting points are uncorrected.

Diethyl ether and tetrahydrofuran (THF) were freshly distilled from sodium benzophenone ketyl. Dry CH_2Cl_2 was distilled from CaH_2. Methyllithium (1.0–1.5 M, low halide content in Et_2O) was obtained from Aldrich Chemical Co. and titrated using *n*-propanol with 1,10-phenanthroline as indicator.[48] Tetramethylstannane[49] and trimethylbromostannane[50] were prepared by literature procedures.

Gas chromatographic (GC) purification was performed on a Varian 90-P3 gas chromatograph with a thermal conductivity detector. A flow rate of approximately 60 mL/min was employed with helium as the carrier gas using a 5-ft × $^{3}/_{8}$-in. column or $^{1}/_{4}$-in. column packed with 20% SE-30 on Chromosarb W AW DMCS 60/80. Product analyses were carried out with the 90P3 or with a Varian 3700 gas chromatograph on a 25-m, 0.33-bore capillary column with a bonded phase of dimethylsiloxane.

Reactions involving lithium reagents were run under an atmosphere of dry N_2 in glassware which had been dried in a 120 °C oven for at least 3 h. All reaction temperatures were measured externally.

Standard Workup. In the standard workup procedure (1 mmol), the reaction mixture was poured into 20 mL of water and extracted with 10 mL of 50% ether–pentane. The organic layer was then washed successively with 10–20 mL of water and 10–20 mL of brine and filtered through a Na_2SO_4 cone. For reactive dienes, approximately 1 mg of 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide (radical inhibitor) was added before evaporation of solvent.

CAUTION. Organoselenium and organotin compounds are toxic and should be handled with due care. Solutions containing volatile organotin compounds were rotary evaporated in a bond.

(Trimethylstannyl)lithium. This is a modification of the procedure of Tamborski, Ford, and Soloski.[51] A dry, 250-mL, 3-neck round-bottom flask with a stopcock drain outlet on the bottom (connected to a 24/40 joint with a nitrogen inlet) was equipped with a condenser, mechanical stirrer, and septum and a glass wool plug for the drain. Lithium wire containing 1% sodium (4.03 g, 580 mmol) cut into ~4-mm pieces was added, and the system was purged with N_2, using a Firestone valve. Trimethylbromostannane (68.9 g, 282.7 mmol) was dissolved in THF to provide a total volume of 120 mL. After addition of 80 mL of THF to the lithium, 30 mL of the Me_3SnBr/THF solution was transferred into the flask by a cannula. The solution spontaneously refluxed and then cooled over a 30-min period. The THF solution of Me_3SnLi was drained into a N_2-flushed receiving flask. The unreacted lithium was again suspended in 80 mL of THF, and this cycle was repeated three times. The resulting THF solutions of (trimethylstannyl)lithium contained a fine suspension of black solids, but these solids did not interfere with syringe measurements and transfers and often settled out during storage. Titration of the solutions obtained using *n*-propanol with 1,10-phenanthroline as indicator[48] provided an easily recognized dark blue endpoint and indicated a total production of 189 mmol (67% yield) of Me_3SnLi in a total volume of 435 mL. These THF solutions were stable for several months at –20 °C under N_2.

2,3-Dichloro-1,3-butadiene was prepared as described by Gibbs and Day:[19] ^{1}H NMR (200 MHz) δ 5.61 (d, J = 1.0 Hz, 2H), 6.01 (d, J = 1.0 Hz, 2H); ^{13}C NMR (90.6 MHz) 117.5 (CH_2), 134.6 (C).

1,4-Bis(trimethylstannyl)-2-butyne (1). A dry, 100-mL airless flask was purged with N_2 using a Firestone valve, and 50 mL of 0.43 M Me_3SnLi in THF (21.5 mmol) was added. After the solution was cooled to –78 °C, 1.32 g (1.05 mL, 10.7 mmol) of 1,4-dichloro-2-butyne was added over 90 s and the solution was stirred an additional 5 min and worked up. The residue was distilled (Kugelrohr). The initial fraction (0.0948 g, 20–55 °C/0.2 mm) contained some product and starting material with other contaminants, and was discarded. The fraction collected at 60–120 °C/3 mmHg provided 3.43 g (9.03 mmol, 84% yield containing 1.3% of **2**) of **1**: ^{1}H NMR (270 MHz) δ 0.15 (s, J_{Sn-H} = 52.5 Hz, 18H), 1.56 (s, J_{Sn-H} = 59, 24 Hz, 4H); ^{13}C NMR (acetone-d_6, 50.10 MHz) δ –9.7 (J_{Sn-C} = 331 Hz), –1.2 (J_{Sn-C} = 290 Hz), 77.5; ^{119}Sn NMR (acetone-d_6, 74.32 MHz) δ 8.87 ($J(^{119}Sn-^{117}Sn)$ = 139 Hz); IR 2994, 2922, 2282 (w), 2227 (w), 1432, 1202, 1183, 782 cm^{-1}; MS M^+ calcd for $C_{10}H_{22}\,^{118}Sn_2$ 377.9764, found 377.9763.

This material was stored at –20 °C under N_2, and although some brown solid material was deposited upon storage, **1** was still pure by NMR after several months.

2,3-Bis(trimethylstannyl)-1,3-butadiene (2). A 250-mL airless flask was purged with N_2 (Firestone valve), 105 mL of 0.33 M Me_3SnLi in THF (34.6 mmol) was added, the flask was placed in an ice bath, and 5.4 g (5.3 mL, 30 mmol) of HMPA (distilled from CaH_2, 73 °C/1.3 mmHg) was added followed by dropwise addition of 1,4-dichloro-1-butyne (1.47 ml, 15.0 mmol) over 2 min. The mixture was allowed to stir for 5 min at 0 °C and then for 40 min at room temperature before being poured into 150 mL of water and 100 mL of pentane. The pentane layer was extracted with two more 100-mL portions of water, washed with brine, and filtered through a Na_2SO_4 cone and the solvent removed. The residue was distilled (65–66 °C/0.80 mmHg) using a 15-cm vacuum-jacketed Vigreux column to give 4.25 g of **2** (11.2 mmol, 75% yield, <0.5% of **1**) as a clear liquid which solidified upon freezer storage (–20 °C) under N_2: ^{1}H NMR (270 MHz) δ 0.18 (s, J_{Sn-H} = 54 Hz, 18H), 5.29 (dd, J = 2.0, 0.5 Hz, J_{Sn-H} = 70, 8 Hz, 2H), 5.67 (dd, J = 2.0, 0.5 Hz, J_{Sn-H} = 148, 7.5 Hz, 2H); ^{13}C NMR (50.10 MHz) δ –8.4 (J_{Sn-C} = 335.5 Hz), 126.8 (J_{Sn-C} = 40.9 Hz), 158.6 (J_{Sn-C} = 406.3, 12 Hz); ^{119}Sn NMR (74.32 MHz, acetone-d_6) δ –29.3; IR 3062, 3005, 2979, 2938, 1581, 1399, 1208, 921, 782 cm^{-1}; UV λ_{max} (hexane) 200 (ϵ 18 300); 228 nm (8790). Anal. Calcd for $C_{10}H_{22}Sn_2$: C, 31.64; H, 5.84. Found: C, 31.74; H, 5.91.

Lithium–Tin Exchange and Silylation of 1 and 2 (Scheme II). A. Normal Addition. To a 0.20 M solution of **1** or **2** (0.1 to 2.0 mmol) in THF which was cooled to –78 °C was added 1.0 equiv of MeLi in ether down the side of the flask. After 5 min, 3.0 equiv of Me_3SiCl was added, the cooling bath was removed, and 0.30 mL of 30% KOH per millimole of MeLi was added followed by 4 mL of pentane. The pentane solution was dried with Na_2SO_4, and a sample was removed for GC analysis. The Na_2SO_4 was filtered and the pentane removed under vacuum.

Capillary GC analysis at 150 °C gave the following retention times: **4** (2.82 min), 1,2-bis(trimethylsilyl)-2,3-butadiene (2.94 min), **3** (3.25 min), **9a** (3.79 min), **8** (5.28 min), **2** (5.93 min), and **1** (10.01 min).

B. **Inverse Addition.** The lithium reagent solution was prepared at –78 °C as above. After 5 min, the solution was transferred with a dry ice cooled syringe or cannula to a flask at –78 °C containing Me_3SiCl in 4 mL of pentane. GC analysis and workup were done as before.

1,4-Bis(trimethylsilyl)-2-butyne (3). A solution of MeLi (0.64 mmol) was added to 0.8 mL of ether in a 10-mm NMR tube with a septum. The NMR tube was cooled to –78 °C, and 0.166 mL (0.64 mmol) of **1** was added. The solution was frozen in a liquid N_2 bath, and MeLi (0.64 mmol) in 2.6 mL of THF was added. The contents were warmed to –78 °C, and the sample was used in NMR experiments. An insoluble precipitate in an orange solution formed between –60 and –27 °C. Addition of 0.330 mL of Me_3SiCl at –78 °C caused the precipitate to dissolve and the orange solution to fade to yellow. Dodecane (0.080 mL) was added as an internal GC standard, and the solution was diluted in 15 mL of pentane. H_2O (3 mL) and 30% KOH (3 mL) were added. GC analysis of the pentane layer identified a 95% recovery of the following products: **3** (93%), **4** (3%), 1,2-bis(trimethylsilyl)-2,3-butadiene (2%), and **9a** (2%). A similar experiment resulted in a 64% purified yield of **3** following workup and Kugelrohr distillation (25–40 °C/1.4 mmHg): ^{1}H NMR (270 MHz) δ 0.08 (s, J_{Si-H} = 6.6 Hz, 18H), 1.42 (s, 4H); ^{13}C NMR (90.6 MHz, 30% ether–THF, –85 °C) δ –2.2 (J_{Si-C} = 51.9 Hz), 6.7 (J_{Si-C} = 51.9 Hz), 75.4; MS M^+ calcd for $C_{10}H_{21}Si_2$ 198.1254, found 198.1260.

2,3-Bis(trimethylsilyl)-1,3-butadiene (4). Diene **2** (0.026 mL, 0.10 mmol) and biphenyl standard (11.6 mg, 0.0753 mmol) were dissolved in 0.6 mL of THF and cooled to –78 °C. To this solution was added MeLi (0.44 mmol). After 5 min, 0.080 mL of Me_3SiCl was added. The solution was allowed to warm to 0 °C, and 0.030 mL of 30% KOH solution was added. The mixture was poured into pentane–H_2O and extracted. The yield by GC analysis before solvent evaporation was 92%. Solvent was removed carefully to give a yield 73% of **4**. A pure sample was prepared

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by preparative GC: ^{1}H NMR (200 MHz) δ 0.11 (s, 18H), 5.35 (d, J = 3.2 Hz, 2H), 5.40 (d, J = 3.2 Hz, 2H); IR 3061, 2962, 2904, 1854, 1411, 1251, 923, 837, 757, 691 cm^{-1}; MS M$^+$ calcd for $C_{10}H_{22}Si_2$ 198.1260, found 198.1252.

Isomerization of Monolithium Reagent 6 at –40 °C. To a cooled (–78 °C) solution of **2** (0.026 mL, 0.10 mmol) in 0.8 mL of THF was added MeLi in ether (0.13 mmol). The mixture was warmed to –40 °C, kept at this temperature for 1.5 h, coooled to –78 °C, and transferred with a cooled (–78 °C) jacketted syringe to a solution of Me_3SiCl (0.026 mL, 0.20 mmol) in 0.80 mL of pentane. After 5 min, a 30% KOH solution was added followed by normal workup. NMR shows the following ratios of starting material and product: **1** (16%), **9a** (18%), **8** (32%), and **3** (34%).

2-Lithio-1-(trimethylstannyl)-2,3-butadiene (5). A solution of MeLi (0.31 mmol) was added to ether (0.8 mL) in an oven-dried, 10-mm NMR tube with a rubber septum. The tube was cooled to –78 °C, 0.170 mL (0.64 mmol) of **1** was added, and the solution was frozen in a liquid N_2 bath. MeLi (0.33 mmol) in THF (2.6 mL) was added, and the contents were warmed to –78 °C. The resultant, bright yellow solution showed no signs of decomposition after 24 h at –78 °C. NMR experiments were performed on a Bruker AM-360 spectrometer operating at 90.56 MHz at temperatures ranging between –27 and –121 °C. ^{7}Li–^{13}C coupling could be detected at –120 °C (but not above –85 °C). In THF–ether solutions, the ^{7}Li–^{13}C quartet was partially collapsed; however, changing to a dimethyl ether solvent system resulted in a sharp 1:1:1:1 quartet with no other changes in the spectrum. Following the conclusion of experiments, the solutions were trapped with Me_3SiCl and analyzed by calibrated GC to give a high yield (95%) of products. ^{13}C NMR data for **5**: (90.6 MHz, 30% ether–THF, –116 °C) δ –9.6 ($J_{\text{Sn–C}}$ = 287.6 Hz, $J_{\text{C–H}}$ (q) = 127.2 Hz), 12.1 ($J_{\text{Sn–C}}$ = 342.6 Hz, $J_{\text{C–H}}$ (t) = 132.0), 41.8 ($J_{\text{C–H}}$ (t) = 158.3 Hz), 97 ($J_{\text{Li–C}}$ = 19 Hz), 176.8 ($J_{\text{Sn–C}}$ = 47.3 Hz, $J_{\text{C–H}}$ (t) = 9.5 Hz).

2-Lithio-3-(trimethylstannyl)-1,3-butadiene (6). Following the procedure outlined for **5**, MeLi in ether (0.64 mmol) and **2** (0.166 mL, 0.64 mmol) were added to a solution of THF (2.4 mL) and ether (1.0 mL). The orange/brown solution of **6** was stored at –78 °C. Above –50 °C, **6** slowly isomerized to the more stable isomer **5**. ^{13}C NMR data for **6**: 90.6 MHz, 10% ether–THF, –121 °C) δ –9.7 ($J_{\text{Sn–C}}$ = 291.5 Hz, $J_{\text{C–H}}$ (q) = 125.6 Hz), 94.2 ($J_{\text{Sn–C}}$ = 38.2 Hz, $J_{\text{C–H}}$ (q) = 153.0 Hz), 103.9 ($J_{\text{Sn–C}}$ = 59.5 Hz, $J_{\text{C–H}}$ (dd) = 153.1, 139.9 Hz), 171.2 ($J_{\text{Sn–C}}$ = 432.6 Hz, $J_{\text{C–H}}$ (dd) = 19.5, 14.1 Hz), 213 (1:1:1:1 q in dimethyl ether, $J_{\text{Li–C}}$ = 27 Hz).

1,4-Dilithio-2-butyne (7). Following the procedure outlined for **5**, MeLi in ether (1.28 mmol) and 0.166 mL (0.64 mmol) of **1** were added to THF (2.6 mL) and ether (0.80 mL). The solution of **7** was stored at –78 °C. Between –60 and –27 °C, a precipitate formed in the orange solution accompanied by a loss of ^{13}C signals. The precipitate would not dissolve upon cooling; however, it dissolved in the presence of Me_3SiCl to give a 95% yield of products determined by GC analysis: **3** (93%), **4** (3.3%), 1,2-bis(trimethylsilyl)-2,3-butadiene (2.5%), and **9a** (1.7%). ^{13}C NMR data for **7**: (90.6 MHz, 30% ether–THF, –90 °C) δ –15.4, –3.6, –2.0, –0.2, 1.3, 2.4, 91.4, 91.5, 93.1, 97.7, 98.1, 120.4. The six upfield resonances were broad (unresolved ^{7}Li–^{13}C coupling?). The six downfield resonances (sharp singlets) were due to quaternary carbons.

2-(Trimethylsilyl)-3-(trimethylstannyl)-1,3-butadiene (9a). To a stirred flask containing 0.51 mL (0.76 g, 2.0 mmol) of **2** in 3 mL of THF at –78 °C was slowly added MeLi in ether (2.2 mmol). After 5 min at –78 °C, the solution of **6** was transferred at –78 °C using a dry ice jacketted syringe to a stirred flask at –78 °C containing 0.32 mL (2.5 mmol) of Me_3SiCl in 2 mL of pentane. The cold bath was removed and 1 mL of a 30% KOH solution added. Standard workup and Kugelrohr distillation (25–40 °C, 0.4 mmHg) gave a clear liquid, **9a**, 0.45 g (78% yield): ^{1}H NMR (200 MHz) δ 0.11 (s, 9H), 0.14 (s, $J_{\text{Sn–H}}$ = 54.1 Hz, 9H), 5.27 (d, J = 2.4 Hz, $J_{\text{Sn–H}}$ = 76.0 Hz, 1H), 5.35 (dd, J = 2.8, 0.7 Hz, $J_{\text{Sn–H}}$ = 10.0 Hz, 1H), 5.43 (d, J = 2.8 Hz, $J_{\text{Sn–H}}$ = 11.0 Hz, 1H), 5.65 (d, J = 2.4 Hz, $J_{\text{Sn–H}}$ = 158 Hz, 1H); ^{13}C NMR (125.76 MHz) δ –8.6 ($J_{\text{Sn–C}}$ = 338.5 Hz), –0.7 ($J_{\text{Si–C}}$ = 52.1 Hz), 124.1 ($J_{\text{Sn–C}}$ = 35.3 Hz), 124.6 ($J_{\text{Sn–C}}$ = 30.5 Hz), 157.0 ($J_{\text{Sn–C}}$ = 10.6 Hz), 157.9 ($J_{\text{Sn–C}}$ = 423.2 Hz); IR 3063, 2959, 2916, 1837, 1566, 1407, 1246, 1187, 911, 834, 759, 688, 646 cm^{-1}; UV $\lambda_{\max}$ (hexane) 194 (ϵ 7150); 228 nm (2490); MS M$^+$ calcd for $C_{10}H_{22}SiSn$ 288.0506, found 288.0512.

2-Lithio-3-(trimethylsilyl)-1,3-butadiene (10a). To a solution of 145 mg (0.5 mmol) of **9a** in THF (3.6 mL) was added MeLi (0.5 mmol) at –78 °C (as in **5**). ^{13}C NMR data for **10a**: (90.6 MHz, 9% ether–THF, –120 °C) δ –1.1 ($J_{\text{Si–C}}$ = 118.5 Hz), 93.1 (CH_2), 104.6 (CH_2), 171.9 ($J_{\text{Si–C}}$ = 61.0 Hz), 214.5 ($J_{\text{Li–C}}$ = 26 Hz).

1,1,4,4-Tetramethyl-2,3-bis(methylene)-1,4-disilacyclopentane (11). A solution of 0.328 g (0.865 mmol) of diene **2** and 20 mL of THF at –78 °C was treated with MeLi in ether (0.87 mmol). The light yellow solution was transferred by cannula 2 min later to a –78 °C solution of 0.175 g (0.867 mmol) of bis(chlorodimethylsilyl)methane in 20 mL of THF. This solution was stirred for 3 min, and another 0.87 mmol of MeLi was added. The reaction mixture was stirred for 10 min at –78 °C, poured into 10 mL of saturated $NaHCO_3$, and extracted with 20 mL of 1:1 Et_2O–pentane. Normal workup and solvent evaporation at 0 °C gave **11** which was used without further purification: ^{1}H NMR (270 MHz) δ –0.21 (s, 2H), 0.16 (s, 12H), 5.16 (d, J = 2.9 Hz, 2H), 5.82 (d, J = 2.9 Hz, 2H).

***N*-Methylmaleimide Adduct of 1,1,4,4-Tetramethyl-2,3-bis(methylene)-1,4-disilacyclopentane (11-NMM).** A solution of freshly prepared **11**, 96.3 mg (0.867 mmol) of *N*-methylmaleimide, and 10 mL of CH_2Cl_2 was stirred for 30 min. The volatiles were removed, and the residue was purified by fractional crystallization using CH_2Cl_2–hexane to give 0.105 g (0.358 mmol, 41% yield, from **2**) of **11-NMM** as a white powder, mp 61–63 °C: ^{1}H NMR (200 MHz) δ –0.38 (s, 2H), –0.05 (s, 6H), 0.09 (s, 6H), 2.16 (dm, J = 14.2 Hz, 2H), 2.80 (d, J = 13.8 Hz, 2H), 2.85 (s, 3H), 3.07 (m, 2H); IR (KBr) 2938, 1700, 1431, 1247, 1034, 827, 794 cm^{-1}; MS M$^+$ calcd for $C_{14}H_{23}NO_2Si_2$ 293.1261, found 293.1263.

2-Chloro-3-(trimethylstannyl)-1,3-butadiene (17). Diene **2** (1.30 g, 3.42 mmol) in 5 mL of THF was cooled to –78 °C. MeLi in ether (5.13 mmol) was added followed by 2.7 mL of a 1.25 M solution of $MgBr_2 \cdot OEt_2$ in 2:1 benzene–ether (3.4 mmol) at –78 °C. A solution of 0.77 mL of $PhSO_2Cl$ (6.0 mmol) in 5 mL of THF was added to the Grignard reagent solution by cannula. The mixture was allowed to warm to room temperature over 10 min. Concentrated NH_4OH (2 mL) was added and the mixture stirred for 10 min. Standard workup gave a 97% yield of **17** (by NMR standard). The residue was distilled (Kugelrohr 25 °C/0.5mm) to yield 0.725 g (84%) of **17**: ^{1}H NMR (200 MHz, resolution enhanced) δ 0.25 (s, $J_{\text{Sn–H}}$ = 56 Hz, 9H), 5.23 (dt, J = 1.6, 0.6 Hz, $J_{\text{Sn–H}}$ = 8.1 Hz, 1H), 5.42 (ddd, J = 1.6, 1.2, 0.5 Hz, $J_{\text{Sn–H}}$ = 3.8 Hz, 1H), 5.47 (ddd, J = 1.8, 1.2, 0.6 Hz, $J_{\text{Sn–H}}$ = 62 Hz, 1H), 6.27 (dt, J = 1.8, 0.6 Hz, $J_{\text{Sn–H}}$ = 124 Hz, 1H); ^{13}C NMR (90.6 MHz) δ –8.4 ($J_{\text{Sn–C}}$ = 357.1 Hz), 115.6 ($J_{\text{Sn–C}}$ = 17.8 Hz), 129.4 ($J_{\text{Sn–C}}$ = 23.8 Hz), 144.6 ($J_{\text{Sn–C}}$ = 69.4 Hz), 148.5 ($J_{\text{Sn–C}}$ = 402.3 Hz); IR 3060, 2980, 2913, 1602, 1577, 1368, 1203, 1076, 925, 896, 869, 769 cm^{-1}; UV $\lambda_{\max}$ (hexane) 192 (ϵ 7630), 228 nm (8480); MS M$^+$ calcd for $C_7H_{13}ClSn$ 251.9728, found 251.9651.

The direct conversion of lithium reagent **6** to **17** produced an optimized yield of 50% when hexachloroethane was used.

***N*-Methylmaleimide Adduct of 2-Chloro-3-(trimethylstannyl)-1,3-butadiene (17-NMM).** 2-chloro-3-(trimethylstannyl)-1,3-butadiene (**17**) (0.160 mmol) and 14.8 mg (0.133 mmol) of *N*-methylmaleimide were dissolved in 0.4 mL of $CDCl_3$ along with a small amount of methylene blue (enough to give the solution a sky-blue color) in an NMR tube and heated at 55 °C for 16 h. At this time, the reaction was complete by NMR analysis. The product was chromatographed on silica gel, eluting with 60% ether–pentane (R_f = 0.30) to yield 42 mg (88%) of the Diels–Alder adduct: ^{1}H NMR (270 MHz) δ 0.19 (s, $J_{\text{Sn–H}}$ = 56.6 Hz, 9H), 2.30 (ddd, J = 14.9, 6.5, 1.8 Hz, $J_{\text{Sn–H}}$ = 11.5 Hz, 1H), 2.69 (ddd, J = 15.8, 7.3, 1.8 Hz, $J_{\text{Sn–H}}$ = 6.5 Hz, 1H), 2.82 (dd, J = 14.9, 2.9 Hz, 1H), 2.88 (dd, J = 15.8, 2.9 Hz, 1H), 2.96 (s, 3H), 3.02 (ddd, J = 9.2, 6.6, 3.0 Hz, 1H), 3.15 (ddd, J = 9.2, 7.3, 2.6 Hz, 1H); ^{13}C NMR (90.6 MHz) δ –8.8 (Me_3Sn), 24.9 (CH_3N), 30.9 (CH_2), 33.4 (CH_2), 38.8 (CH), 40.3(CH), 137.7 (C=), 139.4 (C=), 178.9 (C=O), 179.3 (C=O); IR 2985, 2908, 1778, 1702, 1593, 1436, 1385, 1285, 1265, 1103 cm^{-1}.

2-(Phenylthio)-3-(trimethylstannyl)-1,3-butadiene (18). A two-bulb flask containing 0.380 g (0.256 mL, 1.0 mmol) of **2** in 4 mL of THF on one side and 0.240 g (1.1 mmol) of Ph_2S_2 in 4 mL of THF on the other was cooled to –78 °C (part of the disulfide precipitated), and MeLi in ether (1.06 mmol) was added to the diene solution. Two minutes later, 3.0 mL (1.2 mmol) of 0.4 M $MgBr_2 \cdot OEt_2$ in ether–benzene was added to the solution of **6**. After an additional 2 min, the cold Grignard solution was poured into the cold Ph_2S_2 solution, the cold bath removed, and the mixture stirred for 2.25 h before pouring into 10 mL of 1.5 M NaOH and 10 mL of ether–pentane (1:1). The organic layer was washed with water and then brine and filtered through a Na_2SO_4 cone. Radical inhibitor (~1 mg) was added before evaporation of the solvent, and the residue was purified by preparative TLC (50:1 pentane–ether) to provide 0.242 g (0.74 mmol, 74% yield) of **18**: ^{1}H NMR (270 MHz) δ 0.21 (s, $J_{\text{Sn–H}}$ = 54.9 Hz, 9H), 5.07 (s, 1H), 5.27 (s, $J_{\text{Sn–H}}$ = 8.3 Hz, 1H), 5.38 (d, J = 1.9 Hz, $J_{\text{Sn–H}} \approx$ 68 Hz, 1H), 6.21 (d, J = 1.9 Hz, $J_{\text{Sn–H}}$ = 135.9

Hz, 1H), 7.2–7.4 (m, 5H); IR 3065, 2995, 2930, 1595, 1575, 1491, 1451, 783, 753, 702 cm^{-1}; MS M$^+$ calcd for $C_{13}H_{18}S^{118}Sn$ 324.0150, found 324.0151.

2-(Phenylthio)-3-(trimethylsilyl)-1,3-butadiene (19). A two-bulb flask containing 0.218 g (1.0 mmol) of Ph_2S_2 in 5 mL of THF on one side and 0.380 g (0.256 mL, 1.0 mmol) of **2** in 5 mL of THF on the other side was cooled to −78 °C. The yellow color which developed upon the addition of MeLi in ether (1.0 mmol) faded upon addition of Me_3SiCl (0.127 mL, 1.0 mmol) 3 min later. Another 1.02 mmol of MeLi added 5 min later produced a darker yellow solution. After 5 min, this solution was poured into the Ph_2S_2–THF solution, stirred an additional 5 min at −78 °C, and poured into 25 mL of 1.5 M NaOH solution and 20 mL of 50% ether–pentane. The organic layer was washed successively with another 20 mL of 1.5 M NaOH, 2 × 10 mL of water, and 10 mL of brine. The organic layer was filtered through a cone of Na_2SO_4, the radical inhibitor added, and the solvent evaporated. The yellow residue was purified by preparative TLC (pentane) to give 0.116 g (0.49 mmol, 49% yield) of **19** as a colorless oil: ^{1}H NMR (200 MHz, Cl_3CCHCl_2 as reference, δ 6.11) δ 0.18 (s, $J_{Si-H} = 6.8$ Hz, 9H), 4.93 (s, 1H), 5.22 (s, 1H), 5.51 (d, $J = 2.6$ Hz, 1H), 6.05 (d, $J = 2.6$ Hz, 1H), 7.2–7.4 (m, 5H); IR 3080, 2980, 2918, 1595, 1494, 1457, 1268, 857 cm^{-1}. Anal. Calcd for $C_{13}H_{18}SSi$: C, 66.60; H, 7.74. Found: C, 66.81; H, 7.90.

3-*n*-Hexyl-2-(trimethylstannyl)-1,3-butadiene (20). A solution of 1.30 mL (1.92 g, 5.08 mmol) of **2** in 12 mL of THF was cooled to −78 °C. A solution of MeLi (5.24 mmol) was added over 2.5 min. Two minutes later, 0.750 mL of 1-iodohexane (1.12 g, 5.28 mmol) was added dropwise over 1 min. The solution soon clouded with precipitate. After being stirred for 20 min at −78 °C, the solution was warmed to 0 °C over 40 min. A standard workup was followed by Kugelrohr distillation (collecting the fraction from 90–170 °C/4.2 mmHg) to give 1.22 g (80% yield) of **20**: ^{1}H NMR (200 MHz) δ 0.16 (s, $J_{Sn-H} = 59.9$ Hz, 9H), 0.86 (t, $J = 6$ Hz, 3H), 1.2–1.5 (m, 8H), 2.19 (t, $J = 7$ Hz, 2H), 4.76 (d, $J = 1.3$ Hz, $J_{Sn-H} \approx 10$ Hz, 1H), 4.86 (br s, 1H), 5.26 (d, $J = 2$ Hz, $J_{Sn-H} = 73$ Hz, 1H), 5.84 (d, $J = 2$ Hz, $J_{Sn-H} = 153$ Hz, 1H); IR 2975, 2940, 2870, 1624, 1586, 1480, 1202, 936, 900, 782 cm^{-1}; MS M$^+$ calcd for $C_{13}H_{26}{}^{118}Sn$ 300.1055, found 300.1032. Anal. Calcd for $C_{13}H_{26}Sn$: C, 51.87; H, 8.70. Found: C, 52.06; H, 8.48.

2,3-Di-*n*-hexyl-1,3-butadiene (22). A 10-mL flask containing 0.380 g (1.0 mmol, 0.260 mL) of **2** and 0.424 g (2.0 mmol, 0.295 mL) of 1-iodohexane in 5 mL of THF was cooled to −78 °C. Upon addition of MeLi in ether (2.5 mmol), the solution turned yellow. The yellow color faded away, and after 5 min at −78 °C, the cold bath was removed and the solution stirred at room temperature for 30 min followed by a standard workup. The residue was purified by Kugelrohr distillation (40–59 °C/0.1 mmHg) to give 0.146 g (0.65 mmol, 65% yield) of 22:[52] ^{1}H NMR (200 MHz) δ 0.88 (t, $J = 6.3$ Hz, 6H), 1.2–1.5 (m, 16H), 2.22 (t, $J = 7.2$ Hz, 4H), 4.90 (s, 2H), 5.05 (s, 2H); IR 2983, 2948, 2887, 1613, 1483, 1476, 906 cm^{-1}. Anal. Calcd for $C_{16}H_{30}$: C, 86.40; H, 13.60. Found: C, 86.32; H, 13.59.

2-Carboxy-3-*n*-hexyl-1,3-butadiene (23). MeLi in ether (1.30 mmol) was added to a −78 °C solution of 0.332 g (0.300 mL, 1.10 mmol) of **2** in 5 mL of THF containing ~1 mg of 1,10-phenanthroline as indicator,[48] resulting in a brown coloration. This color persisted upon the addition of 2.8 mL of $MgBr_2\cdot OEt_2$ in 1:1 ether–benzene (0.50 M, 1.4 mmol) 2 min later. After an additional 2 min, CO_2 (passed through a column of $CaSO_4$) was passed through the system causing it to become colorless in ~30 s. The CO_2 flow was continued for another 2 min before the mixture was poured into 10 mL of 1.2 N HCl and 10 mL of 1:1 ether–pentane. The organic layer was extracted twice with 5-mL portions of 1.5 M NaOH solutions. The NaOH solutions were then acidified (litmus) with 1.2 N HCl and extracted twice with 10-mL portions of ether–pentane. The combined organic layers were washed with brine and filtered through a Na_2SO_4 cone. Approximately 1 mg of radical inhibitor was added before the solvent was removed to yield 0.133 g (0.727 mmol, 66% yield) of **23** as a colorless liquid: ^{1}H NMR (200 MHz) δ 0.88 (t, $J = 6.5$ Hz, 3H), 1.15–1.45 (m, 8H), 2.28 (t, $J = 7.1$ Hz, 2H), 5.04 (d, $J = 1.5$ Hz, 1H), 5.16 (br d, $J = 1.5$ Hz, 1H), 5.73 (d, $J = 1.5$ Hz, 1H), 6.18 (d, $J = 1.5$ Hz, 1H), 11.8 (br s, 1H); IR 3460–2400 (s br), 1705, 1625, 1425, 1267, 1156, 920 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.62; H, 9.80.

3-Dodecyl-2-(methylseleno)-1,3-butadiene (24). A flask containing 2.13 g (1.40 mL, 5.62 mmol) of **2** in 15 mL of THF was cooled to −78 °C, and MeLi in ether (5.70 mmol) was added. After 5 min, 1.40 g (1.38 mL, 5.62 mmol) of 1-bromododecane was added. This material froze but went into solution upon removal of the cold bath and warming to room temperature over 20 min. This solution was again cooled to −78 °C, 5.90 mmol of MeLi in ether was added, and 8 min later, 0.444 g (5.62 mmol) of gray Se was added through one neck of the flask while maintaining a flow of N_2 through the system. The cold bath was again removed, and after 20 min, 0.450 mL (1.03 g, 7.23 mmol) of iodomethane was added dropwise over 1 min to the approximately 10 °C solution. The mixture was stirred for 5 min before a standard workup. The resulting yellow liquid obtained was purified by Kugelrohr distillation. The fraction collected between 70 and 106 °C (0.025 mmHg) yielded 0.90 g (2.85 mmol, 51%) of **24**: ^{1}H NMR (200 MHz) δ 0.86 (t, $J = 6.6$ Hz, 3H), 1.22 (br s, 18H), 1.43 (m, 2H), 2.09 (s, $J_{Se-H} = 11.5$ Hz, 3H), 2.28 (t, $J = 7.4$ Hz, 2H), 4.99 (br s, 1H), 5.10 (s, 1H), 5.24 (br s, 1H), 5.62 (s, $J_{Se-H} = 10.8$ Hz, 1H); ^{13}C NMR (90.6 MHz) δ 6.09 (CH_3, $J_{Se-C} = 67.3$ Hz), 14.1 (CH_3), 22.7 (CH_2), 28.2 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.7 (CH_2), 31.9 (CH_2), 34.8 (CH_2), 112.0 (CH_2), 114.2 (CH_2), 142.2 (C, $J_{Se-C} = 108$ Hz), 148.1 (C); IR 3100, 2942, 2870, 1632, 1584, 1476, 1393, 1285, 1136, 914, 874, 736 cm^{-1}; MS M$^+$ calcd for $C_{17}H_{32}{}^{80}Se$ 316.1669, found 316.1670. Anal. Calcd for $C_{17}H_{32}Se$: C, 64.74; H, 10.23. Found: C, 64.62; H, 10.41.

2-Methyl-3-methylene-4-(trimethylstannyl)pent-4-en-2-ol (26a). MeLi in ether (1.10 mmol) was added to 0.380 g of diene **2** (0.260 mL, 1.00 mmol) in 2 mL of 1:1 THF–ether at −78 °C. The yellow solution was transferred with a cooled (−78 °C) syringe to acetone (0.230 mL, 3.13 mmol) in 1 mL of pentane. The yellow color disappeared, and the cold mixture was poured into pentane–water and worked up. The yield of **26a**, determined by NMR standards, was 69% along with 18% of allene **27a**. Kugelrohr distillation (0.5 mmHg, 25–30 °C) gave 0.163 g of a 97:3 mixture of **26a** and **27a** (59% yield). A pure sample of **26a** was prepared by preparative GC: ^{1}H NMR (200 MHz) δ 0.12 (s, $J_{Sn-H} = 54.0$ Hz, 9H), 1.31 (s, 6H), 1.40 (s, 1H), 4.60 (d, $J = 1.5$ Hz, $J_{Sn-H} = 10.9$ Hz, 1H), 4.81 (d, $J = 1.5$ Hz, 1H), 5.28 (d, $J = 3.4$ Hz, $J_{Sn-H} = 72.9$ Hz, 1H), 5.75 (d, $J = 3.4$ Hz, $J_{Sn-H} = 148.1$ Hz, 1H); ^{119}Sn NMR (186.5 MHz) δ −31.9; IR 3450 (s br), 3090, 3035, 2976, 2923, 1614, 1366, 1163, 1106, 960, 928, 900, 770 cm^{-1}; MS M$^+$ − CH_3 calcd for $C_9H_{17}O^{118}Sn$ 259.0299, found 259.0299; UV λ_{max} (hexane) 204 nm (ϵ 7980).

2-Methyl-4-(trimethylstannyl)hexa-4,5-dien-2-ol (27a). A solution of 75.9 mg (0.0513 mL, 0.20 mmol) of **2** in 2 mL of THF was cooled to −78 °C and MeLi in ether (0.22 mmol) added. The yellow color disappeared upon the addition of 0.62 mL of 0.40 M $MgBr_2\cdot OEt_2$ in 1:1 ether–benzene 4 min later. After 2 min, 41.2 mg (0.050 mL, 0.71 mmol) of acetone was added and the solution warmed to room temperature over 30 min before being poured into 10 mL of ether–pentane (1:1). The organic layer was washed twice with 10-mL portions of water and filtered through a Na_2SO_4 cone. Radical inhibitor (~1 mg) was added and the solvent removed. The yield of **27a**, determined by NMR standard (0.012 mL, 0.10 mmol of pentachloroethane), was 82% (≥92% purity, no **26a** detected): ^{1}H NMR (200 MHz) δ 0.18 (s, $J_{Sn-H} = 55$ Hz, 9H), 1.23 (s, 6H), 1.79 (s, 1H), 1.25 (t, $J = 2.6$ Hz, $J_{Sn-H} = 46$ Hz, 2H), 4.19 (t, $J = 2.6$ Hz, $J_{Sn-H} = 41.3$ Hz, 2H); IR 3650–3200 (s, br), 1932.

1,3-Diphenyl-4-methylene-5-(trimethylstannyl)-5-hexen-1-one (28). A two-bulb flask containing 0.759 g (0.513 mL, 2.0 mmol) of **2** in 5 mL of THF on one side and 0.206 g (1.0 mmol) of $CuBr\cdot SMe_2$[35a,b] suspended in 4 mL of THF on the other side was cooled to −78 °C. The yellow solution produced by addition of MeLi in ether (2.13 mmol) to the solution of **2** was added to the suspension of copper salt, and the solution was warmed to −65 °C over 15 min. To the homogeneous cuprate solution was added 0.208 g (1.0 mmol) of 1,3-diphenylpropenone in 1.5 mL of THF over 90 s (blood red color). As this solution was warmed to −20 °C over 45 min, the color faded and became gold. A mixture of 5 mL of concentrated NH_4OH and 5 mL of saturated NH_4Cl solutions was added, and this was extracted with 10 mL of ether–pentane (1:1). The organic layer was washed successively with concentrated NH_4OH solution, twice with water, and with brine. After the organic layer was filtered through a cone of Na_2SO_4, ~1 mg of radical inhibitor was added and solvents were removed. The addition of 0.036 mL (0.3 mmol) of pentachloroethane showed the production of 0.55 mmol (55% yield) of **28** by NMR analysis. Purification by preparative TLC (10:1 pentane–ether) gave 0.220 g (0.52 mmol, 52% yield) of **28**: ^{1}H NMR (200 MHz) δ 0.14 (s, $J_{Sn-H} = 54.2$, 9H), 3.37 (dd, $J = 17.1, 7.5$ Hz, 1H), 3.55 (dd, $J = 17.1, 7.0$ Hz, 1H), 4.47 (br t, $J = 7.2$ Hz, 1H), 4.90 (s, 1H), 4.96 (s, $J_{Sn-H} = 9.6$ Hz, 1H), 5.26 (d, $J = 2.0$ Hz, $J_{Sn-H} = 71.8$ Hz, 1H), 5.87 (d, $J = 2.0$ Hz, $J_{Sn-H} = 147$ Hz, 1H), 7.10–7.60 (m, 8H), 7.92 (d with fine structure, $J = 7$ Hz, 2H); IR 3097, 3070, 3040, 2990, 2922, 1696,

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[52] Hhota, S.; Tosaka, T.; Sonoda, N.; Shimotsuma, W. Eur. Pat. Appl. EP 61,264. CA 98, P99701n, 1983.

1609, 1590, 1505, 1461, 760, 711, 701 cm^{-1}; MS M$^+$ calcd for $C_{22}H_{26}O^{118}Sn$ 424.1005, found 424.1005. Anal. Calcd for $C_{22}H_{26}OSn$: C, 62.15; H, 6.16. Found: C, 62.20; H, 6.23.

2,3-Bis((*N,N*-dimethylamino)methyl)-1,3-butadiene (29). To (*N,N*-dimethylmethylene)ammonium iodide (Eschenmoser's salt, 0.504 g, 2.72 mmol) suspended in 5 mL of dry CH_2Cl_2 under N_2 was added 0.516 g (0.360 mL, 1.36 mmol) of **1**. Most of the suspended solid disappeared after 30 min of stirring. After 6 h, the mixture was poured into 10 mL of 1.2 N HCl. The aqueous layer was neutralized (litmus) with 1.5 M NaOH and the resulting cloudy solution extracted with 15 mL of 1:1 ether–pentane. The organic layer was filtered through a cone of Na_2SO_4 and solvent removed to provide 0.164 g (0.97, 72% yield) of pure **29** (this material could be Kugelrohr distilled in the presence of radical inhibitor, 65 °C/aspirator, 83% recovery): ^{1}H NMR (200 MHz) δ 2.16 (s, 12H), 3.00 (s, 4H), 5.04 (br s with fine structure, 2H), 5.27 (d, J = 2.2 Hz, 2H); IR 3104, 2996, 2960, 2880, 2830, 2790, 1617, 1475, 1373, 1281, 1152, 921, 873 cm^{-1}. Anal. Calcd for $C_{10}H_{20}N_2$: C, 71.38; H, 11.98; N, 16.65. Found: C, 71.10; H, 11.81; N, 16.60.

2,3-Diiodo-1,3-butadiene (31). A solution of **1** (0.314 g, 0.826 mmol) in 2 mL of CH_2Cl_2 was cooled to −78 °C under N_2. Iodine (0.525 g, 2.07 mmol) was added and the mixture stirred for 15 min at −78 °C. The flask was warmed quickly to room temperature and the mixture poured into 10% $NaHSO_3$ solution and ether–pentane. Extraction with $NaHSO_3$ solution removed all the color in the organic layer. Normal workup and NMR analysis with internal standard showed 98% yield of **31**. Me_3SnI was also present (18% of theoretical). Most of the Me_3SnI was removed during solvent evaporation. The product was dissolved in pentane, extracted three times with 10% KF solution (to remove Me_3SnI) and brine, and dried and solvent removed giving a yield of 0.241 g of **31**, 88% pure by NMR (overall 84% yield). Attempted preparative TLC led to significant decomposition: ^{1}H NMR (200 MHZ) δ 7.18 (d, J = 1.5 Hz, 2H), 7.74 (d, J = 1.5 Hz, 2H); IR 2948, 2917, 2858, 1811, 1567, 1387, 1347, 1199, 1146, 1056, 908 cm^{-1}; MS M$^+$ calcd for $C_4H_4I_2$ 305.8406, found 305.8394.

1,1,1-Trifluoro-3-((trimethylstannyl)methyl)penta-3,4-dien-2-one (32). Trifluoroacetic anhydride (0.088 g, 0.060 mL, 0.42 mmol) was added to a 0 °C solution of 0.114 g (0.0792 mL, 0.30 mmol) of **1** and 0.012 mL (0.10 mmol) of pentachloroethane in 0.3 mL of $CDCl_3$ in an NMR tube. The side of the tube was rinsed with another 0.2 mL of $CDCl_3$, and the tube was shaken and removed from the cold bath. NMR analysis after 30 min at room temperature showed a quantitative production of **32**. This solution was poured into 50 mL of pentane and washed successively with saturated $NaHCO_3$, 10% KF, and brine. The solvents were removed, and after filtration through a cone of Na_2SO_4, part of the residue was purified by preparative GC: ^{1}H NMR (270 MHz) δ 0.11 (s, J_{Sn-H} = 54.5 Hz, 9H), 1.71 (t, J = 2.2 Hz, J_{Sn-H} = 34 Hz, 2H), 5.33 (t, J = 2.2 Hz, J_{Sn-H} = 55 Hz, 2H); IR 2998, 2933, 1956, 1930, 1715, 1352, 1286, 1220, 1168, 1094, 935, 870, 784, 759 cm^{-1}; MS M$^+$ − CH_3 calcd for $C_8H_{10}F_3O^{118}Sn$ 296.9705, found 296.9696.

Kinetic Runs for Reactions of *N*-Methylmaleimide and Various 2,3-Disubstituted 1,3-Butadienes. To a solution of 0.05 mmol of the diene in 0.5 mL of C_6D_6 in an NMR tube were added 11.1 mg (0.100 mmol) of *N*-methylmaleimide and enough methylene blue to give the solution a sky-blue color. The tube was cooled in dry ice, sealed, and placed in an oil bath thermostated at 80.0 °C. At appropriate time intervals, the tube was removed and the NMR spectrum recorded and integrated. For the rates that were significantly fast at room temperature, the tube was kept in dry ice except when the spectrum was taken. The second-order rate constant was calculated from both the disappearance of the starting materials and the appearance of the product. Usually six to eight points were taken, and their deviation from the mean was 5–10%.

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Supplementary Material Available: ^{1}H NMR spectra for all significant compounds and experimental procedures and analytical data for the *N*-methylmaleimide adduct of 2,3-dichloro-1,3-butadiene, **2-NMM**, **9b**, **10b**, **12**, **12-NMM**, **13**, **14**, **14-NMM**, **15-SO$_2$**, **16**, **21**, **24-NMM**, **26b**, **26c**, and **27c** (37 pages). Ordering information is given on any current masthead page.