

ORGANOLITHIUM ROUTES TO 1,2-DISUBSTITUTED ETHYLENE DERIVATIVES. AN ATTEMPTED SYNTHESIS OF 1,2-DILITHIOETHYLENE

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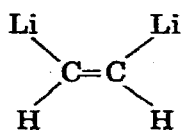
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Summary

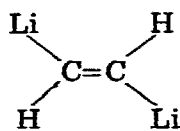
The attempted preparation of *trans*-1,2-dilithioethylene by the action of two molar equivalents of *n*-butyllithium on *trans*-1,2-bis(tri-*n*-butylstannyl)ethylene was unsuccessful, the reaction stopping at the $\text{Bu}_3\text{SnCH}=\text{CHLi} + \text{BuLi}$ stage. However, *trans*-1,2-disubstituted ethylene derivatives could be prepared in good yield by a stepwise sequence in a one-pot process. Thus, *trans*- $\text{Bu}_3\text{SnCH}=\text{CHSnBu}_3$ was treated successively with molar equivalents of *n*-BuLi, Me_3SiCl , *n*-BuLi and $\text{Me}_2\text{C}=\text{O}$ to give *trans*- $\text{Me}_3\text{SiCH}=\text{CHCMe}_2\text{OH}$ in 63% yield. Prepared in similar fashion were *trans*- $\text{Me}_3\text{SiCH}=\text{CHSiMe}_3$, *trans*- $\text{Me}_3\text{SiCH}=\text{CHSnMe}_3$ and *trans*- $\text{Me}_3\text{SiCH}=\text{CHCH}_3$. These products, as well as $(\text{trans}\text{-Me}_3\text{SiCH}=\text{CH})_2\text{Hg}$, also were prepared by appropriate reactions of *trans*- $\text{Me}_3\text{SiCH}=\text{CHLi}$, which was obtained by the transmetalation reaction of phenyllithium with *trans*- $\text{Me}_3\text{SiCH}=\text{CHSnPh}_3$ in diethyl ether solution. The $(\text{Ph}_3\text{P})_4\text{Pd}$ -catalyzed demercuration of $(\text{trans}\text{-Me}_3\text{SiCH}=\text{CH})_2\text{Hg}$ gave *trans,trans*- $\text{Me}_3\text{SiCH}=\text{CH}-\text{CH}=\text{CHSiMe}_3$ in 95% yield.

Introduction

1,2-Dilithioethylene, either the *cis* or the *trans* isomer, Ia or Ib, would be an interesting organolithium reagent, with potential applications in the preparation

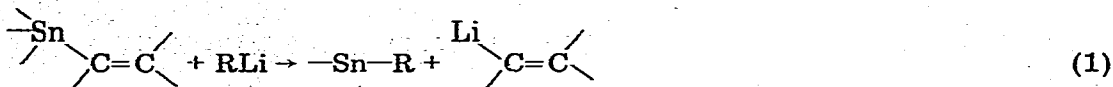


(Ia)



(Ib)

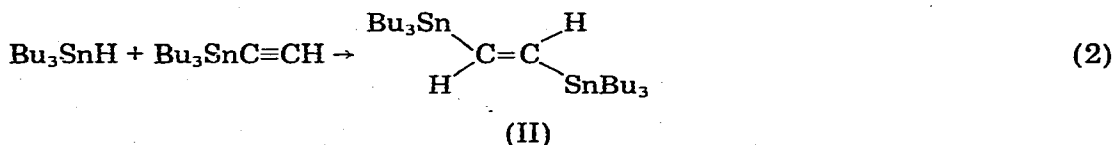
of functionally disubstituted ethylenes and in polymer synthesis. One route to 1,2-dilithioethylene which may be considered is the transmetalation reaction which has served well in the preparation of vinylic lithium reagents such as vinyl-lithium itself [1], propenyl- and isopropenyl-lithium [2], and *trans*- β -styryl-lithium [3] (eq. 1). We report here concerning our attempted preparation of



1,2-dilithioethylene and some related organolithium chemistry.

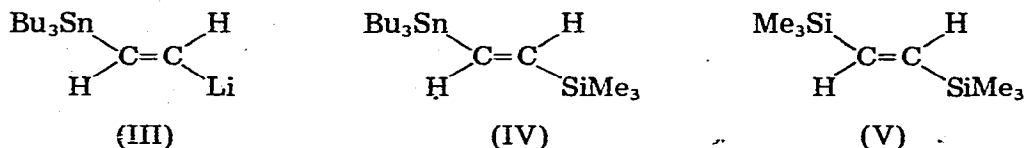
Results and discussion

Nesmeyanov and Borisov reported the preparation of *trans*-1,2-bis(tri-*n*-butylstannyl)ethylene in 1967 (eq. 2) [4]. It was shown later by Corey and



Wollenberg [5] that this compound reacted with one molar equivalent of *n*-butyllithium in tetrahydrofuran (THF) at -78°C to give the monolithium reagent III. Attempts to effect the reaction of II with two molar equivalents of *n*-butyllithium, in order to generate Ib, were not reported, but such a reaction, in principle, presents a good possibility for the preparation of *trans*-1,2-dilithioethylene.

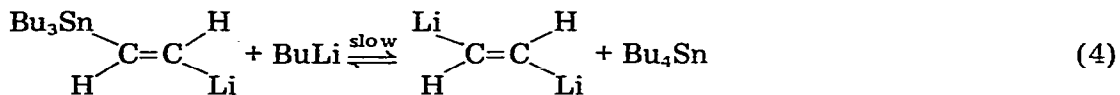
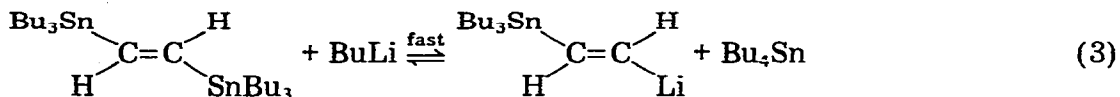
Our initial experiments seemed quite encouraging. Treatment of II with one molar equivalent of *n*-butyllithium at -78°C in THF medium, followed by addition of trimethylchlorosilane to the reaction mixture, gave IV in 60% yield. Addition of two molar equivalents of *n*-butyllithium to a THF solution of II at



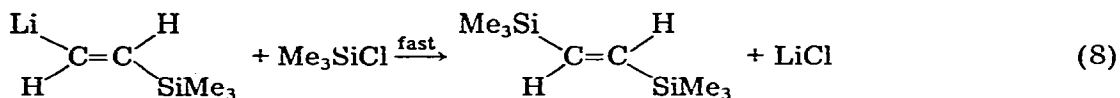
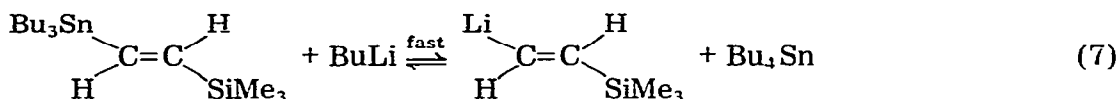
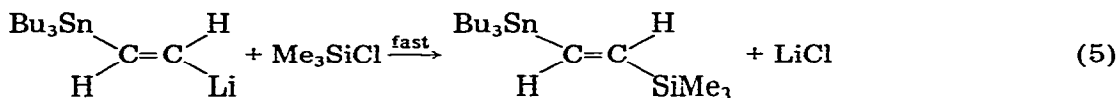
78°C , followed by slow addition of trimethylchlorosilane to the reagent solution, gave *trans*-1,2-bis(trimethylsilyl)ethylene (V), the hoped-for product, in 60% yield. At first sight, this might be taken as evidence that *trans*-1,2-dilithioethylene had indeed been formed. Another experiment (using a ratio of 3 BuLi to 1 II) demonstrated that this reaction could be effected at room temperature, the normal conditions for carrying out the RLi/vinylic tin transmetalation [1–3]. Under those conditions, a 72% yield of V was realized, and so, a practical, easily effected synthesis of *trans*-1,2-dilithioethylene seemed in hand. However, as further investigations showed, such was not the case.

A disquieting element was introduced by the observation that the yield of V in a 3 BuLi/1 II/3 Me₃SiCl reaction depended on the rate of addition of tri-

methylchlorosilane to the reagent solution. Thus, in a reaction in which the trimethylchlorosilane was added rapidly rather than slowly, the yield of V was only 48%. This initially puzzling result could be rationalized by the reaction sequence 3–8. If the relative rates of reactions 3–8 were as indicated, then such



(or an unfavorable equilibrium)



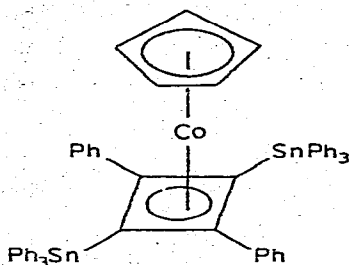
results could be explained. Slow addition of trimethylchlorosilane allowed reaction of the monolithium reagent (eq. 5) and subsequent transmetalation of the product (eq. 7) to occur in successful competition with the slow reaction 6. On the other hand, rapid addition of trimethylchlorosilane allowed reaction 6 to occur to a significant extent, even though it is rather slow*. This picture could be confirmed by means of a suitable experiment. When a reagent solution was prepared by mixing one molar equivalent of II and three of n-butyllithium in THF, and this solution was added to a large excess of trimethylchlorosilane (i.e., inverse addition), the product obtained was not V, rather it was IV in 63% yield. It is thus evident that *trans*-1,2-dilithioethylene is not produced when II is treated with an excess of n-butyllithium under these conditions and that the transmetalation stops at the monolithium stage, III.

These results indicate that the derivativization of new polylithium reagents by the addition of the electrophilic substrate to the lithium reagent solution is fraught with danger. If the relative rates of successive metalation or transmetalation steps and of the reactions of the various lithium species with the substrate tend in the direction of those observed in this study, then a totally erroneous picture could be obtained. Trimethylchlorosilane appears to be an especially

* Many studies have demonstrated that the $\text{Me}_3\text{SiCl}/n$ -alkyllithium reaction is slow relative to many alternate processes, especially at low temperature. The initial observation concerning this point was made by Bey and Weyenberg [6].

poor substrate in this connection. In any event, the lithium reagent solution should be added to an excess of the substrate if meaningful results are to be obtained.

It is interesting to note that the present case is not the only example of the failure of a Li/Sn transmetalation process in the attempted preparation of a dilithium reagent. In earlier work [7], we had been unsuccessful in preparing solutions of 1,2-dilithiobenzene by the reaction of methylithium in THF or *n*-butyllithium in diethyl ether with 1,2-bis(trimethylstannyl)benzene and, more recently, Jutzi et al. [8] reported failure in the attempted preparation of 1,5-dilithio-1,4-pentadiene by Li/Sn transmetalation. In a similar vein, the novel tin compound VI was converted only to the monolithium reagent when treated

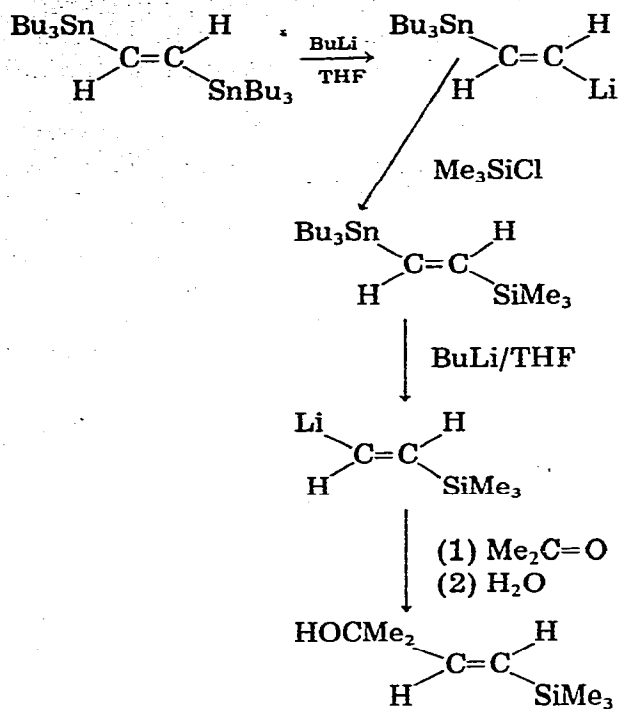


(VI)

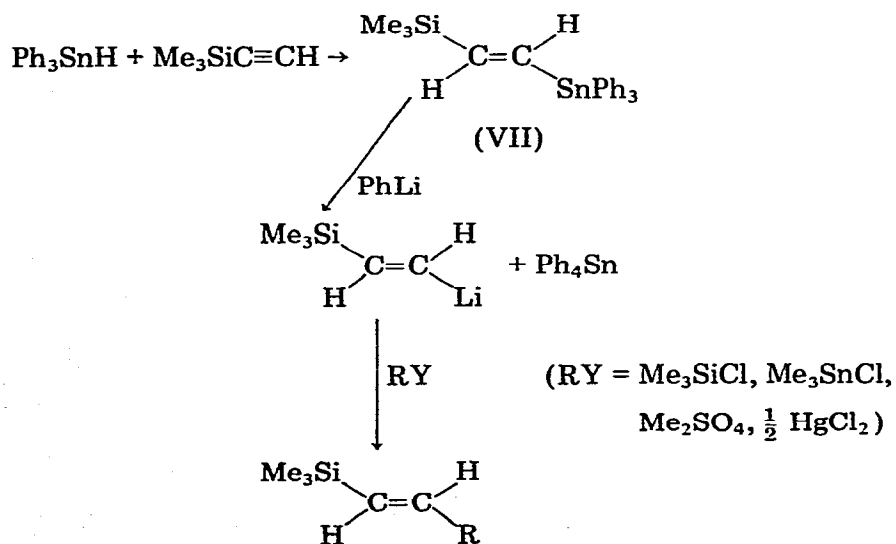
with an excess of phenyllithium in THF [9]. The failure of the transmetalation reaction to provide the desired dilithium reagents does not mean that the latter are not accessible or not stable. For instance, 1,2-dilithiobenzene can be prepared by other means [10], and Jutzi et al. [8] were able to prepare 1,5-dilithio-1,4-pentadiene by lithium-halogen exchange. It would appear that unfavorable thermodynamic and/or kinetic factors are associated with the transmetalation of a tin-containing organolithium species and an organolithium reagent. The transmetalation reaction is known to be an equilibrium process [11], and thus it may be that in the equilibrium 4 the starting materials are more stable than the products, one of which would have vicinal partial negative charges. On the other hand, it may be that nucleophilic attack by *n*-butyllithium at a tin center which is vicinal to a carbon atom with a partial negative charge is kinetically not a favorable process.

Although our attempted synthesis of *trans*-1,2-dilithioethylene was not realized, the application of II as a source of the CH=CH moiety by a two-step Sn/Li transmetalation sequence was of potential utility in organic and organometallic synthesis. This was demonstrated by the reaction sequence shown in Scheme 1. This sequence, which was carried out in one reaction vessel by successive additions of molar equivalents of *n*-butyllithium, trimethylchlorosilane, *n*-butyllithium and acetone to II in THF solution, followed by hydrolysis, gave the indicated allylic alcohol in 63% yield, based on II. Prepared in similar fashion were *trans*-Me₃SiCH=CHCH₃ (70% yield; successive additions of *n*-BuLi, Me₃-SiCl, *n*-BuLi and Me₂SO₄ to II) and *trans*-Me₃SiCH=CHSnMe₃ (54% yield; successive additions of *n*-BuLi, Me₃SiCl, *n*-BuLi and Me₃SnCl to II). These are rather trivial examples, but it is obvious that much more general application of this successive addition principle is possible. The preparation of diverse CH=CH-

SCHEME 1



SCHEME 2

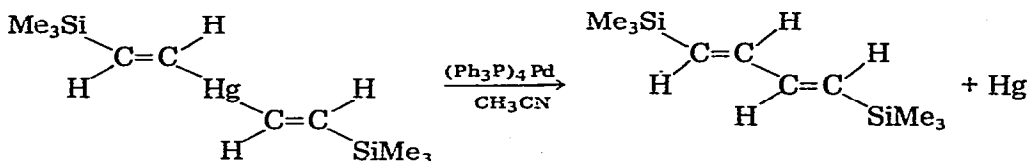


bridged systems of type *trans*-ACH=CHB should be possible by this procedure. The *trans* stereochemistry of II and the fact that the transmetalation reaction between vinylic tin compounds and organolithium reagents proceeds with retention of configuration about the C=C bond of the vinyl group being transferred [2] insure the *trans* stereochemistry of the product.

The compounds containing the *trans*-Me₃SiCH=CH group mentioned above, as well as (*trans*-Me₃SiCH=CH)₂Hg, were prepared by an alternate route during the course of this investigation which is shown in Scheme 2. The vinylic tin compound, VII, is easily prepared in a sealed tube reaction of triphenyltin hydride and ethynyltrimethylsilane at 185°C [12], is easily purified, and reacts essentially quantitatively with phenyllithium in diethyl ether. The lithium reagent formed reacts with all substrates examined to give exclusively *trans* products as shown. Since, as mentioned above, the transmetalation reaction proceeds with retention of configuration at a vinylic carbon atom, the structure of VII, not firmly secured previously, must be that shown in Scheme 2.

This route to *trans*-Me₃SiCH=CHLi was developed independently and published prior to the present report by Cunico and Clayton [13]. These workers also prepared *trans*-Me₃SiCH=CHSnBu₃ and in a low temperature reaction with *n*-butyllithium in THF used this compound to generate *trans*-Me₃SiCH=CHLi. Another route to *trans*-Me₃SiCH=CHLi which used the reaction of *trans*-Me₃-SiCH=CHBr with two molar equivalents of *t*-butyllithium, was reported while the present work was in progress [14]. This procedure actually may prove to be the method of choice since the starting bromide is easily prepared by addition of HBr to ethynyltrimethylsilane.

Finally, we note that the mercury compound prepared during the course of this study, (*trans*-Me₃SiCH=CH)₂Hg, provided a useful route to *trans,trans*-1,4-bis(trimethylsilyl)-1,3-butadiene by a palladium-catalyzed coupling reaction of a type developed by Vedejs and Weeks [15].



Experimental

1. General comments

All reactions were carried out in flame-dried glassware under an atmosphere of prepurified nitrogen. The solvents used were rigorously dried, usually by distillation from sodium benzophenone ketyl prior to use. IR spectra were recorded using a Perkin-Elmer 457A grating infrared spectrophotometer, NMR spectra using a Varian Associates T60 or Perkin-Elmer R20 or R22 spectrometers. Chemical shifts are reported in δ units, ppm downfield from internal tetramethylsilane. Chloroform (δ 7.27 ppm) or dichloromethane (δ 5.30 ppm) often were used as alternative internal standards. Gas-liquid chromatography (GLC) was used routinely for isolation of pure samples of products, determination of purity and for yield determinations by the internal standard method.

n-Butyllithium and t-butyllithium were purchased from Alfa/Ventron. Trimethylchlorosilane was kindly donated by the Union Carbide Corporation, bis-(tri-n-butyltin) oxide, which served as starting material for the butyltin compounds, by the M&T Chemicals, Inc. Ethynyltrimethylsilane was prepared by the method of Kraihanzel and Losee [12], triphenyltin hydride by the procedure reported by Kuivila and Beumel [16], *trans*-1-trimethylsilyl-2-triphenylstannylethylene by the procedure of Kraihanzel and Losee, tri-n-butyltin hydride by the LiAlH_4 reduction of $(n\text{-Bu}_3\text{Sn})_2\text{O}$ [17], ethynyltri-n-butyltin by the Grignard procedure in an adaptation of the method used for ethynyltrimethylsilane and 1,2-bis(tri-n-butylstannyl)ethylene by the procedure of Nesmeyanov and Borisov [4], as modified by Corey and Wollenberg [5].

Preparation of ethynyltrimethylsilane using mono-lithium acetylide

In the later stages of this work, $\text{Me}_3\text{SiC}\equiv\text{CH}$ was prepared by the reaction of $\text{LiC}\equiv\text{CH}$ in THF [18] with trimethylchlorosilane. In a typical preparation, a two-liter round-bottomed flask, equipped with overhead stirring apparatus, no air-stopper, nitrogen inlet tube, and gas inlet tube, was flamed dry and charged with 700 ml of dry THF and cooled to -78°C in a dry ice/acetone bath. Acetylene, after passing through concentrated sulfuric acid and soda lime, was bubbled through the THF to saturate it.

In a separate operation, a solution of 1 mol of n-butyllithium in hexane was trap-to-trap distilled ($22^\circ\text{C}/0.02$ mmHg) to remove the hexane. The n-butyllithium was cooled to -78°C , whereupon 300 ml of dry THF (cooled to -78°C) was added to dissolve the butyllithium. The -78°C n-butyllithium solution was added slowly by cannula over a 1 h period to the -78°C solution of THF saturated with acetylene. During this operation, acetylene bubbling was continued. A clear, colorless solution resulted. Subsequently, 127 ml (1 mol) of trimethylchlorosilane was added all at once. The solution was stirred for an additional 10 min at -78°C and then was allowed to warm slowly to room temperature overnight. The solution was hydrolyzed with saturated aqueous ammonium chloride and extracted with water until no THF remained. Distillation of the organic layer afforded ethynyltrimethylsilane, b.p. 53°C , n_D^{25} 1.3866 (lit. [12] b.p. 53°C , n_D^{26} 1.3870) in 72% yield.

Reaction of trans-1,2-bis(tri-n-butylstannyl)ethylene with one equivalent of n-butyllithium at -78°C and subsequent reaction with trimethylchlorosilane

A 300 ml, round-bottomed flask, equipped with an overhead stirring apparatus, addition funnel, nitrogen inlet, no-air stopper, and low temperature thermometer (henceforth the standard apparatus) was flamed dry and charged with 10.21 g (16.8 mmol) of the title olefin in 50 ml of dry THF. The solution was cooled to -78°C in a dry ice/acetone bath. Then 7.1 ml (17.0 mmol) of 2.4 N n-butyllithium in hexane was added slowly over a 15 min period. The mixture was stirred for 2 h and then 2.5 ml (20.0 mmol) of trimethylchlorosilane was added. The solution was stirred an additional 2 h, was allowed to warm to room temperature, and was hydrolyzed with 200 ml of water. The organic layer was dried over sodium sulfate and was trap-to-trap distilled ($22^\circ\text{C}/0.03$ mmHg) to remove volatile compounds. GLC analysis of the non-volatile liquid showed the presence of 4.77 g (84% yield) of tetra-n-butyltin, identified by comparison of

its GLC retention time with that of an authentic sample, and the presence of 3.80 g (58% yield) of *trans*-1-trimethylsilyl-2-tri-*n*-butylstannylethylene, identified on the basis of GLC retention time and the *trans*-AB coupling pattern (J_{AB} 21 Hz) visible in the vinyl region of the NMR spectrum of the non-volatile liquid. GLC analysis of this particular mixture of compounds is very difficult due to extreme difficulty in separating these two compounds. This form of yield analysis was abandoned in favor of the easier NMR yield analysis which does not require isolation of the material. Attempts to isolate the *trans*-1-trimethylsilyl-2-tri-*n*-butylstannylethylene by distillation failed as the product was always contaminated with tetra-*n*-butyltin.

A reaction carried out at room temperature with 54.8 mmol of *trans*-1,2-bis-(tri-*n*-butylstannyl)ethylene using this general procedure gave *trans*-1-trimethylsilyl-2-tri-*n*-butylstannylethylene in 62% yield (NMR yield determination).

Reaction of trans-1,2-bis(tri-n-butylstannyl)ethylene with two equivalents of n-butyllithium at -78°C and subsequent reaction with trimethylchlorosilane

The standard apparatus was charged with 10.46 g (17.2 mmol) of the title olefin in 50 ml of dry THF. The solution was cooled in a dry ice/acetone bath to -78°C . The addition funnel was charged with 17.0 ml (40.8 mmol) of 2.4 *N* *n*-butyllithium in hexane, which was added slowly to the mixture in the flask. The resulting bright yellow solution was stirred at -78°C for 1.5 h. Then 6.0 ml (47.5 mmol) of trimethylchlorosilane was added slowly. The yellow color was discharged at the completion of this addition. After it had been stirred an additional 1.5 h, the solution was allowed to warm to room temperature and then was hydrolyzed with 200 ml of water. The organic layer was trap-to-trap distilled ($22^{\circ}\text{C}/0.03$ mmHg). GLC analysis of the volatile portion showed the presence of 1.71 g (59% yield) of *trans*-1,2-bis(trimethylsilyl)ethylene, n_{D}^{25} 1.4270 (lit. [19] n_{D}^{20} 1.4303), whose NMR spectrum was identical with that of authentic material [19]. In addition, 2.08 g of *n*-butyltrimethylsilane, n_{D}^{25} 1.4002 (lit. [20a] n_{D}^{20} 1.4030), whose IR spectrum was identical with that of authentic material [20b], was obtained. This accounted for 88% of the *n*-butyllithium initially present.

Reaction of trans-1,2-bis(tri-n-butylstannyl)ethylene with three equivalents of n-butyllithium at room temperature and subsequent reaction with trimethylchlorosilane

The standard apparatus was charged with 5.45 g (9.0 mmol) of the title olefin in 25 ml of dry THF. Then 2.5 ml (27.4 mmol) of 2.19 *N* *n*-butyllithium in hexane was added over a 15 min period. The reaction mixture was stirred an additional 15 min, and then 4.0 ml (31.5 mmol) of trimethylchlorosilane in 20 ml of dry THF was added slowly over a 15 min period. After it had been stirred for an additional 15 min, the mixture was hydrolyzed with 200 ml of water. The organic layer was trap-to-trap distilled ($22^{\circ}\text{C}/0.03$ mm Hg). GLC analysis of the volatile portion showed the presence of 1.11 g (72% yield) of *trans*-1,2-bis(trimethylsilyl)ethylene, n_{D}^{25} 1.4270, whose NMR spectrum was identical with that of authentic material.

Reaction of trans-1,2-bis(tri-n-butylstannyl)ethylene with three equivalents of n-butyllithium at room temperature and subsequent reaction with trimethylchlorosilane; reverse addition

The standard apparatus was charged with 11.20 g (18.5 mmol) of the title olefin in 35 ml of dry THF. To the solution was added slowly, over a 15 min period, 25 ml (60.0 mmol) of 2.5 N n-butyllithium in hexane. The mixture was stirred for 15 min and then was transferred via cannula to the addition funnel of a similarly equipped flask which contained 8.3 ml (excess) of trimethylchlorosilane in 25 ml of dry THF. The lithium reagent solution was added slowly to the chlorosilane solution over a 15 min period. After it had been stirred for an additional 15 min, the solution was hydrolyzed with 200 ml of water. The organic layer was trap-to-trap distilled (22°C/0.03 mmHg). GLC analysis of the volatile portion did not show the presence of *trans*-1,2-bis(trimethylsilyl)ethylene. NMR yield analysis of the non-volatile liquid (Varian Associates T-60, CH₂Cl₂ internal standard) showed the presence of 4.57 g (63% yield) of *trans*-1-trimethylsilyl-2-tri-n-butylstannylethylene, identified on the basis of the *trans*-AB coupling pattern (J_{AB} 21 Hz) visible in the vinyl region of the NMR spectrum of the non-volatile liquid.

Reaction of trans-1,2-bis(tri-n-butylstannyl)ethylene, successively, with one equivalent of n-butyllithium, trimethylchlorosilane, n-butyllithium and dimethyl sulfate

The standard apparatus was charged with 10.93 g (18.0 mmol) of the title olefin in 35 ml of dry THF. Then 8.2 ml (18.0 mmol) of 2.19 N n-butyllithium in hexane was added all at once. The reaction mixture was stirred for 15 min, and then 2.23 ml (18.0 mmol) of trimethylchlorosilane was added in one portion. After an additional 15 min period, 8.2 ml (18.0 mmol) of n-butyllithium solution was added all at once. Fifteen min later, 1.75 ml (excess) of dimethyl sulfate was added. The entire reaction mixture then was stirred for an additional hour and subsequently was hydrolyzed with 200 ml of water. The organic layer was trap-to-trap distilled (22°C/0.03 mmHg). GLC analysis of the volatile portion showed the presence of 1.45 g (70% yield) of *trans*-1-propenyltrimethylsilane whose IR and NMR spectra were identical to those of an authentic sample [21].

Reaction of trans-1,2-bis(tri-n-butylstannyl)ethylene, successively, with one equivalent of n-butyllithium, trimethylchlorosilane, n-butyllithium and acetone

The standard apparatus was charged with 11.87 g (19.6 mmol) of the title olefin in 35 ml of dry THF. Then 9.5 ml (19.6 mmol) of 2.07 N n-butyllithium in hexane was added all at once. The reaction mixture was stirred for 15 min, and then 2.5 ml (19.6 mmol) of trimethylchlorosilane was added in one portion. After an additional 15 min period, 9.5 ml (19.5 mmol) of n-butyllithium in hexane was added all at once. Fifteen min later, 3.0 ml (40.7 mmol) of acetone was added. The entire reaction mixture was stirred for an additional hour and subsequently was hydrolyzed with 200 ml of water. The organic layer was trap-to-trap distilled (22°C/0.04 mmHg). GLC analysis of the volatile portion showed the presence of 12.4 mmol (63% yield) of *trans*-3-hydroxy-3-methyl-1-trimethylsilyl-1-butene, Me₃SiCH=CHCMe₂OH, n_D^{25} 1.4428. (Found: C, 60.70; H, 11.72. C₈H₁₈OSi calcd.: C, 60.69; H, 11.46%.) NMR (CCl₄/CHCl₃): δ 0.10 (s, 9H, Me₃Si),

1.29 (s, 6H, CMe₂), 1.45 (s, 1H, OH) and 5.50–6.29 ppm (AB pattern, J_{AB} 18 Hz, 2H, vinyl H). IR (film): $\nu(\text{C}=\text{C})$ 1615 cm⁻¹.

Reaction of trans-1,2-bis(tri-n-butylstannyl)ethylene, successively, with one equivalent of n-butyllithium, trimethylchlorosilane, n-butyllithium and trimethyltin chloride

The standard apparatus was charged with 10.75 g (17.7 mmol) of the title olefin in 35 ml of dry THF. Then 8.6 ml (17.7 mmol) of 2.07 N n-butyllithium in hexane was added all at once. The reaction mixture was stirred for 15 min, and then 2.25 ml (17.7 mmol) of trimethylchlorosilane was added in one portion. After an additional 15 min period, 8.6 ml (17.7 mmol) of n-butyllithium solution was added all at once. Fifteen min later, 3.6 g (17.7 mmol) of trimethyltin chloride was added. The entire reaction mixture was stirred for an additional hour and subsequently was hydrolyzed with 200 ml of water. The organic layer was trap-to-trap distilled (22°C/0.04 mmHg). GLC analysis of the volatile portion showed the presence of 9.51 mmol (54% yield) of *trans*-1-trimethylsilyl-2-trimethylstannylethylene, n_D^{25} 1.4723. (Found: C, 36.49; H, 7.71. C₈H₂₀SiSn calcd.: C, 36.53; H, 7.66%.) NMR (CCl₄/CH₂Cl₂): δ 0.12 (s, 9H, Me₃Si), 0.17 (s, 9H, Me₃Sn, $J(^{117}\text{Sn}-^1\text{H})$ 52 Hz, $J(^{119}\text{Sn}-^1\text{H})$ 55 Hz), and 6.30–7.20 ppm (AB pattern, J_{AB} 22 Hz, 2H, vinyl H).

Preparation of trans-2-trimethylsilylvinyllithium by the reaction of trans-1-trimethylsilyl-2-triphenylstannylethylene with phenyllithium in diethyl ether

A 500 ml, round-bottomed flask, equipped with reflux condenser, addition funnel, magnetic stir bar, no-air stopper and nitrogen inlet tube, was flamed dry and charged with 26.00 g (57.9 mmol) of the title olefin and 75 ml of anhydrous diethyl ether. The addition funnel was charged with 50.0 ml (63.0 mmol) of 1.26 N phenyllithium in diethyl ether. The phenyllithium was added slowly over a 1 h period. The reaction mixture was cooled with an ice water bath to complete precipitation of the tetraphenyltin and stirred for an additional h. Subsequently, the addition funnel was charged with 9.5 ml (75.0 mmol) of trimethylchlorosilane. This was added slowly to the lithium reagent solution over a 30 min period, and the mixture was stirred at room temperature overnight. The mixture was hydrolyzed and extracted with 200 ml of water, and the organic layer was trap-to-trap distilled (22°C/0.05 mmHg). The trap-to-trap residue was washed with ether, filtered and dried to give 23.35 g (94% yield) of tetraphenyltin, m.p. 226–227°C (lit. [22] m.p. 225°C). GLC analysis of the volatile portion showed the presence of 8.59 g (86% yield) of *trans*-1,2-bis(trimethylsilyl)ethylene, n_D^{25} 1.4274 (lit. [19] n_D^{20} 1.4303 whose IR and NMR spectra were identical to those of an authentic sample [19]).

Reactions of Me₃SiCH=CHLi prepared in this manner with dimethyl sulfate, trimethyltin chloride and acetone gave *trans*-Me₃SiCH=CHCH₃ (76% yield), *trans*-Me₃SiCH=CHSnMe₃ (88% yield) and *trans*-Me₃SiCH=CHCMe₂OH (69%), respectively. The products were identified by comparison of their properties with those of the products of the reactions described above.

Preparation of bis(trans-2-trimethylsilylvinyl)mercury and its palladium-catalyzed demercuration

The Me₃SiCH=CHLi reagent was prepared by the procedure described above

from 15.0 g (33.4 mmol) of the title olefin and 30.2 mmol of phenyllithium in 75 ml of diethyl ether. Then 3.85 g (14.0 mmol) of mercuric chloride in 30 ml of ether was added. The mixture was stirred at room temperature overnight and subsequently was hydrolyzed and extracted with 200 ml of water. The precipitated tetraphenyltin (12.5 g, 98%), m.p. 226–228°C, was filtered from the organic layer and washed with ether. The filtrates were combined, and the ether was removed by rotary evaporation. The remaining viscous liquid was distilled at reduced pressure to give 4.83 g (81% yield) of bis(*trans*-2-trimethylsilylvinyl)-mercury as a clear colorless liquid, b.p. 78–79°C/0.03 mmHg, n_D^{25} 1.5264. (Found: C, 30.66; H, 5.59. $C_{10}H_{22}Si_2Hg$ calcd.: C, 30.09; H, 5.56%.) NMR (CCl_4/CH_2Cl_2): δ 0.10 (s, 18H, Me_3Si) and 6.07–7.37 ppm (AB pattern, J_{AB} 22 Hz, 4H, vinyl H).

The demercuration of this compound was carried out as follows. A 100 ml, round-bottomed flask, equipped with reflux condenser and nitrogen inlet, was flamed dry and charged with 7.59 g (19.0 mmol) of the title mercurial in 50 ml of reagent-grade acetonitrile. To this was added 0.24 g (0.19 mmol) of tetrakis-(triphenylphosphine)palladium (Pressure Chemical Co.). The solution became dark grey immediately, with fine particles suspended in the liquid. The mixture was stirred overnight at room temperature. The reaction mixture was filtered to yield 3.64 g (96% yield) of mercury. The filtrate was trap-to-trap distilled (22°C/0.03 mmHg), leaving a light yellow liquid residue. GLC analysis of this liquid showed the presence of one product, which was collected and identified as 1,4-bis(trimethylsilyl)-*trans,trans*-1,3-butadiene, n_D^{20} 1.4685 (lit. [23] n_D^{20} 1.4679), the NMR spectrum of which was consistent with the proposed structure; NMR ($CCl_4/CHCl_3$): δ NMR 0.15 (s, 18H, Me_3Si) and 5.57–6.74 ppm (AA'BB' pattern, 4H, vinyl-H). NMR yield analysis (Varian Associates T-60, methanol internal standard) showed the presence of 3.56 g (95% yield).

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