THE PREPARATION OF ORGANOLITHIUM COMPOUNDS BY THE TRANSMETALATION REACTION
PART VIII. β-STYRYLLITHIUM[*]

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Although a number of authors have described the preparation of β-styrylmagnesium bromide and β-styryllithium, satisfactory methods for producing these reagents in high yield and purity still are lacking. Early work in this area was carried out by Gilman and co-workers[2], who reported the preparation of β-styrylmagnesium bromide in refluxing ether in 90 % yield. However, the yield was determined solely by titration and no derivatives were prepared. More extensive reactions were carried out by Wright[3], who prepared both the *cis-* and *trans-β*-styryl Grignard reagents and characterized them by carbonation. From *trans-β*-bromostyrene a 62 % yield of cinnamic acid was obtained (60 % *trans*, 40 % *cis*). Use of *cis-β*-bromostyrene gave a 35 % yield of cinnamic acid (isomer ratio 32 % *trans*, 68 % *cis*). Attempted preparation of β-styryllithium by Wright was only partially successful, the reaction of β-bromostyrene with lithium giving a 4:1 mixture of *trans-β*-styryllithium and phenylethynyllithium in 25 % yield. Wright was the first to point out that two serious side reactions accompany attempts to prepare the β-styryl Grignard (or lithium) reagent. The first is a coupling reaction which gives 1,4-diphenylbutadiene. The second, a dehydrohalogenation reaction (which Cristol[4] has shown very likely proceeds by an α elimination mechanism), is the one which leads ultimately to phenylethynyllithium.

An attempt by Gilman[5] to prepare β-styryllithium by a metal–halogen exchange reaction between β-bromostyrene and *n*-butyllithium also was only partially successful. When the reaction mixture was added to solid carbon dioxide after it had been refluxed in petroleum ether solution for 24 h, a 23 % yield of *trans*-cinnamic acid was obtained. When the solvent was ether, only phenylpropiolic acid (42 %) was isolated. Further work[6] showed that β-styryllithium could be prepared, apparently as a pure reagent in moderate yield, in diethyl ether via the direct reaction by working on a small (0.05 mole) scale and limiting the reaction time to 20 min. However, when

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[*] (a) For Part VII see ref. 1; (b) Also part XX of the series *Vinyl Derivatives of Metals*; for part XIX, see ref. 1.

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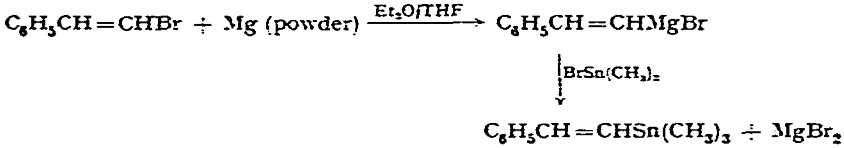
preparations on a larger scale were attempted, derivatives of phenylethynyllithium were the sole products.

This unsatisfactory state of affairs prompted us to investigate the transmetalation reaction, which served well in the preparation of other vinylic organolithium reagents[1,7,8,9], as a possible high yield route to β-styryllithium, since the complication presented by dehydrohalogenation and consequent formation of phenylethynyllithium would be avoided in such a reaction. Of interest also was the possibility of specific preparation of *cis*-β-styryllithium and *trans*-β-styryllithium by this procedure and the characterization of these isomeric lithium reagents by physical techniques.

β-Styryltrimethyltin was selected as the starting tin compound in order to have a volatile precursor that could be analyzed by gas chromatography. The compound was prepared in 63% yield by the Grignard route, using a 7:1 ratio of ether/THF as the solvent. A 28% yield of 1,4-diphenylbutadiene was also obtained.



$$\begin{tikzcd} C_6H_5CH{=}CHBr + Mg\ (powder) \arrow[r, "Et_2O/THF"] & C_6H_5CH{=}CHMgBr \arrow[d, "BrSn(CH_3)_3"] \\ & C_6H_5CH{=}CHSn(CH_3)_3 + MgBr_2 \end{tikzcd}$$

The β-bromostyrene used in this preparation was found by gas chromatography (cyanoethylsilicone column) to consist of two isomers in a ratio of 92:8. As the equilibrium ratio is known to be *ca.* 90% *trans* and 10% *cis*[10], it was assumed that the major isomer was the *trans* isomer. This was confirmed by infrared, ultraviolet and NMR spectra of the two isomers (see EXPERIMENTAL). It was of some surprise, therefore, to find that the styryltrimethyltin product consisted of two isomers in a ratio of 72:28. A partial *trans* to *cis* isomerization appeared to have occurred at some step in the reaction.

Assignment of geometrical configuration to these isomers was made on the basis of their infrared, NMR and ultraviolet spectra. The less volatile isomer (72% isomer) exhibited a strong infrared band at 990 cm^{-1} and tentatively was assigned the *trans* structure. Absorption in this region is known to be highly characteristic of *trans* olefins[11]. The less volatile isomer (28% isomer) showed no infrared absorption between 920 and 1020 cm^{-1} and was tentatively assigned the *cis* structure.

The NMR spectrum* of the *trans* isomer showed the phenyl protons at 7.3 p.p.m. and a sharp, unsplit peak at 6.70 p.p.m. The relative areas of these two peaks was 5:2, leaving no doubt that this peak represented the signals from both (non-equivalent) olefinic protons. Thus, an extreme example of an AB type spectrum occurs. A similar AB type spectrum has been observed for the olefinic protons of *trans*-propenylbenzene[12]. Small satellite signals arising from coupling of the ^{117}Sn and ^{119}Sn isotopes with the geminal proton were observed at 6.07 and 7.33 p.p.m. A coupling constant of 75.6 c.p.s. is indicated. In the NMR spectrum of the *cis* isomer one olefinic proton occurred as a doublet (J = 13.9 c.p.s.) at 7.50 p.p.m., the five aromatic protons as a sharp signal at 7.15 p.p.m., and the second olefinic proton as a doublet (J = 13.9 c.p.s.) at 6.09 p.p.m. It may be noted that this coupling constant is in the range of

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* Chemical shifts are given in p.p.m. downfield from tetramethylsilane.

J_{cis} for vinylic tin compounds (14.2 c.p.s. for *cis*-$CH_3CH{=}CHSn(CH_3)_3$; 13.2 c.p.s. for $(CH_2{=}CH)_4Sn$ and (*cis*-$CH_3CH{=}CH)_4Sn$).

The ultraviolet spectra of the two isomers provided independent evidence supporting the isomer assignments made on the basis of the infrared spectra. It has been well established[13] that simple *trans* olefins absorb at longer wavelengths and with higher extinction coefficients than the corresponding *cis* isomers. This was found to be true for the β-styryltrimethyltin isomers. The *trans* isomer had λ_{max} 259 mμ (ε = 21,400) while the *cis* isomer had λ_{max} 250 mμ (ε = 9,230).

When this work had been completed, it was learned that these isomers had also been prepared as part of a Purdue thesis project by the addition of trimethyltin hydride to phenylacetylene[14]. The physical properties and isomer assignments were identical in both cases.

An attempt to prepare the pure *cis*-β-styryltrimethyltin isomer also led to a *cis*–*trans* mixture of products. *cis*-β-Bromostyrene was prepared in 79 % yield by the decarboxylative debromination of *trans*-crotonic acid dibromide, according to the procedure of Cristol and Norris[15]. The Grignard reagent was prepared in THF, and after addition of trimethyltin bromide, a 50 % yield of β-styryltrimethyltin was obtained. The isomer ratio in this product was found by gas chromatographic analysis (Dow Corning 710 Silicone Oil Column) to be 79 % *cis* and 21 % *trans*.

In anticipation of characterizing *cis*- and *trans*-β-styryllithium with trimethylchlorosilane, the synthesis of *cis*- and *trans*-β-styryltrimethylsilane was undertaken. The preparation of the *trans* isomer presented no difficulties, as it had been previously described (without rigorous structural proof) by several workers[16–18]. The method actually used was that of Sommer and co-workers[18], in which the ether in the Grignard solution is partially replaced by benzene before the addition of trimethylchlorosilane. A 64 % yield of β-styryltrimethylsilane was obtained, which gas chromatographic analysis (General Electric SE 30 Silicone Gum short column) showed was a single isomer. It tentatively was assumed that this was the *trans* isomer, as the β-bromostyrene used was the equilibrium mixture of 90 % *trans* and 10 % *cis**. However, confirmation of this isomer assignment could not be made with certainty until a sample of the (supposed) *cis* isomer was available for a comparison of spectral characteristics.

The preparation of the *cis* isomer proved to be more difficult. A compound previously thought to be this isomer had been described by Benkeser[16] and was prepared by the partial catalytic hydrogenation of (phenylethynyl)trimethylsilane. Accordingly, (phenylethynyl)trimethylsilane was prepared and a partial reduction using palladium-on-charcoal poisoned with pyridine attempted. Several workers have reported excellent results in the use of various palladium catalysts for the partial reduction of acetylenic silanes to *cis* olefins[20–23]. After the absorption of one equivalent of hydrogen the hydrogenation was stopped and the product distilled. A compound with properties similar to those described by Benkeser[16] was obtained. Although but one peak was observed on gas chromatographic analysis (General Electric SE 30 Silicone Gum short column), the ultraviolet spectrum of the product clearly revealed that it was not the *cis* isomer. The spectrum was identical with that of (phenylethynyl)trimethylsilane,

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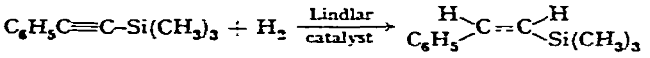
* This is in contrast to the 72:28 *trans*- to *cis*-β-styryltrimethyltin ratio obtained using the same β-bromostyrene. The solvents used were different, and recent work[19] has indeed demonstrated that the solvent effects on the isomer ratio of *cis*- and *trans*-$C_6H_5CH{=}CHMgBr$ are significant.

but the extinction coefficients for all peaks were about half the values for the pure compound. Thus, it was clear that reduction under these conditions had led largely to the saturated compound, (β-phenylethyl)trimethylsilane (subsequently prepared by the catalytic hydrogenation of *trans*-β-styryltrimethylsilane), and unreacted (phenylethynyl)trimethylsilane. An NMR spectrum of the product confirmed this conclusion, showing strong signals where peaks from (β-phenylethyl)trimethylsilane occurred, but only weak signals in the region where the olefinic protons of *cis*-β-styryltrimethylsilane were subsequently found to occur.

A similar reduction was then tried using a Lindlar catalyst[24], and it was found that *ca.* a 75 % yield of the *cis* olefin was obtained. However, since the retention time



$$C_6H_5C{\equiv}C\text{–}Si(CH_3)_3 + H_2 \xrightarrow[\text{catalyst}]{\text{Lindlar}} \begin{matrix} H & & H \\ & C{=}C & \\ C_6H_5 & & Si(CH_3)_3 \end{matrix}$$

of this isomer was identical with that of both the starting acetylene and the fully saturated silane on several common gas chromatographic columns, analytically pure samples could not be obtained by this procedure.

A satisfactory method for obtaining the pure *cis* isomer was ultimately developed by a photochemical procedure. It was found that when the pure *trans* isomer was irradiated (*n*-hexane solution), a slow *trans* to *cis* isomerization occurred. After 23 hours of irradiation, the ratio was 63 % *trans* and 37 % *cis*. The irradiation was stopped at this point and analytical samples of the *cis* isomer were collected by gas chromatography (General Electric SE 30 Silicone Gum short column). Excellent separation of the *cis* and *trans* isomers could be obtained on this column. Since the irradiation was not continued for longer times, it was not established if the photochemical steady-state had been reached in this 23 hour period. A high recovery of products (96 %) indicated no dimerization or polymerization occurred during the irradiation.

With both isomers available, decisive structural assignments could now be made. The less volatile isomer showed a strong infrared band at 985 cm^{-1} and was thus assigned the *trans* structure. The more volatile isomer showed only very weak absorption in this region and was assigned the *cis* structure.

The NMR spectra gave further proof for these assignments. In the spectrum of the *trans* isomer the five phenyl protons occurred as a broad peak at 7.3 p.p.m. The two olefinic protons occurred as two doublets (J = 19.2 c.p.s.) at 6.90 and 6.33 p.p.m. In the spectrum of the *cis* isomer the five phenyl protons occurred as a sharp peak at 7.40 p.p.m. One olefinic proton occurred as a doublet (J = 15.6 c.p.s.) at 5.92 p.p.m., while the upfield half of the second doublet (midpoint at 7.55 p.p.m.) was obscured by the strong phenyl signal at 7.40 p.p.m. The larger coupling constant for the *trans* protons is in agreement with numerous studies[25–31].

The ultraviolet spectra of the two isomers provided additional evidence for these structural assignments[13]. The *trans* isomer had its maximum at 258 mμ (ε = 21,100), while the *cis* isomer had its maximum at 248 mμ (ε = 11,300).

In our initial studies *trans*-β-styryllithium was obtained via the transmetalation reaction by the addition of one equivalent of methyllithium to *trans*-β-styryltrimethyltin. The NMR spectrum of the styryllithium reagent* (deep red solution) showed one

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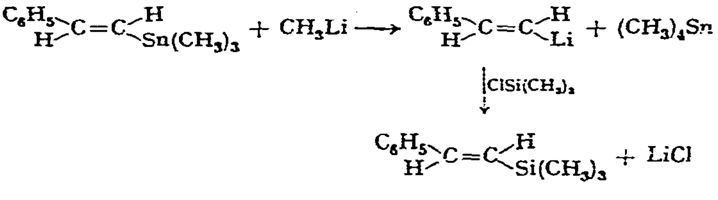
* The tetramethyltin formed in the transmetalation reaction does not interfere.

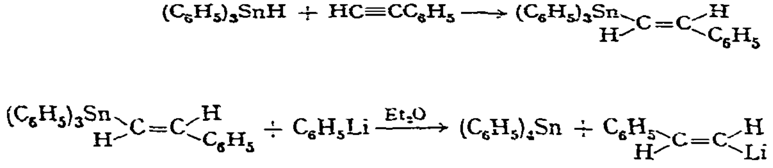
olefinic proton as a doublet ($J = 22.8$ c.p.s.) at 8.01 p.p.m. The upfield component of the second doublet was obscured by the broad phenyl signal at 7.3 p.p.m. It is to be noted here that this coupling constant falls within the range of J_{trans} reported for vinylic lithium reagents: 22.2 c.p.s. for *trans*-$CH_3CH{=}CHLi$ and 23.9 c.p.s. for $CH_2{=}CHLi$[1]. Addition of trimethylchlorosilane to this lithium reagent produced only



$$\overset{C_6H_5}{\underset{H}{}}\!>\!C{=}C\!<\!\overset{H}{\underset{Sn(CH_3)_3}{}} + CH_3Li \longrightarrow \overset{C_6H_5}{\underset{H}{}}\!>\!C{=}C\!<\!\overset{H}{\underset{Li}{}} + (CH_3)_4Sn \xrightarrow{ClSi(CH_3)_3} \overset{C_6H_5}{\underset{H}{}}\!>\!C{=}C\!<\!\overset{H}{\underset{Si(CH_3)_3}{}} + LiCl$$

trans-β-styryltrimethylsilane. The refractive index, infrared spectrum and retention time (General Electric SE 30 Silicone Gum short column) of this product were identical with those of an authentic sample.

A possibly more practical route to *trans*-β-styryllithium is afforded by the following reaction sequence:



$$(C_6H_5)_3SnH + HC{\equiv}CC_6H_5 \longrightarrow \overset{(C_6H_5)_3Sn}{\underset{H}{}}\!>\!C{=}C\!<\!\overset{H}{\underset{C_6H_5}{}}$$

$$\overset{(C_6H_5)_3Sn}{\underset{H}{}}\!>\!C{=}C\!<\!\overset{H}{\underset{C_6H_5}{}} + C_6H_5Li \xrightarrow{Et_2O} (C_6H_5)_4Sn + \overset{C_6H_5}{\underset{H}{}}\!>\!C{=}C\!<\!\overset{H}{\underset{Li}{}}$$

The addition of triphenyltin hydride to phenylacetylene proceeds in virtually quantitative yield at room temperature to give a single isomer[32], which has been shown[14] to be that with the *trans* structure. The addition of phenyllithium to an ether solution of *trans*-β-styryltriphenyltin resulted in immediate precipitation of tetraphenyltin (isolated in 90 % recrystallized yield). Addition of trimethylchlorosilane to the solution of *trans*-β-styryllithium thus formed gave *trans*-β-styryltrimethylsilane as the sole product in 86 % yield. It is apparent that the transmetalation reaction represents a superior route to *trans*-β-styryllithium. The reagent is formed in very high yield and none of the by-products which complicate matters when β-bromostyrene is used as starting material are present. Furthermore, isomerization does not appear to be a problem in this reaction, since an isomerically pure product was formed in very high yield in the most favorable case reported. For reasons which will become apparent in the discussion below, we cannot say with complete confidence that there occurs no isomerization at all. These experiments do, however, suggest that *trans*-β-styryllithium is configurationally stable in ether solution at room temperature*.

An attempt was made to prepare *cis*-β-styryllithium by the transmetalation procedure. When one equivalent of ethereal methyllithium was added to *cis*-β-styryltrimethyltin in ether, a dark red solution was formed, which appeared to be rather viscous. The NMR spectrum of this solution showed no sharp peaks, but only a broad,

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* A summary of the configurational stability of vinylic lithium reagents is given in ref. 33.

unresolved series of signals between 6.0 and 8.3 p.p.m. Addition of trimethylchlorosilane to this solution gave a vigorous reaction, and a viscous residue which contained no volatiles remained when the ether was distilled off. This strange behavior lacks a ready explanation. The possibility exists that the action of methyllithium on *cis*-β-styryltrimethyltin results in polymerization of the tin-containing olefin rather than in a transmetalation reaction. The possibility must also be considered that the transmetalation reaction does occur and that the resulting *cis*-β-styryllithium polymerizes in some unknown manner.

EXPERIMENTAL

Methods

All reactions and manipulations involving organolithium reagents were performed under an atmosphere of argon or prepurified nitrogen. Carefully purified solvents were used throughout these studies. Analyses were performed by Dr. S. M. NAGY (M.I.T.) and by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Infrared spectra were recorded using a Baird Model B or a Perkin-Elmer Model 21 infrared spectrophotometer, NMR spectra in ether solution using a Varian Associates A60 NMR spectrometer, and ultraviolet spectra using a Cary 14 Recording Spectrophotometer. The columns used for gas chromatographic analyses and separations were 265 cm in length (1 cm i.d. Pyrex tubing). For certain high-boiling compounds the use of 90 cm columns proved advantageous. The cyanoethylsilicone used was General Electric Co. XF-1150 Fluid.

β-Bromostyrenes

trans-β-Bromostyrene. A sample of commercial β-bromostyrene (Eastman) was examined by gas chromatography (cyanoethylsilicone column, jacket temperature 160°, preheater temperature 160°, 15 p.s.i. He) and was found to consist of two isomers in a ratio of 92:8. An analytical sample of the major isomer was collected and had n_D^{25} 1.6071 (lit.[34] n_D^{25} 1.6071 reported for *trans*-β-bromostyrene). The infrared and ultraviolet spectra of this isomer were identical with published spectra[34] for *trans*-β-bromostyrene. In the NMR spectrum, the five aromatic protons occurred as a sharp signal at 7.15 p.p.m. The two olefinic protons occurred as two doublets ($J = 13.8$ c.p.s.) at 7.03 and 6.60 p.p.m.

cis-β-Bromostyrene was prepared by the procedure of Cristol and Norris[15] in 79 % yield, b.p. 42–44°/0.4 mm. Gas chromatographic analysis (cyanoethylsilicone column, jacket temperature 140°, 15 p.s.i. He) revealed the isomer ratio to be 97 % *cis* and 3 % *trans*. An analytical sample of the major isomer was collected and had n_D^{25} 1.5980 (lit.[34] n_D^{25} 1.5980 reported for *cis* isomer). The infrared and ultraviolet spectra of this isomer were identical with published spectra of *cis*-β-bromostyrene[34]. In the NMR spectrum, the five aromatic protons occurred as a group of two at 7.60 p.p.m. and as a group of three at 7.25 p.p.m. The two olefinic protons occurred as two doublets ($J = 7.8$ c.p.s.) at 6.93 and 6.30 p.p.m. The larger coupling constant ($J = 13.8$ c.p.s.) observed for the *trans* isomer is in agreement with expectations.

Preparation of β-styryltrimethyltin from trans-β-bromostyrene

In a 500 ml flask, equipped with a stirrer, reflux condenser, addition funnel and protected by an argon atmosphere, was placed 4.1 g (0.17 g-atom) of magnesium powder. The magnesium then was covered with 175 ml of ether and 25 ml of THF, and several drops of methyl iodide were added to initiate the reaction. A solution of 33.9 g (0.185 mole) of β-bromostyrene (92 % *trans*, 8 % *cis*) in 50 ml of THF was added dropwise over a half hour period. It was observed that the solution turned dark red soon after this addition was started. When the addition was complete, the mixture was refluxed for 20 hours. To the mixture was added 34.1 g (0.14 mole) of trimethyltin bromide, followed by a two hour reflux period. The mixture was hydrolyzed with a saturated ammonium chloride solution and the salts were washed with an additional 50 ml of ether. After the combined ether layers were filtered and dried over anhydrous sodium sulfate, the ether and THF were distilled off. Fractional distillation of the residue furnished 23.8 g (63 % yield) of product, b.p. 110–114°/3.5 mm. When the pot residue was allowed to cool, 6.9 g (28 % yield) of a crystalline product, subsequently identified as 1,4-diphenylbutadiene, was obtained.

The product was analyzed by gas chromatography (Dow Corning 710 Silicone Oil short column, jacket temperature 152°, 12 p.s.i. He) and was found to consist of two isomers in a 72:28 ratio. The 28 % isomer was subsequently identified as the *cis* isomer and the 72 % isomer as the *trans* isomer, analytical samples being collected by gas chromatography.

cis-β-styryltrimethyltin: n_D^{25} 1.5530; infrared spectrum (pure liquid) 3040(m), 2950(s), 2900(m), 1590(m), 1570(m), 1495(s), 1445(m), 1190(m), 1075(m), 1025(w), 915(m), 775(s), 700(s) cm^{-1}. The ultraviolet spectrum (*n*-heptane) showed λ_{max} 250 (ε = [illegible]230), λ_{sh}285 (ε = 809), and λ_{max}293 (ε = 382). (Found: C, 49.59; H, 6.10. $C_{11}H_{16}Sn$ calcd.: C, 49.49; H, 6.04 %.)

trans-β-styryltrimethyltin: n_D^{25} 1.5666; infrared spectrum (pure liquid) 3040(m), 2960(s), 2900(m) 1595(m), 1570(m), 1495(s), 1450(m), 1190(m), 1175(m), 1070(w), 1030(m), 990(s), 775(s), 725(s), 690(s) cm^{-1}. The ultraviolet spectrum (*n*-heptane) showed λ_{max} 259 (ε = 21,400), λ_{max} 284 (ε = 2900), λ_{max} 293 (ε = 1764). (Found: C, 49.60; H, 6.15 %.)

The crystalline residue obtained at the end of the distillation was recrystallized twice from chloroform and had m.p. 147–149° (lit.[35] m.p. 150.5° reported for *trans–trans*-1,4-diphenyl-1,3-butadiene). The Diels-Alder adduct was prepared by heating 0.30 g (1.46 mmole) of the diene with 0.145 g (1.48 mmoles) of maleic anhydride in 10 ml of xylene for eight hours. The product was recrystallized twice, first from chloroform, then from acetonitrile, and had m.p. 208–209.5° (lit.[36] m.p. 206° reported for 3,6-diphenyl-1,2,3,6-tetrahydrophthalic anhydride). A total of 0.29 g (65 % yield) was obtained.

Preparation of β-styryltrimethyltin from cis-β-bromostyrene

In a 500 ml flask, equipped with a stirrer, reflux condenser, addition funnel and protected by an argon atmosphere, was placed 3.1 g (0.13 g-atom) of magnesium turnings. The turnings were covered with 50 ml of THF and reaction was initiated by the addition of several drops of 1,2-dibromoethane. An additional 250 ml of THF then was added, and over a one hour period a solution of 25.0 g (0.136 mole) of *cis-β*-bromostyrene (97 % isomeric purity) in 50 ml of THF was added. The solution turned dark red soon after this addition was started. When the addition was complete, the mixture was refluxed for two hours. A solution of 20.0 g (0.082 mole) of trimethyltin bromide in 50 ml of THF was added dropwise, and the mixture was refluxed overnight.

The reaction mixture was worked up as described above. After the THF was distilled off, fractional distillation of the residue gave 10.8 g (50% yield) of product, b.p. 70–73°/0.35 mm. A viscous residue remained in the flask, but attempts to obtain a crystalline product (from chloroform) were unsuccessful.

Gas chromatographic analysis (Dow Corning 710 Silicone Oil short column, jacket temperature 142°, 12 p.s.i. He) of the distillation product revealed that it consisted of two isomers in a 79:21 ratio. The more volatile isomer (79% isomer) had n_D^{25} 1.5532 and had an identical retention time as the previously characterized sample of *cis*-β-styryltrimethyltin. The infrared spectra of the two compounds were identical. The less volatile isomer (21% isomer) had a retention time identical with that of the previously characterized sample of *trans*-β-styryltrimethyltin. The infrared spectra of these two compounds were also identical.

Preparation of trans-β-styryltrimethylsilane

In a 500 ml flask equipped with a stirrer, reflux condenser, addition funnel, and protected by an argon atmosphere, was placed 20.0 g (0.83 g-atom) of magnesium powder. The magnesium was covered with 100 ml of ether, and reaction was initiated by the addition of 0.1 g of iodine and several drops of β-bromostyrene. Over a five hour period, a solution of 70.0 g (0.38 mole) of β-bromostyrene (92% *trans*, 8% *cis*) in 200 ml of ether was added to the mixture. External heating was used during this entire period to insure vigorous refluxing. Dry benzene (100 ml) then was added to the reaction flask and ether was distilled off until the pot temperature reached 60°. The solution was allowed to cool and 41.0 g (0.38 mole) of trimethylchlorosilane was added over a ten minute period. The mixture was refluxed for 40 hours. After hydrolysis with saturated ammonium chloride solution, the ether–benzene layer was decanted and the solvent removed by rotary evaporation. Fractional distillation of the residue gave 43.1 g (64% yield) of product, b.p. 80–83°/3 mm. Gas chromatographic analysis (General Electric SE 30 Silicone Gum short column, jacket temperature 135°, preheater temperature 150°, 15 p.s.i. He) revealed the product to contain but one isomer, subsequently identified as the *trans* isomer. An analytical sample had n_D^{25} 1.5241 (lit.[15] b.p. 98°/10.5 mm, n_D^{20} 1.5270). The infrared spectrum (pure liquid) had bands at 3040(m), 3000(m), 2930(s), 2880(m), 1600(s), 1575(m), 1495(s), 1450(m), 1330(m), 1285(w), 1250(s), 1215(m), 1200(m), 1070(w), 1030(m), 985(s), 865(s), 840(s), 755(s), 725(s), 690(s) cm^{-1}. The ultraviolet spectrum of this isomer (*n*-heptane) had maxima at 218 mμ (ε = 13,000), 258 (ε = 21,100), 284 (ε = 2380) and 294 (ε = 1460). (Found: C, 74.84; H, 9.20. $C_{11}H_{16}Si$ calcd.: C, 74.92; H, 9.15%.)

Preparation of (phenylethynyl)trimethylsilane

In a 300 ml flask, equipped with magnetic stirrer, reflux condenser, addition funnel, and protected by an argon atmosphere was placed 30.0 g (0.294 mole) of phenylacetylene and 20 ml of ether. Over a one hour period, 200 ml of 1.5 *N* *n*-butyllithium (0.30 mole) in ether was added to the solution. Then, 39.0 g (0.36 mole) of trimethylchlorosilane was added over a 15 minute period, and the mixture was refluxed overnight. The mixture then was filtered through a sintered glass filter to remove the precipitated lithium chloride, and the ether removed by rotary evaporation. Fractional distillation of the residue gave 38.0 g (74% yield) of product, b.p. 59–60°/1.0 mm, n_D^{25} 1.5255 (lit.[16] b.p. 67°/5 mm, n_D^{20} 1.5284). The infrared spectrum of this compound (pure liquid) had bands at 3030(m), 2930(m), 2880(m), 2160(s), 1595(m), 1570(w), 1490(s), 1445(m), 1410(m), 1280(m), 1250(s), 1220(s), 1180(w), 1070(m), 1030(m), 930(m), 915(m), 865(s), 840(s), 760(s), 690(s), 645(s) cm^{-1}. The ultraviolet spectrum (*n*-heptane) had λ_{max} 237 (ε = 16,500), λ_{sh} 243 (ε = 18,200), λ_{max} 247 (ε = 27,400), λ_{max} 253 (ε = 16,200), λ_{max} 258 (ε = 26,000), λ_{max} 273 (ε = 769), λ_{max} 281 (ε = 560). (Found: C, 75.87; H, 8.42. $C_{11}H_{14}Si$ calcd.: C, 75.79; H, 8.09%.)

Catalytic hydrogenation of (phenylethynyl)trimethylsilane (palladium catalyst)

In a 250 ml hydrogenation flask was placed 11.5 g (0.066 mole) of (phenylethynyl)-trimethylsilane, 100 ml of ethyl acetate, 506 mg of 10% palladium-on-charcoal catalyst, and 300 mg of distilled pyridine. Over a five hour period, 1640 cc of hydrogen (theoretical amount for absorption of one equivalent) was absorbed. The mixture then was filtered and the ethyl acetate removed by rotary evaporation. Fractional distillation of the residue furnished 8.9 g of product, b.p. 60–61°/1.0 mm, n_D^{25} 1.5072. Gas chromatographic analysis (General Electric SE 30 Silicone Gum short column, jacket temperature 135°, preheater temperature 130°, 19 p.s.i. He) showed only one peak for this product. The ultraviolet spectrum (*n*-heptane) was identical (in peak position) with that of (phenylethynyl)trimethylsilane; λ_{max} 247 (ε = 14,000), λ_{max} 258 (ε = 13,100). The NMR spectrum showed strong bands at 2.6 and 1.0 p.p.m. arising from the fully saturated silane. A moderate intensity doublet at 5.9 p.p.m. showed that at least some of the desired *cis* isomer was present.

Catalytic hydrogenation of (phenylethynyl)trimethylsilane (Lindlar catalyst)

In a 200 ml hydrogenation flask was placed 7.5 g (0.043 moles) of (phenylethynyl)-trimethylsilane, 80 ml of ethyl acetate, 0.75 g of Lindlar catalyst and 0.2 g of synthetic quinoline. Over a 17 hour period, 780 cc of hydrogen (75% of the theoretical amount for absorption of one equivalent) was absorbed. The reaction was stopped, the reaction mixture filtered, and the ethyl acetate removed by rotary evaporation. Fractional distillation of the residue gave 6.6 g of product, b.p. 45°/0.1 mm. The NMR spectrum of this product showed a strong doublet at 5.9 p.p.m., subsequently shown to arise from the *cis* isomer. Weak signals also were seen at 2.6 and 1.0 p.p.m., arising from the saturated silane. No signals attributable to the *trans* isomer were detected.

Preparation of (β-phenylethyl)trimethylsilane

In a 200 ml hydrogenation flask was placed 11.2 g (0.0636 mole) of *trans*-β-styryl-trimethylsilane, 60 ml of ethyl acetate, and 0.214 g of 10% palladium-on-charcoal catalyst. Over a two hour period, the solution absorbed 1630 cc of hydrogen (105% of theoretical amount). The solution was filtered and the ethyl acetate removed by rotary evaporation. Distillation of the residue furnished 9.2 g (81% yield) of (β-phenylethyl)trimethylsilane, b.p. 48–50°/0.5 mm, n_D^{25} 1.4832 (lit.[18] b.p. 78°/8.5 mm, n_D^{20} 1.4863). In the NMR spectrum of this compound, the five aromatic protons occurred as a sharp peak at 7.3 p.p.m. The two benzylic protons occurred as a complex multiplet (> quintet) at 2.65 p.p.m., while the second set of methylene protons also occurred as a complex multiplet (> sextet) at 1.0 p.p.m. The trimethylsilyl group occurred as a sharp singlet at 0.0 p.p.m. Rotation about the carbon–carbon bond is apparently restricted by the steric requirements of the phenyl and trimethylsilyl groups, thus causing this spectrum to be unexpectedly complex.

Preparation of cis-β-styryltrimethylsilane

In a 50 ml quartz flask, equipped with a reflux condenser, a side arm with a no-air rubber stopper, and protected by an argon atmosphere, was placed 10.5 g of *trans-β*-styryltrimethylsilane and 10 ml of *n*-hexane. The top of the flask was covered completely with aluminum foil. The *trans-β*-styrylsilane solution was irradiated with an ultraviolet lamp (Hanovia Lamp Division Cat. No. 30600, 100 watts) placed 3.5 cm below the flask. Samples were withdrawn periodically with a syringe and isomer ratios were determined by gas chromatography (General Electric SE 30 Silicone Gum short column, jacket temperature 112°, preheater temperature 140°, 20 p.s.i. He).

Irradiation Time	*trans-β-Styryl Isomer, %*	*cis-β-Styryl Isomer, %*
0	100	0
10 min	100	0
20 min	100	0
2 h	97	3
5 h	88	12
23 h	63	37

The irradiation was stopped at the end of 23 hours and the *n*-hexane was distilled off. Distillation of the residue gave 10.1 g (96% recovery) of product, b.p. 50–52°/0.2 mm. An analytical sample of the *cis* isomer collected by gas chromatography had n_D^{25} 1.5144. The infrared spectrum (pure liquid) had bands at 3000(m), 2920(s), 2880(m), 1940(w), 1590(s), 1570(s), 1495(s), 1445(m), 1410(m), 1250(s), 1155(w), 1070(m), 1030(m), 985(w), 915(m), 850(s), 765(s), 700(s) cm^{-1}. The ultraviolet spectrum of this isomer (*n*-heptane) had maxima at 248 mμ ($\varepsilon = 11{,}300$) and 294 mμ ($\varepsilon = 270$). (Found: C, 75.08; H, 9.41. $C_{11}H_{16}Si$ calcd.: C, 74.92; H, 9.15%.)

Preparation of trans-β-styryllithium by the transmetalation reaction

In a small flask, thoroughly flushed with argon, was placed 2.27 g (8.5 mmoles) of *trans-β*-styryltrimethyltin. To the flask then was added 5.0 ml of 1.7 *N* methyllithium (8.5 mmoles) and the solution was swirled occasionally for one hour. The solution immediately turned red, and the color seemed to darken over the one hour period. A 1/4 cc sample was transferred to a NMR tube and the spectrum of the solution was obtained. This sample was returned to the reaction flask, and 1.0 g (9.25 mmoles) of trimethylchlorosilane was added dropwise over a 15 minute period (vigorous reaction). After the solution was allowed to stand overnight, it was filtered to remove the precipitated lithium chloride and the ether was distilled off. Gas chromatography (General Electric SE 30 Silicone Gum short column, jacket temperature 131°, preheater temperature 140°, 19 p.s.i. He) was used to collect 0.76 g (51% yield) of *trans-β*-styryltrimethylsilane, n_D^{25} 1.5242. The retention time, refractive index, and infrared spectrum of this product were identical with those of a sample of authentic *trans-β*-styryltrimethylsilane. The yield is on the low side due to the workup procedure used and to the small scale on which this reaction was run. It is to be noted that the NMR spectrum of the reagent solution, obtained before addition of trimethylchlorosilane, indicated that essentially no unreacted *trans-β*-styryltrimethyltin was left.

Preparation of trans-β-styryllithium from trans-β-styryltriphenyltin: recommended preparative procedure

In a 200 ml flask equipped with magnetic stirrer, addition funnel, reflux condenser, under an argon atmosphere, was placed 9.1 g (0.02 mole) of *trans*-β-styryltriphenyltin[32] in 150 ml of ether. To this solution was added during 15 min 26.5 ml of 0.75 *N* phenyllithium in ether. White solid precipitated immediately, and the solution became dark in color. The mixture was stirred at room temperature for 1.5 h and then 2.6 g (0.22 mole) of trimethylchlorosilane was added. The reaction mixture was allowed to stand overnight, then was filtered and the filtrate distilled to give 3.0 g (86 %) of *trans*-β-styryltrimethylsilane, b.p. 78–80°/3 mm. The infrared spectrum and refractive index were identical with that of authentic material.

The white solid which had been filtered was recrystallized from benzene to give 8.2 g of pure tetraphenyltin, a yield of 90 %.

Preparation of cis-β-styryllithium by the transmetalation reaction

In a small flask, thoroughly flushed with argon, was placed 0.764 g (2.86 mmoles) of *cis*-β-styryltrimethyltin. To the flask then was added 1.7 ml of 1.7 *N* methyllithium (2.89 mmoles) and the solution was swirled occasionally for one hour. The solution turned dark red immediately, and was almost black at the end of the one hour period. The viscosity of the solution seemed to increase somewhat over this period also. A 0.4 cc sample was then transferred to a NMR tube and the spectrum of the solution was obtained. No sharp peaks were observed in the aromatic region, but only a broad, unresolved series of signals between 6.0 and 8.3 p.p.m. This sample was returned to the reaction flask and 0.33 g (3.0 mmoles) of trimethylchlorosilane was added dropwise over a 15 minute period (vigorous reaction). After the solution was allowed to stand for 30 hours, it was filtered to remove the precipitated lithium chloride and the ether was distilled off. A viscous residue remained, in which no volatile products could be detected by gas chromatographic analysis (General Electric SE 30 Silicone Gum short column, jacket temperature 112°, preheater temperature 140°, 20 p.s.i. He).

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SUMMARY

trans-β-Styryllithium can be prepared conveniently by the transmetalation reaction occurring between *trans*-β-styryltin compounds and organolithium reagents. This procedure is superior to others previously used, since neither acetylenic by-products nor 1,4-diphenylbutadiene are formed. The preparation and characterization of the *cis* and *trans* isomers of β-styryltrimethylsilane and -tin are described.

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