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THE PREPARATION OF ORGANOLITHIUM REAGENTS BY THE TRANSMETALATION REACTION

XI*. CROTYLLITHIUM

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Summary

Both *cis*- and *trans*-crotyltrimethyltin react with *n*-butyl- and methyl-lithium in ether to give crotyllithium in high yield. In each case, reaction of the reagent solution with trimethylchlorosilane gives an approximately 3/2 mixture of *trans*- and *cis*-crotyltrimethylsilane. These transmetalation equilibria permit the isomerization of *cis*- and *trans*-crotyltrimethyltin to a 3/2 *trans/cis* mixture by small amounts of *n*-butyl- or methyl-lithium. Metallic lithium also causes isomerization of the *cis*- and *trans*-crotyllithium isomers via a metal displacement process which generates a small amount of crotyllithium which is capable of exchanging crotyl groups with unconverted crotyltrimethyltin. The possible mechanism of the isomerization reactions observed is discussed.

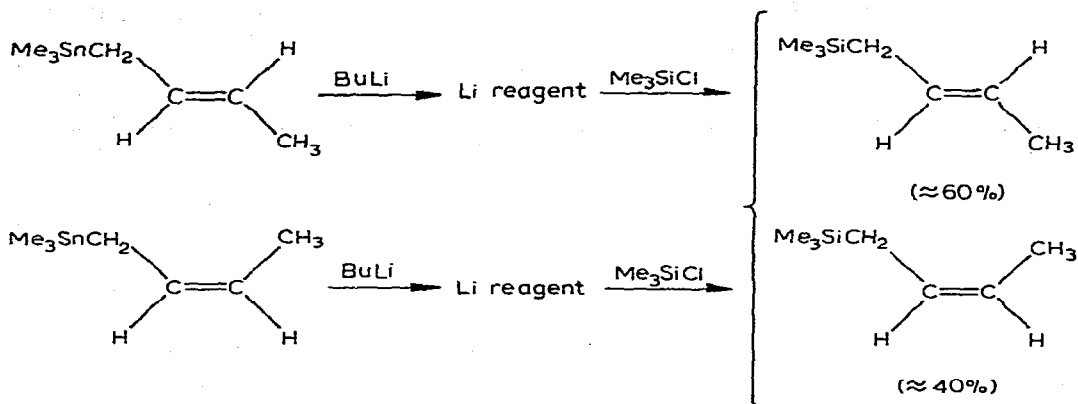
Introduction

In previous studies [3] we had prepared and separated the *cis*- and *trans*-isomers of crotyltrimethyltin. Their availability suggested to us a study of the preparation of crotyllithium, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Li}$, by the transmetalation reaction, which had been used previously in these laboratories to generate allyl- and methallyllithium [4]. The stereochemical question which could be investigated since both *cis*- and *trans*-crotyltrimethyltin were in hand was an interesting one in view of the apparent fluxional nature of allyllithium in diethyl ether and in THF [5]. The work reported here was completed in 1967 and was the subject of a preliminary communication [2]. Although we were unable to continue this study in the manner indicated [2] during the course of the intervening years, we felt that it would be useful to publish full details of the preparative portions of our work on crotyllithium.

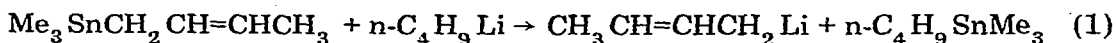
* For Part X see ref. [1]; for preliminary communication see ref. [2].

Results and discussion

Crotyllithium was obtained in high yield by the transmetalation reaction occurring between crotyltin compounds and organolithium reagents. The reaction, however, did not proceed with retention of configuration about the C=C bond. When crotyllithium was generated from either *cis*- or *trans*-crotyltrimethyltin, both *cis*- and *trans*-crotyltrimethylsilane were obtained in each case in ca. 2/3 ratio when the reaction mixture was quenched with trimethylchlorosilane:



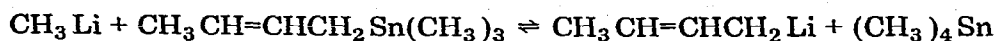
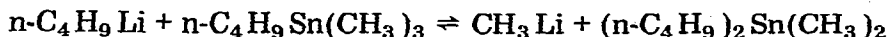
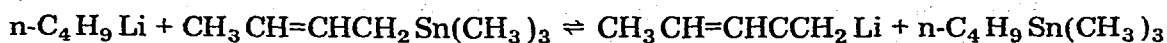
The reaction of pure *trans*-crotyltrimethyltin with an equivalent amount of *n*-butyllithium in diethyl ether/hexane for 30 min, followed by the dropwise addition of trimethylchlorosilane, gave crotyltrimethylsilane (61% *trans*, 39% *cis*) in 94% yield, but the recovery of *n*-butyltrimethyltin was only 45% of theory, based on eqn. (1). Similar treatment of *cis*-crotyltrimethyltin with



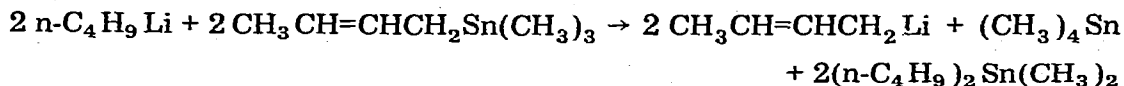
n-butyllithium followed by the addition of trimethylchlorosilane gave crotyltrimethylsilane (61% *trans*, 39% *cis*) in 98% yield, but again the recovery of *n*-butyltrimethyltin was low (47%). Further analysis of the reaction mixtures by gas-liquid chromatography (GLC) showed that no *n*-butyltrimethylsilane was present, but that di-*n*-butyldimethyltin as well as some tetramethyltin had been produced. The high yield of crotyltrimethylsilane, compared to the amount of *n*-butyltrimethyltin obtained, implied that the formation of di-*n*-butyldimethyltin and tetramethyltin had occurred before the trimethylchlorosilane was added. Since such transmetalation reactions are known to be equilibrium processes [6,7], a complex series of equilibria favoring the formation of crotyllithium must be considered in place of the simple process implied by eqn. (1). Scheme 1 shows the reactions which must take place. To confirm the generality of the displacement of methyl groups from tin by *n*-butyllithium under our reaction conditions, tetramethyltin was treated with about 2.5 molar equivalents of *n*-butyllithium in diethyl ether/hexane at room temperature for 90 min. Analysis of the reaction mixture by GLC after hydrolysis showed that *n*-butyltrimethyltin had been formed in 57% yield.

SCHEME 1

Formation of crotyllithium

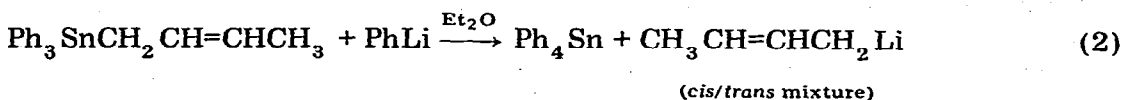


with the net result:



Since the reaction of *n*-butyllithium with crotyltrimethyltin was complicated by the formation of the redistribution products, methylithium also was used to prepare crotyllithium by the transmetalation reaction. In this case, the effects of secondary transmetalation equilibria are eliminated. A 1/1 molar ratio of methylithium and crotyltrimethyltin was insufficient to produce useful yields of crotyllithium and even when *trans*-crotyltrimethyltin was treated with a two-fold excess of methylithium in ether for 30 min, the yield of crotyltrimethylsilane (58% *trans*, 42% *cis*) was only 66% after treatment of the reagent solution with trimethylchlorosilane. Some crotyltrimethyltin remained unconverted. Complete consumption of *trans*-crotyltrimethyltin was achieved when such a 2/1 reaction mixture in ether was heated at reflux for 30 min before the chlorosilane was added. When such a procedure was used, the yield of crotyltrimethylsilane (58% *trans*, 42% *cis*) was 98%, based on crotyltrimethyltin. Similar observations were made with *cis*-crotyltrimethyltin.

Since a mixture of *cis*- and *trans*-crotyllithium appears to result irrespective of the crotyltrimethyltin isomer used in the transmetalation reaction, preparative applications of crotyllithium do not require isomerically pure crotyltin compounds. The procedure of choice involves the use of crotyltriphenyltin as a mixture of *cis* and *trans* isomers in a reaction with phenyllithium in diethyl ether [3]. Tetraphenyltin precipitates in high yield and an ether solution of crotyllithium remains [eqn. (2)]. In one example of the application of this



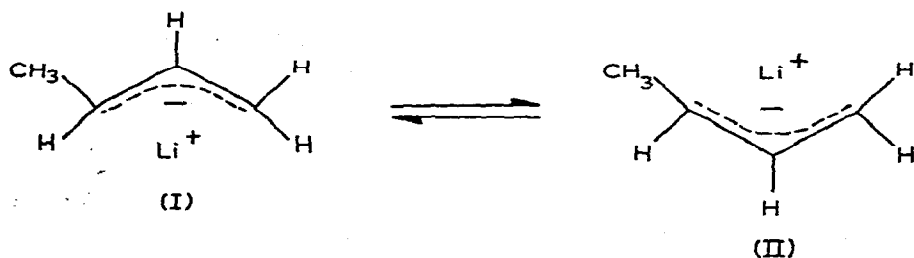
reaction, the reagent solution was treated with trimethylchlorosilane to give crotyltrimethylsilane in 80% yield [3]. Tetraphenyltin was isolated in 98% yield.

Solid crotyllithium also may be obtained by the transmetalation reaction. Treatment of tetracrotyltin with one molar equivalent of ethyllithium in benzene resulted in formation of a white precipitate whose solution in dimethyl ether at low temperature showed NMR signals due only to the solvent and to crotyllithium. *n*-Butyllithium could not be used in place of ethyllithium since the solid precipitate was found to contain both crotyl and butyl groups in about 1/1 ratio (via reaction with trimethylchlorosilane). A similar 1/1 solid

complex of type $n\text{-BuLi}\cdot\text{RLi}$ had been encountered in the attempted preparation of pure cyclopropyllithium by the transmetalation reaction occurring between tetracyclopropyltin and *n*-butyllithium in pentane [8].

A consideration of the stereochemical outcome of these reactions is of interest. The formation of *cis*- and *trans*-crotyltrimethylsilane in about 2/3 ratio in these reactions implied that the reactive intermediate, crotyllithium, provided a pathway by which the isomerization could occur, since both of the pure crotyltrimethylsilane isomers were configurationally stable under the reaction conditions, i.e., in the presence of ethereal *n*-butyllithium.

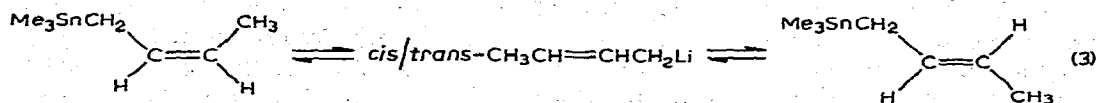
Solution spectroscopic studies of allylic lithium reagents* have provided important information concerning the constitution of allyllithium, crotyllithium and higher homologs, $\text{RCH}=\text{CHCH}_2\text{Li}$. Of most direct application to this study, the variable temperature proton NMR spectra of crotyllithium in dimethyl ether have been explained in terms of an ionic model: contact ion pairs, the anions of which have the crotyl form with *syn* and *anti* configurations of the methyl group [13].



A path for the *cis/trans* isomerization which must occur in our reactions could be provided by isomerization of the ionic species directly or, as we [2] and others [11] have suggested, by intervening covalent forms in which the α -methylallyllithium structure provides the means of destroying the *cis* and *trans* geometry of the species initially generated from *cis*- or *trans*-crotyltrimethyltin. In this connection, we note that it has been reported [14] that both crotyltriphenyltin and α -methylallyltriphenyltin in ether reacted with phenyllithium to give allylic lithium reagent solutions which had identical electronic spectra.

It is noted that (α -methylallyl)trimethylsilane was not among the products when our crotyllithium solutions were allowed to react with trimethylchlorosilane. In a later study of the constitution and reactivity of a higher homolog, neopentylallyllithium, in hydrocarbon [10] and in ether solvents [12], similar regioselectivity on reaction with trimethylchlorosilane was observed.

Since, as already mentioned, the transmetalation reactions occurring between organotin and organolithium compounds are equilibrium processes, the addition of a small amount of an organolithium reagent in ether to pure *cis*- or *trans*-crotyltrimethyltin should cause isomerization of the respective tin com-



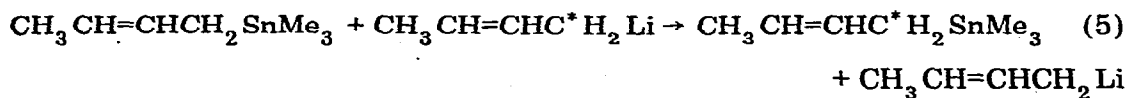
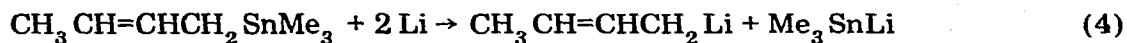
*See ref. [9 - 12] for the latest work in this area. These papers by Glaze and his coworkers, in addition to interesting experimental studies, present a good literature survey on the constitution of allylic lithium reagents in hydrocarbon and in ether solvents.

pound [eqn. (2)]. This was found to be the case. When about 10 mole % of *n*-butyllithium was added to pure *cis*- or *trans*-crotyltrimethyltin in diethyl ether with subsequent hydrolysis after 30 min, the recovered crotyltrimethyltin contained both the *cis* and *trans* isomers, in about 2/3 ratio in each instance. Similar results were obtained when 10 mole % of methylithium was used instead and the reaction mixture heated at reflux for 30 min prior to hydrolysis.

The observations that in these crotyltrimethyltin isomerizations the *trans/cis* ratio is 3/2 and that the reaction of crotyllithium with trimethylchlorosilane gives crotyltrimethylsilane with a *trans/cis* ratio of 3/2 as well suggest that the *anti/syn* [(I)/(II)] ratio of the crotyllithium isomers in solution also may be 3/2. It is noteworthy that the variable temperature NMR study of crotyllithium in dimethyl ether detected the presence of two species in 3/2 ratio [13]. Furthermore, in the case of neopentylallyllithium, NMR spectroscopy indicated that an *anti/syn* ratio of 3/1 was present in diethyl ether solution [11], and reaction of such a neopentylallyllithium solution with trimethylchlorosilane gave $\text{Me}_3\text{CCH}_2\text{CH}=\text{CHCH}_2\text{SiMe}_3$ with a *trans/cis* ratio of 2.7 [12]. It would seem that the reaction products with trimethylchlorosilane do indeed reflect the composition of $\text{RCH}=\text{CHCH}_2\text{Li}$ reagents in solution, if not exactly, then certainly as a good first approximation. The rates of coupling of (I) and (II) with trimethylchlorosilane must be quite similar, but this certainly is not expected to be the case with any other substrate.

Metallic lithium also was found to cause such isomerization of the pure crotyltrimethyltin isomers under appropriate experimental conditions. When an excess of *trans*-crotyltrimethyltin was treated with a dispersion of metallic lithium containing 2% sodium in diethyl ether medium, no isomerization occurred. However, after enough 1,2-dimethoxyethane (DME) had been added to give a solution of about 12 vol % DME and this mixture had been stirred at room temperature for 1 h, then isomerization did occur. This was determined by hydrolyzing an aliquot and analyzing the recovered crotyltrimethyltin by GLC; a 2/3 ratio of *cis* to *trans*-crotyltrimethyltin was found. This ratio was not changed by further exposure of this crotyltrimethyltin isomer mixture to metallic lithium. In contrast, the pure *cis* and *trans* isomers of crotyltrimethylsilane did not undergo such isomerization when treated with lithium in 1/1 diethyl ether/DME for 24 h.

These results suggest that the isomerization of the crotyltrimethyltin isomers occurred by a metal displacement mechanism, in which small amounts of crotyllithium are formed which then can equilibrate with the remaining crotyltrimethyltin [eqn. (4) and (5)].



Such metal displacement processes are well known in organotin chemistry (e.g., ref. [15] for an example involving propenyltin compounds and some indication concerning mechanism).

One may conclude from this study that crotyllithium may be generated by the transmetalation reaction in high yield and that this procedure has excel-

TABLE I
REACTIONS OF CROTYLTRIMETHYLTIN ISOMERS WITH ORGANOLITHIUM REAGENTS

CH ₃ CH=CHCH ₂ SnMe ₃ Isomer (mmol)	RLi (mmol)	Reaction conditions	Me ₃ SiCl added (mmol)	CH ₃ CH=CHCH ₂ SiMe ₃ (% yield)	Other products (% yield)
96% <i>trans</i> (25.6)	n-BuLi (25.4)	In Et ₂ O, 30 min at room temp.	25.4	93 (61% <i>trans</i> , 39% <i>cis</i>)	n-BuSnMe ₃ (45), Me ₄ Sn (n-Bu) ₂ SnMe ₂
99% <i>cis</i> (13.0)	n-BuLi (13.0)	Same	13.0	98 (61% <i>trans</i> , 39% <i>cis</i>)	n-BuSnMe ₃ (47), (n-Bu) ₂ SnMe ₂ , Me ₄ Sn
96% <i>trans</i> (15.3)	n-BuLi (15.4)	Same; subsequent hydrolysis with aq. NH ₄ Cl	53.5	66 (58% <i>trans</i> , 42% <i>cis</i>)	Recovered CH ₃ CH= CHCH ₂ SnMe ₃ (60), 57% <i>trans</i> , 43% <i>cis</i>
94% <i>trans</i> (26.1)	MeLi (52.5)	In Et ₂ O, 30 min at room temp.	48.0	98 (58% <i>trans</i> , 42% <i>cis</i>)	CH ₃ CH=CHCH ₂ SnMe ₃ (mixed isomers), Me ₄ Sn
94% <i>trans</i> (23.8)	MeLi (48)	In Et ₂ O, 30 min at reflux	48.0	92 (57% <i>trans</i> , 43% <i>cis</i>)	Not determined
90% <i>cis</i> (14.5)	MeLi (29)	In Et ₂ O, 30 min at reflux	28.0	Not determined	Not determined
94% <i>trans</i> (16.0)	MeLi (1.7)	In Et ₂ O, 30 min at reflux; subsequent hydrolysis with NaH ₂ PO ₄ /NaOH pH 7 buffer solution.		Recovered CH ₃ CH=CHCH ₂ SnMe ₃ (68), 56% <i>trans</i> , 44% <i>cis</i>	Recovered
90% <i>cis</i> (14.5)	MeLi (1.7)	Same		Recovered CH ₃ CH=CHCH ₂ SnMe ₃ (71), 56% <i>trans</i> , 44% <i>cis</i>	Recovered
Ph ₃ SnCH ₂ CH=CHCH ₃ mixed isomers (230)	PhLi (232)	In Et ₂ O (650 ml), 30 min at room temp.	230	80 (distillation yield) (60% <i>trans</i> , 40% <i>cis</i>)	Ph ₄ Sn (98) (precipitated during the transmetalation step, recovered by filtration)

lent synthetic utility. However, a limitation is provided by the nature of the system which does not allow the preparation of isomerically pure crotyl products.

A further detailed investigation of the synthetic utility of crotyllithium in organic and organometallic synthesis, as well as a comparison of its reactivity with that of the crotyl Grignard reagent, would be of interest, but such studies are beyond the scope of our present interests.

Experimental

General comments

All of the reactions were conducted in standard glass equipment with ground-glass joints under pre-purified nitrogen with rigorous exclusion of air until the solutions were hydrolyzed. The reagents and solvents were transferred and weighed under nitrogen in a glass syringe equipped with a small "Luer-Lok" stopcock.

Solutions of methyllithium in diethyl ether and n-butyllithium in n-hexane were purchased from Foote Mineral Company, and were standardized before use by the double titration method of Gilman using freshly distilled 1,2-dibromoethane.

The diethyl ether was anhydrous reagent grade from freshly opened containers which were fitted with no-air stoppers. Trimethylchlorosilane was obtained from the Dow Corning Corp. and distilled under nitrogen before use into a flask equipped with a no-air stoppered side-arm with a Teflon stopcock. The lithium dispersion in petroleum jelly (30% by weight of lithium containing 2% sodium) was used as purchased from Orgmet, Inc.

The preparation of crotyltrimethyltin and crotyltrimethylsilane and the separation and characterization of the pure *cis* and *trans* isomers are discussed in detail in ref. [3]. The crotyltrimethyltin was stored in foil-covered 5 ml no-air stoppered vials under nitrogen, and no isomerization occurred in samples stored in this manner for several weeks. The purity of the crotyltrimethyltin was checked by GLC prior to each experiment. The analyses of the starting materials and of the reaction products were done by GLC using a 9 ft. x 10 mm i.d. glass column filled with 15% by weight of General Electric XF-1150 Silicone Oil on Johns-Manville Chromosorb P, 80 - 100 mesh. Quantitative analysis of the reaction mixtures was carried out by the internal standard method.

IR spectra were recorded using a Perkin-Elmer Model 337 grating infrared spectrophotometer, proton magnetic resonance spectra with a Varian Associates A60 spectrometer.

Reaction of the crotyltrimethyltin isomers with organolithium reagents

The reaction of *trans*-crotyltrimethyltin with n-butyllithium is described in detail. The other reactions carried out are summarized in Table 1.

In a 100 ml three-necked flask equipped with a 15 ml pressure-equalized dropping funnel, reflux condenser, and magnetic stirring bar was placed *trans*-

crotyltrimethyltin (5.60 g, 25.6 mmol, containing 4% of the *cis* isomer) dissolved in 20 ml of anhydrous ethyl ether under nitrogen. The dropping funnel was charged with 16.5 ml of a 1.54 *N* n-butyllithium solution in hexane (25.4 mmol) which was added rapidly to the ether solution of *trans*-crotyltrimethyltin. A clear yellow solution formed which was stirred at room temperature for 30 min.

When trimethylchlorosilane (2.75 g, 25.4 mmol) was added dropwise to the stirred solution of crotyllithium, the yellow color was discharged, and a white solid formed.

The mixture was stirred an additional two hours at room temperature, and then hydrolyzed with saturated ammonium chloride solution*. The ether layer was separated, and dried over sodium sulfate before analysis on the XF-1150 column at 70° with a helium pressure of 10 psi using benzene as an internal standard. Pure samples of each component were collected by GLC and used to prepare mixtures for the calculation of the response factors: *trans*-crotyltrimethylsilane [3] (RF 1.09), *cis*-crotyltrimethylsilane [3] (RF 1.12), and butyltrimethyltin (RF 0.646).

Analysis of the reaction mixture using these values showed that a total of 23.8 mmole of crotyltrimethylsilane was formed (containing 61% *trans*, 39% *cis*), a yield of 93% based on crotyltrimethyltin. The yield of butyltrimethyltin was 11.4 mmol or 45% based on crotyltrimethyltin, while the remaining crotyltrimethyltin was only 0.5 mmol or about 2% of the original amount.

The original reaction mixture was also analyzed on an 8 ft. × 6 mm i.d. glass column filled with a mixture of 20% General Electric SE 30 Silicone Rubber Gum on Chromosorb P, 80 - 100 mesh, operated at 187° with a helium pressure of 15 psi. Under these conditions a higher boiling component was observed with a retention time of 8.7 min. An authentic sample of di-n-butyl-dimethyltin** added to the ether solution of reaction products had the same retention time and symmetrically enlarged the peak. The presence of some tetramethyltin was also observed when the mixture was analyzed using a 9 ft. × 10 mm i.d. glass column packed with 20% Dow Corning Silicone Oil No. 710 on Chromosorb P, 80 - 100 mesh, operated isothermally at 56° with 15 psi of helium. Under these conditions the retention time of the crotyltrimethylsilane isomers was over thirty minutes, while the resolution of the lower boiling components of the mixture was greatly increased. A component with a retention time of 12.4 min was identified as tetramethyltin by comparison of its retention time to an authentic sample (M & T Chemicals).

The reaction of n-butyllithium with tetramethyltin

A solution of tetramethyltin (3.05 g, 17.0 mmol, M & T Chemicals, Inc.) in 10 ml of anhydrous ether was treated with 26.0 ml of a 1.54 *N* solution of n-butyllithium (40.0 mmol) in hexane under nitrogen in a 50 ml three-necked flask equipped with a magnetic stirring bar and a condenser. The solution was stirred for 90 min at room temperature, and then hydrolyzed with water. The organic layer was separated and dried over magnesium sulfate and filtered.

*No isomerization occurred when *trans*-crotyltrimethylsilane in ether was shaken for several minutes with saturated ammonium chloride.

**Prepared by the reaction of dimethyltin dichloride (M & T Chemicals) with n-butyllithium in ether.

Analysis of the organic layer by GLC using the XF-1150 column at 72° with a helium pressure of 12 psi showed that in addition to the solvent and tetramethyltin, a higher boiling compound was formed. This product was identified as n-butyltrimethyltin by comparison of its retention time to an authentic sample. The yield of n-butyltrimethyltin (RF 0.65) was 9.80 mmol or 57% of the amount of tetramethyltin as determined by GLC analysis using benzene as an internal standard.

The preparation of tetracrotyltin

A solution of crotylmagnesium chloride in ether was prepared following the method of Young and co-workers [16]. In a dry 2 l three-necked flask equipped with a reflux condenser, mechanical stirrer, and 500 ml dropping funnel was placed 30.0 g (1.23 mol) of magnesium in 200 ml of diethyl ether under nitrogen. A single crystal of iodine was added, and the dropping funnel was charged with 100 g (1.11 mol) of crotyl chloride (Aldrich Chemical Co.). A small portion of the crotyl chloride was added to initiate the reaction. When the reaction became vigorous, the flask was immersed in an ice bath, and the remaining crotyl chloride was diluted with 300 ml of ether and added dropwise to the mixture. The reaction was stirred for an additional 2 h at 0°, and then warmed to room temperature.

A smooth suspension of stannic chloride (62.5 g, 0.25 mol, B & A reagent grade) (as the etherate) in 500 ml of ether was added in small portions to the reagent from the dropping funnel, and the resulting mixture was heated at reflux overnight. Most of the ether was distilled from the mixture under nitrogen, and the residue was hydrolyzed with saturated ammonium chloride solution. The pale yellow organic layer was decanted, and the solid residue was washed with several portions of ether which were combined with the organic layer.

The ether was removed with a rotary evaporator connected to a water aspirator through a dry-ice/acetone trap, and the liquid residue (72.4 g) was separated from the non-volatile material in a trap-to-trap distillation (130° to -196°/0.03 mm) to give 58.1 g of a pale yellow liquid. A very viscous brown liquid remained in the pot and was discarded.

The crude product was distilled through a 15 cm vacuum-jacketed Vigreux column to give a small amount of forerun and a major fraction of 40.6 g, b.p. 116 - 120°/1.7 mm, n_D^{25} 1.5360. This fraction was dissolved in an equal volume of pentane and the solution was treated with anhydrous ammonia to precipitate any remaining tin chloride. The solution was filtered to remove the small amount of solid that formed, and the pentane was evaporated at reduced pressure. The residue was redistilled through a short-path distillation head to give 31.4 g of tetracrotyltin, b.p. 111 - 113°/0.95 mm, n_D^{25} 1.5330.

An infrared spectrum of the neat liquid showed absorptions at 3030 (sh), 2995 (s), 2940 (sh), 2890 (s), 2860 (sh), 2840 (m), 2700 (w), 1690 (w), 1655 (w), 1640 (m), 1450 (m), 1440 (sh), 1420 (sh), 1390 (m), 1375 (sh), 1355 (m), 1310 (w), 1260 (w), 1162 (m), 1100 (m), 1072 (m), 1038 (m), 995 (m), 965 (s), 905 (m), 791 (m), 755 (sh), and 722 (s), cm^{-1} .

The NMR spectrum in carbon tetrachloride showed a complex overlapping pattern between 1.2 and 2.2 ppm (5 H) and a complex pattern of at least 12 lines between 4.9 and 5.9 ppm (2 H).

Preparation of solid organolithium reagents

The organolithium reagents were prepared and handled with rigorous exclusion of air and moisture. The dry solids were violently pyrophoric in air, although they could be stored under nitrogen for several days without apparent change.

The NMR samples were prepared by transferring the solid organolithium reagent into a tared Pyrex sample tube (6 mm o.d.) which was flushed with nitrogen from a long 15 ga. syringe needle before use. The sample tube was immersed in a dry-ice/acetone bath while a brisk current of nitrogen was passed into the open neck of the tube through a syringe needle. When dimethyl ether (The Matheson Co., Inc., N.J.) was used as a solvent, a second syringe needle connected to the ether container was positioned so that the dimethyl ether condensed onto the solid. The sample tube was sealed with a tight-fitting polyethylene cap, (NMR Specialities, Inc., New Kensington, Pa.) and warmed to room temperature. Solutions of crotyllithium prepared in dimethyl ether were lemon-yellow in color, and could be kept for several hours at room temperature without noticeable change in the NMR spectrum.

The reaction of tetracrotlytin with n-butyllithium

In a 25 ml pear-shaped flask under nitrogen tetracrotlytin (2.13 g, 6.30 mmol) was treated with 8.0 ml. of a 1.56 N solution of n-butyllithium (12.5 mmol) in hexane. A precipitate formed which was filtered, washed with dry pentane, and dried in a current of nitrogen to give a white, finely divided powder.

A portion of the solid (50.2 mg) was transferred into an NMR sample tube and dissolved in 300 μ l of dimethyl ether. The NMR spectrum of this sample showed a quartet at about δ 5.8 ppm similar to that observed in the NMR spectrum of crotyllithium prepared from methylolithium and crotyltrimethyltin [2], but the presence of a complex overlapping pattern at 1.0 to 1.5 ppm as well as a high field triplet at about -1.2 ppm (J 8 Hz) indicated that n-butyllithium was also present. Since n-butyllithium is ordinarily a liquid soluble in pentane [17], another sample of the solid was prepared following the above procedure, but this time the solid precipitate was washed repeatedly with pentane (ten 5 ml portions) before drying. However, the NMR spectrum of this sample in dimethyl ether showed resonances due to both crotyllithium and n-butyllithium.

The original sample of the solid was dissolved in 10 ml of anhydrous diethyl ether, and the resulting yellow solution was transferred in a syringe to a 50 ml three-necked flask equipped with a condenser, dropping funnel, and magnetic stirring bar under nitrogen. When an excess of trimethylchlorosilane (2.39 g, 22 mmol) was added dropwise to the solution, the yellow color was

discharged and a white solid formed. The reaction mixture was heated to reflux for 1 h, and then hydrolyzed with saturated ammonium chloride solution.

The ether solution was separated and analyzed by GLC on the XF-1150 preparative column at 58° with a helium pressure of 12 psi. The chromatogram showed that *n*-butyltrimethylsilane, *trans*-crotyltrimethylsilane, and *cis*-crotyltrimethylsilane had been formed in the reaction of trimethylchlorosilane with the ethereal solution of the organolithium reagent. The products were identified by comparison of their infrared spectra with those of known samples. The solution was analyzed quantitatively using trichloroethylene as an internal standard. The total yield of *n*-butyltrimethylsilane (RF 0.811) was 2.38 mmol, and the combined yield of *cis*- and *trans*-crotyltrimethylsilane [RF 0.842 (*cis*), 0.826 (*trans*)] was 2.62 mmol. The molar ratio of *n*-butyltrimethylsilane to crotyltrimethylsilane was 0.9, while the latter contained 44% of the *cis* and 56% of the *trans* isomer.

The reaction of ethyllithium with tetracrotyltin

When tetracrotyltin (1.92 g, 5.65 mmole) was treated with recrystallized, lithium halide-free ethyllithium [18] in benzene (16.0 ml of a 0.734 *N* solution, 11.7 mmol) under nitrogen, a pale yellow solid formed which was filtered, washed with dry pentane, and dried in a current of nitrogen. An NMR spectrum of the solid in dimethyl ether showed that crotyllithium was present, but a triplet near 1.0 ppm and a quartet at near -1.2 ppm (*J* 8 Hz) indicated that some ethyllithium was still present.

Treatment of tetracrotyltin (1.88 g, 5.55 mmole) with one equivalent of ethyllithium in benzene (7.0 ml of a 0.734 *N* solution, 5.14 mmole) following the same procedure gave pure crotyllithium as a white solid which was filtered, washed with benzene, and dried under nitrogen. A portion of the solid was dissolved in dimethyl ether (39.7 mg in 250 μ l) in an NMR sample tube to give a clear lemon-yellow solution. The NMR spectrum of this sample showed only the resonances due to crotyllithium and the solvent, and no resonances due to ethyllithium were observed.

Since no internal reference was present, the resonances were arbitrarily referred to the center of the high field doublet (*J* 10.5 Hz) of crotyllithium (the α -CH₂ resonance). The methyl resonance appeared as a doublet (*J* 6 Hz) at -23 Hz, and the four line pattern due to the β -CH appeared at -303 Hz. The γ -CH resonance was obscured by the strong solvent resonance at -126 Hz, and four peaks symmetrically positioned around this resonance (-77, -101, -151, and -171 Hz) were shown to be due to spinning side bands in the solvent. Two additional peaks at -56 and -196 Hz were identified as ¹³C proton satellite resonances of the solvent.

The reaction of trans-crotyltrimethyltin with metallic lithium

In a 50 ml three-necked flask equipped with a reflux condenser with nitrogen inlet tube and a magnetic stirring bar was placed *trans*-crotyltrimethyltin (2.59 g, 8.56 mmol, containing ca. 6% of the *cis* isomer) in 10.0 ml of

anhydrous ether, and 58.7 mg of a lithium dispersion* (ca. 2.5 mmol of lithium) was added to the solution. About 0.1 ml of a 5% solution of benzophenone in ether was added to the reaction mixture, and a pale blue color developed.

The mixture was stirred under nitrogen at room temperature for 19 h. At the end of this period a 0.25 ml sample of the blue solution was withdrawn in a syringe and hydrolyzed by injecting the sample into 0.5 ml of water contained in a small vial. The ether solution was decanted and analyzed by GLC using the XF-1150 column at 75° with a helium pressure of 15 psi and no change in the ratio of *cis*- to *trans*-crotyltrimethyltin was observed.

1,2-Dimethoxyethane (DME) was twice distilled from potassium, and 2.0 ml of the DME was added to the mixture along with an additional 0.10 ml of the benzophenone solution. The resulting blue solution slowly developed a purple color which became dark red after 1 h.

At the end of this period, a 0.25 ml sample of the solution was withdrawn, hydrolyzed, and analyzed on the XF-1150 column, and the ratio of *trans/cis*-crotyltrimethyltin was 60/40. Additional samples were taken at 30 min intervals, but the isomer ratio remained unchanged at the end of 3 h.

The attempted reaction of cis- and trans-crotyltrimethylsilane with metallic lithium

A solution of *trans*-crotyltrimethylsilane (1.28 g, 10.0 mmol, containing 6% of the *cis*-isomer) in a mixture of 5.0 ml each of DME and ethyl ether was treated with 55.6 mg of the lithium dispersion (ca. 2.4 mmol lithium) and 0.15 ml of the benzophenone solution for 24 h following the method described in the previous experiment. At the end of this period the ratio of *trans/cis*-crotyltrimethylsilane remained 96/4.

Similar treatment of *cis*-crotyltrimethylsilane (0.82 g, 6.4 mmol, containing 2% of the *trans*-isomer) with 41.4 mg of the lithium dispersion (ca. 2.0 mmol lithium) in a mixture of 4.0 ml each of ether and DME produced no change in the isomer ratio at the end of 24 h.

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*The dispersion contained 30% by weight of lithium (containing 2% sodium) in a petroleum jelly base (Orgmet, Inc.) The sample was weighed on a small piece of Teflon sheet which was added to the solution.

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