The Lithium Metal Induced Isomerization of Propenyl Derivatives of Tin, Silicon, and Germanium[1]

Dietmar Seyferth,[2a] Reiichi Suzuki,[2b] and Lawrence G. Vaughan[2c]

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received July 28, 1965*

Abstract: A study of the action of metallic lithium on tetra-*cis*- and tetra-*trans*-propenyltin in ether showed that isomerization of propenyl groups attached to tin occurs in addition to the expected metal displacement reaction (eq. 2). The action of lithium on the isomeric propenyltrimethyl compounds of carbon, silicon, germanium, and tin also was investigated. No isomerization occurred in the case of the carbon compounds. The silicon and the germanium derivatives were not isomerized in diethyl ether solution but in tetrahydrofuran were converted to the pure *trans* isomer and to a mixture of 92% *trans* and 8% *cis* isomers, respectively. *cis*- and *trans*-propenyltrimethyltin were isomerized in ether solution to a mixture of 79% *trans* and 21% *cis* isomer; in tetrahydrofuran total cleavage of the propenyl group (giving propenyllithium and trimethyltinlithium) and partial cleavage of methyl groups (giving methyllithium) were observed. A mechanism involving radical-anion intermediates, $[(CH_3)_3M{-}CH{=}CHCH_3]^{\dot{-}}$, which are stabilized by C(2p)→metal(nd) π-bonding is suggested for the observed isomerizations. A mechanism for the alkali metal displacement reaction involving electron transfer from the alkali metal to the metal alkyl followed by migration of an organic group to the reagent metal is discussed: $\cdot M + R{-}M' \rightarrow M^+[R{-}M']^{\dot{-}} \rightarrow R{-}M + \cdot M'$.

In a previous study[3] we had determined that the transmetalation reaction occurring between propenyltin compounds and organolithium reagents proceeds with retention of the geometric configuration of the propenyl group transferred from tin to lithium. It seemed of interest to investigate in similar fashion the stereochemistry of the metal displacement reaction, a reaction which finds preparative application in organolithium chemistry.[4] In general, metallic lithium will displace a less electropositive metal from its wholly or partially organic compounds. This reaction is of practical advantage when M in eq. 1 is mercury, lead, or tin. Pertinent to this study is the previously reported preparation of vinyllithium from tetravinyllead (in 90% yield) and from tetravinyltin (in 55% yield) using this procedure.[5] In these reactions it is customary to use a trace of benzophenone as a catalyst.

$$R_nM + nLi \longrightarrow nRLi + M \qquad (1)$$

A complex situation was encountered when the lithium metal displacement reaction was carried out with tetra-*cis*- and tetra-*trans*-propenyltin with benzophenone present in catalytic amounts. (The lithium wire used contained 1.1% sodium.) The reaction scheme outlined in Chart I was used in our study of the stereochemistry of these reactions. Reaction of an excess of lithium with tetra-*trans*-propenyltin (benzophenone catalyst) followed by characterization of the lithium reagent formed with trimethylchlorosilane (reaction 3, a reaction known to occur with retention of configuration of the propenyl group[3]) gave a 16% yield of propenyltrimethylsilane. Gas chromatographic and infrared spectroscopic analyses showed this to be the pure *trans* isomer. A 54% recovery of tetrapropenyltin was obtained. However, it was obvious from its infrared spectrum and refractive index that partial isomerization of *trans*-propenyl groups to *cis*-propenyl groups had taken place. To determine quantitatively the extent of this isomerization (not possible by instrumental methods directly), the recovered tetrapropenyltin was cleaved with an excess of *n*-butyllithium, and the propenyllithium thus formed (stereospecifically[3]) was characterized using trimethylchlorosilane. The propenyltrimethylsilane obtained consisted of 78% *trans* and 22% *cis* isomer. A separate exploratory experiment carried out in the same way showed that tetra-*cis*-propenyltin also was isomerized under these conditions. The tetrapropenyltin recovered was shown to contain 79% *cis*- and 21% *trans*-propenyl groups.

Chart I

$$\underset{\substack{\text{(pure } cis \text{ or}\\ \text{pure } trans)}}{(CH_3CH{=}CH)_4Sn} + 4Li \xrightarrow{Et_2O} 4CH_3CH{=}CHLi + Sn \qquad (2)$$

$$CH_3CH{=}CHLi + (CH_3)_3SiCl \longrightarrow (CH_3)_3SiCH{=}CHCH_3 + LiCl \qquad (3)$$

$$\begin{array}{ll} (CH_3CH{=}CH)_4Sn + 4n\text{-}C_4H_9Li \longrightarrow & \\ \text{(recovered)} \qquad 4CH_3CH{=}CHLi + (n\text{-}C_4H_9)_4Sn & (4) \\ \qquad\qquad \Big\downarrow {\scriptstyle (CH_3)_3SiCl} & \\ \qquad\qquad (CH_3)_3SiCH{=}CHCH_3 & \end{array}$$

The agent responsible for the observed isomerization of the propenyltin compounds could have been either metallic lithium or the ketyl formed by the reaction of lithium with benzophenone. Further experiments showed that the ketyl did not cause isomerization of tetrapropenyltin isomers, but that lithium did. Thus a similar experiment with tetra-*trans*-propenyltin using lithium wire with no benzophenone present gave propenyllithium (19%, determined as propenyltrimethylsilane) which was the pure *trans* isomer, and the recovered tetra-*trans*-propenyltin contained both *trans*- (86%) and *cis*- (14%) propenyl groups. With tetra-*cis*-propenyltin the same experimental procedure yielded

---

[1] Part XXII of the series "Vinyl Derivatives of Metals"; part XXI: L. G. Vaughan and D. Seyferth, *J. Organometal. Chem.*, in press.

[2] (a) Alfred P. Sloan Foundation Fellow, 1962–1966; (b) Postdoctoral Research Fellow, 1963–1965; on leave from the Nitto Chemical Industrial Company Ltd., Osaka, Japan; (c) National Science Foundation Cooperative Graduate Fellow, 1961–1963; National Science Foundation Summer Graduate Fellow, 1963.

[3] D. Seyferth and L. G. Vaughan, *J. Am. Chem. Soc.*, **86**, 883 (1964).

[4] R. G. Jones and H. Gilman, *Chem. Rev.*, 54, 841 (1954).

[5] E. C. Juenge and D. Seyferth, *J. Org. Chem.*, **26**, 563 (1961).

propenyllithium (21%), which was 47% *cis* and 53% *trans* isomer and recovered (71%) tetrapropenyltin which contained 58% *cis*- and 42% *trans*-propenyl groups.

It would be more informative to be able to study the isomerization of propenyltin compounds in the absence of the complicating metal displacement which produces propenyllithium. Propenyltrimethyltin proved to be a compound which did not undergo metal displacement when treated with metallic lithium in diethyl ether medium. In this solvent pure lithium, lithium wire containing 1.1% sodium, and lithium dispersion containing 2% sodium caused a relatively rapid isomerization of both *cis*- and *trans*-propenyltrimethyltin to an equilibrium mixture composed of 79% of the *trans* isomer and 21% of the *cis* isomer. Isomerization of the *cis* isomer appeared to be somewhat more rapid. In tetrahydrofuran, on the other hand, complete destruction of the propenyltrimethyltin resulted on treatment with lithium at room temperature. The reaction mixture was in this case quenched with triethylchlorosilane and hydrolyzed. Among the products identified (in the case of *cis*-propenyltrimethyltin) were *cis*- (38% yield) and *trans*-propenyltriethylsilane (23% yield), triethylmethylsilane (18%), and triethylsilyltrimethyltin (45%), in addition to higher boiling products which were not isolated in the pure state. These products indicate that the displacement reaction of tetraorganotin compounds occurs stepwise. In the present case the first step involves formation of propenyllithium and trimethyltinlithium

$$(CH_3)_3SnCH{=}CHCH_3 + 2Li \longrightarrow (CH_3)_3SnLi + CH_3CH{=}CHLi \qquad (5)$$

Methyllithium could be formed either by further attack by lithium on trimethyltinlithium or by partial methyl group displacement from propenyltrimethyltin

$$(CH_3)_3SnLi + 2Li \longrightarrow (CH_3)_2SnLi_2 + CH_3Li \qquad (6)$$

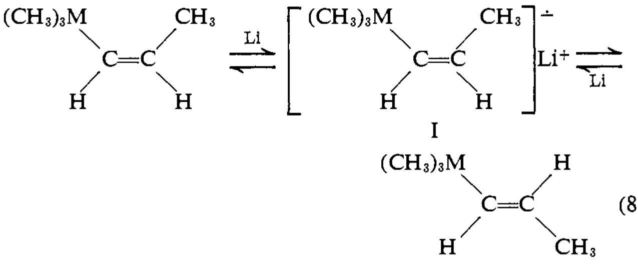
or

$$(CH_3)_3SnCH{=}CHCH_3 + 2Li \longrightarrow (CH_3)_2(CH_3CH{=}CH)SnLi + CH_3Li \qquad (7)$$

This investigation was extended to include a study of the action of metallic lithium on the propenyltrimethyl derivatives of carbon, silicon, and germanium as well. Neither *cis*- nor *trans*-4,4-dimethyl-2-pentene (propenyltrimethylmethane) was isomerized by the action of lithium dispersion containing 2% sodium in tetrahydrofuran, nor were any higher boiling products formed. In diethyl ether neither pure lithium nor sodium-containing lithium caused any isomerization of the pure *cis* or *trans* isomers of propenyltrimethylsilane or propenyltrimethylgermane during a 28-day contact time. In tetrahydrofuran, however, lithium dispersion caused isomerization of *cis*-propenyltrimethylsilane to the pure *trans* isomer within 6 hr. The *trans* isomer was itself unaffected with respect to isomerization by lithium in this solvent. In both cases, after hydrolysis, the recovery of propenyltrimethylsilane was only 45–50%, and other products were present as well. *n*-Propyltrimethylsilane was formed in low yield. Three high-boiling organosilicon compounds were isolated but were not identified. It was established that they were not reductive dimerization products which might have been expected, either 1,4-bis(trimethylsilyl)-2,3-dimethylbutane or 3,4-bis(trimethylsilyl)hexane.

In tetrahydrofuran both propenyltrimethylgermane isomers were converted by the action of lithium dispersion to an equilibrium mixture containing 92% *trans*-propenyltrimethylgermane and 8% of the *cis* isomer. Here, however, recovery of propenyltrimethylgermane was high (80–86%), and neither *n*-propyltrimethylgermane nor high-boiling organogermanium compounds were found.

All of these observations are consistent with an isomerization mechanism involving a radical-anion intermediate (I, eq. 8) in which an electron has been donated from a lithium atom into a π-antibonding orbital of the olefin. The resulting weakening of the C_{2p}–C_{2p} π overlap would permit rotation about the C–C axis and isomerization could occur. Alkali metal induced isomerization of olefins is rare; the isomerization of *cis*- to *trans*-stilbene by lithium in tetrahydrofuran and of *cis,cis*- and *cis,trans*-1,2,3,4-tetraphenylbutadiene to the *trans,trans* isomer was reported recently by Doran and Waack.[6] The observed isomerization of the propenyl compounds of silicon, germanium, and tin (but not of carbon) by the action of metallic lithium suggests that the radical anions formed in these cases are stabilized in some manner. The formation of the radical anion from triphenylvinylsilane (*via* lithium in tetrahydrofuran at −75°) and the reductive dimerization of the latter species (giving $(C_6H_5)_3SiCH(Li)CH_2CH_2CH(Li)Si(C_6H_5)_3$) have been described recently,[7] and stabilization of the radical anion by Si(dπ)–C(pπ) interaction was discussed. The uninegative radical anions derived from 4-trimethylsilyl- and 4-trimethylgermylbiphenylene have been studied by Curtis and Allred using electron spin resonance spectroscopy and oscillopolarographic analysis.[8] The e.s.r. spectra were interpreted and discussed in terms of a simple molecular orbital model involving d orbitals of the group-IV substituent; and for the C–Si and C–Ge bonds, π-bond orders of 0.18 and 0.13, respectively, were calculated. Thus it seems reasonable to suggest that the decisive factor which permits isomerization of the propenyl compounds of silicon, germanium, and tin, but not of carbon, is the stabilization through dπ–pπ bonding of the radical anions of the former. Such stabilization is, of course, not possible for the radical anion derived from propenyltrimethylmethane, carbon not having available d orbitals of suitably low energy, and thus electron transfer may not be energetically favorable in this particular system.



(8)

---

[6] M. A. Doran and R. Waack, *J. Organometal. Chem.*, 3, 94 (1965).

[7] J. J. Eisch and R. J. Beuhler, *J. Org. Chem.*, **28**, 2876 (1963).

[8] M. D. Curtis and A. L. Allred, *J. Am. Chem. Soc.*, **87**, 2554 (1965).

The fact that reduction and reductive dimerization products were obtained in the present study not at all or only in low yield suggests that only a small fraction of the olefin was converted to its radical anion. However, this is sufficient for complete isomerization to occur with time through electron-transfer reactions between radical anion and olefin. A concise discussion of the mechanism for geometric isomerization of olefins *via* their radical anions is given in the paper of Doran and Waack.[6]

The decreasing *trans/cis* ratio as the metal in $(CH_3)_3MCH{=}CHCH_3$ was varied from Si to Ge to Sn is believed to reflect a steric factor, since steric interactions between the three methyl substituents on the group-IV atom with a *cis*-methyl group would be expected to decrease with increasing size of M.

This isomerization study of propenyltin and -silicon compounds now permits us to understand better reactions 2 and 3 of Chart I. The observed results of the metal displacement reaction study are compatible with the following picture. Metallic lithium causes isomerization of tetra-*trans*- and tetra-*cis*-propenyltin in diethyl ether solution. The lithium displacement of propenyl groups from tin, however, most likely occurs without geometrical isomerization of the propenyl groups undergoing displacement. The observed isomer distribution of the propenyllithium produced in this displacement provides support for this belief. With tetra-*trans*-propenyltin, *only trans*-propenyllithium was formed, although, at the time the mixture was quenched with trimethylchlorosilane, isomerization had already resulted in a tetrapropenyltin isomer mixture containing up to 22% of the *cis* structure. Similarly, in the lithium cleavage of tetra-*cis*-propenyltin the propenyllithium produced was somewhat richer in the *trans* structure than was the isomerized, unreacted tetrapropenyltin. This preference for displacement of *trans*-propenyl groups from tin by lithium recalls the favored formation of *trans*-propenyllithium (over the *cis* compound) in the metal exchange (transmetalation) reaction.[3] The isomeric composition of the propenyltrimethylsilane formed in the trimethylchlorosilane quench (eq. 3) accurately reflects the isomeric composition of the propenyllithium produced in the displacement reaction. We have shown already that neither propenyltrimethylsilane isomer is affected by lithium *in diethyl ether medium.* The configurational stability of *cis*- and *trans*-propenyllithium in ether has been established,[3] and we have now shown as well that the geometrical configuration of both propenyllithium isomers in ether is unaffected by the presence of excess lithium dispersion containing 2% sodium.

We suggest a mechanism for the metal displacement reaction involving electron transfer from lithium to the propenyltin compound, followed by migration of the organic group from tin to lithium. In the case of the lithium cleavage of propenyltrimethyltin, this would lead to the following scheme.

$$(CH_3)_3SnCH{=}CHCH_3 + Li\cdot \longrightarrow Li^+[(CH_3)_3(CH_3CH{=}CH)Sn]^{\cdot-}$$

$$Li^+[(CH_3)_3(CH_3CH{=}CH)Sn]^{\cdot-} \longrightarrow LiCH{=}CHCH_3 + (CH_3)_3Sn\cdot$$

$$(CH_3)_3Sn\cdot + Li\cdot \longrightarrow (CH_3)_3SnLi$$

Such a mechanism might be expected to occur with retention of configuration *in the second step* in view of our previous results on the propenyltin–organolithium exchange reaction,[3] and it would be expected that the most stable anion would be lost from the initially formed radical-anion complex. In the case of a tin compound containing both *cis*- and *trans*-propenyl groups (owing to isomerization occurring during the first step above), one would expect favored formation of *trans*-propenyllithium in line with the results of our transmetalation reaction study,[3] and this was found to occur.

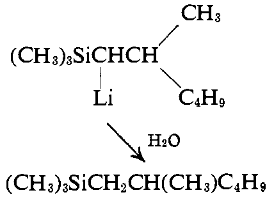
The fact that such metal displacement was found with propenyltin compounds and not with the propenyl derivatives of silicon and germanium most likely is a consequence of the lower Sn–C bond energy when compared to equivalent Si–C and Ge–C bond energies. The significant solvent effects observed in this study are interesting but not well understood. Solvation of the radical anion and its counterion and of the incipient propenyl carbanion should be factors of some importance, but in the absence of further data, a discussion of this point at this time would not be fruitful.

The metal displacement reaction is not a practical route to the preparation of pure *cis*- or *trans*-propenyllithium owing to facile isomerization induced by metallic lithium of propenyl groups attached to a heavy metal.[9] This study has, however, provided results which suggest a possible mechanism for the metal displacement reaction.

$$\cdot M^I + R{-}M \longrightarrow [M^I]^+[R{-}M]^{\cdot-} \longrightarrow R{-}M^I + M\cdot$$

The action of *n*-butyllithium in tetrahydrofuran-hexane medium on propenyltrimethylsilane also was studied. We were prompted to do so by the report of Waack and Doran[10] that organolithium reagents caused isomerization of 1,2,3,4-tetraphenylbutadiene in tetrahydrofuran solution. However, when a molar equivalent of *n*-butyllithium was added to propenyltrimethylsilane (32% *cis*, 68% *trans*), the recovered (50%) silane after a 20-hr. contact time followed by hydrolysis had unchanged isomeric composition. 2-Methylhexyltrimethylsilane also was isolated in about 30% yield; thus *n*-butyllithium addition to the olefinic double bond had occurred.

$$(CH_3)_3SiCH{=}CHCH_3 + n\text{-}C_4H_9Li \longrightarrow$$



$$(CH_3)_3SiCH(Li)CH(CH_3)C_4H_9 \xrightarrow{H_2O} (CH_3)_3SiCH_2CH(CH_3)C_4H_9$$

Similar β addition of organolithium reagents to vinylsilanes[11] and vinyltriphenylgermane[12] is known from previous work.

Experimental Section

General Comments. All reactions involving metallic lithium or organolithium reagents were carried out under a dry argon or prepurified nitrogen atmosphere. Ether solvents were distilled from lithium aluminum hydride or calcium hydride before use. The gas chromatographic techniques applicable to the analysis of the

---

[9] Propenylmercury compounds react similarly with metallic lithium: D. Seyferth and L. G. Vaughan, *J. Organometal. Chem.*, in press.

[10] R. Waack and M. A. Doran, *ibid.*, 3, 92 (1965).

[11] L. F. Cason and H. G. Brooks, *J. Am. Chem. Soc.*, 74, 4582 (1952); *J. Org. Chem.*, 19, 1278 (1954).

[12] D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.*, 84, 361 (1962).

Table I. Lithium-Induced Isomerization of *cis*- and *trans*-Propenyltrimethyltin in Diethyl Ether Solution[a]

Compound	Reaction time, hr.	Lithium wire		Lithium wire (1.1% Na)		Lithium dispersion (2% Na)	
		% *cis*	% *trans*	% *cis*	% *trans*	% *cis*	% *trans*
cis-CH$_3$CH=CHSn(CH$_3$)$_3$	0	100	0	98	2	100	0
	1	...	...	95	5	84	16
	2	95	5	69	31	62	38
	3	70	30	...	...	...	...
	4	...	...	55	45	40	60
	6	...	...	23	77	22	78
	6.5	30	70	...	...	...	...
	7.5	22	78	...	...	...	...
	8.5	21	79	...	...	...	...
	9	...	...	22	78	22	78
	24	21	79	22	78	22	78
		(81% recovery by distillation)		(78% recovery by distillation)		(83% recovery by distillation)	
trans-CH$_3$CH=CHSn(CH$_3$)$_3$	0	0	100	3	97	0	100
	1	...	...	4	96	1	99
	3	3	97	5	95	5	95
	6	...	...	16	84	16	84
	6.5	12	88	...	...	...	...
	8.5	20	80	...	...	...	...
	9	...	...	21	79	21	79
	12	21	79	22	78	22	78
	24	21	79	22	78	22	78
		(86% recovery by distillation)		(88% recovery by distillation)		(88% recovery by distillation)	

[a] G.l.c. analysis of isomers was effected using 20% G.E. XF-1150 cyanoethylsilicone fluid on Chromosorb P at 72°.

cis and *trans* isomers of the propenyltrimethyl compounds of silicon, germanium, and tin have been described in a previous paper of this series.[13] The propenyl compounds of these elements used in this study were prepared by procedures outlined in the latter paper.[13] (For more informative n.m.r. data on tetra-*trans*-propenyltin and *trans*-propenyltrimethylgermane, see part XXI).[1] The *cis*- and *trans*-4,4-dimethyl-2-pentene were purchased from Chemical Samples, Inc., Columbus, Ohio. G.l.c. analysis (silver nitrate column) attested to their isomeric purity. The lithium samples used in this work were purchased from the Lithium Corporation of America. Analyses were performed by Dr. S. M. Nagy (MIT Microchemical Laboratory) and by the Galbraith Laboratories, Knoxville, Tenn.

Reaction of Lithium Metal with Tetra-*trans*-propenyltin. In a 100-ml. Morton flask equipped with a high-speed stirrer, reflux condenser, and addition funnel, and protected by an argon atmosphere, was placed 2.60 g. (0.371 g.-atom) of sliced lithium wire (1.1% sodium content) and 30 ml. of diethyl ether. To the flask then was added 30 mg. of benzophenone and 8.65 g. (30.5 mmoles) of tetra-*trans*-propenyltin. Stirring was begun, and after 15 min. the solution had developed a blue color. After 30 min. the mixture was black, and the lithium surface had become somewhat shiny. Stirring was continued for a total of 4 hr. at room temperature, after which time 7.0 g. (61.5 mmoles) of trimethylchlorosilane (Dow Corning Corp.) was added. The resulting mixture was stirred at room temperature overnight. It then was filtered to remove excess lithium and precipitated lithium chloride. The filtrate was fractionally distilled to give 2.1 g. (16% yield) of propenyltrimethylsilane, b.p. 87–89°. Gas chromatographic analysis (silver nitrate column,[13] at 50°, 14 p.s.i. helium) revealed the product to be the pure *trans* isomer. Further fractional distillation produced 4.65 g. (54% recovery) of tetrapropenyltin, b.p. 60–61° (0.15 mm.), $n^{25}\mathrm{D}$ 1.5091. To determine the isomer ratio of propenyl groups in the recovered product, 4.15 g. (14.6 mmoles) was treated with 50.0 ml. of 1.5 *N* *n*-butyllithium (75 mmoles) in ether. The propenyllithium formed was quenched with 8.55 g. (79 mmoles) of trimethylchlorosilane. After filtration, fractional distillation of the ether solution furnished 4.4 g. (55% yield) of propenyltrimethylsilane. G.l.c. analysis revealed the isomer ratio to be 22% *cis* and 78% *trans*.

A similar experiment was carried out using 0.371 g.-atom of lithium wire (1.1% Na) and 29.6 mmoles of tetra-*trans*-propenyltin during 4 hr. in ether in the absence of benzophenone. The same work-up procedure after the trimethylchlorosilane quench gave 2.5 g. (19%) of propenyltrimethylsilane, which g.l.c. analysis showed to be the pure *trans* isomer, and 5.7 g. (68% recovery) of tetrapropenyltin. The latter (5.3-g. sample) was treated with 80 mmoles of *n*-butyllithium in ether, and the reaction mixture was quenched with trimethylchlorosilane. Propenyltrimethylsilane, 5.5 g. (65%), 86% *trans* and 14% *cis* by g.l.c., was obtained by this procedure.

Reaction of Lithium Metal with Tetra-*cis*-propenyltin. Tetra-*cis*-propenyltin, 7.05 g., 25 mmoles, was added to 2.07 g. (0.3 g.-atom) of lithium wire (1.1% Na) in 25 ml. of ether (no benzophenone present). After 30 min., the mixture had turned black; it was stirred for a total of 4 hr. at room temperature and was quenched with 75 mmoles of trimethylchlorosilane. The resulting mixture was stirred overnight. The solution was filtered and the ether removed by fractional distillation. The higher-boiling volatiles were separated by a high-vacuum trap-to-trap distillation and redistilled to give 2.4 g. (21%) of propenyltrimethylsilane (47% *cis*, 53% *trans*) and 5.0 g. (71% recovery) of tetrapropenyltin, b.p. 58–60° (0.25 mm.). Treatment of the latter (4.0-g. sample) with 75 mmoles of *n*-butyllithium in ether, followed by addition of 80 mmoles of trimethylchlorosilane, gave propenyltrimethylsilane (58% *cis*, 42% *trans*) in 61% yield.

Investigation of the Action of Lithium Benzophenone Ketyl on the Tetrapropenyltin Isomers. In a 200-ml. three-necked flask equipped with magnetic stirrer, reflux condenser, and addition funnel was placed 0.88 mmole of benzophenone and 0.89 mg.-atom of lithium (1.1 % Na) and 15 ml. of ether. The lithium was consumed within 1.5 hr., and a blue solution resulted. Tetra-*cis*-propenyltin (5.0 g., 17.7 mmoles) was added and the mixture stirred at room temperature for 5 hr. *n*-Butyllithium (71 mmoles) in ether then was added with a resulting color change to dark red. After the mixture had been stirred for 4 hr. at room temperature, 71 mmoles of trimethylchlorosilane was added. The reaction mixture was stirred overnight and worked up in the usual way to give propenyltrimethylsilane (98% *cis*) in 63% yield and tetra-*n*-butyltin, b.p. 94–96° (0.4 mm.), in 69% yield.

A similar experiment with tetra-*trans*-propenyltin was carried out. No isomerization of propenyl groups was observed.

The Action of Lithium on the *cis* and *trans* Isomers of the Propenyltrimethyl Derivatives of Carbon, Silicon, Germanium, and Tin. Isomerizations in diethyl ether using lithium wire pieces were carried out in a 200-ml. Morton flask equipped with a high-speed stirrer and a side arm with a no-air rubber stopper under an inert atmosphere. In the flask was placed an excess of lithium (0.15 g.-atom for 30 mmoles of propenyl compound; 0.2 g.-atom for 40 mmoles) in 25–50 ml. of diethyl ether. The propenyl compound was added and the mixture stirred for the specified time. Samples (250 μl.) were withdrawn periodically with a syringe, hydrolyzed with 1 ml. of distilled water, and then analyzed for isomeric com-

---

(13) D. Seyferth and L. G. Vaughan, *J. Organometal. Chem.*, **1**, 138 (1963).

position by g.l.c. The experimental data for the propenyltrimethyltin isomers are given in Table I. The pure *cis-* and *trans*-propenyltrimethyl derivatives of silicon and germanium were unchanged even after 28 days of this treatment *in diethyl ether*. This was the case also when lithium dispersion containing 2% sodium was used.

At the end of the reaction the mixture was hydrolyzed carefully with 100 ml. of saturated ammonium chloride solution. The organic phase was fractionally distilled and the yield of recovered propenyl compound was determined by means of this distillation. Its isomeric composition was determined by g.l.c.

Isomerizations using lithium dispersion containing 2% sodium[14] were carried out in 200-ml., three-necked flasks equipped with a magnetic stirrer, reflux condenser, and a side arm with a no-air rubber stopper. The general procedure described above was followed. The results obtained with the tin compounds are given in Table I, with the propenyltrimethyl compounds of germanium and silicon in Table II. Pure *cis-* and *trans*-4,4-dimethyl-2-pentene were not affected by the action of lithium dispersion (containing 2% sodium) in tetrahydrofuran during a 120-hr. contact time; neither isomerization nor formation of higher boiling compounds was observed.

Table II. Isomerization of the *cis* and *trans* Isomers of Propenyltrimethylsilane and -germane by Means of Lithium Dispersion (Containing 2% Sodium) in Tetrahydrofuran[a]

Compound	Reaction time, hr.	% *cis*	% *trans*
cis-$CH_3CH{=}CHSi(CH_3)_3$	0	100	0
	2	35	65
	4	9	91
	6	0	100
	72	0	100
		(41.5% recovery by distillation)	
trans-$CH_3CH{=}CHSi(CH_3)_3$	0	0	100
	2	0	100
	6	0	100
	72	0	100
		(46% recovery by distillation)	
cis-$CH_3CH{=}CHGe(CH_3)_3$	0	99	1
	2	94	6
	4	89	11
	6	31	69
	9	26	74
	11	14	86
	27	8	92
	72	8	92
		(72% recovery by distillation)	
trans-$CH_3CH{=}CHGe(CH_3)_3$	0	100	0
	2	100	0
	4	98	2
	6	95	5
	27	92	8
	72	92	8
		(86% recovery by distillation)	

[a] G.l.c. analysis of these isomers was effected using a silver nitrate column.[13]

Hydrolysis also followed those reactions carried out in tetrahydrofuran. The aqueous phase was extracted with pentane and the combined organic solutions were washed with portions of water until g.l.c. showed that tetrahydrofuran was no longer present. The remaining pentane solution then was dried and distilled and starting material recovery and isomeric composition were determined.

As will be noted in Table II, the recovery of propenyltrimethylsilane when the isomerization was carried out in tetrahydrofuran was rather low. In the case of *cis*-propenyltrimethylsilane (40-mmole scale reaction) distillation of the pentane solution gave 2.1 g. of liquid, b.p. 85–87°, and 0.9 g., b.p. 85° (10 mm.), n^{25}D 1.4567. The 85–87° boiling fraction was shown by g.l.c. (silver nitrate column) to consist of *trans*-propenyltrimethylsilane (92%) and *n*-propyltrimethylsilane (8%). The latter was identified by comparison of its g.l.c. retention time, infrared spectrum, and refractive index with those of an authentic sample. In the case of the *trans* compound (40-mmole scale), distillation gave 2.3 g., b.p. 85–88°, and 0.95 g., b.p. 85° (10 mm.), n^{25}D 1.4566. The former fraction contained 91% *trans*-propenyltrimethylsilane and 9% *n*-propyltrimethylsilane. The higher-boiling fractions were examined by g.l.c. (XF 1150 column at 95°). In both cases three peaks appeared in the g.l.c. chart in a ratio of 57:35:8 in order of increasing retention time. The three peaks were collected: (I) n^{25}D 1.4552, $(CH_3)_3Si$ group present, as shown by bands in the infrared spectrum at 1255, 840, and 760 cm.$^{-1}$ (*Anal.* Found: C, 62.12; H, 12.11); (II) n^{25}D 1.4606, $(CH_3)_3Si$ group present (infrared) (*Anal.* Found: C, 61.91; H, 11.90); (III) only enough for an infrared spectrum could be collected; the presence of a $(CH_3)_3Si$ group was indicated. The n.m.r. spectra of the first two peaks also were obtained, but they could not be reconciled with any structure, especially the expected reductive dimers, either $(CH_3)_3SiCH_2CH(CH_3)CH(CH_3)CH_2Si(CH_3)_3$ or $(CH_3)_3SiCH(C_2H_5)CH(C_2H_5)Si(CH_3)_3$.

Reaction of *cis*-Propenyltrimethyltin with Lithium in Tetrahydrofuran. In a 200-ml., three-necked flask equipped with magnetic stirrer and reflux condenser was placed 0.15 g.-atom of lithium (dispersion containing 2% sodium), 50 ml. of tetrahydrofuran, and 30 mmoles of *cis*-propenyltrimethyltin. The mixture was stirred at room temperature. After 1 hr. it had turned brown and deposition of dark solid was observed after 12 hr. The mixture was stirred for a total of 24 hr. and then was quenched with 120 mmoles of triethylchlorosilane (Peninsular ChemResearch, Inc.). The resulting dark gray reaction mixture was stirred for 16 hr. at room temperature, then was hydrolyzed with 75 ml. of saturated ammonium chloride solution. Gray solid (most probably metallic tin, 0.8 g., 22.4%) was filtered off. The aqueous phase was extracted with pentane and the extracts and the organic phase were combined and washed with water until all of the tetrahydrofuran had been removed. The dried pentane solution was distilled *in vacuo* into a receiver at −78° and the distillate was analyzed by g.l.c. (General Electric Co. SE-30 silicone gum column at 100°; General Electric Co. XF-1150 cyanoethylsilicone column at 92°; General Electric Co. SE-30 column at 200°). The following products were identified: (1) triethylsilane (10.3 mmoles), n^{25}D 1.4095 (lit.[15] n^{25}D 1.4092); (2) triethylmethylsilane (16.2 mmoles, 18% yield based on available methyl groups), n^{25}D 1.4163 (lit.[16] 1.4160); (3) triethylsilanol (yield not determined); (4) *cis*-propenyltriethylsilane (11.5 mmoles, 38% yield), n^{25}D 1.4443; (5) *trans*-propenyltriethylsilane (7 mmoles, 23% yield), n^{25}D 1.4400; (6) triethylsilyltrimethyltin (13.6 mmoles, 45.4% yield), n^{25}D 1.4921; (7) and (8) two minor unidentified products of lower volatility. The first five products were identified by comparison of their g.l.c. retention times, refractive indices, and infrared spectra with those of authentic samples. Triethylsilyltrimethyltin is a new compound. *Anal.* Calcd. for $C_9H_{24}SiSn$: C, 38.70; H, 8.65. Found: C, 38.35; H, 8.84. Its infrared spectrum (pure liquid)[17] showed bands at 2960 (vs), 2910 (s), 2880 (s), 2800 (w), 2740 (w), 2350 (w), 1470 (m), 1420 (m), 1380 (m), 1240 (m), 1190 (w), 1020 (s), 1010 (s), 978 (w), 770 (s), 730 (vs), 720 (vs), and 700 (vs) cm.$^{-1}$.

Authentic *cis-* and *trans*-propenyltriethylsilane were prepared by the reaction of propenylmagnesium bromide (isomeric mixture) with triethylchlorosilane in tetrahydrofuran. The mixture of *cis-* and *trans*-propenyltriethylsilane had b.p. 69–69.5° (24 mm.), and the isomers were separated by g.l.c. (General Electric Co. XF-1150 column at 105°).

***cis*-Propenyltriethylsilane** has n^{25}D 1.4444. Its infrared spectrum (pure liquid)[17] showed bands at 3010 (w), 2960 (vs), 2920 (vs), 2880 (vs), 2810 (w), 2740 (w), 2190 (w), 1625 (s), 1470 (m), 1450 (sh), 1425 (m), 1390 (w), 1360 (w), 1245 (m), 1060 (w), 1020 (s), 975 (w), 730 (vs), 690 (sh), and 650 cm.$^{-1}$.

***trans*-Propenyltriethylsilane** has n^{25}D 1.4400. Its infrared spectrum (pure liquid)[17] showed absorption at 3010 (sh), 2960 (vs), 2920 (vs),

---

[14] Supplied as a 30% by weight dispersion in petrolatum. The petrolatum was washed away with two 50-ml. portions of ether and the lithium then was suspended either in ether or tetrahydrofuran.

[15] R. N. Meals, *J. Am. Chem. Soc.*, **68**, 1880 (1946).

[16] F. C. Whitmore, L. H. Sommer, P. A. diGiorgio, W. A. Strong, R. E. van Strein, D. L. Bailey, H. K. Hall, E. W. Pietrusza, and G. T. Kerr, *ibid.*, **68**, 475 (1946).

[17] Obtained using a Perkin-Elmer Model 337 grating infrared spectrophotometer.

2880 (vs), 2850 (sh), 2810 (w), 2740 (w), 1625 (s), 1470 (m), 1450 (sh), 1425 (m), 1390 (w), 1315 (w), 1245 (m), 1070 (w), 1020 (s), 985 (s), 770 (vs), 740 (s), 720 (s), and 662 (w) cm.$^{-1}$.

The strong band at 985 cm.$^{-1}$ in the spectrum of the latter and its absence in the spectrum of the other isomer are to be noted, since they provide the basis for our isomer assignment. In support of this assignment, *trans*-propenyltrimethylsilane has a strong band at 987 cm.$^{-1}$, and this absorption is absent in the spectrum of the *cis* isomer; in this case, n.m.r. spectroscopy confirmed the isomer assignment.[13]

Reaction of Propenyltrimethylsilane with *n*-Butyllithium. In a 100-ml. flask equipped with magnetic stirrer, reflux condenser, and dropping funnel was placed 11.7 mmoles of propenyltrimethylsilane (32% *cis*, 68% *trans*) and 15 ml. of tetrahydrofuran. To this solution was added 8.3 ml. of 1.42 *N* (11.7 mmoles) *n*-butyllithium in hexane (Foote Mineral Co.) during 15 min. The reaction was slightly exothermic and the solution turned orange. Stirring was continued at room temperature for 20 hr. The mixture was hydrolyzed with saturated ammonium chloride and the aqueous layer was extracted with *n*-hexane. The combined extracts and organic phase were washed free of tetrahydrofuran with water and then dried. The hexane solution was distilled *in vacuo* into a receiver at −78° and the distillate was analyzed by g.l.c. (silver nitrate column at 50°; SE-30 column at 165°). It was determined in this manner that propenyltrimethylsilane had been recovered in 50% yield; the isomer ratio was 32% *cis*, 68% *trans*. Also present (in 30% yield) was 2-methylhexyltrimethylsilane, $n^{25}\text{D}$ 1.4204, $n^{20}\text{D}$ 1.4223, lit.[18] $n^{20}\text{D}$ 1.4222. *Anal.* Calcd. for $C_{10}H_{24}Si$: C, 69.68; H, 14.04. Found: C, 69.18; H, 13.74. The alternate structure, 1-ethylamyltrimethylsilane, has $n^{25}\text{D}$ 1.4268.[19]

Investigation of the Action of Lithium on *cis*- and *trans*-Propenyllithium. *cis*- and *trans*-propenyllithium were prepared as described previously[13] using enough lithium dispersion (containing 2% sodium) in excess so that the Li/RLi ratio was 5. The mixture in each case was stirred for 24 hr. at room temperature, filtered through a sintered disk, and quenched as usual with trimethylchlorosilane. G.l.c. examination of the product propenyltrimethylsilane in each case showed that no isomerization had occurred.

Preparation of Authentic 2,3-Dimethyl-1,4-bis(trimethylsilyl)butane. *meso*-2,3-Dimethyl-1,4-dibromobutane was prepared as follows: ethyl α-bromopropionate → diethyl 2,3-dimethylsuccinate[20] → *meso*-2,3-dimethylsuccinic acid[20] → diethyl *meso*-2,3-dimethylsuccinate[21] → *meso*-2,3-dimethylbutane-1,4-diol[22] → *meso*-2,3-dimethyl-1,4-dibromobutane.[22]

The di-Grignard reagent was prepared from 0.03 mole of 2,3-dimethyl-1,4-dibromobutane using 0.08 g.-atom of magnesium turnings in 30 ml. of tetrahydrofuran. To this reagent solution was added 0.08 mole of trimethylchlorosilane, and the mixture was heated at reflux overnight. The reaction mixture was hydrolyzed; the organic layer was separated, dried, and distilled to give 2.8 g. of liquid, b.p. 84–88° (10 mm.). G.l.c. indicated contamination with 4-hydroxybutyltrimethylsilane (from solvent cleavage by the trimethylchlorosilane–Mg combination[23]). A pure sample of product was obtained by preparative g.l.c. (General Electric SE-30 silicone gum column at 168°); its refractive index at 25° was 1.4368; lit.[24] $n^{20}\text{D}$ 1.4400. Its infrared and n.m.r. spectra were compatible with the assigned structure but were quite different from those of the high-boiling products of the $CH_3CH{=}CHSi(CH_3)_3$–Li in tetrahydrofuran reaction. *Anal.* Calcd. for $C_{12}H_{30}Si_2$: C, 62.48; H, 13.12. Found: C, 62.00; H, 13.41.

Acknowledgments. The authors are grateful to the National Science Foundation (Grant NSF-GP 2511) and to the Alfred P. Sloan Foudation for generous support of this work and to M & T Chemicals, Inc. and the Germanium Information Center for gifts of chemicals.

---

(18) A. D. Petrov and U. P. Lavrichev, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1125 (1952).

(19) J. C. Saam and J. L. Speier, *J. Am. Chem. Soc.*, **80**, 4104 (1958).

(20) C. Hell and M. Rothberg, *Ber.*, **22**, 62 (1889).

(21) N. Zelinsky and S. Krapivin, *ibid.*, **22**, 646 (1889).

(22) G. E. McCasland and S. Proskow, *J. Am. Chem. Soc.*, **76**, 3486 (1954).

(23) U. Krüerke, *Chem. Ber.*, **95**, 174 (1962).

(24) A. D. Petrov and V. F. Mironov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 635 (1952).