VINYL DERIVATIVES OF METALS

XVIII. PREPARATION, CHARACTERIZATION AND ISOMERIZATION OF PROPENYL DERIVATIVES OF SILICON, GERMANIUM AND TIN[*]

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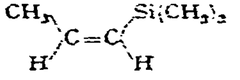
Studies concerned with the stereochemistry of the transmetalation reaction[2] required the synthesis of isomerically pure *cis*- and *trans*-propenyltin compounds. The scope of this synthetic study was expanded to include the *cis*- and *trans*-propenyltrimethyl compounds of silicon and germanium as well. Previous work by A. N. Nesmeyanov and A. E. Borisov and their coworkers has dealt with the preparation and the conversions of *cis*- and *trans*-propenyl derivatives of a number of metals: mercury, thallium, tin, and antimony.[†] The availability of nuclear magnetic resonance spectroscopy as a routine experimental tool has made possible more rigorous structural assignments in the present study than were possible in the previous Soviet studies cited.

SILICON

Propenyltrimethylsilane was prepared in 57 % yield by the reaction of propenylmagnesium bromide[4] (from the equilibrium mixture of *cis*- and *trans*-1-bromopropene) with trimethylchlorosilane in tetrahydrofuran (THF). Gas chromatographic analysis of the product revealed the presence of two isomers in a ratio of 68:32. This ratio was identical to the *cis*–*trans* isomer ratio of the starting 1-bromopropene, a ratio known to be that of the equilibrium mixture[5]. The two silane isomers were separated cleanly on a silver nitrate gas chromatography column, the 68% isomer being the more strongly retained. As *cis* olefins are known to form stronger complexes with silver ion than the corresponding *trans* isomers[6], the *cis* structure, (I), was assigned tentatively to this isomer, while the 32 % isomer was assigned the *trans* configuration, (II).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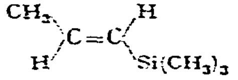
(II)

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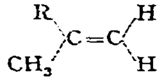
[*] Presented in part at the International Colloquium on Organometallic Chemistry of the Centre National de la Recherche Scientifique, Paris, September 24–28, 1962. For Part XVII, see ref. 1.

[**] Alfred P. Sloan Research Fellow.

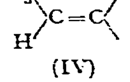
[***] National Science Foundation Cooperative Graduate Fellow, 1961–1963; General Electric Foundation Fellow, 1961.

[†] This work is summarized (with references to the middle of 1961) in ref. 3.

The infrared and NMR spectra of these isomers completely confirmed these assignments. The assumed *trans* isomer showed strong infrared bands at 1620 and 987 cm^{-1}; absorption in the latter region is known to be highly characteristic of *trans* olefins[7]. The assumed *cis* isomer had a strong band at 1610 cm^{-1}, but showed no absorption in the 925–1025 cm^{-1} region. In the NMR spectrum[*] of the *trans* isomer (Fig. 2), one olefinic proton occurred as a pair of quartets ($J = 5.4$ c.p.s.) at 6.41 and 6.11 p.p.m., the second as a doublet ($J = 18.6$ c.p.s.) at 5.76 p.p.m., and the methyl group protons of the propenyl substituent as a doublet ($J = 5.4$ c.p.s.) at 1.95 p.p.m. In the spectrum of the *cis* isomer (Fig. 1), one olefinic proton occurred as a sextet ($J = 7.2$ c.p.s.) at 6.35 p.p.m., the second as a doublet ($J = 14.4$ c.p.s.) at 5.40 p.p.m., and the methyl group as a doublet ($J = 7.2$ c.p.s.), further split into a quartet with $J = 1.5$ c.p.s., at 1.75 p.p.m. As numerous studies[8,9] have revealed that coupling between *trans* olefinic protons is always greater than coupling between *cis* protons, the above spectra provide complete confirmation of the initial isomer assignments[**]. No rigorous evidence was obtained as to which olefinic proton occurred at lower field in these spectra, but several factors strongly suggest that it is the β proton of the propenyl substituent. Studies[11] of a number of 2-substituted propenes of type (III) have shown that the coupling constant between the methyl groups and the olefinic protons is in the range of 1–2 c.p.s. for a wide variety of substituents. The validity of this generalization for organosilicon and organotin substituents has been verified by the NMR spectra of isopropenyltrimethylsilane [III, R = $Si(CH_3)_3$] and isopropenyltrimethyltin [III, R = $Sn(CH_3)_3$]. In the spectrum of the former, the methyl group appeared at 1.80 p.p.m. as a triplet, being coupled equally to both protons with a coupling constant of 1.0 c.p.s. The two olefinic protons appeared as multiplets (J_{H-H} = *ca.* 2.0 c.p.s.) at 5.07 and 5.61 p.p.m. In the tin compound, the methyl group protons also appeared as a triplet ($J = 1.5$ c.p.s.) at 1.94 p.p.m. The olefinic protons appeared as partially split peaks (J_{H-H} = *ca.* 1.0 c.p.s.) at 5.07 and 5.61 p.p.m. Geminal coupling of type (IV) is known to produce coupling constants in the order of 4–10 c.p.s.[3]. Thus the magnitude of the coupling constants observed in *cis*- and *trans*-propenyltrimethylsilane (5.4 and 7.2 c.p.s.) clearly indicates that it is the β proton which is being split by the methyl group. Consideration of $d\pi$–$p\pi$ overlap[***], which would produce deshield-



(III)



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[*] NMR spectra were recorded using a Varian Associates A60 NMR spectrometer. Chemical shifts are given in p.p.m. downfield from tetramethylsilane.

[**] It may be noted that in trimethylvinylsilane J_{cis} = 14.6 c.p.s. and J_{trans} = 20.2 c.p.s.; see ref. 10.

[***] For NMR-derived evidence for $d\pi$–$p\pi$ bonding in vinylsilanes, see refs. 10 and 12.

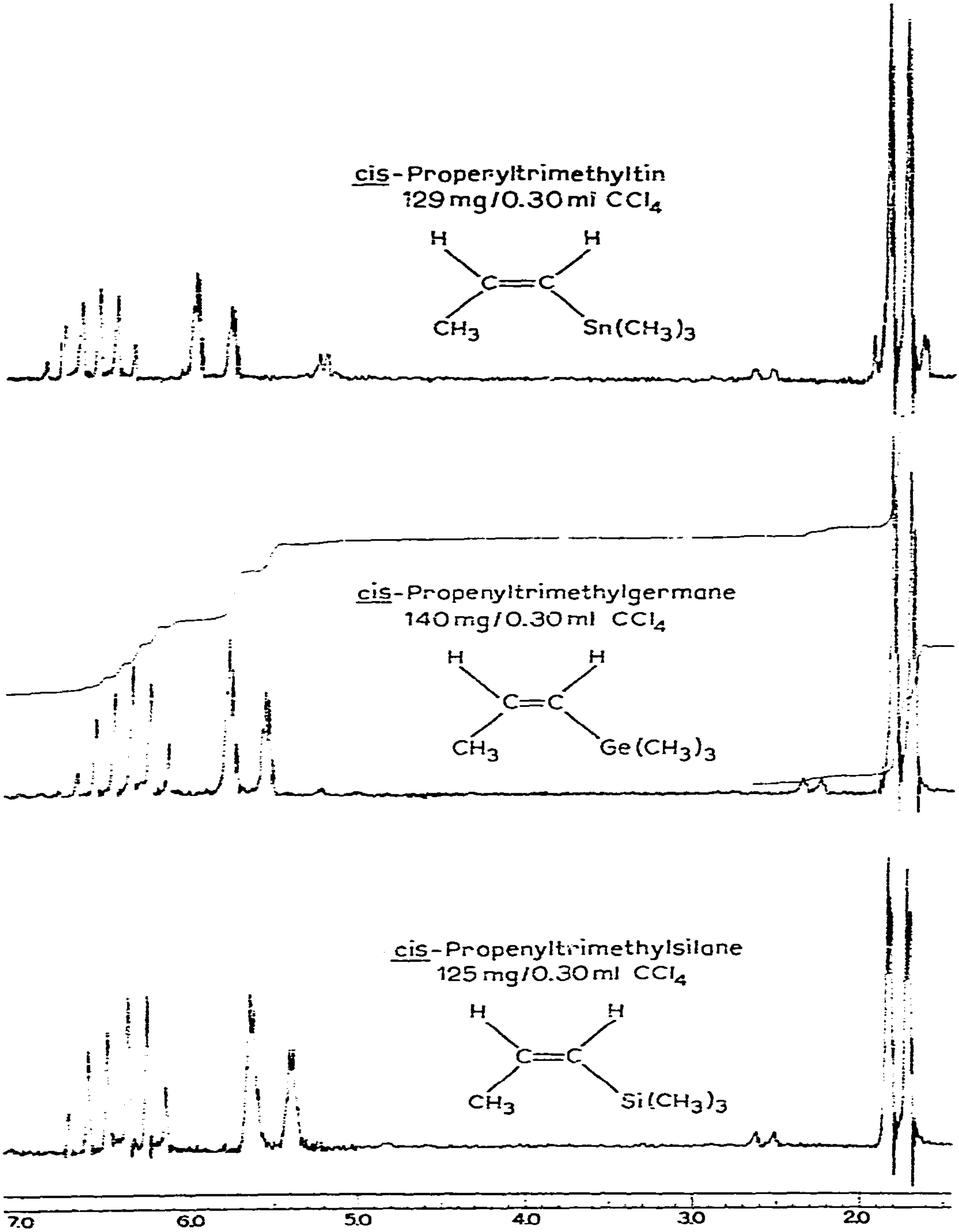


Fig. 1. NMR spectra of the *cis*-propenyltrimethyl compounds of tin, germanium and silicon. Chemical shifts are recorded in p.p.m. downfield from tetramethylsilane. Olefinic and methyl protons not necessarily recorded at same spectrum amplitude.

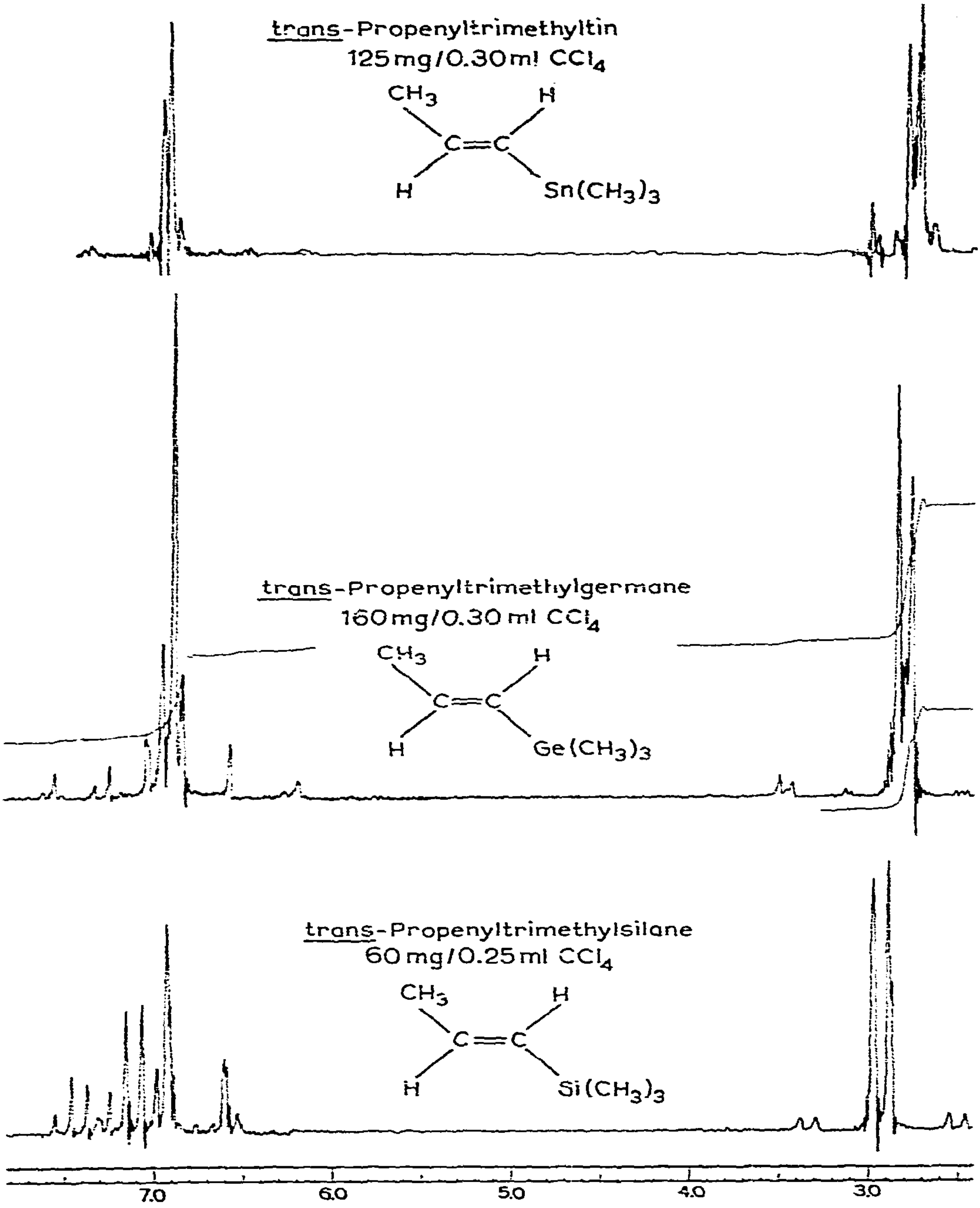
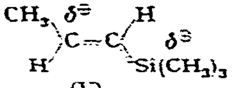


Fig. 2. NMR spectra of the *trans*-propenyltrimethyl compounds of tin, germanium and silicon. Chemical shifts are recorded in p.p.m. downfield from tetramethylsilane. Olefinic and methyl protons not necessarily recorded at same spectrum amplitude.

ing of the β-proton (as in V) lead to the prediction that this proton should occur at a lower field than the α proton. The observed spectra are in agreement with both this



(V)

prediction and the magnitude of the methyl-olefinic proton coupling constants mentioned above.

GERMANIUM

Propenyltrimethylgermane was prepared in 75% yield by the reaction of propenyllithium (from 1-bromopropene and lithium metal[13]) with trimethylgermanium chloride. The product was found to consist of two isomers in 70:30 ratio.

It should be noted that in all reactions involving the use of propenyllithium reagents prepared by the reaction of lithium metal with 1-bromopropenes no acetylenic products (*e.g.*, $(CH_3)_3GeC{\equiv}CCH_3$ in this case) were found. This is in contrast to the findings of ref. 13a and 13b. In the case of the preparation of propenyltrimethyltin compounds (see below), separate experiments showed that $(CH_3)_3SnC{\equiv}CCH_3$ would have been detected in the reaction mixture if it had been present. Thus when a mixture of *cis*- and *trans*-$CH_3CH{=}CHSn(CH_3)_3$ and $CH_3C{\equiv}CSn(CH_3)_3$ was analyzed by gas chromatography (cyanoethylsilicone column, jacket temperature 88°, 12 p.s.i. He) relative retention times for these compounds were 7.6 minutes, 6.4 minutes, and 10.5 minutes, respectively. We believe that the absence of acetylenic products in our reactions reflects a difference in experimental conditions: (a) carrying out the propenyllithium preparation *at 0°* rather than at the reflux temperature of the system; (b) use of an excess of lithium and very slow addition of the 1-bromopropenes *with high speed stirring*.

The 70% propenyltrimethylgermane isomer was more strongly retained on a silver nitrate gas chromatography column and was assigned tentatively the *cis* configuration. This assignment was confirmed by its infrared spectrum, which showed a strong band at 1610 cm^{-1}, but which was completely devoid of absorption in the 925–1025 cm^{-1} region. In the NMR spectrum of this isomer striking similarities to that of the corresponding *cis*-propenylsilane were observed, olefinic protons occurring as as sextet (J = 6.6 c.p.s.) at 6.39 p.p.m. (H_β), and as a doublet J = 13.2 c.p.s.) at 5.65 p.p.m. (H_α), the methyl group as a doublet (J = 6.6 c.p.s.), further split into a quartet with J = 1.5 c.p.s., at 1.77 p.p.m., and the trimethylgermyl group protons as a singlet at 0.25 p.p.m. (Fig. 1).

The presumed *trans* structure of the other isomer also was confirmed by spectral data. The infrared spectrum of this isomer showed a strong band at 980 cm^{-1} in addition to $\nu_{C=C}$ at 1620 cm^{-1}. In its NMR spectrum, the two olefinic protons were found as an unresolved multiplet at 5.9 p.p.m. This multiplet was dominated by a sharp, unsplit peak at 5.88 p.p.m. A considerably smaller unsplit peak occurred at 5.56 p.p.m., and these peaks apparently are the doublet due to the α proton. If this assignment is correct, then the coupling constant between the two olefinic protons is 19.2 c.p.s. The methyl group appeared as a doublet (J = 4.8 c.p.s.) at 1.8 p.p.m., the trimethylgermyl group protons as a singlet at 0.18 p.p.m. (Fig. 2).

TIN

The synthetic problem in the case of the isomeric propenyltin derivatives was more demanding, since larger quantities of pure isomers were required for subsequent studies. Propenyltrimethyltin initially was prepared in 42% yield by the reaction of propenylmagnesium bromide with trimethyltin bromide in THF. Subsequently, it was found that a considerably better yield (88%) could be achieved by using propenyllithium in ether. In both cases the product consisted of two isomers in a ratio of 64:36, and by analogy with the propenylsilane and -germane cases, the 64% isomer tentatively was assigned the *cis* structure. Both isomers were decomposed completely on attempted gas chromatographic analysis on a silver nitrate column, an observation not surprising in view of the known facile cleavage of the aryl-tin linkage by alcoholic silver nitrate[14]. However, it was found that a satisfactory gas chromatographic separation of *cis*- and *trans*-propenyltrimethyltin could be achieved by using a cyano ethylsilicone column. This procedure allowed the collection of analytical samples of both isomers, but was not suited for work on a larger scale, due to the low capacity of such columns. An experimentally simpler approach used the isomerically pure *cis*- and *trans*-propenyllithium reagents, as obtained from the reaction of lithium with *cis*-1-bromopropene and *trans*-1-chloropropene respectively. In this manner, *cis*- and *trans*-propenyltrimethyltin were obtained in high yield.

The presumed structures of these isomers again were confirmed by means of spectral studies. The *trans* isomer had strong infrared bands at 1605 and 985 cm^{-1}, while the *cis* isomer showed absorption at 1605 cm^{-1}, but none in the 925–1050 cm^{-1} region. In the NMR spectrum of the *trans* isomer (Fig. 2), a doubly split peak occurred in the olefinic region at 5.90 p.p.m. along with a smaller complex multiplet pattern. The area of this peak was equivalent to two protons, but no first order splitting pattern was discernible. An extreme example of an ABX_3 system obviously is involved. The methyl group occurred as a doublet ($J = 4.2$ c.p.s.) at 1.80 p.p.m., the trimethyltin group protons as a sharp singlet at 0.08 p.p.m. A small double satellite signal, arising from splitting of the trimethyltin proton peak by the ^{117}Sn and ^{119}Sn isotopes (7.7 and 8.7% abundant, respectively) was observed at 0.53 p.p.m. ($J = 54$ c.p.s.). This signal was observed in all NMR spectra of compounds containing the $(CH_3)_3Sn$ group. The expected upfield half of this signal was observed in several spectra at 0.45 p.p.m. above the main trimethyltin peak. In the NMR spectrum of *cis*-propenyltrimethyltin, one olefinic proton occurred as a sextet ($J = 6.6$ c.p.s.) at 6.40 p.p.m., the second as a doublet ($J = 14.2$ c.p.s.) at 5.75 p.p.m. The methyl group appeared as a doublet ($J = 6.6$ c.p.s.), further split into a quartet with $J = 1.0$ c.p.s., at 1.75 p.p.m., while the trimethyltin signal was found at 0.15 p.p.m. (Fig. 1).

In addition to the propenyltrimethyltin isomers, both tetra-*cis*-propenyltin and tetra-*trans*-propenyltin were prepared in high yield by the organolithium route using pure *cis*- and *trans*-propenyllithium respectively. The infrared spectra of both isomers were similar to those of the corresponding propenyltrimethyltin isomers. The olefinic region of the NMR spectrum of tetra-*trans*-propenyltin showed an unresolved multiplet at 6.0 p.p.m., which was dominated by a strong, sharp peak at 5.98 p.p.m., while a smaller, unsplit peak occurred at 5.68 p.p.m. It is possible (and seems probable to us) that these peaks represent the doublet due to the α proton of the propenyl group. If this is the case, then the *trans* coupling constant is 19.2 c.p.s. (*vs.* a *cis* coupling

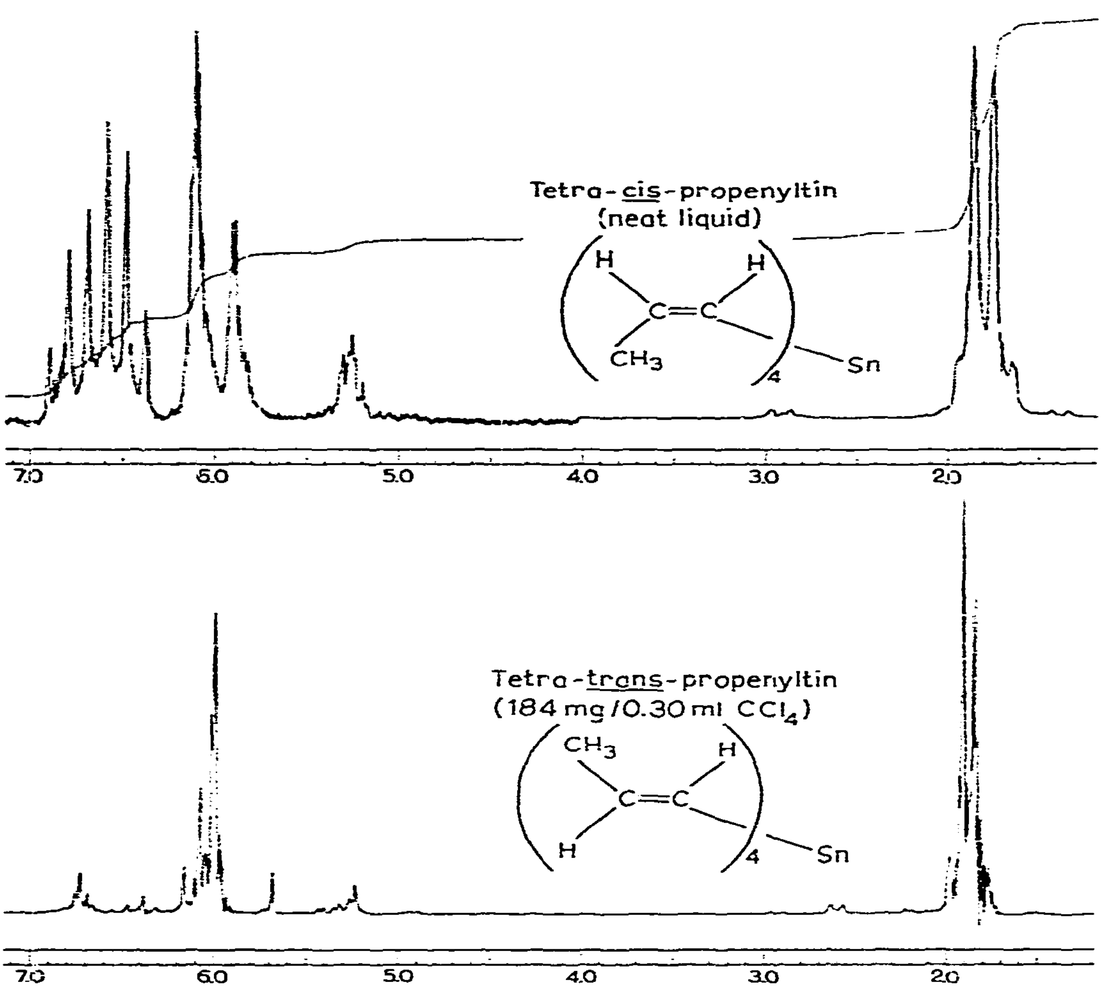


Fig. 3. NMR spectra of tetra-*cis*- and tetra-*trans*-propenyltin. Chemical shifts are recorded in p.p.m. downfield from tetramethylsilane. Olefinic and methyl protons not recorded at same spectrum amplitude.

constant of 13.2 c.p.s. in tetra-*cis*-propenyltin*). The methyl group protons occurred as a doublet ($J = 4.2$ c.p.s.) at 1.88 p.p.m. (Fig. 3). The NMR spectrum of tetra-*cis*-propenyltin (Fig. 3) showed one olefinic proton as a sextet ($J = 6.6$ c.p.s.) at 6.62 p.p.m., the second as a doublet ($J = 13.2$ c.p.s.) at 6.00 p.p.m., and the methyl protons as a doublet ($J = 6.6$ c.p.s.) at 1.81 p.p.m. Also clearly seen in this spectrum is an additional broad peak at 5.25 p.p.m. It seems possible that this peak is the upfield half of the signal to be expected from splitting of the α proton by the ^{117}Sn and ^{119}Sn isotopes. The downfield half of the signal is obscured by the sextet due to the β proton, but a coupling constant of *ca.* 90 c.p.s. is indicated. Confirmation of this assignment is obtained from the spectrum of tetra-*trans*-propenyltin, which shows two small peaks

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* J_{trans} and J_{cis} in tetravinyltin were found to be 20.3 c.p.s. and 13.2 c.p.s., respectively.[15]

at 6.73 and 5.23 p.p.m., symmetrical about the major peak at 5.98 p.p.m. If this is indeed splitting due to the tin isotopes, the coupling constant is 90 c.p.s.

Other possible routes to pure *cis*- and *trans*-propenyltin compounds were considered. The addition of organotin hydrides to olefins and acetylenes has been described by Van der Kerk and Noltes*. In all cases described, addition of the organotin moiety to the terminal CH_2 or CH groups of monosubstituted olefins and acetylenes was reported to occur. Furthermore, in most of the cases where a triorganotin hydride reacted with an acetylene, only one product, not a mixture of isomers, was found. On mechanistic grounds, this isomer was believed to be the *trans* olefin, this being formed by *cis* addition of the Sn–H linkage to the acetylene. Our expectation, based on this previous work, that the addition of trimethyltin hydride to methylacetylene would give exclusively *trans*-propenyltrimethyltin, was not met. When this addition reaction was carried out in a sealed tube at 100° during 18 hours, a 30% yield of propenyltrimethyltin was obtained. Gas chromatographic analysis revealed this product to be a mixture of all three possible isomers, *trans*-, *cis*-, and isopropenyltrimethyltin, in a ratio of 68:28:4. More recent work[17] has shown that the addition of organotin hydrides to organic unsaturation can occur *via* a radical route. It seems likely, therefore, that the lack of specificity in our addition reaction can be attributed to the operation of a radical chain addition mechanism. In view of work described below concerning the thermal stability towards configurational change of *cis*- and *trans*-propenyltrimethyltin, it does not seem likely that the observed mixture of isomers resulted by isomerization of either *cis*- or *trans*-propenyltrimethyltin as formed in the addition reaction.**

The formation of a mixture of isomers in the above reaction and the alternate possibility of converting a mixture of *cis*- and *trans*-propenyltrimethyltin to either of the pure isomers led us to investigate the question of isomerization in the propenyltrimethyl compounds of silicon, germanium and tin. Both radical-catalyzed and photochemical isomerizations were considered.

Heating propenyltrimethyltin (71% *cis*, 29% *trans*) for long periods in the presence of benzoyl peroxide or 2,2′-azobisisobutyronitrile caused a negligible amount of isomerization. In both cases, the ratio changed to 65% *cis*- and 35% *trans*-propenyltrimethyltin. Experiments using ultraviolet radiation were more successful. Twenty minutes of irradiation of a mixture containing 71% *cis*- and 29% *trans*-propenyltrimethyltin resulted in a change to an isomer composition of 25% *cis* and 75% *trans*. This ratio was not changed after an additional 20 hours of irradiation.

This facile isomerization to an apparent steady-state mixture prompted a more detailed investigation of the isomerization of pure *cis*- and *trans*-propenyltrimethyltin. Under comparable experimental conditions *cis*-propenyltrimethyltin was isomerized to the 3:1 *trans*–*cis* mixture after five minutes of irradiation, the pure *trans* isomer after ten minutes. No change in this ratio occurred during an additional 20 hours of irradia-

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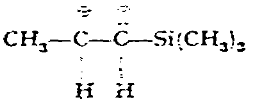
* For a review see ref. 16a; for later work ref. 16b.

** *Note added in proof:* A report (R. F. Fulton, Ph. D. Thesis, Purdue University, 1960) not available to us when this paper was being written describes the trimethyltin hydride catalyzed isomerization of *cis*-β-styryl-trimethyltin to the *trans*-isomer. Since trimethyltin hydride was still present at the end of our reaction, it is possible that the mixture of *cis*- and *trans*-propenyltrimethyltin also resulted through isomerization of the kinetically controlled product, either *cis*- or *trans*-propenyltrimetyltin. Further investigation of this point is no longer within the scope of this study.

tion. An 85% recovery of propenyltrimethyltin was obtained, indicating that only little or no dimerization and/or polymerization had occurred.

Ultraviolet irradiation of *trans*- and *cis*-propenyltrimethylsilane was required for considerably longer times, 29 and 71 hours respectively, to produce a steady-state mixture (81% *trans*, 19% *cis*). With *cis*- and *trans*-propenyltrimethylgermane an equilibrium mixture (83% *trans*, 17% *cis*) also was obtained on irradiation. The rates of isomerization of the germanium-containing isomers were considerably slower than those observed for the analogous tin compounds, but faster than those of the corresponding silicon compounds. *Cis*-propenyltrimethylgermane required 5.5 hours of irradiation, the *trans* isomer 51.75 hours, for the attainment of the steady-state *trans*–*cis* ratio. In one preparatively oriented isomerization carried out in ether solution (5 g propenyltrimethylgermane, 5 ml ether), the initial isomer ratio of 70% *cis*, 30% *trans* changed to 9% *cis*, 91% *trans* after a 4.5 hour irradiation period. This illustrates the striking effect of solvent on both the rate of isomerization and the position of equilibrium.

While nothing is known of the transition state in these isomerizations, an attractive possibility is the dipolar species, (VI). Metals having vacant d orbitals of sufficiently low energy are known to stabilize an adjacent carbanionic center *via* dπ–pπ overlap*, while little, if any, stabilization is given to an adjacent radical center, at least in the case of organosilicon compounds[15].



$$CH_3{-}\underset{\textstyle H}{\overset{+}{C}}{-}\underset{\textstyle H}{\overset{\ominus}{\ddot{C}}}{-}Si(CH_3)_3$$

(VI)

Simple thermal isomerization of the propenyltrimethylsilicon, -germanium, and -tin compounds studied appears not to occur readily. All could be distilled at atmospheric pressure without isomerization. In the case of the tin compounds this represents temperatures of 125–130°.

EXPERIMENTAL**

(1) *Cis- and trans-1-halopropenes*

Cis- and *trans*-1-chloropropene were obtained by fractional distillation of a mixture of 1- and 2-chloropropenes through a 6-foot packed column: 2-chloropropene, b.p. 23.2–24.5°; *cis*-1-chloropropene, b.p. 30.0–30.4°; *trans*-1-chloropropene, b.p. 37.0–38.0°. Gas chromatography (cyanoethylsilicone column***, 17% on 60–80 mesh Johns-Manville Chromosorb P, jacket temp. 28°, 12 p.s.i. He) showed the *cis* and *trans* isomers thus obtained to have a purity greater than 99%. *Cis*-1-bromopropene was obtained by fractional distillation of a mixture of *cis*- and *trans*-1-bromopropene through a 6-foot packed column. Pure *cis*-1-bromopropene was collected from

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* Ref. 3, pp. 137–141.

** All reactions involving reactive organometallic reagents were carried out in an atmosphere of dry argon or prepurified nitrogen. Analyses were performed by Dr. S. M. Nagy (M.I.T.), the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y., and A. Schoeller, Kronach, Ofr.

*** General Electric Company XF 1150 Fluid. We are indebted to the Silicone Products Department of the General Electric Company for samples of this material.

56.9–57.5°. Gas chromatography (cyanoethylsilicone column, jacket temp. 54°, 14 p.s.i. He) showed this fraction to have a purity of greater than 99%. No separation of *cis*- and *trans*-1-halopropenes occurred on a silver nitrate column. Apparently silver ion complexes much more strongly with the halogen atom than with the π system of the double bond.

(2) *Propenyltrimethylsilane*

In a 500 ml three-neck flask (equipped with a mechanical stirrer, reflux condenser and dropping funnel) was placed 9.3 g (0.39 g-atom) of magnesium turnings. The latter were covered with 100 ml of THF, and 5 ml of 1-bromopropene (equilibrium mixture of *cis* and *trans* isomers) was added to start the reaction; once it had started, an additional 150 ml of THF was added. 1-Bromopropene (57.0 g, 0.47 mole) in 30 ml THF then was added dropwise at a rate sufficient to maintain a gentle reflux. The mixture was heated at reflux for 1 h upon completion of the addition. Trimethylchlorosilane (Dow Corning Corporation), 32.4 g, 0.3 mole, in 30 ml THF, was added in portions during 30 min; the resulting mixture was heated at reflux overnight, then was hydrolyzed with saturated ammonium chloride solution. The organic layer was separated and the salts were dissolved in dilute HCl. The resulting solution was extracted with 100 ml of THF. The combined THF layers were dried, and 200 ml of THF was distilled off. This distillate was diluted with 600 ml of water and the organic phase which separated was added to the undistilled residue. This residue (*ca.* 100 ml) was diluted with 500 ml of water, and the organic layer which separated was dried over sodium sulfate. Fractional distillation gave 19.2 g (57%) of pure (by gas chromatography) propenyltrimethylsilane, b.p. 85–88°, n_D^{20} 1.4121. The *cis* and *trans* isomers were separated on a silver nitrate gas chromatography column* (jacket temp. 25°, 9 p.s.i. He).

Trans-propenyltrimethylsilane: n_D^{25} 1.4062; infrared spectrum (5% in CCl_4), 2950(s), 1620(s), 1450(m), 1430(w), 1375(w), 1250(s), 985(s), 850(s) cm^{-1}. (Found: C, 62.87; H, 12.48. $C_6H_{14}Si$ calcd.: C, 63.06; H, 12.35%.)

Cis-propenyltrimethylsilane: n_D^{25} 1.4105; infrared spectrum (5% in CCl_4): 2950(s), 1610(s), 1450(m), 1430(m), 1410(m), 1385(m), 1360(w), 1295(w), 1250(s), 1055(w), 925(w), 850(s) cm^{-1}. (Found: C, 63.15; H, 12.24%.)

Isopropenyltrimethylsilane

This silane was prepared in 55% yield by the reaction of isopropenylmagnesium bromide with trimethylchlorosilane in THF using the procedure described above; b.p. 82–84°, n_D^{25} 1.4048; lit.[19] b.p. 83°/760, n_D^{20} 1.4070. Infrared spectrum: 3000(w.), 2910(s.), 1600(w.), 1445(m.), 1405(m.), 1365(w.), 1340(w.), 1250(s.), 1210(w.), 1000(w.), 940(m.), 920(s.), 850(s.) cm^{-1}.

(3) *Propenyltrimethylgermane*

In a 200 ml three-neck flask (equipped with magnetic stirrer, reflux condenser and addition funnel) was placed 70 ml of anhydrous ether and 1.12 g (0.16 g-atom) of sliced

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* Prepared in the following way: To a solution of 45.2 g of tetraethylene glycol in 800 ml methanol was added 30 g of powdered silver nitrate. When solution was complete, the solution was filtered and 140 g Chromosorb P firebrick added. The methanol was allowed to evaporate overnight, and drying was completed by heating in a vacuum oven at 75° for 3 h. The column was conditioned by passing a slow stream of nitrogen through it for 15 h at 175°.

lithium wire containing 1 % sodium (Lithium Corp. of America). Ten g (0.083 mole) of 1-bromopropene (mixture of isomers) in 15 ml of ether then was added dropwise at a rate sufficient to maintain a vigorous reflux. To the resulting lithium reagent solution was added 10.2 g (0.067 mole) of trimethylgermanium chloride, and the reaction mixture was refluxed for 30 min, then was hydrolyzed with saturated ammonium chloride solution. Fractional distillation of the dried organic layer gave 7.9 g (75%) of product, b.p. 100–103°. The isomers (70 % *cis*, 30 % *trans*) were separated by gas chromatography on a silver nitrate column (jacket temp. 57°, 13 p.s.i. He).

Trans-propenyltrimethylgermane: n_D^{25} 1.4269; infrared spectrum (pure liquid): 2950(s), 2900(s), 2820(m), 1620(s), 1445(m), 1415(m), 1370(w), 1310(w), 1240(s), 1005(w), 980(s), 825(s), 765(s), 680(m) cm^{-1}. (Found: C, 45.57; H, 8.81. $C_6H_{14}Ge$ calcd.: C, 45.39; H, 8.88 %.)

Cis-propenyltrimethylgermane: n_D^{25} 1.4319; infrared spectrum (pure liquid): 2960(s), 2900(s), 2800(w), 1610(s), 1450(m), 1415(m), 1380(m), 1345(m), 1240(m), 1050(w), 1035(w), 915(w), 850(s), 760(s), 655(s) cm^{-1}. (Found: C, 45.46; H, 8.94 %.)

(4) *Propenyltrimethyltin*

(*a*) *Grignard procedure.* Propenylmagnesium bromide was prepared as described above from magnesium and 1-bromopropene (equilibrium mixture of isomers) on a 0.66 mole scale in 300 ml of THF. To this solution was added 119.0 g (0.49 mole) of trimethyltin bromide in 100 ml THF during 1 h. The reaction mixture was heated at reflux overnight and then hydrolyzed with saturated ammonium chloride solution. Distillation of the dried organic layer gave 42 g of crude product, b.p. 126–127°. This was purified by treating its ether solution with anhydrous gaseous ammonia for 2 h. The precipitated organotin halide–ammonia adduct was filtered and the filtrate distilled to give pure propenyltrimethyltin, b.p. 125–126°, n_D^{25} 1.4655. The isomers (64 % *cis*, 36 % *trans*) were separated on a cyanoethylsilicone column (jacket temp. 65°, 8 p.s.i. He).

Trans-propenyltrimethyltin: n_D^{25} 1.4638; infrared spectrum (5% in CCl_4): 2980(s), 2910(s), 1605(s), 1445(m), 1375(w), 1315(w), 1220(s), 1195(w), 985(s) cm^{-1}. (Found: C, 35.28; H, 6.79. $C_6H_{14}Sn$ calcd.: C, 35.17; H, 6.89 %.)

Cis-propenyltrimethyltin: n_D^{25} 1.4690; infrared spectrum (5 % in CCl_4): 2970(s), 2920(s), 1605(s), 1450(m), 1380(w), 1335(m), 1250(m), 1190(m), 1040(w), 910(w), 865(s) cm^{-1}. (Found: C, 35.26; H, 6.99 %.)

(*b*) *Organolithium procedure.* Propenyllithium was prepared on a 0.24 mole scale in 240 ml of ether as described above. To this solution was added 49 g (0.2 mole) of trimethyltin bromide in 50 ml of ether during 30 min. The reaction mixture was heated at reflux for 2 h, then was hydrolyzed with saturated ammonium chloride solution. Fractional distillation of the dried organic layer gave 35.3 g (88%) of propenyltrimethyltin, b.p. 124–126°. Gas chromatography (cyanoethylsilicone column) showed that the *cis–trans* ratio was 67:33.

(5) *Cis-propenyltrimethyltin*

In a 200 ml three-neck flask (equipped with high speed stirrer, reflux condenser and dropping funnel) was placed 1.65 g (0.236 g-atom) of sliced lithium wire (low sodium content) and 100 ml of ether. The flask contents were cooled to 0° and 14.3 g (0.118 mole) of pure *cis*-1-bromopropene in 10 ml ether was added dropwise during 1 h. The temperature was maintained at 0° during the addition. To the lithium reagent solution was added 24.4 g (0.1 mole) of trimethyltin bromide in 20 ml ether and the reaction mixture was allowed to stand overnight. Hydrolysis with saturated sodium bicarbonate followed. The ether layer was treated with anhydrous, gaseous ammonia and filtered. Fractional distillation of the filtrate gave 14.8 g (72%) of *cis*-propenyltrimethyltin, b.p. 127–130°, n_D^{25} 1.4690. Gas chromatographic analysis indicated that less than 1% of the *trans* isomer was present.

(6) *Trans-propenyltrimethyltin*

In a 500 ml three-neck flask (equipped with stirrer, dry-ice condenser and addition funnel) was placed 4.6 g (0.66 g-atom) of lithium wire containing 1% sodium and 200 ml of ether. Over a three h period a solution of 27.0 g (0.35 mole) of pure *trans*-1-chloropropene in 20 ml of ether was added dropwise (moderate refluxing). A solution of 59.0 g (0.24 mole) of trimethyltin bromide in 20 ml of ether then was added to the lithium reagent during 30 min. The reaction mixture was stirred for 1 h and then hydrolyzed with saturated ammonium chloride solution. Fractional distillation of the organic layer gave 39.2 g (79%) of *trans*-propenyltrimethyltin, b.p. 125–128°, n_D^{25} 1.4638. Gas chromatography indicated that less than 1% of the *cis* isomer was present.

(7) *Tetra-cis-propenyltin*

Cis-propenyllithium was prepared from *cis*-1-bromopropene on a 0.34 mole scale as described above in a 1-liter Morton flask. To the resulting solution was added 33.0 g (0.075 mole) of tin tetrabromide in 50 ml of ether during 1 h. The reaction mixture was allowed to stand overnight, then was hydrolyzed with a saturated solution of sodium bicarbonate. The separated ether layer was treated with gaseous ammonia and filtered. Fractional distillation of the filtrate gave 16.1 g (76%) of product, b.p. 57–59°/0.2; n_D^{25} 1.5178; infrared spectrum (pure liquid): 2940(s), 1600(s), 1450(s), 1380(m), 1325(s), 1205(w), 1040(m), 995(w), 985(w), 925(m) cm^{-1}. (Found: C, 51.03; H, 7.09. $C_{12}H_{20}Sn$ calcd.: C, 50.93; H, 7.12%.)

(8) *Tetra-trans-propenyltin*

Trans-propenyllithium was prepared as described above from pure *trans*-1-chloropropene on a 0.615 mole scale in 550 ml of ether. To this solution was added 45.7 g (0.104 mole) of tin tetrabromide in 50 ml of ether during 45 min. The reaction mixture was heated at reflux overnight, then was hydrolyzed with saturated ammonium chloride. Fractional distillation of the organic phase gave 24.5 g (83%) of product, b.p. 53–56°/0.05; n_D^{25} 1.5064; infrared spectrum (pure liquid): 2940(s), 2840(m), 1600(s), 1440(s), 1370(m), 1315(m), 1210(s), 1055(m), 1035(m), 980(s), 935(w), 705(m), 650(s) cm^{-1}. (Found: C, 51.26; H, 7.18. $C_{12}H_{20}Sn$ calcd.: C, 50.93; H, 7.12%.)

(9) *Propenyltrimethyltin by the hydride addition method*

In a Pyrex combustion tube, flushed with argon and cooled to —78°, was placed 2.7 g of methylacetylene (Matheson Co.) (0.068 mole, 40% excess) and 8.0 g (0.0485 mole) of trimethyltin hydride. The tube then was stoppered, placed in liquid nitrogen and sealed. After being placed in a steel reactor, it was allowed to warm to room temperature and subsequently heated at *ca.* 100° for 18 h. Fractional distillation of the reaction mixture gave 2.8 g of recovered trimethyltin hydride and 1.9 g of liquid boiling at 120–130° (30% yield, based on unrecovered trimethyltin hydride). Gas chromatographic analysis (20% Dow Corning 710 Silicone Fluid on Chromosorb P, jacket at 70°, 7 p.s.i. He) showed that a mixture of iso-, *cis*-, and *trans*-propenyltrimethyltin (4:28:68 ratio) was present.

(10) *Isopropenyltrimethyltin*

To 3.5 g (0.5 g-atom) of lithium wire pieces in 300 ml of ether was added 31.0 g (0.26 mole) of 2-bromopropene during 1 h. To the resulting solution was added 45.0 g (0.18 mole) of trimethyltin bromide. The reaction mixture was heated at reflux for 10 h and hydrolyzed with saturated ammonium chloride solution. Fractional distillation of the ether layer gave 25.5 g (67%) yield of product, b.p. 118–120°; n_D^{25} 1.4608; infrared spectrum: 2900(s), 1600(w), 1440(s), 1360(w), 1190(m), 995(m), 935(m), 905(s), cm^{-1}. (Found: C, 35.46; H, 6.91. $C_6H_{14}Sn$ calcd.: C, 35.17; H, 6.89%.)

(11) *Attempted isomerization of propenyltrimethyltin with radical catalysts*

In a 100 ml flask equipped with a reflux condenser was placed 13.1 g (0.064 mole) of propenyltrimethyltin (71% *cis*, 29% *trans*) and 25 ml of carbon tetrachloride. Benzoyl peroxide (0.116 g, 0.48 mole) was added, and the mixture was refluxed for 4 h. Gas chromatographic analysis (cyanoethylsilicone column) indicated that no change in the isomer ratio had occurred. The mixture was heated at reflux for an additional 72 h. After this time the isomer ratio had changed to 65% *cis*, 35% *trans*. Propenyltrimethyltin was recovered quantitatively.

A similar experiment was carried out on the same scale using propenyltrimethyltin of the same isomeric composition and 0.142 g of 2,2′-azobisisobutyronitrile in carbon tetrachloride solution. The mixture was heated at reflux for 65 h. Gas chromatography showed the isomer ratio to be 65% *cis*, 35% *trans* after this treatment. The recovery of starting material again was nearly quantitative.

(12) *Ultraviolet irradiations*

All ultraviolet irradiations were carried out in a quartz flask equipped with a condenser and a side arm with a no-air rubber stopper. The top of the flask was covered completely with Al foil. The ultraviolet lamp used* was placed below the flask at a distance of 3.5 cm, and an argon atmosphere was maintained. *n*-Hexane was used as the solvent. Samples were withdrawn periodically with a syringe, and isomer ratios were determined by gas chromatography as described above. All isomers examined were shown to be stable configurationally in refluxing *n*-hexane in the absence of the ultraviolet source. The experimental data are given in Table 1.

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* Hanovia Lamp Division Cat. No. 30600, 100 watts.

TABLE 1

UV ISOMERIZATION OF PROPENYLTRIMETHYL DERIVATIVES OF TIN, GERMANIUM AND SILICON

Compound	*Irradiation Time*	*trans-Propenyl Isomer, %*	*cis-Propenyl Isomer, %*
trans-$CH_3CH=CHSn(CH_3)_3$	0	100	0
(0.9 g in 8 ml of hexane)	5 min	75	25
	10 min	75	25
	20 h	75	25
cis-$CH_3CH=CHSn(CH_3)_3$	0	0	100
(1.0 g in 8 ml of hexane)	5 min	52	48
	10 min	75	25
	15 min	75	25
	20 h	75	25
trans-$CH_3CH=CHGe(CH_3)_3$	0	100	0
(1.0 g in 8 ml of hexane)	5 min	100	0
	22 min	96	4
	1 h	94	6
	2 h	89	11
	3.5 h	87	13
	5.5 h	83	17
	23 h	83	17
cis-$CH_3CH=CHGe(CH_3)_3$	0	0	100
(1.0 g in 8 ml of hexane)	10 min	1	99
	20 min	2	98
	30 min	3.5	96.5
	1 h	8	92
	2 h	17	83
	3.25 h	27.5	72.5
	4.5 h	41	59
	6 h	50	50
	7.67 h	57.5	42.5
	23.75 h	79.5	20.5
	29.75 h	81	19
	51.75 h	83	17
trans-$CH_3CH=CHSi(CH_3)_3$	0	100	0
(0.85 g in 8 ml of hexane)	2 h	99	1
	3.5 h	97	3
	5 h	95	5
	6.33 h	92.5	7.5
	22.5 h	86	14
	29 h	81	19
cis-$CH_3CH=CHSi(CH_3)_3$	0	0	100
(0.6 g in 7 ml of hexane)	15 min	2	98
	30 min	3	97
	1 h	5	95
	2.2 h	9	91
	3 h	13.5	86.5
	4.5 h	19	81
	6 h	24	76
	7 h	29	71
	27.8 h	74	26
	71 h	81	19

SUMMARY

Pure *cis*- and *trans*-propenyltrimethylsilane, -germane, and -tin, as well as tetra-*cis*- and tetra-*trans*-propenyltin, have been prepared by the organolithium or the Grignard routes. Assignment of configuration for all isomers was made on the basis of their infrared and nuclear magnetic resonance spectra. The isomerization of these compounds to apparently steady-state *cis-trans* isomer mixtures by ultraviolet radiation is described.

REFERENCES

1 D. Seyferth and M. Takamizawa, *J. Org. Chem.*, 28 (1963), 1142.
2 D. Seyferth and L. G. Vaughan, paper in preparation.
3 D. Seyferth, *Vinyl Compounds of Metals*, in: F. A. Cotton, *Progress in Inorganic Chemistry*, Interscience Publishers, New York, 1962, p. 129–280.
4 H. Normant, *Bull. Soc. Chim. France*, (1957) 728.
5 K. E. Harwell and L. F. Hatch, *J. Am. Chem. Soc.*, 77 (1955) 1682.
6 M. A. Muhs and F. T. Weiss, *J. Am. Chem. Soc.*, 84 (1962) 4697.
7 L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, 2nd ed., 1958, p. 45–48.
8 L. M. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy to Organic Chemistry*, Pergamon Press, London, 1959, p. 57.
9 J. D. Roberts, *Nuclear Magnetic Resonance*, McGraw-Hill Book Co., New York, 1959, p. 54.
10 R. T. Hobgood, J. H. Goldstein and G. S. Reddy, *J. Chem. Phys.*, 35 (1961) 2038.
11 L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, (1960) 2881.
12 G. V. D. Tiers, J. S. Peake and N. P. Sweeney, *Abstracts of Papers, 140th National Meeting of the American Chemical Society*, Chicago, Ill., September 1961, p. 27-N.
13 (a) E. A. Braude and J. A. Coles, *J. Chem. Soc.*, (1951) 2078, 2085.
(b) D. Y. Curtin and J. W. Crump, *J. Am. Chem. Soc.*, 80 (1958) 1922.
14 R. K. Ingham, S. D. Rosenberg and H. Gilman, *Chem. Rev.*, 60 (1960) 460.
15 D. W. Moore and J. A. Happe, *J. Phys. Chem.*, 65 (1961) 224.
16 (a) G. J. M. van der Kerk, J. G. A. Luijten and J. G. Noltes, *Angew. Chem.*, 70 (1958) 298.
(b) J. G. Noltes and G. J. M. van der Kerk, *Rec. Trav. Chim.*, 80 (1961) 623; *ibid.*, 81 (1962) 41.
17 W. P. Neumann, H. Niermann and R. Sommer, *Angew. Chem.*, 73 (1961) 768; *Ann. Chem.*, 659 (1962) 27.
18 C. E. Scott and C. C. Price, *J. Am. Chem. Soc.*, 81 (1959) 2670.
19 A. D. Petrov and G. I. Nikishin, *Dokl. Akad. Nauk SSSR*, 93 (1953) 1049.