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ETHYNYLSILANES
II. SYNTHESES AND CHARACTERIZATION OF SOME GROUP IV DIMETALLOID ACETYLENES AND OLEFINS

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INTRODUCTION

Although numerous organometallic vinyl[1] and ethynyl[2] derivatives have been synthesized and studied in recent years, very little has been reported on compounds with the general formulas $R_nM(C{\equiv}CM'R_3)_{4-n}$ or $R_nM(CH{=}CHM'R_3)_{4-n}$, where M and M′ are different Group IV elements. A substantial number of ethynyl compounds with $M=M'$ are known[2] and a few ethylene derivatives with $M=M'=Si$ are known[3]. The first examples of ethylene derivatives with $M=M'=Ge$ and with $M=Ge\neq M'=Si$ have only recently been synthesized[4]. In this paper we wish to report our results on the syntheses of some mixed dimetalloid acetylenes and olefins for which terminal ethynylsilanes serve as the starting materials. Infrared and proton magnetic resonance (PMR) spectral data are utilized in the assignments of structures.

EXPERIMENTAL

General

Infrared spectra were obtained with a Perkin–Elmer Model 21 Spectrophotometer; all compounds were examined in 10% carbon tetrachloride solutions. PMR spectra of products either in carbon tetrachloride solutions or as pure liquids were recorded with a Varian Associates A-60 Spectrometer. Tetramethylsilane was used as an internal standard in all instances. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Reagents were obtained from various sources. Tetrahydrofuran (Fisher Scientific Co., histiological grade) was found to be sufficiently dry for laboratory use as received. Diphenylmethylchlorosilane, phenyldimethylchlorosilane, triphenylchlorosilane, triphenylsilane, phenylmethylchlorosilane, phenylmethyldichlorosilane from Peninsular Chemresearch, Inc. and diphenyldichlorosilane, dimethyldichlorosilane and triphenyltin chloride from Alfa Inorganics, Inc. were normally used as received. Trimethylchlorosilane (J. T. Baker Chemical Co.) was purified by distillation under nitrogen prior to use.

All reactions reported here were carried out in an atmosphere of prepurified nitrogen. Melting points and boiling points are uncorrected.

Syntheses of terminal ethynylsilanes

Although certain of the terminal ethynylsilanes listed in Table 1 are not new compounds, we have still listed our results primarily because of the failures of previous authors to report their experimental yields or details.

Trimethylethynylsilane. A three-necked flask was equipped with a dropping funnel, mechanical stirrer, water condenser and gas inlet tube. About 500 ml of dry tetrahydrofuran was added to the flask, cooled in ice and then saturated with acetylene gas which had been passed through a long column of activated alumina. A solution of ethylmagnesium bromide (0.8 mole) in 400 ml of tetrahydrofuran was added in increments at such a rate that evolution of ethane had ceased before more of the Grignard reagent was introduced. Acetylene was bubbled into the solution during this step and during the initial stages of addition of the trimethylchlorosilane.

TABLE 1

PHYSICAL PROPERTIES, YIELDS AND ANALYSES OF ETHYNYL COMPOUNDS

Ethynyl compounds	*B.p. [°C(mm)] or M.p. (°C)*	*Yield (%)*	*Analyses (%)*		
				Calcd.	*Found*
$(CH_3)_3SiC{\equiv}CH^a$	52.5–53.5 (atm.)	70			
$(C_6H_5)(CH_3)_2SiC{\equiv}CH$	91.5–93.5 (21)	37	C	75.00	74.78
			H	7.50	7.68
$(C_6H_5)_2CH_3SiC{\equiv}CH$	97.5–99.5 (0.25)	57	C	81.81	81.20
			H	6.31	6.46
$(C_6H_5)(CH_3)HSiC{\equiv}CH^b$	83–85 (21)	41			
$(CH_3)_2Si(C{\equiv}CH)_2^c$	83–84.5 (atm.)	30			
$(C_6H_5)(CH_3)Si(C{\equiv}CH)_2^d$	113–115 (21)	41			
$(C_6H_5)_2Si(C{\equiv}CH)_2^e$	136–137 (1); 43–44	59			
$(CH_3)_3SiC{\equiv}CSn(C_6H_5)_3$	74–76	61	C	61.75	61.32
			H	5.39	5.45
$(C_6H_5)(CH_3)_2SiC{\equiv}CSn(C_6H_5)_3$	41–42.5	48	C	65.90	65.65
			H	5.11	5.11
$(C_6H_5)(CH_3)Si[C{\equiv}CSn(C_6H_5)_3]_2$	100.5–102	33	C	64.98	64.68
			H	4.38	4.60
$(C_6H_5)_2Si[C{\equiv}CSn(C_6H_5)_3]_2$	124–125	38	C	67.10	67.70
			H	4.30	4.16
$(CH_3)_3SiC{\equiv}CSi(C_6H_5)_3$	42–44	73	C	77.53	77.60
			H	6.74	6.68

[a] Ref. 5: b.p. 53.5°; yield 52%. [b] Ref. 6: b.p. 92.5° (42 mm); no yield given. [c] Ref. 7: b.p. 85.5–86.5°; no yield given. [d] Ref. 8: b.p. 105° (20 mm); no yield given. [e] Ref. 8: m.p. 44–45°; yield 72%.

Trimethylchlorosilane (0.7 mole) was added in a dropwise manner to the freshly prepared ethynylmagnesium bromide. After the addition was finished, the solution was stirred for 5 h at room temperature. Hydrolysis was effected with 500 ml of ice–water and the upper layer was retained. A preliminary distillation of the upper layer permitted a separation of the trimethylethynylsilane from the bulk of the tetrahydrofuran. The distillate was washed a number of times with water, dried over anhydrous magnesium sulfate and redistilled to give about 48 g of trimethylethynylsilane, b.p. 52.5–53.5° (lit.[5] 53.5°). The average yield was approximately 70% for ten trials by this method.

Other terminal acetylenes. The synthetic results for the terminal acetylenes are reported in Table 1. The synthetic procedures were similar to that for trimethylethynylsilane up to the point of addition of the pertinent chlorosilane. After the addition of the chlorosilane was complete, these reaction mixtures were heated at 40–50° for 2 h and then allowed to stand overnight. The tetrahydrofuran was distilled from the upper layer obtained in the hydrolysis step. Each product was then purified by one or more distillations. The reported yields are of the final, redistilled products.

Syntheses of $[(C_6H_5)_3SnC{\equiv}C]_nSiR'_{4-n}$ *compounds*

All of the (stannylethynyl)silanes were prepared according to the preparation given below. Analyses, melting points and yields (based on the amount of triphenyltin chloride used) are listed in Table 1.

$(CH_3)_3SiC{\equiv}CSn(C_6H_5)_3$. A Grignard exchange reaction was effected by adding 0.06 mole of trimethylethynylsilane in 50 ml of tetrahydrofuran to 0.06 mole of ethylmagnesium bromide in 50 ml of tetrahydrofuran. When the evolution of ethane had ceased, 0.05 mole of triphenyltin chloride in 50 ml of tetrahydrofuran was added. The mixture was heated at 45° for 1.5 h. Hydrolysis with 100 ml of saturated aqueous ammonium chloride solution was then carried out. The upper layer was separated and dried over anhydrous magnesium sulfate. After filtration, the tetrahydrofuran was removed from the filtrate under aspirator vacuum. The oily residue was recrystallized twice from 2-propanol to give 8.1 g (61 %) of [(triphenyltin)-ethynyl] trimethylsilane, m.p. 74–76°.

Synthesis of $(CH_3)_3SiC{\equiv}CSi(C_6H_5)_3$. Trimethylethynylsilane (9.8 g; 0.1 mole) was added slowly to a solution of ethylmagnesium bromide (0.1 mole) in 125 ml of tetrahydrofuran. After the evolution of ethane had ceased and while the solution was still warm, a solution of triphenylchlorosilane (29.5 g; 0.1 mole) in 30 ml of tetrahydrofuran was added. The mixture was heated at reflux for 9 h and allowed to stand an additional 9 h at room temperature. Cooling the solution in ice precipitated magnesium salts which were removed by filtration. The filtrate was reduced in volume and cold hexane was added to complete the precipitation of magnesium salts. All solvent was removed from the filtrate obtained in the last precipitation procedure. The residue was recrystallized from 50 ml of hot n-hexane to which 50 ml of 2-propanol was added. White crystals slowly formed in the solution after standing in the refrigerator. Recrystallization from a 1:3 mixture of n-hexane and 2-propanol yielded 25.8 g of a white crystalline solid.

Hydrostannation of ethynylsilanes

A mixture of the ethynylsilane and one or two equivalents of freshly prepared triphenyltin hydride[9], depending upon the functionality of the ethynylsilane, was prepared and heated at 100–125° under nitrogen for 12–20 h. Normally between 10–20 mmoles of triphenyltin hydride were used in a reaction. After this time, the reaction mixture was stirred well with n-hexane and insoluble hexaphenylditin was removed by filtration. An oil or partly crystalline solid was usually obtained after removal of the solvent from the filtrate. These materials were recrystallized several times from n-hexane, 2-propanol or a mixture of these solvents.

The low boiling point of trimethylethynylsilane required that the reaction with this compound be carried out in a stainless steel bomb. A temperature of 175–185°

was maintained for 18 h. This appeared to be an optimum time.

The melting points, yields and analyses for these compounds are listed in Table 2. The percentage yields are of analytically pure products.

TABLE 2

MELTING POINTS, YIELDS AND ANALYSES OF *trans*-$R_nSi[CH{=}CHM(C_6H_5)_3]_{4-n}$ COMPOUNDS

Vinyl compounds	*M.p.* (°C)	*Yield* (%)	*Analyses* (%)		
				Calcd.	*Found*
$(CH_3)_3SiCH{=}CHSn(C_6H_5)_3$	72.5–74.5	70	C	61.50	61.15
			H	5.78	5.98
$(C_6H_5)(CH_3)_2SiCH{=}CHSn(C_6H_5)_3$	48.5–50.5	60	C	65.75	65.87
			H	5.47	5.63
$(C_6H_5)(CH_3)Si[CH{=}CHSn(C_6H_5)_3]_2$	95.5–96.5	36	C	64.68	64.73
			H	4.81	4.64
$(C_6H_5)_2Si[CH{=}CHSn(C_6H_5)_3]_2$	142–144	72	C	66.80	66.95
			H	4.70	4.64
$(CH_3)_3SiCH{=}CHSi(C_6H_5)_3$	92.5–94	91	C	77.10	77.05
			H	7.27	7.43
			Si	15.63	15.85
$(CH_3)_2Si[CH{=}CHSi(C_6H_5)_3]_2$	131–133	96	C	80.25	79.59
			H	6.36	6.30
			Si	13.38	13.62
$(C_6H_5)_2(CH_3)SiCH{=}CHSi(C_6H_5)_3$	126–128	48	C	82.20	82.29
			H	6.23	6.42
$(C_6H_5)(CH_3)Si[CH{=}CHSi(C_6H_5)_3]_2$	117–119	47	C	81.75	81.43
			H	6.09	6.09
$(C_6H_5)_2Si[CH{=}CHSi(C_6H_5)_3]_2$	146–148	42	C	82.90	83.00
			H	5.84	5.96

Hydrosilation of ethynylsilanes

The reactions between equivalent amounts of triphenylsilane (7–20 mmoles) and the mono- or diethynylsilane were carried out under nitrogen with the aid of approximately 5 mg of solid hexachloroplatinic acid as a catalyst. Varying reaction conditions were necessary to obtain the yields reported in Table 2. The reaction with trimethylethynylsilane was carried out at 35–40° for 0.5 h, while dimethyldiethynylsilane required a reaction time of 2.5 h at 50°. Methyldiphenylethynylsilane, diphenyldiethynylsilane and methylphenyldiethynylsilane were hydrosilated to give somewhat poorer yields of the vinylsilanes in spite of reaction at 90–100° for 20 h. Dark tars were also obtained in these reactions at the higher temperatures. The products were purified by recrystallization several times from n-hexane. The yields given in Table 2 are of analytically pure substances.

Polymer syntheses

Reaction of $(C_6H_5)(CH_3)Si(C{\equiv}CH)_2$ *with* $(C_6H_5)_2SiH_2$. Phenylmethyldiethynylsilane (5.1 g; 0.030 mole), diphenylsilane (5.5 g; 0.030 mole) and approximately 5 mg of solid hexachloroplatinic acid were mixed in a small flask under nitrogen. The contents of the flask became warm and solidified completely after stirring for 15 min. The dark mixture was taken up in hot benzene and treated with activated charcoal. The tacky solid which remained after evaporation of the benzene was triturated repeatedly with hot n-hexane. Evaporation of the filtered extracts and final removal of solvent under high vacuum gave 9.4 g (89%) of a yellow, tacky polymer which slowly solidified to a glassy, brittle solid after several weeks. (Found: C, 78.53; H, 6.99. $C_{23}H_{22}Si_2$ calcd.: C, 78.36; H, 5.96%.)

Reaction of $(CH_3)_2Si(C{\equiv}CH)_2$ *with* $(C_6H_5)_2SiH_2$. Dimethyldiethynylsilane (3.24 g; 0.030 mole) reacted exothermically with diphenylsilane (5.52 g; 0.030 mole) and the product was purified as described in the preceding preparation. A brown, viscous polymer weighing 7.2 g was obtained which became a brittle glass after several weeks. (Found: C, 75.35; H, 7.78. $C_{18}H_{20}Si_2$ calcd.: C, 73.97; H, 6.90%.)

RESULTS OF SYNTHESES

Although nearly three hundred alkynylsilanes have been listed in the literature[2], only approximately twenty of these are terminal ethynylsilanes. Furthermore the synthetic procedures for most of these monosubstituted acetylenes have not been well described, and frequently the yields are not reported. Therefore, we have reported here some of our results on the syntheses of ethynylsilanes even though these compounds are not all new.

With the availability of reasonable quantities of these terminal ethynylsilanes, we have been able to investigate certain of their chemical properties and uses. As a first step we have synthesized a number of new dimetalloid acetylenes and olefins. Unsymmetrical disubstituted acetylenes were prepared by the standard procedures shown in reactions (1) and (2). The terminal ethynylsilanes used as starting materials and the new dimetalloid acetylenes are listed in Table 1.

$$(4-n)C_2H_5MgBr+R_nSi(C{\equiv}CH)_{4-n} \rightarrow R_nSi(C{\equiv}CMgBr)_{4-n}+(4-n)C_2H_6 \quad (1)$$

$$R_nSi(C{\equiv}CMgBr)_{4-n}+(4-n)\,ClM(C_6H_5)_3 \rightarrow R_nSi[C{\equiv}CM(C_6H_5)_3]_{4-n}+(4-n)\,MgBrCl \quad (2)$$

where $n = 1, 2$; $M = Si$ or Sn; $R = CH_3, C_6H_5$ and/or H

The hydrometallation reactions of ethynylsilanes were found to proceed smoothly in fair to excellent yields according to reaction (3). It would seem reasonable to expect that the hexachloroplatinic acid catalyzed addition of triphenylsilane to terminal acetylenes would proceed by *cis*-addition[10], and that the sterically favorable *trans*-isomers would be formed. *trans*-Olefins would also be expected to result in the thermal hydrostannation reactions with triphenylstannane[11]. Infrared and PMR spectral data to be considered in the next section indicate that the *trans*-isomers appear to be formed exclusively.

$$R_nSi(C{\equiv}CH)_{4-n}+(4-n)\,(C_6H_5)_3MH \rightarrow R_nSi[CH{=}CHM(C_6H_5)_3]_{4-n} \quad (3)$$

where $R = CH_3$, C_6H_5 and $M = Sn$ or Si

Two hydrosilation reactions were carried out which yielded polymers. Diphenylsilane added very readily to dimethyldiethynylsilane or methylphenyldiethynylsilane in the presence of hexachloroplatinic acid according to reaction (4).

$$(C_6H_5)_2SiH_2+R_2Si(C{\equiv}CH)_2 \xrightarrow{\text{"Pt"}} -\!\!\left[CH{=}CH{-}SiR_2{-}CH{=}CH{-}Si(C_6H_5)_2\right]_n\!\!- \quad (4)$$

where $R_2 = (CH_3)_2$ or $(CH_3)(C_6H_5)$

Spectral evidence indicates that these polymers have *trans*-dimetalloid structures. A few examples of polymeric substances similar to those made here have been reported without structural assignment[12].

DISCUSSION

(1) *Infrared spectra*

(*a*) *Acetylenes.* Listed in Table 3 are selected infrared bands observed for the various acetylenes. The characteristic infrared active acetylenic CH and C≡C stretching vibrations for the ethynylsilanes in carbon tetrachloride appear in the very narrow spectral regions of 3295 ± 5 and 2043 ± 10 cm^{-1}, respectively. Asymmetrical disubstituted acetylenes show at most a weak C≡C stretching band near 2085 cm^{-1}. The fact that these C≡C stretching frequencies for the group IV acetylene derivatives are some 80–130 cm^{-1} lower than the corresponding absorption bands of analogous organic compounds has been previously considered and shown to be only partially accounted for in terms of mass effects on the vibrational modes[13]. Other absorption bands in the region 1400–980 cm^{-1} which arise from perturbed phenyl vibrations characteristic of the phenyl–silicon and phenyl–tin groupings[14] as well as other less specific phenyl modes are listed in Table 3 for assistance in the interpretation of the infrared spectra of the dimetalloid olefins to be considered in the next section.

(*b*) *Olefins.* The infrared spectra in the region 1400–900 cm^{-1} of the *trans*-dimetalloid olefins exhibit all of the bands observed for the corresponding acetylenes in this same region. A direct correspondence of the characteristic phenyl–silicon and phenyl–tin bands at 1110 ± 3 and 1074 ± 1 cm^{-1} and the other phenyl bands at 1026 ± 4 and 998 ± 1 cm^{-1} for the related *trans*-olefins and acetylenes is obvious upon comparison of the frequencies listed in Tables 3 and 4. This point is lucidly illustrated in Fig. 1 in which the actual spectra of $(C_6H_5)_3SnCH{=}CHSi(CH_3)_2(C_6H_5)$ and $(C_6H_5)_3SnC{\equiv}CSi(CH_3)_2(C_6H_5)$ are shown. The well-known band at 1250 cm^{-1} is characteristic of the CH_3–Si group and has not been listed in the Tables; it is present where expected. Further inspection of the two spectra shown in Fig. 1 reveals two

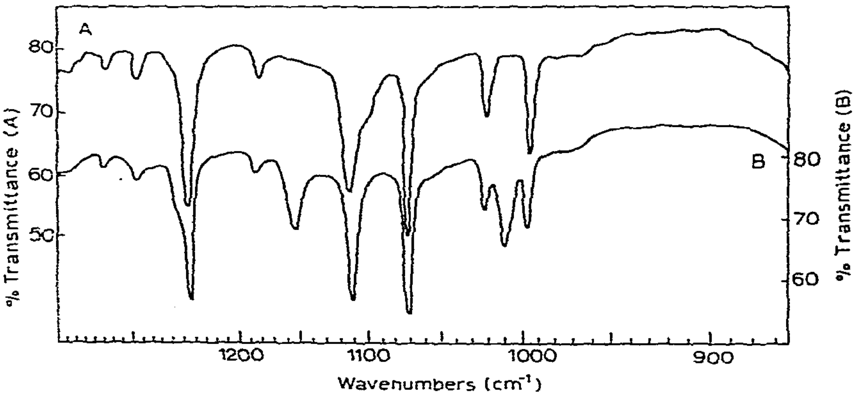

Fig. 1. Infrared Spectra of $(C_6H_5)(CH_3)_2SiC{\equiv}CSn(C_6H_5)_3$ (A) and of $(C_6H_5)(CH_3)_2SiCH{=}CHSn(C_6H_5)_3$ (B).

additional bands at 1159 and 1012 cm^{-1} for the *trans*-olefin which are not observed for the acetylene. We suggest that these bands arise from the vinyl CH in-plane [β(CH)] and out-of-plane [γ(CH)] vibrational modes. In general, the β(CH) and γ(CH) bands for trans organic olefins are found in the regions 1310–1290 and 980–960 cm^{-1}, respectively[15]. No other absorption bands of consequence are found in these regions for the dimetalloid olefins that are not also present in the spectra of the parent acetylene. It is interesting to note that one can differentiate between the Si/Si and Si/Sn derivatives since β(CH) for the former is found at 1170–1174 cm^{-1} whereas in the latter it appears at 1159–1160 cm^{-1}.

In the recent report by Mironov *et al.*[4] on the syntheses of some 1,2-digermyl- and 1-silyl-2-germylethylene derivatives, the presence of the *trans*-dimetalloid structure was proven by the weakness of the C=C stretching band in the infrared and its corresponding greater intensity in the Raman spectrum. We note in their published infrared spectra of these *trans*-olefins that bands, unassigned by them, are to be found in the regions 1000–1010 and 1180–1195 cm^{-1} which appear to correspond to those observed by us for our Si/Si and Si/Sn disubstituted olefins. Therefore, our observations complement those of the Russian workers and provide a simple method for the characterization of the *trans*-dimetalloid structure.

The two polymers reported here also appear to have an exclusive 1,2-*trans*-structure as their infrared spectra in the 1400–900 cm^{-1} region are virtually indistinguishable from those of the *trans*-disilicon substituted olefins.

(2) *Proton magnetic resonance spectra*

(*a*) *Acetylenes.* The existence of p_π–d_π bonding between vacant silicon 3*d* levels and the bonding π orbitals of the acetylenic triple bond has been said to account for the enhanced hydrogen bonding acidity[13], the diminished hydrogen bonding basicity[13], and the more rapid exchange of the acetylenic proton of an ethynylsilane relative to the corresponding properties of analogous organic acetylenes. This idea gains further support from the chemical shifts of the acetylenic protons of the ethynylsilanes as shown in Table 3. These signals appear at a significantly deshielded position (τ 7.5–7.8 ppm) compared to those of alkyl acetylenes (τ *ca.* 8.2 ppm) and suggest that the trimethylsilyl group is approximately as effective as the phenyl group as an electron withdrawing group when the silicon atom adjoins the unsaturated system. By contrast, when the silicon atom is insulated from the triple bond by a methylene group as in $(CH_3)_3SiCH_2C{\equiv}CH$, the chemical shift for the acetylenic proton is τ 8.33 ppm (10% in CCl_4)[17]. This indicates that bonding in this last compound between silicon and carbon is no longer synergic as the trimethylsilyl group is revealing its strong electron-donating capacity but can not remove charge from the triple bond through a back-π-bonding mechanism.

The data in Table 3 indicate that there is no unexpected deviation in the chemical shifts of the various types of protons with respect to the inductive properties of groups bonded to silicon. For example, in the series $(CH_3)_3Si$–, $(CH_3)_2(C_6H_5)Si$–, and $(CH_3)(C_6H_5)_2SiC{\equiv}CH$ the chemical shifts observed in 10% carbon tetrachloride solutions for both the methyl and the ethynyl protons are shifted to lower field in a stepwise manner as the methyl groups are replaced by phenyl groups. Other similar trends are readily apparent.

(*b*) *Olefins.* The pertinent PMR signals are reported in Table 4. The effect of

TABLE 3

SPECTRAL CHARACTERISTICS OF GROUP IV ACETYLENES

Compound	*Infrared* $(cm^{-1})^a$						*PMR (ppm)*^{b}	
	$\nu(CH)$	$\nu(C{\equiv}C)$	SiC_6H_5	SnC_6H_5	C_6H_5		$\tau({\equiv}CH)$	$\tau(SiCH_3)$
$(CH_3)_3SiC{\equiv}CH$	3292 s	2033 s					7.79	9.82
$(CH_3)_2(C_6H_5)SiC{\equiv}CH$	3300 s	2041 s	1117 s		1028 w	999 w	7.65	9.60
$(CH_3)(C_6H_5)_2SiC{\equiv}CH$	3295 s	2043 s	1114 s		1027 w	997 w	7.57	9.34
$(CH_3)_2Si(C{\equiv}CH)_2$	3292 s	2038 s					7.63	9.65
$(CH_3)(C_6H_5)Si(C{\equiv}CH)_2$	3300 s	2052 s	1117 s		1028 w	999 w	7.52^c	9.45^c
$(C_6H_5)_2Si(C{\equiv}CH)_2$	3297 s	2044 s	1110 s 1118 s		1028 w	999 w	7.46	
$(CH_3)(C_6H_5)(H)SiC{\equiv}CH$	3291 s	2038 s	1117 s		1028 w	998 w	7.64^d	9.60^d
$(CH_3)_3SiC{\equiv}CSi(C_6H_5)_3$		inact.	1112 s		1025 w	998 w		9.73
$(CH_3)_3SiC{\equiv}CSn(C_6H_5)_3$		2080 w		1075 s	1023 w	998 w		9.75
$(CH_3)_2(C_6H_5)SiC{\equiv}CSn(C_6H_5)_3$		2079 w	1116 s	1075 s	1023 w	998 w		9.53
$(CH_3)(C_6H_5)Si[C{\equiv}CSn(C_6H_5)_3]_2$		2087 w	1113 s	1076 s	1023 w	999 w		9.32
$(C_6H_5)_2Si[C{\equiv}CSn(C_6H_5)_3]_2$		2087 w	1111 s 1116 s	1076 s	1023 w	999 w		

[a] 10% in CCl_4; intensities: s = strong, m = medium, w = weak. [b] Approximately 10% in CCl_4 except [c] as pure liquid. [d] Doublet; $\tau(SiH)$ appears as octet centered at 5.27 ppm; $J(H\text{-}Si\text{-}C\text{-}H)$ 4.0 cps, $J(H\text{-}Si\text{-}C{\equiv}C\text{-}H)$ 1.1 cps.

TABLE 4

SPECTRAL CHARACTERISTICS OF *trans*-DIMETALLOID OLEFINS

	Infrared (cm^{-1})[a]						PMR (ppm)[a]	
	$\beta(CH)$[b]	SiC_6H_5	SnC_6H_5	C_6H_5	$\gamma(CH)$[b]	C_6H_5	$\tau(SiCH_3)$	$\tau(HC{=}CH)$[c]
$(CH_3)_3SiCH{=}CHSi(C_6H_5)_3$	1174 m	1108 s		1030 w	1014 m	999 w	9.89	3.06 (28.4; 22.8)
$(CH_3)_3SiCH{=}CHSn(C_6H_5)_3$	1160 mw		1073 s	1022 w	1011 mw	998 w	9.88	2.95 (28.2; 22.6)
$(CH_3)_2(C_6H_5)SiCH{=}CHSn(C_6H_5)_3$	1159 mw	1113 s	1075 s	1023 w	1012 mw	999 w	9.62	2.83[d] (J 22.8)
$(CH_3)(C_6H_5)_2SiCH{=}CHSi(C_6H_5)_3$	1172 mw	1110 s		1030 w	1015 mw	998 w	9.37	[e]
$(CH_3)_2Si[CH{=}CHSi(C_6H_5)_3]_2$	1172 m	1111 s		1029 w	1013 m	998 w	9.77	3.03 (31.6; 22.8)
$(CH_3)(C_6H_5)Si[CH{=}CHSi(C_6H_5)_3]_2$	1172 mw	1109 s		1029 w	1013 mw	998 w	9.50	2.89 (29.0; 22.8)
$(CH_3)(C_6H_5)Si[CH{=}CHSn(C_6H_5)_3]_2$	1159 mw	1111 m	1075 s	1023 w	1013 mw	999 mw	9.47	2.73 (29.2; 22.5)[d]
$(C_6H_5)_2Si[CH{=}CHSi(C_6H_5)_3]_2$	1172 mw	1111 s		1029 w	1015 mw	998 mw		[e]
$(C_6H_5)_2Si[CH{=}CHSn(C_6H_5)_3]_2$	1159 mw	1109 m	1074 s	1023 w	1012 mw	999 w		[e]
$\left[CH{=}CHSi(C_6H_5)(CH_3)CH{=}CHSi(C_6H_5)_2\right]_n$	1170 s	1109 s		1028 w	1016 s	998 w		
$\left[CH{=}CHSi(CH_3)_2CH{=}CHSi(C_6H_5)_2\right]_n$	1170 m	1110 s		1029 w	1012 m	998 w		

[a] Approximately 10% in CCl_4. [b] See text. [c] Center of AB quartet; Q and J values (in cps) in parentheses, respectively. [d] Estimated. [e] Indeterminable with certainty.

p_π–d_π bonding between silicon and the olefinic double bond on the lowering of the chemical shift of vinyl protons has been discussed[18]. For the dimetalloid olefins studied here, the chemical shifts appear in the τ 3 ppm region. This indicates that there is an additive deshielding effect when two Group IV atoms are attached to the double bond. The PMR spectrum of *trans*-$(CH_3)_3SiCH{=}CHSi(C_6H_5)_3$ is shown in Fig. 2. The vinyl protons in this compound are seen to interact to yield an AB quartet. Three lines of this quartet are observable at τ 3.00, 3.12 and 3.49 ppm; the fourth line, expected to appear at τ 2.73 ppm, is hidden beneath the signals of the aromatic protons. Values for Q_{AB} and J_{AB} were obtained for the various compounds and are listed in Table 4[19]. The J_{AB} values of 22–23 cps are in excellent agreement with trans coupling constants observed for simpler silicon and tin vinyl systems[18,20,21]. The relative intensities of the inner lines to the outer lines of the AB quartet are expected to be around 9 : 1 when calculated from Q_{AB} and J_{AB}. This ratio is observed experimentally in each case where a comparison between theory and observation is possible. For $(CH_3)_2(C_6H_5)$-$SiCH{=}CHSn(C_6H_5)_3$ only the two high field lines, one weak and one strong, were observable and so only an estimate of the center of the AB quartet is listed in Table 4. With $(CH_3)(C_6H_5)Si[CH{=}CHSn(C_6H_5)_3]_2$, the two weak outer lines were observed straddling the aromatic proton signals; one band within the aromatic proton envelope appeared to correspond well with the expected position for one of the stronger lines of the AB quartet and was used to determine the Q_{AB} and J_{AB} values for this compound. It appears from the data in Table 4 that the triphenyltin group is slightly more effective in the deshielding of vinyl protons than is the triphenylsilyl group. The spectrum of the last compound readily illustrates this point. This deshielding effect of tin has been recognized before and would seem to be explicable as a result of p_π–d_π bonding between vacant 5*d* orbitals on tin and the filled π orbitals of the double bond[18].

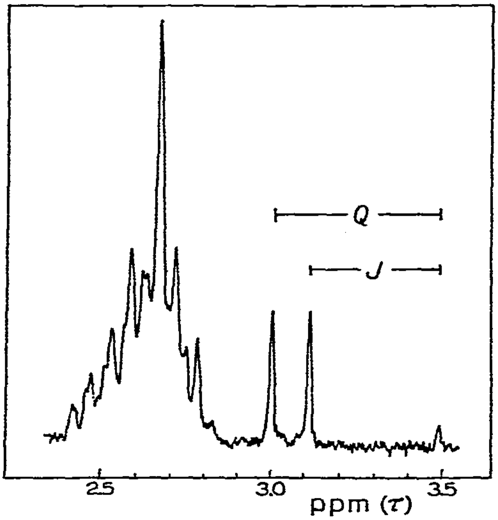

Fig. 2. PMR spectrum of $(CH_3)_3SiCH{=}CHSi(C_6H_5)_3$ in CCl_4. See text for assignments.

Simple inductive effects are operative in these olefinic systems as they were for the acetylenes. As expected, the vinyl protons appear to be more shielded when the silicon atoms bear methyl groups rather than phenyl groups.

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SUMMARY

Syntheses are reported for new dimetalloid acetylenes and olefins with the general structures $R_nSi[C{\equiv}CSi(C_6H_5)_3]_{4-n}$, $R_nSi[C{\equiv}CSn(C_6H_5)_3]_{4-n}$, *trans*-$R_nSi[CH{=}CHSi(C_6H_5)_3]_{4-n}$ and *trans*-$R_nSi[CH{=}CHSn(C_6H_5)_3]_{4-n}$ where $n = 2$ or 3 and $R = CH_3$ and/or C_6H_5. Characteristic infrared and proton magnetic resonance spectral data are given.

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