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THE SYNTHESIS OF 2-SILANORCARANES*,**

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SUMMARY

2,2-Dimethyl-2-silanorcarane has been prepared by the stepwise reduction of 7,7-dibromo-2,2-dimethyl-2-silanorcarane with tri-n-butyltin hydride. Treatment of the dibromonorcarane with silver ion or pyrolysis with quinoline releases hydrogen bromide and decomposes the ring system. Trimethyl(dimethylamino)stannane reduces the dibromo compound to a 1.5/1 mixture of the *endo*- and *exo*-isomers of 7-bromo-2,2-dimethyl-2-silanorcarane in the first known reaction of the tin–nitrogen bond to proceed by a radical mechanism. β-Elimination of bromine is favored *endo* > *exo* in the mass spectrometer.

The 7,7-dibromo compound is prepared by a series of steps which include the hydrosilylation of 5-chloro-1-pentyne by trichlorosilane, the intramolecular Barbier cyclization of the product, the methylation of the resulting 1,1-dichloro-1-sila-2-cyclohexene, and the action of a dihalocarbene generated from phenyl(tribromomethyl)mercury on this silacyclohexene. The dibromonorcarane is formed in 50% yield, but a side reaction produces 5-(dimethylbromosilyl)-1-pentene, which was identified as its hydrolysis product, $[CH_2{=}CH(CH_2)_3Si(CH_3)_2]_2O$. Deuteration experiments establish that the process of ring-opening is concerted, and the observation of resonances due to a transient β-addition product in the NMR leads to the proposal of an HBr-addition β-elimination mechanism for ring-opening which appears to apply to several examples of unsaturated sila- and germacarbocycles in general. Hydrostannation of 5-chloro-1-pentyne by dimethyltin hydride chloride leads to the dimethylchlorostannyl-substituted 5-chloro-1-pentene which undergoes alkyl group redistribution to form a mixture of alkyltin chlorides.

INTRODUCTION

Subtle differences between carbon and the lower members of the fourth group may be studied in the role these elements play in the chemistry of carbocyclic systems where heteroatoms are substituted for ring carbons. Bicyclic systems undergo easy

* A preliminary account of this work was presented at the 158th National Meeting, A.C.S., New York City, September, 1969.
** 2-Silanorcarane = 2-silabicyclo[4.1.0]heptane.
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rearrangement, and have an even richer chemistry still. An investigation of the chemistry of 7-norbornadiene derivatives has recently been completed in this laboratory[1]. We now report synthesis and some reactions of the related fused-ring system, the 2-silanorcaranes.

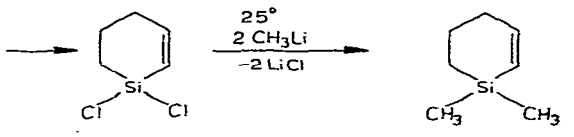
RESULTS AND DISCUSSION

The organic 7,7-dihalo[4.1.0]bicycloheptane is readily synthesized from cyclohexene and a dihalocarbene. The analogous 1,1-dichloro- and 1,1-diphenyl-1-sila-2-cyclohexenes have been synthesized by hydrosilylation of 5-chloro-1-pentyne followed by an intramolecular Barbier reaction[2]:

$$Cl_3SiH + HC{\equiv}C(CH_2)_3Cl \longrightarrow Cl_3SiCH{=}CH(CH_2)_3Cl \xrightarrow[\text{ether}]{Mg}$$

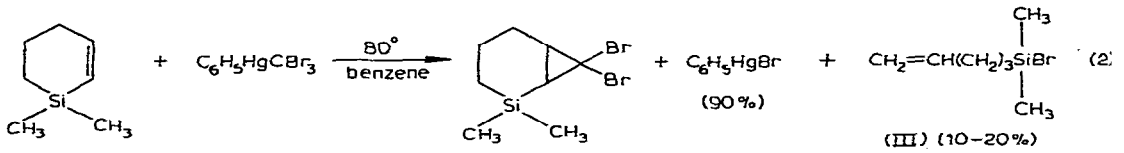
cis/*trans* 3/1

(1)



(I)

1,1-Dimethyl-1-sila-2-cyclohexene (I), prepared as shown in eqn. (1), proved to be excellent starting point for the preparation of the bicyclic compound since the methyl groups confer both greater volatility and ease of spectroscopic identification on the resulting product. We chose to generate the dihalocarbene by thermolysis of phenyl-(tribromomethyl)mercury, since the closely-related 1,1-dibromo-2-(trimethylsilyl)-cyclopropane could be prepared from trimethylvinylsilane in good yield using this reagent[3]. Standard methods of producing dihalocarbene afford the silyl-substituted cyclopropanes in very small yield (ca. 0.1%)[4]. The thermolysis of the mercurial reagent[5,6] was carried out in benzene in the presence of a 2/1 molar excess of (I):

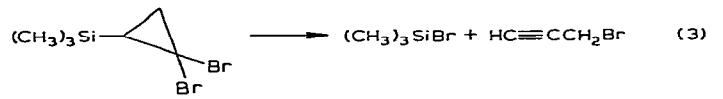


(2)

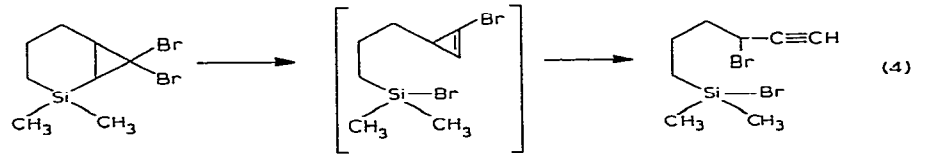
Compound (III), 5-(dimethylbromosilyl)-1-pentene, was identified as its hydrolysis product, $[CH_2{=}CH(CH_2)_3Si(CH_3)_2]_2O$ which exhibits a molecular ion $m/e=270$ (mol.wt.=270) and intense $P-69^+$ and $P-97^+$ fragments which can be assigned to the structures $[CH_2{=}CH(CH_2)_3Si(CH_3)_2OSi(CH_3)_2]^+$ and $[CH_2{=}CHCH_2Si(CH_3)_2OSi(CH_3)_2]^+$, respectively.

2,2-Dimethyl-7,7-dibromo-2-silanorcarane (II) (b.p. 65°/0.02 mm) exhibits two methylsilane resonances in the NMR, consistent with the puckered geometry of

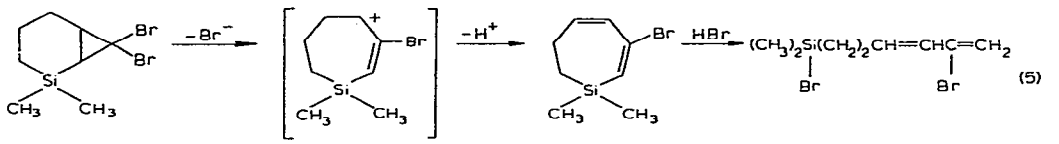
the ring system, but the mass spectrum lacks a parent ion. The two most abundant fragments are found at *m/e* 203 (a polyisotopic 1/2/1 pattern) and 138 (a 1/1 pattern), characteristic of di- and monobromine fragments, respectively. We assign these as $CH_3SiBr_2^+$ and $(CH_3)_2SiBr^+$, where the formation of the latter can be rationalized in terms of a β-elimination mechanism. The formation of the dibromosilane probably occurs in a secondary rearrangement. The apparent facility with which (II) undergoes β-elimination in the low-density, gas phase in the mass spectrometer is consistent with the known solution behavior of silyl-substituted, *gem*-dihalocyclopropanes[7]:



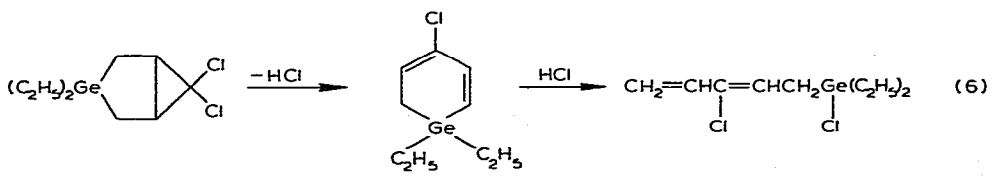
The formation of (III) warrants further discussion. Ring-opening of (II) by β-elimination would be expected to give a terminal acetylene by analogy with the behavior depicted in eqn. (3):



Expansion of the ring, on the other hand, followed by or accompanied by silicon–carbon bond cleavage, would be expected to give a silacycloheptadiene by analogy with the rearrangement of the organic 7,7-dibromonorcarane to 1,3,5-cycloheptatriene which has been shown to proceed through disrotatory opening of the fused cyclopropyl ring to an allylic cation, followed by loss of a proton[8,9]:



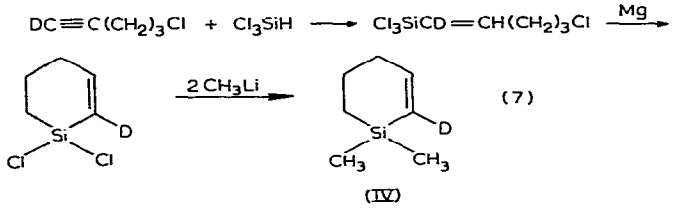
This latter type of rearrangement has been shown recently to take place in the thermolysis of the closely-related 3,3-diethyl-6,6-dichloro-3-germa[3.1.0]bicyclohexane[10], but neither of the rearrangements depicted in eqns. (4) or (5) leads to a terminal olefin of the type represented by (III).



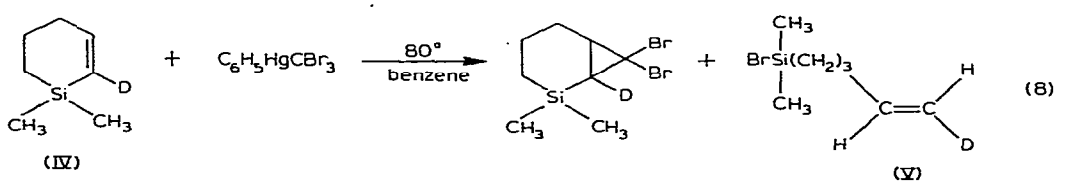
Pyrolysis of (II) in the presence of quinoline, a procedure which serves to convert the organic 7,7-dibromonorcarane to cycloheptatriene[9], results in the

formation of quinoline hydrobromide at 200°, but no volatile silicon-containing compounds are formed. Silver ion, which serves to rearrange 7,7-dibromonorcaranes to cycloheptenones under mild conditions[11], precipitates silver bromide from (II) immediately at room temperature, but GLC analysis reveals at least nineteen components with none predominating. The instability of (II) toward hydrogen bromide release is also shown by its behavior on prolonged heating in refluxing benzene where extensive charring accompanies hydrogen bromide evolution or even at room temperature where 10–20% decomposition occurs in 4 weeks.

In order to elucidate further the pathway to (III), we synthesized the 2-deuterio derivative of (I) by deuterium oxide exchange with the starting acetylene; hydrosilylation of the resulting 1-deuterio-5-chloro-1-pentyne, Barbier reaction and methylation:

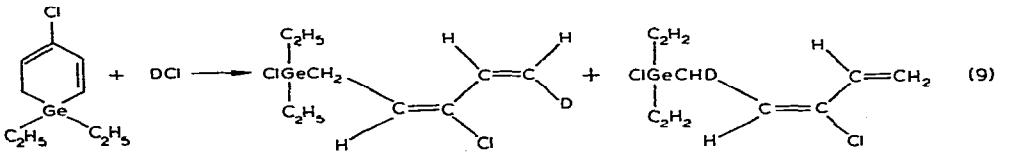


The reaction of the 2-deuterio-1,1-dimethyl-1-sila-2-cyclohexene (IV) with the mercurial reagent[5,6] gave, in addition to the 1-deuterio-substituted derivative of (II), *trans*-1-deuterio-5-(dimethylbromosilyl)-1-pentene (V) as the only ring-opened product:



The NMR spectrum of the olefinic region of (V) is shown in Fig. 1. The splitting pattern is consistent only with the *trans*-isomer. This establishes the stereospecific nature of the cleavage of the silicon–carbon bond in the 1,2-position of (I).

During the course of this work it was reported that the cleavage of 1,1-diethyl-4-chloro-1-germa-2,4-cyclohexadiene by deuterium chloride is stereospecific as well[10]:



and produces only the *cis*-product. Decomposition of (II) could be the source of the hydrogen bromide needed to give the ring-opened product (III).

Treatment of (I) with anhydrous hydrogen bromide gas in benzene gives (III)

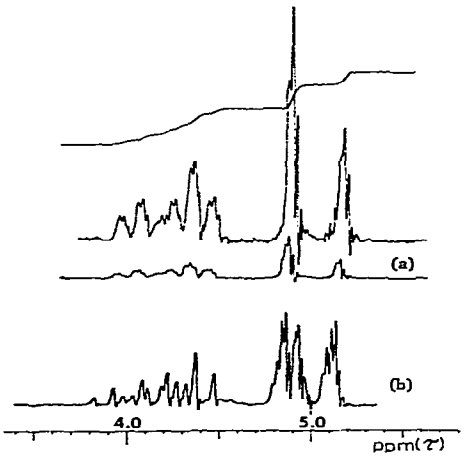
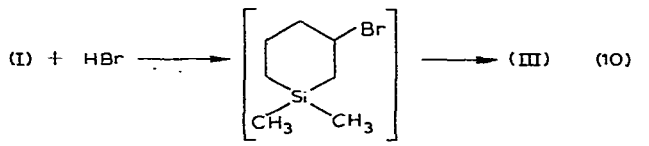


Fig. 1. (a) olefinic region of the NMR spectrum of (V); (b) olefinic region of the NMR spectrum of (III).

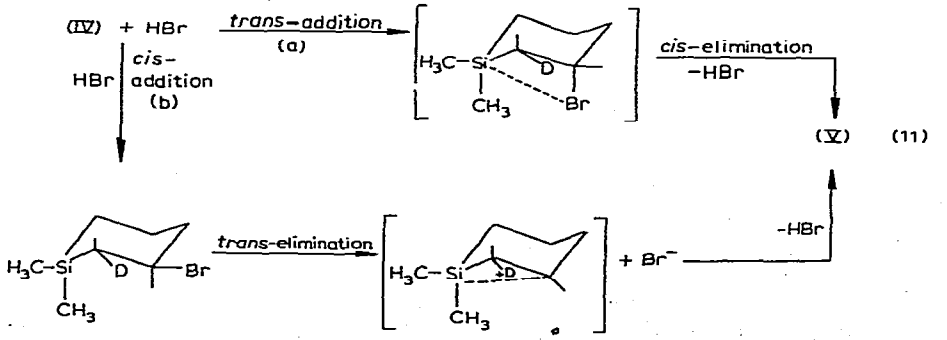
quantitatively. During the conversion the spectrum of the product was accompanied by a transient multiplet which developed on successive NMR sweeps at room temperature in the region associated with halo-substituted methylene groups (6.7 τ) and then vanished on refluxing. This observation is consistent with the intermediate addition product (VI):



(VI)

Hydrogen bromide addition to the acyclic trimethylvinylsilane gives the β-substituted product exclusively[12]. The resulting 2-bromoethylsilane decomposes under mild conditions to ethylene and trimethylbromosilane, while the α-substituted product is stable[13,14]. Phenylmercuric bromide has no effect on (I) under the conditions of the preparation of (III) in eqn. (2). Hydrogen bromide addition to allylsilanes gives the β-halo product as well which decomposes above 40° [15].

There are two possible reaction paths leading to (V):



Pathway (b), proceeding through the silicon-bridged, non-classical carbonium ion, has been suggested as an explanation for the *trans*-β-elimination observed in (β-

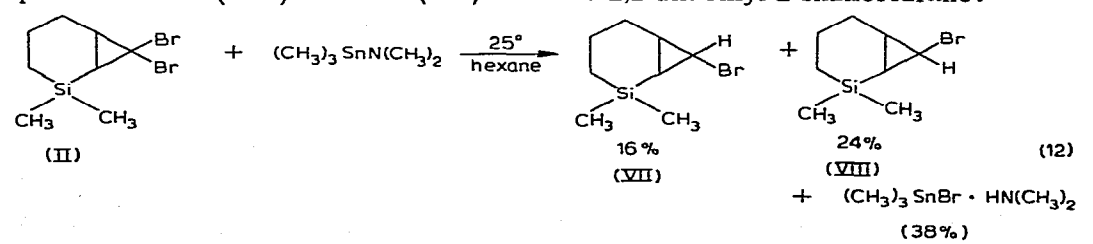
haloalkyl)silanes in highly polar media[16,17]. The four-centered intermediate in pathway (a) has been suggested to explain the thermal decomposition of (β-haloalkyl)-silanes in non-polar media and the gas phase[18]. That addition of HBr to cyclohexene is predominantly *trans*-[19], and that the stereochemistry of the cyclohexane ring system would permit easy formation of a four-centered intermediate lends credence to pathway (a). However, in a medium capable of supporting ions, *cis*-addition would predominate. This is unlikely in our reactions since evidence for the existence of the ionic intermediate in pathway (b) has been obtained only for highly polar media such as acetic acid or aqueous alcohol. The four-centered intermediate is more likely in a thermal decomposition in benzene.

Vinylgermanes undergo exclusive β-addition of HX, and the products can be isolated; allylgermanes undergo cleavage during addition of HX[19]. Our system (I) contains only a vinylsilane bond. The (β-bromoethyl)silanes are known to lack thermal stability[12], and as expected, we observe the ring-opening of (I) with hydrogen bromide. It appears, therefore, that the *axial*-positions of the halide atoms in the silacyclohexane system as initially formed facilitate ring opening by a concerted β-elimination which is enhanced by *juxta*-position to the ring metalloid atom of the already specially reactive β-halogen.

The easy decomposition of (II) to release hydrogen bromide can also be rationalized by a β-elimination mechanism. The puckered shape of the 7,7-dibromo-norcarane ring system places the *endo*-bromine atom directly above the ring silicon in all possible conformations of the ring. The ring opening at the 1,2-position could proceed via formation of a silicon–bromine bond. The isolation of quinolinium hydrogen bromide, followed by further decomposition [see eqn. (5)]. Seyferth *et* tion of silver bromide on treatment with alcoholic silver nitrate suggests, however, that ring expansion to the silacycloheptadiene may be occurring first with release of hydrogen bromide, followed by further decomposition [see eqn. (5)]. Seyferth, *et al.*[10] have made a rough measure of the relative rates of these two competing decomposition processes in the rearrangement of the related 6,6-dichloro-3-germa-[3.1.0]bicyclohexanes [see eqn. (6)]. Concerted germanium–carbon bond cleavage was found to be approximately four times faster than hydrogen chloride elimination[10]. On this basis we reason that the decomposition of (II) is taking place with β-elimination as the initial step. Definitive proof must await isolation of the intermediate (VI).

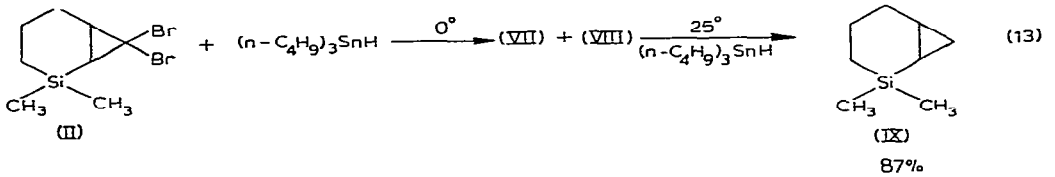
The recent interest generated by the discovery by Cardin and Lappert[2] of the use of (dimethylamino)trimethylstannane as a powerful and highly specific dehydrohalogenating agent led us to try the reaction of (II) with this compound. The mild conditions and ease of separation of the solid complex $(CH_3)_3SnX \cdot HN(CH_3)_2$ product make this method particularly attractive.

Surprisingly, the reaction proceeds at room temperature to give the reduction products *endo*- (VIII) and *exo*- (VII) 7-bromo-2,2-dimethyl-2-silanorcarane:



The mass spectrum of each compound shows a molecular ion with the polyisotopic bromine features centered at *m/e* 219, a $P-15^+$ fragment ion, and a bromine-bearing ion at *m/e* 138 which can be assigned to $(CH_3)_2SiBr^+$. This latter ion was the most prominent feature in the mass spectra of both compounds. It is interesting to note that the relative intensities of the other ions are approximately 10% lower in the *endo*-isomer (VIII) where β-elimination would be expected to be favored. The two isomers could be distinguished by their NMR spectra. The *endo*-isomer (VIII) with its cyclopropyl protons *cis*- would be expected to show larger spin–spin coupling than the *exo*-isomer (VII) where these protons are *trans*[22]. Thus (VIII) exhibits a doublet of doublets centered at 6.5 τ with *J* values of 6.4 and 8.4 Hz, while (VII) shows a doublet of doublets centered at 7.3 τ with *J* values of 3.0 and 5.0 Hz.

A reasonable mechanism for the observed reduction of (II) to (VII) and (VIII) involves a free radical. The same products are obtained in the absence of solvent. Tin-containing radicals are known to abstract hydrogen from reactants or from solvent[23]. The radical inhibitor galvinoxyl slowed the reaction rate, as expected, but the same products were obtained, suggesting short radical chain lengths[24]. *gem*-Dibromocyclopropanes are reduced readily by tri-n-butyltin hydride, and such reactions have been shown to be radical chain processes[25,26]. The reaction of tri-n-butyltin hydride with (II) proceeds stepwise:



(13)

The product carbosilane heterocycle exhibits a parent molecular ion and an intense fragment at $P-15^+$ in the mass spectrum. A cracking scheme is proposed in Fig. 2, where a McLafferty rearrangement occurs to generate the most intense feature in the spectrum at *m/e* 97 ($P-43^+$) which we assign as shown. The NMR spectrum contains two methylsilicon resonances.

The slow rate of the second step of eqn. (13) enables the stereochemistry of the first step to be studied. The ratio of (VI) to (VII) remained at 1.5/1 throughout the course of the reaction, the same as that observed in the reaction of (II) with the tin amide, suggesting a similar mechanism for both reactions. Thus the reaction depicted in eqn. 12 may constitute the first example of a tin amide, which normally reacts by polar mechanisms[21], taking part in a radical process. There is precedent, however, in the reaction of 7,7-dibromonorcarane by a radical process with methylmagnesium bromide, another reagent which usually reacts in a polar fashion[27], to give the reduction products where the ratio of *endo*- to *exo*- was found to be 2.5/1, the same as that obtained in the reduction of 7,7-dibromonorcarane with tri-n-butyltin hydride[25]. The slight loss of stereospecificity (*endo*/*exo*-changes from 2.5/1 to 1.5/1) in our reaction is probably associated with additional crowding by the methyl groups at silicon. These unusual reaction pathways may be due in part to the general inability of halocyclopropane systems to undergo polar displacement reactions[28]. For example, we find (II) to be inert toward lithium aluminum hydride reduction. Proof of the mechanism must await identification of the source of the abstracted hydrogen.

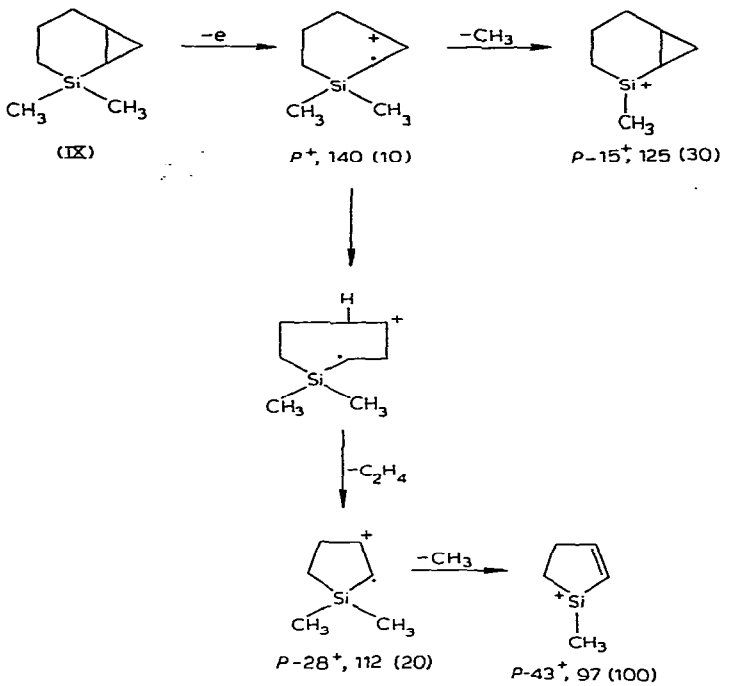


Fig. 2. Cracking scheme for silicon-containing fragments from (VIII).

We have carried out a preliminary investigation into the synthesis of the tin analogue of (I). We chose to use the very reactive dimethyltin hydride chloride[29] for the hydrostannation of 5-chloro-1-pentyne. Following the procedure of Kennedy and Kuivila[29], we were able to produce the hydride chloride *in situ* by a 1/1 exchange between dimethyltin dichloride and dihydride.

$$(CH_3)_2SnCl_2 + (CH_3)_2SnH_2 \overset{-70°}{\rightleftharpoons} 2\,(CH_3)_2SnHCl$$

$$\overset{25°,\ HC{\equiv}C(CH_2)_3Cl}{\downarrow}$$

$$(CH_3)_2\underset{Cl}{Sn}CH{=}CH(CH_2)_3Cl \qquad (14)$$

65%; [*cis*/*trans* = 3/1]

The NMR spectrum of the product revealed three sets of methyltin resonances, each consisting of two absorptions in a ratio of 3/1. This suggests that redistribution has taken place:

$$2\,(CH_3)_2\underset{Cl}{Sn}CH{=}CH(CH_2)_3Cl \rightleftarrows CH_3\overset{Cl}{\underset{Cl}{Sn}}CH{=}CH(CH_2)_3Cl + (CH_3)_3SnCH{=}CH(CH_2)_3Cl \qquad (15)$$

Tin tetrachloride, another possible component of the mixture, would not be detected.

This result is not surprising in light of the known lability of the alkyl groups in organotin halides[30]. Redistribution of the chloropentene groups could not be established with confidence because of the complexity of the olefinic region in the NMR spectrum. Attempts to cyclize the crude reaction product of eqns. (14) and (15) by an intramolecular Barbier reaction have failed.

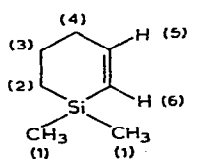
EXPERIMENTAL

General

Melting points were recorded on a Townson and Mercer melting point apparatus and are uncorrected. Boiling points are uncorrected. IR spectra were recorded using Perking–Elmer Infracord 237 and 337 and Beckman IR-8 models. UV spectra were recorded using a Cary Model 14. Varian A-60, A-60A and HA-100D spectrometers were used for recording the NMR spectra with tetramethylsilane or benzene as the internal standard. Gas chromatographic analyses were performed on F & M Model 810 and Hewlett–Packard Model 5750 Laboratory Chromatographs equipped with thermal conductivity detectors with helium as the carrier gas. The columns used in all cases were a six foot, 1/8 inch column containing 10% UCW-98 (silicon oil) on Chromosorb W for analytical purposes and a 12 foot, 1/2 inch column containing UCW-98 (silicone oil) on Chromosorb W for preparative work. Volatiles were collected at −196° in U-tubes. Mass spectra were measured on an AEI-MS902 high resolution mass spectrometer at 70 eV. Elemental analyses and molecular weight determinations were performed by Galbraith Analytical Laboratories, Knoxville, Tennessee. Analysis for silicon and tin were performed gravimetrically by conversion to their respective dioxides. Commercial starting materials were distilled before use. All reactions were carried out in an atmosphere of prepurified nitrogen.

Preparation of 1,1-*dimethyl*-1-*sila*-2-*cyclohexene* (*I*)

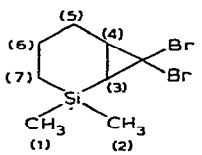
Methyllithium–lithium bromide complex in ether (126 ml, 0.71 g/cc, 0.82 mole) was added to a three-necked flask fitted with a dropping funnel, a Friedrichs condenser, a gas inlet tube and a magnetic stirrer while a positive pressure of nitrogen was maintained. 1,1-Dichloro-1-sila-2-cyclohexene[3] (28.5 g, 0.23 mole) in anhydrous ether (35 ml) was added dropwise with stirring. After addition of the silane was complete the reaction mixture was stirred for an additional 30 min, cooled to 0° with an ice bath, and the excess lithium reagent hydrolyzed with water (150 ml). The ether layer was washed with water (50 ml) and the water layer extracted twice with ether (50 ml). The combined ether layer and extracts were dried over anhydrous magnesium sulfate and the ether distilled at atmospheric pressure using a 12 cm Vigreux column. The residue distilled at 130–132° to give the product in 83% yield (18.0 g) and GLC analysis of the distillate at 120° showed the compound to have greater than 95% peak purity: (Found: C, 66.11, H, 10.97. $C_7H_{14}Si$ calcd.: C, 66.66; H, 11.11%.)



UV in cyclohexane: λ_{max} 213 nm. IR neat on KBr plates: 2960 s, 2940 s, 2920 s, 2860 m, 1600 m(sh), 1460 m, 1440 m, 1250 s, 1120 m, 900 m, 850 s, 800 s, 760 m, 710 m, 650 m cm^{-1}. NMR in CCl_4: τ(H1) 10.0 (6H, s); τ(H2) 9.1–9.5 (2H, m); τ(H3) and τ(H4) 7.3–8.1 (4H, m); τ(H5) 1.9 (1H, 2t); τ(H6) 3.2 (1H, 2t); J(H5–H6) 14.0 Hz; J(H4–H6) 1.5 Hz; J(H4–H5) 4.0 Hz. Mass spectrum: *m/e* 126 (P^+, 50%), 111 (P–15$^+$, 100%), 98 (P–28$^+$, 20%, $[CH_2CH{=}CHSi(CH_3)_2]^+$), 83 ($P$–43$^+$, 30%).

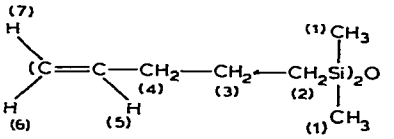
Preparation of 7,7-dibromo-2,2-dimethyl-2-silanorcarane (II).

Phenyl(tribromomethyl)mercury[5,6] (72.5 g, 0.137 mole) was placed in a 500 ml three-necked flask fitted with a condenser, a gas inlet and a magnetic stirrer. The flask was evacuated, filled with nitrogen, and benzene (200 ml) dried over potassium metal was distilled in. 1,1-Dimethyl-1-sila-2-cyclohexene (34.0 g, 0.27 mole) was added and the mixture brought to reflux while stirring. Almost all of the phenyl(tribromomethyl)mercury had dissolved by the time reflux temperature was reached. After refluxing for 2 h the reaction mixture was cooled and then filtered. Phenylmercuric bromide (45.8 g, 93%, m.p. 283–285°) was recovered. Benzene was removed from the filtrate on a rotary evaporator at 25°/16 mm and excess olefin was removed by trap to trap distillation at 25°/10^{-3} mm. The residue distilled at 67–70°/0.02 mm to give the product in 50% yield (20.8 g). The product was purified further by distillation on a Teflon-coated spinning band column at 65°/0.02 mm, and GLC analysis at 150° showed the product to be greater than 95% pure: (Found: C, 32.46; H, 4.70; Br, 53.12; Si, 9.18; mol.wt., osmometric in benzene, 310. $C_8H_{14}Br_2Si$ calcd.: C, 32.23; H, 4.73; Br, 53.61; Si, 9.42%; mol.wt., 298.)



IR in CCl_4: 2920 m, 2850 m, 1545 m, (br), 1250 s, (sh), 995 s, 875 m cm^{-1}. NMR in CCl_4: τ(H1) 9.9 (3H, s); τ(H2) 9.7 (3H, s); τ(ring protons) 8.0–9.8 (8H, m). Mass spectrum: *m/e* 203 {t, 1/2/1, 10%. $[(CH_3)_2SiBr_2]^+$}, 138 {d, 1/1, 100% $[(CH_3)_2SiBr]^+$}.

The distillate from the trap to trap distillation at 25°/10^{-3} mm contained a second compound (3.5 g, 15%) in addition to 1,1-dimethyl-1-sila-2-cyclohexene. The compound was purified by preparative GLC at 175° and identified as 6,6,8,8-tetramethyl-7-oxa-6,8-disila-1,12-tridecadiene. (Found: C, 61.65; H, 10.88. $C_{14}H_{34}OSi_2$ calcd.: C, 62.22; H, 11.11%.)



UV in CCl_4: λ_{max} 230 nm. IR neat on KBr plates: 3090 m, 2970 s, 2930 s, 2890 s, 2870 s, 1645 m, 1440 m, 1415 m, 1255 s, 1065 s, (br), 910 m, 840 s, 790 s cm^{-1}.

NMR in CCl_4: τ(H1) 9.9 (6H, s); τ(H2) 9.5–9.8 (2H, m); τ(H3) 8.5–8.9 (2H, m); τ(H4) 7.8–8.2 (2H, m); τ(H5) 4.0–4.5 (1H, m); τ(H6) and τ(H7) 4.9–5.2 (2H, m); J(H5–H7) 17.0 Hz, J(H4–H5) 7.0 Hz. Mass spectrum: *m/e* 270 (P^+, 1%), 255 (P–15^+, 5%), 201 {P–69^+, 80%, $[CH_2{=}CH(CH_2)_3Si(CH_3)_2OSi(CH_3)_2]^+$}, 173 {$P$–$97^+$, 100%, $[CH_2{=}CHCH_2Si(CH_3)_2OSi(CH_3)_2]^+$}.

Reaction of 7,7-dibromo-2,2-dimethyl-2-silanorcarane with quinoline

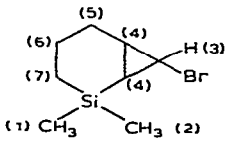
Quinoline (16.34 g, 0.127 mole) was distilled *in vacuo* from calcium hydride into a 50 ml three-necked flask fitted with a 9 cm Vigreux column and a gas inlet tube. 7,7-Dibromo-2,2-dimethyl-2-silanorcarane (0.07 g, 0.017 mole) was added and the mixture heated under a nitrogen atmosphere at 200°. No volatile compounds distilled after 2 h. The reaction mixture was allowed to cool and then heated slowly to 150° at 16 mm pressure. A small amount of a white solid collected in the distillation receivers which was identified from its mass spectrum as quinolinium hydrobromide (P–HBr^+, *m/e* 129).

In a separate experiment the quinoline/2,2-dibromo-2,2-dimethyl-2-silanorcarane mixture was heated for 1 h at each 10° interval between 100 and 200°. After cooling, at each interval the mixture was heated at 16 mm pressure. Again, no volatile products were collected. Charring of the reaction mixture appeared to begin at 170°.

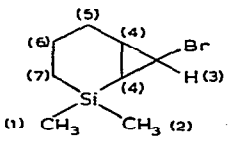
Reaction of 7,7-dibromo-2,2-dimethyl-2-silanorcarane with (dimethylamino)trimethylstannane

n-Hexane (50 ml), 7,7-dibromo-2,2-dimethyl-2-silanorcarane (10.3 g, 0.035 mole) and (dimethylamino)trimethylstannane[31] (19.7 g, 0.087 mole) were combined in a 100 ml flask. After stirring for 1 h a white precipitate appeared in 38% yield (3.8 g) which was filtered and identified as the dimethylamine complex of trimethyltin bromide [m.p. 78°, NMR in CH_2Cl_2: τ9.3 (3H, s); τ 7.4 (2H, d); J 10 Hz; J(Sn–C–H) 64.0 Hz; pos. test for Br^-]. Excess tin amide was hydrolyzed with water (100 ml), the hexane layer dried over anhydrous magnesium sulfate and the solvent evaporated at 25°/100 mm. Analysis of the residue by GLC showed two major products in 16 and 24% yield. The products were identified as *exo*-7-bromo-2,2-dimethyl-2-silanorcarane (VII) (16%) and *endo*-7-bromo-2,2-dimethyl-2-silanorcarane (VIII) (24%) after purification by preparative GLC at 175°.

Exo-isomer: IR in CCl_4: 2940 m, 2900 s, 2840 m, 1455 m, 1435 m, 1340 m, 1245 s, 1200 m, 1130 m, 1020 m, (sh), 980 s, 900 m cm^{-1}. NMR in CCl_4: τ(H1) 10.0 (3H, s); τ(H2) 9.9 (3H, s); τ(H3) 7.3 (1H, dd); τ(H4), τ(H5) and τ(H6) 8.3–9.2 (6H, m); τ(H7) 9.7–9.9 (2H, m). J(H3–H4) 3.0 and 5.0 Hz. Mass spectrum: *m/e* 219 (P^+, 20%, d, 1/1), 204 (P–15^+, 15% d, 1/1), 177 (P–42^+, 35%, d, 1/1), 138 {d, 1/1, 100%, $[(CH_3)_2SiBr]^+$}.



(VII)



(VIII)

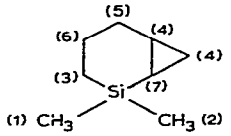
Endo-isomer: IR in CCl_4: 2940 m, 2910 s, 2840 m, 1440 m, 1400 m, 1245 s, 1140 m, 990 m cm^{-1}. NMR in CCl_4: τ(H1) 9.9 (3H, s); τ(H2) 9.8 (3H, s); τ(H3) 6.5 (1H, dd); τ(H4), τ(H5) and τ(H6) 8.0–9.0 (6H, m); τ(H7) 9.5–9.7 (2H, m); J(H3–H4) 8.4 and 6.4 Hz. Mass spectrum: *m/e* 219 (P^+, 30%, d, 1/1), 204 (P–15$^+$, 10%, d, 1/1), 177 (P–42$^+$, 25%, d, 1/1), 138 amu, {d, 1/1, 100%, $[(CH_3)_2SiBr]^+$}.

In a separate experiment 7,7-dibromo-2,2-dimethyl-2-silanorcarane and (dimethylamino)trimethylstannane were combined neat. Analysis of the reaction mixture by GLC showed the presence of the same two products as above in approximately 16 and 24% yield.

An additional experiment was done in the presence of the free radical inhibitor, galvinoxyl[26]. After 1 h no reaction had taken place. Upon heating the reaction mixture for 3 h at 100° and stirring at room temperature for a further 12 h the formation of *endo*- and *exo*-7-bromo-2,2-dimethyl-2-silanorcarane was observed by GLC analysis of the reaction mixture in approximately the same yield as above.

Preparation of 2,2-dimethyl-2-silanorcarane (IX)

Tri-n-butyltin hydride[32] (2.00 g, 0.007 mole) was placed in a 50 ml three-necked flask fitted with a syringe cap and a reflux condenser. 7,7-Dibromo-2,2-dimethyl-2-silanorcarane (1.00 g, 0.003 mole) was added by syringe after the flask has been cooled to 0° in an ice bath. After stirring at 0° for 1 h the mixture was stirred at room temperature for 24 h. During this time aliquots for GLC analysis were taken at 1 h, 3 h, 10 h, and 24 h. The chromatograms of each of these aliquots showed the presence of *exo*- and *endo*-7-bromo-2,2-dimethyl-2-silanorcarane in ratio of 1/1.5 (identified by their retention times at 150°). The product was isolated by preparative GLC at 150° in 87% yield (0.40 g). (Found: C, 68.31; H, 11.31. $C_8H_{16}Si$ calcd.: C, 68.57; H, 11.43%.)



IR in CCl_4: 2960 m, 2900 m, 2880 s, 2830 m, 1260 m, 1230 s, 1120 m, 1020 m cm^{-1}. NMR in CCl_4: τ(H1) 10.0 (3H, s); τ(H2) 9.9 (3H, s); τ(H3) 9.7–9.9 (2H, m); τ(H4), τ(H5) and τ(H6) 7.8–8.7 (6H, m); τ(H7) 10.1–10.3 (2H, m). Mass spectrum: *m/e* 140 (P^+, 10%), 125 (P–15$^+$, 30%), 112 {P–28$^+$, 20%, $[CH_2(CH_2)_3Si(CH_3)_2]^+$}, 97 {$P$–43$^+$, 100%, $[CH{=}CH(CH_2)_2SiCH_3]^+$}.

Reaction of 7,7-dibromo-2,2-dimethyl-2-silanorcarane with silver nitrate

7,7-Dibromo-2,2-dimethyl-2-silanorcarane (5.3 g, 0.018 mole) was added to silver nitrate (3.6 g, 0.020 mole) in 95% methanol (100 ml). An immediate precipitate formed. The reaction mixture was stirred for 1 h and then the silver bromide (2.5 g, 0.013 mole) was filtered, Methanol was evaporated from the filtrate at 25°/16 mm, and the residue extracted with chloroform (20 ml), filtered and dried over calcium chloride. Evaporation of the chloroform at 25°/16 mm followed by GLC analysis of the residue showed recovery of approximately 70% of the starting material in addition to minor components. This mixture was reacted further with an excess

of silver nitrate (5.4 g, 0.030 mole) in 95% methanol (100 ml) and the reaction worked up as above. Analysis of the reaction residue by GLC showed a nineteen component mixture. Attempts to isolate some of these components by preparative GLC failed to yield enough compound for characterization.

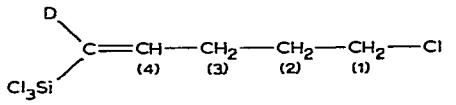
Preparation of 1-*deuterio*-5-*chloro*-1-*pentyne*

5-Chloro-1-pentyne [(100 g, 0.99 mole) Farchan Chem. Co.] in carbon tetrachloride (100 ml) was added to a solution of sodium deuteroxide in deuterium oxide (0.1 *M*, 100 ml, 99.8% deuterium). This solution was prepared by reacting sodium metal (0.23 g, 0.01 mole) with a 5% solution of deuterium oxide in dry tetrahydrofuran (100 ml), evaporating the solvent at 25°/16 mm, and diluting the residue to 100 ml with deuterium oxide. The reaction mixture was stirred for 24 h, the phases separated, and the carbon tetrachloride layer dried over anhydrous magnesium sulfate. The exchange was then repeated using a fresh solution of sodium deuteroxide in deuterium oxide (0.1 *M*, 100 ml). After stirring for two days the exchange was greater than 90% complete as followed by IR spectroscopy (≡C–H stretching mode, 3300 cm^{-1}, ≡C–D stretching mode, 2600 cm^{-1}). The carbon tetrachloride layer was dried over anhydrous magnesium sulfate and the solvent evaporated at 25°/16 mm, giving the product in 90% yield (91 g). Analysis by GLC showed the product to be greater than 95% pure NMR, neat: τ(H1) and τ(H2) 7.9 (4H, m); τ(H) 6.5 (2H, t); J(H2–H3) 6.5 Hz.

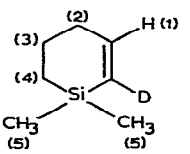
$$\underset{(1)}{D{-}C{\equiv}C{-}}\underset{(2)}{CH_2{-}}\underset{(3)}{CH_2{-}}CH_2{-}Cl$$

Preparation of 2-*deuterio*-1,1-*dimethyl*-1-*sila*-2-*cyclohexene*

Hydrosilation of 1-deuterio-5-chloro-1-pentyne (72 g, 0.70 mole) with trichlorosilane (200 g, 1.5 mole) following the procedure of Benkeser and Cunico[3] gave 1-deuterio-1-(trichlorosilyl)-5-chloro-1-pentene (*cis*/*trans*=3) in 50% yield (81 g). NMR neat (*cis*- and *trans*-): τ(H1) 6.5 (2H, t); τ(H2) 8.0 (2H, m); τ(H3) 7.5 (2H, m); τ(H4) 3.3 (1H, tt). J(H3–H4) 7.0 Hz; J(D–H4) 2.0 Hz.

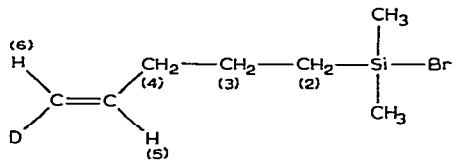


Cyclization of 1-deuterio-1-(trichlorosilyl)-5-chloro-1-pentene (36 g, 0.15 mole) following the procedure of Benkeser and Cunico[3] gave 2-deuterio-1,1-dichloro-1-sila-2-cyclohexene in 45% yield (10.4 g). Treatment of this amount of 1,1-dichloro-1-sila-2-cyclohexene with a 2/1 molar excess of methyllithium–lithium bromide complex in ether as previously described gave 2-deuterio-1,1-dimethyl-1-sila-2-cyclohexene in 55% yield (4.5 g). NMR, neat τ(H1) 3.1 (1H, m); τ(H2) and τ(H3) 7.3–8.1 (4H, m); τ(H4) 9.1–9.5 (2H, m); τ(H5) 10.0 (6H, s); J(H1–H2) 4.0 Hz; J(D–H1) 2.0 Hz.



Reaction of 2-deuterio-1,1-dimethyl-1-sila-2-cyclohexene with phenyl(tribromomethyl)-mercury.

2-Deuterio-1,1-dimethyl-2-sila-2-cyclohexene (3.8 g, 0.03 mole), phenyl(tribromomethyl)mercury (15.7 g, 0.03 mole) and benzene (50 ml) dried by refluxing with potassium, were combined under nitrogen atmosphere. The mixture was refluxed for 4 h, cooled and then filtered. Benzene was evaporated from the filtrate at 25°/16 mm. The residue was trap to trap distilled at 25°/16 mm, the distillate purified by preparative GLC at 150° and the sole component identified as *trans*-1-deuterio-5-



(dimethylbromosilyl)-1-pentene. This compound gave a positive test for hydrolyzable bromine. NMR, neat: τ(H1) 9.6 (6H, s); τ(H2) 9.5–9.8 (2H, m); τ(H3) 8.5–8.9 (2H, m); τ(H4) 7.8–8.2 (2H, m); τ(H5) 4.0–4.5 (1H, 2tt); τ(H6) 4.9–5.2 (1H, 2t); J(H5–H6) 17.0 Hz; J(H4–H5) 7.0 Hz; J(D–H5) 1.5 Hz.

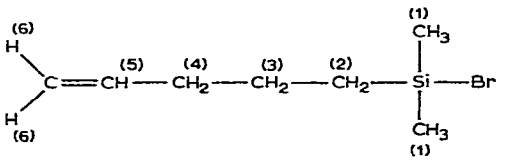
The residue of the trap was distilled at 65°/0.02 mm and the major component was identified as 1-deuterio-7,7-dibromo-2,2-dimethyl-2-silanorcarane by its GLC retention time at 150°.

Decomposition of 7,7-dibromo-2,2-dimethyl-2-silanorcarane in benzene

7,7-Dibromo-2,2-dimethyl-2-silanorcarane (1.0 g, 0.003 mole) was refluxed in benzene (5 ml) for 18 h. Extensive charring was noticed at this point with the evolution of acid fumes which precipitated silver halide from aqueous silver nitrate. Evaporation of the benzene at 25°/16 mm followed by vacuum distillation of the residue recovered only starting material (0.3 g, 30%).

Reaction of 1,1-dimethyl-1-sila-2-cyclohexene with HBr

1,1-Dimethyl-1-sila-2-cyclohexene (1.0 g, 0.008 mole) and dry benzene (5 ml) were combined in a 50 ml flask. The flask was flushed with nitrogen and then anhydrous HBr gas was bubbled slowly through the solution for 5 min. After refluxing for 30 min the solution was flushed with nitrogen. An NMR spectrum taken of an aliquot of this solution showed that the starting material has been converted quantitatively to 5-(dimethylbromosilyl)-1-pentene. NMR in benzene: τ(H1) 9.6 (6H, s); τ(H2) 9.5–9.8 (2H, m); τ(H3) 8.5–8.9 (2H, m); τ(H4) 7.8–8.2 (2H, m); τ(H5) 4.0–4.5 (1H, m); τ(H6) 4.9–5.2 (2H, m).



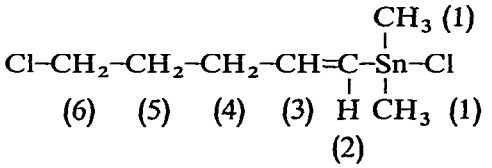
In a separate reaction anhydrous HBr gas was bubbled through a solution

of 1,1-dimethyl-1-sila-2-cyclohexene (1.0 g, 0.008 mole) in benzene (5 ml). An NMR spectrum taken before heating the solution showed a multiplet at τ 6.7 in addition to the resonances associated with 5-(dimethylbromosilyl)-1-pentene. This multiplet vanished after the solution had been allowed to reflux for 30 min.

Preparation of 1-*(dimethylchlorostannyl)-5-chloro-1-pentyne*

Dimethyltin dichloride (4.4 g, 0.020 mole) was added to a Schlenk tube fitted with gas inlet and a magnetic stirrer. The tube was evacuated, filled with nitrogen and cooled to $-77°$ in a Dry Ice–acetone bath. Dimethyltin dihydride[35] (3.00 g, 0.020 mole) was slowly added by syringe and the mixture was allowed to reach room temperature with stirring. 5-Chloro-1-pentyne (4.5 g, 0.044 mole) was added to the resulting clear solution. After stirring for 1.5 h a vigorous reaction ensued with formation of a small amount of grey solid (probably due to the decomposition of some of the hydride chloride). The reaction mixture was filtered and excess acetylene removed *in vacuo* to give the crude product in 65% yield (7.4 g). (Found: Sn, 40.06. $C_7H_{14}Cl_2Sn$ calcd.: Sn, 41.26%.)

IR neat on KBr plates: 2960 m, 2940 m, 1605 m, 1455 m, 1310 m, (br), 785 s, (br), 650 m, (br), 545 s cm^{-1}. NMR in CCl_4 (*cis*+*trans*): τ(H1) 9.3 (6H, 2s); τ(H2) 4.6–5.2 (1H, m); τ(H3) 3.7–4.1 (1H, m); τ(H4) 7.8–8.2 (2H, m); τ(H5) 7.4–7.8 (2H, m); τ(H6) 6.5 (2H, t); J(H5–H6) 7.0 Hz.



In a separate reaction an attempt to purify the product by distillation at 0.01 mm resulted in partial decomposition, the small amount of product that did distill showed three sets of methyltin resonances in the NMR at 9.9, 9.3 and 8.8 τ. The *cis*- and *trans*-ratio could not be accurately determined by GLC due to decomposition, but was estimated to be 3/1 from the relative intensities of the partially resolved methyltin resonances of the *cis*- and *trans*-isomers.

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