Journal of Organometallic Chemistry, 225 (1982) 177—191
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

HEXAMETHYLSILIRANE

II *. RING-OPENING REACTIONS WITH SOME SIMPLE REAGENTS **

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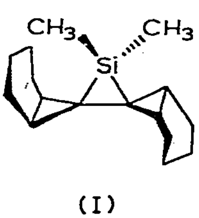
(Received May 8th, 1981)

Summary

Ring-opening reactions formally of the type $Me_2\overline{SiCMe_2C}Me_2 + X{-}H \rightarrow Me_2XSiCMe_2CMe_2H$ occur on reaction of hexamethylsilirane with water, alcohols, ammonia, amines, HCl and carboxylic acids and germanium and tin hydrides. More complicated ring opening reactions are observed with halogens, tetrahalomethanes and molecular oxygen. The oxidation and protolysis (H_2O, ROH, HCl, RCO_2H, NH_3, amines) reactions of hexamethylsilirane are exothermic at room temperature.

Introduction

In previous papers we have reported concerning the synthesis [2], structure [3] and the exceptionally high reactivity [4] of silacyclopropanes (siliranes) with the 7-siladispiro[2.0.2.1]heptane structure, I, II and III. As noted in Part I [1], in search of siliranes of lower molecular weight and simpler structure, we prepared hexamethylsilirane, IV. Although of relatively low thermal stability, this compound was sufficiently stable at room temperature to permit



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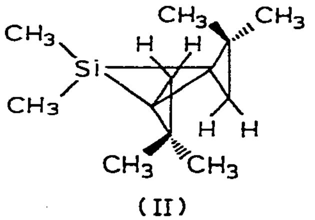

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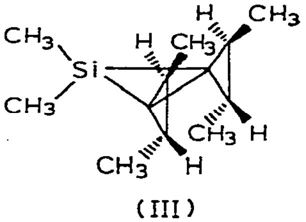

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* Part I: Ref. 1.

** Dedicated to Professor Henry Gilman in recognition of a long and distinguished career as a pioneer in research in organometallic chemistry.

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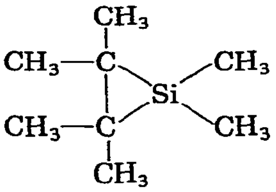
studies of its reactivity. The chemical reactions of the extremely air- and



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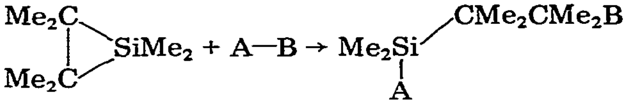
moisture-sensitive hexamethylsilirane are of three principal types: ring-opening reactions which give acyclic products (eq. 1), ring-insertion reactions (eq. 2) and dimethylsilylene-extrusion reactions (eq. 3). We report here concerning reactions of type 1.



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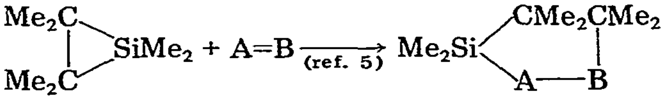

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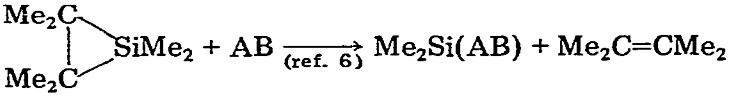

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Results and discussion

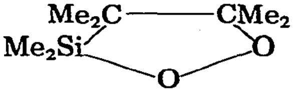
In our investigation of the reactivity of silacyclopropane II we had studied its reactions with diverse common reagents: oxygen, water, alcohols, primary and secondary amines, ammonia, hydrogen sulfide, strong and weak acids, organolithium compounds. In our examination of the reactions of hexamethylsilirane with many of the reagents on this list, as well as with some others, we have found this silacyclopropane to be as reactive, if not more reactive, than II.

Oxidation

The nature of the oxidation process remains obscure. Neat hexamethylsilirane fumes profusely immediately upon exposure to air and a cloudy paper developed over a solution of the silirane which had been allowed to come in contact with the atmosphere. Although hexamethylsilirane is not pyrophoric, its oxidation is vigorously exothermic. Thus, a 40°C temperature rise was observed when oxygen was passed over a solution of 0.9 g of the silirane in 10 ml of heptane.

In order to produce a more controlled reaction, oxygen was passed over a solution of hexamethylsilirane in pentane at —55°C. Removal of volatiles after completion of the oxidation left a white, amorphous solid which was soluble in carbon tetrachloride and which could be precipitated from this solvent by addition of methanol. The proton NMR spectrum of this material showed only

Si—CH_3 and C—CH_3 resonances. Chemical studies showed this solid to be peroxidic: it oxidized iodide ion in acid medium to elemental iodine and triphenylphosphine to triphenylphosphine oxide. Examination of the volatiles from such a silirane oxidation by GLC showed the presence of tetramethylethylene in yields ranging ~30—36% based on starting silirane, a finding which implies the loss of Me_2Si or a fragment containing this unit, such as Me_2SiO_2. On the basis of the presently available information, discussion of the possible structure of the obviously polymeric peroxide formed in the oxidation reaction would be speculation. However, it is tempting to suggest that, in line with known two-atom insertions into hexamethylsilirane [5,6], the initially formed oxidation product is the cyclic peroxide, V, a compound which could decompose either by extrusion of Me_2SiO_2 to give the observed tetramethylethylene or by

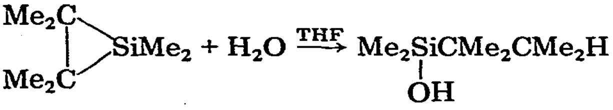


(V)

O—O homolysis to give the diradical $^{\cdot}O—Me_2SiCMe_2CMe_2—O^{\cdot}$, which could be the source of the polymeric peroxide. This reaction obviously requires further experimental study.

Hydrolysis and alcoholysis

Hexamethylsilirane was found to be very moisture sensitive. A stoichiometric reaction of a THF solution of the silirane with water was exothermic and gave the expected silanol in quantitative yield (eq. 4). The silanol could be isolated without difficulty by gas chromatography without apparent condensa-



(4)

tion to the disiloxane. Without doubt, this is due to the presence of the bulky thexyl group *, which sterically hinders the bimolecular condensation reaction.

A few general comments on the identification of reaction products are in order before further delineation of the ring-opening reactions of hexamethylsilirane. Mass spectroscopy and proton NMR spectroscopy were the most useful methods for product characterization. In mass spectroscopic analysis, products of type $Me_2XSiCMe_2CMe_2H$ usually gave the molecular ion. In all cases, the parent ion corresponded to Me_2XSi^+ and the next most intense peak was observed at *m/e* 84, $Me_2C{=}CMe_2^+$. The proton NMR spectra of such ring-opening products were not always straightforward. In many cases, the singlet due to the protons of the methyl groups on the carbon atom α to the silicon atom and the doublet due to the protons of the methyl groups on the carbon atoms β to the silicon atom gave two resonances integrating 3 : 9; clearly one-half of the doublet coincided with the singlet resonance. In some instances this difficulty

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[*] The thexyl group = 2,3-dimethyl-2-butyl, $(CH_3)_2CH(CH_3)_2$-, using the nomenclature of H.C. Brown [7].

was solved by obtaining the NMR spectrum at 90 MHz rather than at the usual 60 MHz. The NMR spectrum of the silanol shown in eq. 4 was not resolved by this means, but in a spectrum obtained at 220 MHz the singlet and the doublet were clearly separated. A coupling constant of 6 Hz was measured for the doublet. The singlet and doublet methyl resonances also could be separated by application of the lanthanide shift reagent, $Eu(dpm)_3$, as detailed in the Experimental section.

Hexamethylsilirane was found to react with most alcohols and with phenol to give ring-opened products, $Me_2(RO)SiCMe_2CMe_2H$, in high yield. Exothermic reactions were observed with methanol, ethanol, isopropanol and phenol. However, hexamethylsilirane did not react with tert-butanol, even when the THF solution containing these reactants was heated (for 24 h at 50°C, 20 h, at 60°C and 6 h at 70°C). The only product which was detected was tetramethylethylene (88% yield), which indicated that the application of heat merely caused Me_2Si extrusion. In view of the failure of tert-butanol to react, a reaction of hexamethylsilirane with lithium tert-butoxide was attempted at room temperature. However, after an 18 h reaction time the silirane remained unchanged, as indicated by the formation of $Me_2(HO)SiCMe_2CMe_2H$ in an exothermic reaction when water was added to the reaction mixture. It would seem that the six methyl substituents of hexamethylsilirane can provide decisive steric hindrance to attack by especially bulky reagents *.

Reactions with ammonia and amines

A THF solution of hexamethylsilirane at 0°C reacted readily with gaseous ammonia which was passed over it to give the aminosilane, $Me_2(H_2N)SiCMe_2CMe_2H$, in 88% yield. The product, a volatile liquid, could be isolated by gas chromatography (120°C column temperature) and, like the silanol, it appeared to be stable to condensation to the disilazane. Similar exothermic reactions with gaseous dimethylamine and with aniline gave $Me_2(Me_2N)SiCMe_2CMe_2H$ (81%) and $Me_2(PhNH)SiCMe_2CMe_2H$ (62%), respectively.

Reactions with acids

Hexamethylsilirane reacted exothermally when gaseous hydrogen chloride was passed over its THF solution at room temperature, giving the expected chlorosilane, $Me_2ClSiCMe_2CMe_2H$, in 90% yield. The reaction with the weak acetic acid in THF also was exothermic and complete within a few minutes. Similar reactions were carried out with chloroacetic acid and cyclopropanecarboxylic acid to give the expected silyl carboxylates, $Me_2(RCO_2)SiCMe_2CMe_2H$, in essentially quantitative yield.

Reactions with halogens

The reaction of chlorine with hexamethylsilirane might be expected to give $Me_2ClSiCMe_2CMe_2Cl$. This product very likely would undergo β-elimination to produce Me_2SiCl_2 and $Me_2C{=}CMe_2$. When hexamethylsilirane was allowed to react with gaseous chlorine at room temperature in THF solution none of

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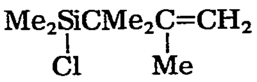
* Silirane II appears to be less hindered at silicon: it reacted smoothly with tert-butanol at room temperature to give an 80% yield of the expected silirane-ring-opening product [4].

these products was formed; instead, the observed product, formed in 90% yield, was the formal HCl cleavage product, $Me_2ClSiCMe_2CMe_2H$. It is possible (but by no means proven) that this product resulted from hydrogen abstraction from the solvent by an intermediate $Me_2ClSiCMe_2CMe_2^{\cdot}$ radical. A similar reaction of the silirane with bromine, carried out in chloroform-d_1 at temperatures below 0°C, gave $Me_2BrSiCMe_2CMe_2H$ as sole product in quantitative yield. Here also the provenance of the hydrogen atom incorporated into the thexyl substituent is unknown. Although a $DCCl_3$ solution was used, the concentrate of the silirane preparation [1] still contained some THF. We note that silirane II also reacted with chlorine to give the formal HCl cleavage product rather than the expected dichloro compound [4,8].

Reactions with tetrahalomethanes

We had found earlier that siliranes I and II reacted exothermally with carbon tetrachloride [4]. Hexamethylsilirane also reacts with carbon tetrachloride in THF solution at room temperature. The vigorously exothermic reaction gave three organosilicon products, VI, VII and VIII, in yields of 34%, 41% and 19%, respectively, as well as some tetramethylethylene when the CCl_4 was added to the silirane/THF solution. Similar products, IX (23%), X (54%), VII (17%) and VIII (8%), were obtained when bromotrichloromethane was added dropwise to a THF solution of hexamethylsilirane at 0°C. These products are indicative of radical chemistry. The trichloromethyl products VII and VIII could result from $CCl_3^{\cdot}$ radical attack at the silicon atom of the silirane ring to give the $Me_2(Cl_3C)$-$SiCMe_2CMe_2^{\cdot}$ radical. It is less apparent how VI, IX and X could have been formed, although one may speculate in terms of the intermediate $^{\cdot}SiMe_2CMe_2$-$CMe_2^{\cdot}$ radical. In view of the facile autoxidation of hexamethylsilirane, its solutions must invariably contain low concentrations of radicals which could serve as initiators of other radical processes.


$\underset{Cl}{Me_2Si}CMe_2\underset{Me}{C}{=}CH_2$

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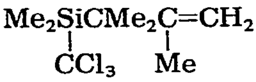
$\underset{CCl_3}{Me_2Si}CMe_2\underset{Me}{C}{=}CH_2$

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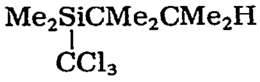
$\underset{CCl_3}{Me_2Si}CMe_2CMe_2H$

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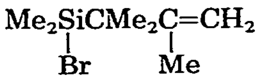
$\underset{Br}{Me_2Si}CMe_2\underset{Me}{C}{=}CH_2$

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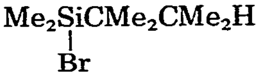
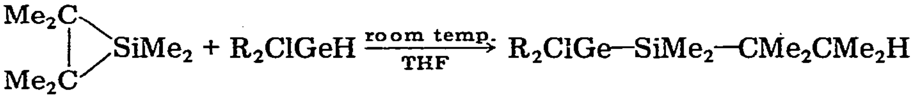

$\underset{Br}{Me_2Si}CMe_2CMe_2H$

(X)

Reactions with organogermanium and organotin hydrides

In view of the ready reaction of hexamethylsilirane with CCl_4 and $CBrCl_3$ in an obviously radical process, it was no surprise to find that the silirane reacted readily with organogermanium and organotin hydrides whose metal—hydrogen bonds are subject to facile homolytic cleavage. Organochlorogermanium hydrides of type R_2ClGeH (R_2 = Et, Et; Ph, Ph; Ph, Et) and triphenylgermane reacted with hexamethylsilirane in THF solution at room temperature to give high yields of the ring-opened product (eq. 5). In the case of diethylchlorogermane the reaction was complete within 2 h, but in most reactions a reaction time of 15 h was used. Phenyldichlorogermane also was very reactive, giving $PhCl_2GeSiMe_2CMe_2CMe_2H$ in 70% yield in a 2 h reaction time. Tri-n-butylgermane and tributyltin hydride were less reactive and required either thermal or photo-activation (eq. 6 and 7).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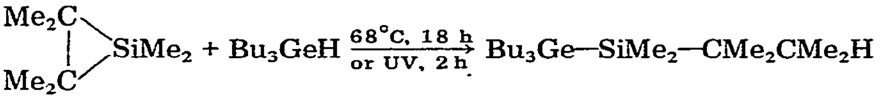
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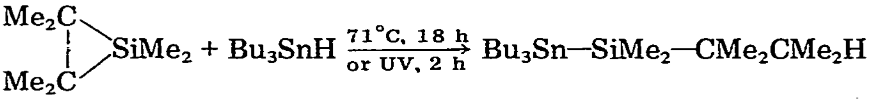
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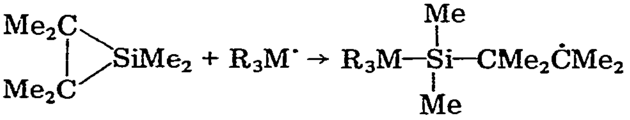
The reactivity of organogermanium hydrides in their addition reactions to simple olefins and acetylenes is in the order $RCl_2GeH > R_2ClGeH > R_3GeH$. These reactions, as well as analogous addition reactions of trialkyltin hydrides, have been shown to occur by a free radical chain process [9,10]. We suggest that a free radical chain process also is operative in the reactions of hexamethylsilirane with these germanium and tin hydrides. As mentioned above, a radical initiator must invariably be present in the silirane solutions as a result of unavoidable traces of oxygen introduced during their transfer and handling. With the less reactive hydrides, photoinitiation was effective. The steps of the radical chain process which we propose must then parallel those of the hydride/olefin reactions (eq. 8—10).

$$R_3M{-}H \rightarrow R_3M^{\cdot} + H^{\cdot} \qquad (8)$$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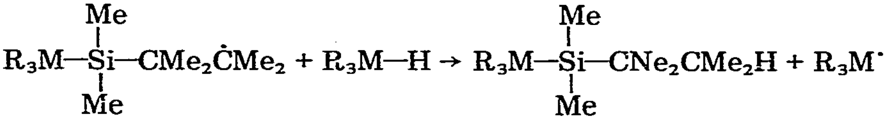
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$$R_3M{-}\underset{Me}{\overset{Me}{Si}}{-}CMe_2\dot{C}Me_2 + R_3M{-}H \rightarrow R_3M{-}\underset{Me}{\overset{Me}{Si}}{-}CNe_2CMe_2H + R_3M^{\cdot} \qquad (10)$$

etc.

These reactions provide a new method for the formation of Si—Ge and Si—Sn bonds.

Conclusions

We have reported here some simple ring-opening reactions of hexamethylsilirane. In view of the highly strained SiC_2 ring of the silacyclopropanes ($\angle$C—Si—C of silirane I = 49.2° [3]), these reactions are not surprising, although the facility and vigor with which they take place is unusual and impressive. In every case it was the Si—C bond (rather than the C—C bond) of the SiC_2 ring which was cleaved. This is as expected since the Si—C bond is polar ($Si^{\delta+}$—$C^{\delta-}$) and is susceptible to nucleophilic attack at silicon and electrophilic attack at carbon, and, very likely, homolytic attack at silicon as well.

Without doubt, many other nucleophilic, electrophilic and radical reagents would react with hexamethylsilirane to open the SiC_2 ring, but in our initial studies we have concentrated on the more common reagents. In other papers we already have reported (with full details) concerning such ring-opening reactions with methylenetrimethylphosphorane [11] and tert-butanethiol [12], and in our initial communication on hexamethylsilirane we have mentioned its cleavage by organolithium reagents [13], a reaction which is still under study. In any case, the observed hyper-reactivity of hexamethylsilirane leads us to suggest that a rich and, very likely, surprising (in terms of known Si—C bond reactions) chemistry remains to be uncovered in future investigations of the silacyclopropanes.

Future papers will bring full details of our investigations of the "two-atom" insertion reactions and the dimethylsilylene extrusion reactions of hexamethylsilirane.

Experimental

General comments

The general comments of Part I [1] are applicable. In Part I the preparations of hexamethylsilirane and its precursors are described in detail, as are the methods used for the determination of the yield of hexamethylsilirane, for the preparation of solutions of hexamethylsilirane in solvents other than THF and for the handling of hexamethylsilirane and its solutions. We stress again the high reactivity of hexamethylsilirane towards atmospheric oxygen and moisture and the need to perform all operations involving this compound with complete exclusion of air in rigorously dried glassware using rigorously dried and degassed reagents and solvents.

Autoxidation of hexamethylsilirane

A solution of 1.30 mmol of hexamethylsilirane in 10 ml of pentane was prepared (cf. Part I [1] for procedure) in a 50 ml three-necked, round-bottomed flask equipped with a pentane thermometer, a dry ice/acetone condenser topped with a nitrogen inlet tube and a no-air stopper through which a disposable pipet was inserted which was connected to an oxygen cylinder. Oxygen was passed over the magnetically stirred solution for 5 min at −55°C. The cooling bath then was removed and the solution was allowed to warm to room temperature over a period of 5 min while the oxygen flow was continued. The volatiles then were trap-to-trap distilled (room temperature/0.02 mmHg) into a receiver cooled to −78°C. GLC analysis of the distillate showed the presence of 0.38 mmol (30%) of tetramethylethylene (identified by GLC retention time, IR and NMR). The distillation residue consisted of a white, amorphous solid which softened at ~82°C when it was heated. This material was readily soluble in CCl_4 and could be precipitated from that solvent by addition of methanol. The following data were obtained on a sample of this precipitated solid. Anal. Found: C, 50.75; H, 9.87. Calcd. for $C_8H_{18}O_2Si$ (i.e., a polymer of V): C, 55.12; H, 10.41%. ^{1}H NMR ($CCl_4/CHCl_3$): δ 0.27 (broadened singlet; Si—CH_3) and 1.00 and 1.27 ppm (broadened singlets, C—CH_3) in 1 : 1 : 1 ratio. IR (CCl_4, cm^{-1}): 2970vs, 2910(sh), 2880m, 1465m, 1455m, 1410w, 1390m, 1375m, 1360m, 1255vs, 1205m, 1180m, 1145m, 1095m, 1020m, 885s cm^{-1}.

a) Reaction of the autoxidation product with sodium iodide. Following the procedure of Johnson and Siddiqi [14], 0.2626 g of the oxidation product was dissolved in 50 ml of freshly boiled acetic acid and then 6 g of NaI and 2 ml of 37% HCl were added. An identical blank solution also was prepared. The product solution immediately changed from colorless to orange to the deep red-brown color of iodine. The blank solution also became colored, but at a much slower rate. The solutions were heated at reflux for 45 min, diluted to precisely 100 ml with distilled water, and then aliquots were withdrawn and titrated with 0.0560 *M* $Na_2S_2O_3$. After subtracting for the blank solution, it was determined that 0.45 mmol of iodine had been formed. If one assumes that the formula weight of the peroxide is 174.32 ($C_8H_{18}O_2Si$), then this would correspond to a 30% yield.

b) Reaction of the autoxidation product with triphenylphosphine. A solution of 0.047 g of the oxidation product and 1.79 g (6.8 mmol) of triphenylphosphine in 10 ml of toluene was stirred and heated at reflux for 20 h. To the cooled solution was added 2 ml of iodomethane and the resulting mixture was stored at room temperature for several hours. The precipitated $MePh_3P^+I^-$ (2.703 g, 6.69 mmol) was filtered. The solvents were removed from the filtrate and the residue was extracted with pentane. Filtration gave 0.04 g (0.14 mmol) of triphenylphosphine oxide, m.p. 152—153°C (lit. [15] m.p. 153°C). The yield of Ph_3PO is 51% based on the assumption made in (a) above.

Hydrolysis of hexamethylsilirane

Into a 50 ml three-necked, round-bottomed flask equipped with a thermometer, a reflux condenser topped with a nitrogen inlet tube, a magnetic stir-bar and a no-air stopper was charged a THF solution containing 2.2 mmol of hexamethylsilirane and then 0.20 ml of distilled water was added dropwise by syringe. An exothermic reaction (15°C temperature rise) occurred. The mixture was stirred at room temperature for several hours and then was trap-to-trap distilled (room temperature/0.01 mmHg). Examination of the distillate by GLC (20% UC-W98 silicone rubber gum, 130°C) showed the presence of the hydrolysis product, $Me_2(HO)SiCMe_2CMe_2H$, in 100% yield. Pure samples were isolated by GLC; n_D^{25} 1.4505. Anal. Found: C, 59.59; H, 12.64. Calcd. for $C_8H_{20}OSi$: C, 59.92; H, 12.57%. The IR spectrum (neat film) had a strong and broad band at 3330 cm^{-1}, indicative of the Si—OH function. The NMR spectra obtained using 60 or 90 MHz spectrometers were not resolved, but the ^{1}H NMR spectrum obtained using a 220 MHz spectrometer was satisfactory: δ 0.133 (s, 6 H, Me_2Si), 0.90 (s, 6 H, CCH_3), 0.95 (d, *J* 6 Hz, 6 H, $CHCH_3$), 1.48 (s, 1 H, OH) and 1.20—1.93 ppm (heptet, 1 H, *J* 6 Hz, Me_2CH).

The use of a lanthanide shift reagent (LSR), $Eu(dpm)_3$, also gave a fully resolved spectrum. About 0.04 mmol of the LSR was added to about 0.06 mmol of the hydrolysis product in three portions. A spectrum was recorded before the addition of any reagent and after each addition, allowing the sample to spin at the probe temperature (ca. 35°C) for 45 min before recording the spectrum in order to dissolve the LSR completely. The results are shown in Table 1.

Alcoholysis of hexamethylsilirane

The reaction with ethanol is typical. A THF solution containing 0.76 mmol of the silirane was added to 0.5 ml (8.7 mmol) of absolute ethanol in the "standard reaction apparatus" (experiment above) at room temperature. An exothermic reaction ensued. The solution was shaken for 10 min and then was examined by GLC. The ethanolysis product, $Me_2(EtO)SiCMe_2CMe_2H$, was present in 82% yield. Samples were isolated by GLC; n_D^{25} 1.4269. Anal. Found: C, 63.50; H, 13.00. Calcd. for $C_{10}H_{24}OSi$: C, 63.75; H, 12.84%. In the mass spectrum important ions were those with *m/e* 188 (M^+), 103 ($Me_2(OEt)Si^+$) and 84 ($Me_4C_2^+$). ^1H NMR (CCl_4, $CHCl_3$) δ 0.117 (s, 6 H, Me_2Si), 0.88 (s, 6 H, $C(CH_3)_2$), 0.93 (d, J 6 Hz, $CH(CH_3)_2$), 1.18 (t J 7 Hz, 3 H, CH_3 of OEt), 1.36—1.98 (heptet, J 6 Hz, 1 H, $CHMe_2$) and 3.65 ppm (q, J 7 Hz, 2 H, CH_2 of OEt).

Similar reactions were carried out with methanol, isopropanol and phenol. Methanol product: $Me_2(MeO)SiCMe_2CMe_2H$, n_D^{25} 1.4295, in quantitative yield. Anal. Found: C, 61.65; H, 12.74. Calcd. for $C_9H_{22}OSi$: C, 61.99; H, 12.72%. Mass spectrum: important ions with *m/e* 174 (M^+), 89 ($Me_2(MeO)Si^+$) and 84 ($Me_4C_2^+$). ^1H NMR ($CCl_4/CHCl_3$): δ 0.083 (s, 6 H, Me_2Si), 0.83 (s, 6 H, $C(CH_3)_2$), 0.88 (d, J 6 Hz, 6 H, $CH(CH_3)_2$) 1.36—1.91 (heptet, 1 H, $CHMe_2$) and 3.40 ppm (s, 3 H, OCH_3). Isopropanol product, $Me_2(Me_2CHO)SiCMe_2CMe_2H$, n_D^{25} 1.4239, in 62% yield. Anal. Found: 65.38; H, 12.92; Calcd. for $C_{11}H_{26}OSi$: C, 65.27; H, 12.95%. ^1H NMR ($CCl_4/CHCl_3$): δ 0.09 (s, 6 H, $SiMe_2$), 0.86 (s, 6 H, $C(CH_3)_2$), 0.90 (d, J 6 Hz, 6 H, $CH(CH_3)_2$), 1.14 (d, J 6 Hz, $OCH(CH_3)_2$), 1.67 (m, 1 H, $CHMe_2$) and 3.98 ppm (m, 1 H, $OCHMe_2$). Phenol product: $Me_2(C_6H_5O)SiCMe_2CMe_2H$, n_D^{25} 1.4915, in 70% yield. Anal. Found: C, 70.84; H, 10.42. Calcd. for $C_{14}H_{24}OSi$: C, 71.12; H, 10.23%. Mass spectrum: important ions with *m/e* 236 (M^+), 1.51 ($Me_2(PhO)Si^+$) and 84 ($Me_4C_2^+$). ^1H NMR ($CCl_4/CHCl_3$): δ 0.21 (s, 6 H, Me_2Si), 0.97 (s, 6 H, $C(CH_3)_2$), 0.97 (d, J 6 Hz, 6 H, $CH(CH_3)_2$). 1.54—1.90 (heptet, 1 H, $CHMe_2$) and 6.65—7.25 ppm (m, 5 H, OPh).

In a similar experiment, 2.56 mmol of hexamethylsilirane and 3.22 mmol of freshly distilled (from calcium hydride) tert-butanol in THF solution were

TABLE 1

EFFECT OF ADDING $Eu(dpm)_3$ [a] TO $HCMe_2—CMe_2—SiMe_2OH$ [b]

	δ $Si(CH_3)_2$ (ppm)	δ $C(CH_3)_2$ (ppm)	δ $CH(CH_3)_2$ (ppm)
no LSR	0.10	0.87	0.93 (d)
1st LSR addition	1.50	1.93	1.60 (d)
2nd LSR addition	4.15	3.95	2.90 (s) [c]
3rd LSR addition	5.37	4.89	3.52 (s)

[a] dpm = dipivaloylmethanato. [b] Chemical shifts are given in ppm downfield from internal tetramethylsilane, using $CHCl_3$ as the internal standard and CCl_4 as the solvent. [c] After addition of the second portion of LST, the methine proton, $CHMe_2$, was decoupled from the methyl groups and the methyl group signal became a singlet.

stirred at room temperature for 2 days. No reaction occurred during this time, according to periodic monitoring by GLC. The mixture then was heated at 50°C for 24 h, at 60°C for 20 h, and at 70°C for 6 h. According to examination by GLC, the silirane did not react with the alcohol even at higher temperature, but it did decompose to give tetramethylethylene in 88% yield. In another experiment, hexamethylsilirane and a small excess of tert-butanol in THF were stirred at room temperature for 24 h. At this point, an excess of methanol was added (strong exotherm) to give $Me_2(MeO)SiCMe_2CMe_2H$ in 95% yield.

Reactions of hexamethylsilirane with ammonia and amines

An apparatus as was used in the autoxidation experiment was charged with a THF solution containing 1.8 mmol of the silirane and cooled to 0°C. Gaseous ammonia (Matheson) was passed over the solution and condensed into it via the dry-ice/acetone condenser. The reaction mixture was stirred for 2 h, while the ammonia refluxed and then the excess of ammonia was vented and the remaining solution trap-to-trap distilled (room temperature/0.02 mmHg). GLC examination of the volatiles (20% UC-W98, 120°C) showed the presence of the ammonolysis product, $Me_2(H_2N)SiCMe_2CMe_2H$, n_D^{25} 1.4440, in 88% yield. Anal. Found: C, 60.08; H, 13.29; N, 8.45. Calcd. for $C_8H_{21}NSi$: C, 60.29; H, 13.28; N, 8.79%. ^1H NMR ($CCl_4/CHCl_3$): δ −0.017 (s, 6 H, Me_2Si), 0.80 (s, 6 H, $C(CH_3)_2$), 0.85 (d, J 6 Hz, 6 H, $CH(CH_3)_2$), 1.28—1.93 ppm (heptet, 1 H, $C\mathit{H}Me_2$). The IR spectrum (neat film) showed bands at 3470 and 3400 cm^{-1} (ν(N—H)).

A similar reaction carried out with gaseous dimethylamine gave $Me_2(Me_2N)$-$SiCMe_2CMe_2H$, n_D^{25} 1.4525, in 81% yield. Anal. Found: C, 63.59; H, 13.24; N, 7.35. Calcd. for $C_{10}H_{25}NSi$: C, 64.08; H, 13.45; N, 7.48%. ^1H NMR ($CCl_4/CHCl_3$): δ 0.16 (s, 6 H, Me_2Si), 0.89 (s, 6 H, $C(CH_3)_2$), 0.92 (d, J 6 Hz, 6 H, $CH(C\mathit{H}_3)_2$), 1.44—1.90 (heptet, 1 H, $C\mathit{H}Me_2$) and 2.54 ppm (s, 6 H, NMe_2).

A reaction of 2.7 mmol of hexamethylsilirane with 12 mmol of aniline in THF (exotherm) at room temperature gave, after trap-to-trap removal of solvent and unconverted aniline, $Me_2(C_6H_5NH)SiCMe_2CMe_2H$, n_D^{25} 1.5231, in 62% yield. Pure samples were isolated by GLC (20% SE-30 silicone rubber gum, 155°C). Anal. Found: C, 71.07; H, 10.58; N, 5.90. Calcd. for $C_{14}H_{25}NSi$: C, 71.41; H, 10.70; N, 5.95%. ^1H NMR (CCl_4/CH_2Cl_2): δ 0.36 (s, 6 H, Me_2Si), 0.99 (s, 6 H, $C(CH_3)_2$), 0.99 (d, J 6 Hz, 6 H, $CH(C\mathit{H}_3)_2$), 1.50—1.95 (heptet, 1 H, $C\mathit{H}Me_2$), 3.10—3.34 (broad s, 1 H, NH) and 6.45—7.15 ppm (m, 5 H, Ph).

Reactions of hexamethylsilirane with acids

Dry gaseous hydrogen chloride (Matheson) was passed over a THF solution containing 2.85 mmol of hexamethylsilirane at room temperature. An exotherm of 15° was noted. The reaction mixture was cooled to room temperature and additional HCl was passed over it for about 1 min. GLC analysis (20% SE-30 at 100°C) indicated the presence of one product in 90% yield. A sample collected by GLC was identified as $Me_2ClSiCMe_2CMe_2H$, n_D^{25} 1.4480. Anal. Found: C, 53.47; H, 10.57; Cl, 19.91. Calcd. for $C_8H_{19}ClSi$: C, 53.74; H, 10.71; Cl, 19.83%. ^1H NMR ($CCl_4/CHCl_3$): δ 0.45 (s, 6 H, Me_2Si), 0.96 (s, 6 H, CMe_2), 0.96 (d, J 6 Hz, 6 H, $C\mathit{Me}_2H$) and 1.47—1.93 ppm (m, 1 H, CH).

The addition of 1.0 g (16 mmol) of glacial acetic acid to a solution of 2.4

mmol of the silirane in THF at room temperature resulted in a strong exotherm. The mixture was shaken briefly and then was analyzed by GLC (20% SE-30 at 100°C). The single product which was present, $Me_2(O_2CCH_3)SiCMe_2CMe_2H$, n_D^{25} 1.4320, was isolated and characterized. Anal. Found: C, 59.07; H, 11.05. Calcd. for $C_{10}H_{22}O_2Si$: C, 59.34; H, 10.96%. IR (film, cm^{-1}): ν(C=O) 1750(sh), 1735(sh), 1725vs. ^1H NMR ($CCl_4/CHCl_3$): δ 0.29 (s, 6 H, Me_2Si), 0.87 (s, 6 H, CMe_2), 0.91 (d, J 6 Hz, 6 H, CMe_2H), 1.40—1.83 (m, 1 H, CH) and 2.01 ppm (s, 3 H, $CH_3C(O)$).

In a similar reaction of the silirane with chloroacetic acid, a THF solution containing 3.11 mmol of the silirane was added at room temperature to a solution of 3 g (32 mmol) of chloroacetic acid in 2.5 ml of THF. After the initial exothermic reaction had subsided, the mixture was stirred for 2 h, at room temperature. GLC analysis then indicated the formation of $Me_2(O_2CCH_2Cl)SiCMe_2CMe_2H$, n_D^{25} 1.4541, in quantitative yield. Anal. Found: C, 50.68; H, 8.87. Calcd. for $C_{10}H_{21}O_2ClSi$: C, 50.71; H, 8.94%. IR (thin film, cm^{-1}): ν(C=O) 1742vs, 1720vs. ^1H NMR ($CCl_4/CHCl_3$): δ 0.36 (s, 6 H, Me_2Si), 0.88 (d, J 7 Hz, CMe_2H), 0.93 (s, 6 H, CMe_2), 1.30—1.83 (heptet, 1 H, CH) and 3.94 ppm (s, 2 H, CH_2Cl).

In another experiment, 6.3 mmol of cyclopropanecarboxylic acid (Aldrich) was added at room temperature to a solution of 2.78 mmol of hexamethylsilirane in THF/benzene. After the initial exotherm, the mixture was stirred at room temperature for 1 h. The product, $Me_2(O_2CC_3H_5\text{-cyclo})SiCMe_2CMe_2H$, n_D^{25} 1.4522, was isolated by GLC. Anal. Found: C, 63.10; H, 10.62. Calcd. for $C_{12}H_{24}O_2Si$: C, 63.10; H, 10.59%. IR (film, cm^{-1}): ν(C=O): 1700vs. ^1H NMR ($CCl_4/CHCl_3$): δ 0.22 (s, 6 H, Me_2Si), 0.83 (d, J 11 Hz, 6 H, CMe_2H), 0.83 (s, 6 H, CMe_2), 0.57—1.90 ppm (m, 6 H, CMe_2H + cyclopropyl H). The product yield was quantitative.

Reactions of hexamethylsilirane with halogens

Gaseous chlorine was passed over a THF solution containing 1.83 mmol of hexamethylsilirane for one min. An exothermic reaction was noted. GLC analysis (10% UC-W98) showed that a single product had been formed in 90% yield. A sample collected by GLC was found to be identical (IR, NMR, analysis) with the hydrochlorination product of the silirane, $Me_2ClSiCMe_2CMe_2H$.

Bromination was carried out at low temperature. A concentrated THF solution containing 4.16 mmol of the silirane was diluted with 5 ml of $CDCl_3$ and cooled to —78°C. Once the solution had frozen, the cooling bath was removed and bromine was added dropwise at such a rate that the added bromine was consumed between additions while the solution gradually warmed. When the bromine color of such an added drop did not disappear after a few minutes, the addition was stopped and the reaction mixture was stirred at room temperature for 1 h. Subsequent GLC analysis showed that a single product had been formed in quantitative yield. A collected sample was identified as $Me_2BrSiCMe_2CMe_2H$, m.p. 34—35.5°C (GLC sample). Anal. Found: C, 43.16; H, 8.46. Calcd. for $C_8H_{19}BrSi$: C, 43.04; H, 8.58%. ^1H NMR ($CCl_4/CHCl_3$): δ 0.55 (s, 6 H, Me_2Si), 0.91 (d, J 7 Hz, 6 H, CMe_2H), 0.95 (s, 6 H, CMe_2) and 1.40—2.06 ppm (heptet, 1 H, CH).

Reactions of hexamethylsilirane with tetrahalomethanes

(a) Carbon tetrachloride. A concentrated THF solution containing 3.64 mmol of hexamethylsilirane was added dropwise with stirring to 3.0 ml (ca. 28.5 mmol) of carbon tetrachloride at 0°C. (The reaction is strongly exothermic at room temperature). After the mixture had been stirred (from 0°C as it warmed to room temperature) for 1 h it was analyzed by GLC (10% SE-30, 90—200°C temperature program). The following products were found to be present (in order of increasing retention time): (1) tetramethylethylene; (2) $Me_2ClSiCMe_2$-$CMe{=}CH_2$, 0.730 mmol, 20% yield based on silirane, m.p. 73—74.5°C (GLC sample). Anal. Found: C, 54.74; H, 9.54; Calcd. for $C_8H_{17}ClSi$: C, 54.35; H, 9.70%. IR (CCl_4/CS_2, cm^{-1}): $\nu(C{=}C)$ 1634s, 1631(sh). ^1H NMR ($CCl_4/CHCl_3$): δ 0.42 (s, 6 H, Me_2Si), 1.22 (s, 6 H, CMe_2), 1.83 (s, 3 H, $CMe{=}$) and 4.63, 4.82 ppm, (2 AB m, 2 H, $=CH_2$); (3) $Me_2(CCl_3)SiCMe_2CMe{=}CH_2$, 1.5 mmol (41%), n_D^{25} 1.5029. Anal. Found: C, 41.58; H, 6.80; Cl, 40.34. Calcd. for $C_9H_{17}Cl_3Si$: C, 41.62; H, 6.60; Cl, 40.96%. IR (film, cm^{-1}): $\nu(C{=}C)$ 1620. ^1H NMR (CCl_4/$CHCl_3$): δ 0.43 (s, 6 H, Me_2Si), 1.38 (s, 6 H, CMe_2), 1.85 (broad s, 3 H, $CMe{=}$) and 4.75 and 4.85 (broad s, J(AB) 6 Hz, $=CH_2$); (4) $Me_2(CCl_3)SiCMe_2CMe_2H$, 0.69 mmol, (19%), n_D^{25} 1.4969. Anal. Found: C, 40.95; H, 7.29; Cl, 40.45. Calcd. for $C_9H_{19}Cl_3Si$: C, 41.30; H, 7.32; Cl, 40.64%. ^1H NMR ($CCl_4/CHCl_3$): δ 0.46 (s, 6 H, Me_2Si), 0.95 (d, J 6 Hz, 6 H, CMe_2H), 1.13 (s, 6 H, Me_2C) and 1.70—2.27 ppm (heptet, 1 H, CH).

Similar product yields were obtained in a reaction carried out in this manner at room temperature.

(b) Bromotrichloromethane. Using the procedure in (a), a concentrated THF solution containing 3.44 mmol of hexamethylsilirane was added to 3.0 ml (ca. 30.5 mmol) of bromotrichloromethane at 0°C. The mixture was stirred for 1 h at room temperature after the initially exothermic reaction. GLC analysis showed the presence of five products: (1) tetramethylethylene; (2) $Me_2BrSiCMe_2CMe{=}CH_2$, apparently thermally not very stable and very moisture-sensitive (a pure sample could not be isolated), 23% yield; ^1H NMR ($CCl_4/CHCl_3$): δ 0.57 (s, 6 H, Me_2Si), 1.23 (s, 6 H, CMe_2), 1.83 (s, 3 H, $CMe{=}$) and 4.65 and 4.85 ppm (broad s, J(AB) 6 Hz, 2 H, $=CH_2$); (3) $Me_2BrSiCMe_2CMe_2H$, 33%, previously characterized in the bromination experiment; (4) $Me_2(CCl_3)SiCMe_2CMe{=}CH_2$, 25%; (5) $Me_2(CCl_3)SiCMe_2CMe_2H$, 6%.

Reactions of hexamethylsilirane with germanium hydrides

(a) Tri-n-butylgermane. A solution of THF concentrate containing 2.17 mmol of hexamethylsilirane and 1.89 g (7.7 mmol) of n-Bu_3GeH was prepared in 5.0 ml of dry benzene under argon. The mixture was stirred and heated under argon at 68°C (±3°) for 18 h. Subsequent GLC analysis showed the presence of one major product, identified as n-$Bu_3GeSiMe_2CMe_2CMe_2H$, n_D^{25} 1.4883, in 28% yield. Anal. Found: C, 61.88; H, 11.86. Calcd. for $C_{20}H_{46}SiGe$: C, 62.02; H, 11.97%. ^1H NMR ($CCl_4/CHCl_3$): δ 0.15 (s, Me_2Si), 0.87 (d, J 6 Hz, 6 H, CMe_2H), 0.88 (s, 6 H, CMe_2) and 0.49—1.63 ppm (m, butyl H and CH).

In a separate experiment, a solution of 1.50 ml of n-Bu_3GeH and 4.52 mmol of the silirane (as a THF concentrate) in 5.0 ml of dry benzene was irradiated (Hanovia 100 watt UV lamp) under argon in a quartz round-bottomed flask for 2 h. GLC analysis showed that n-$Bu_3GeSiMe_2CMe_2CMe_2H$ (identified by NMR and n_D^{25}) had been formed in 70% yield.

(b) Chlorogermanes. The reaction between hexamethylsilirane and diethylchlorogermane is typical. The standard apparatus was charged with 0.90 g of a THF solution containing 1.62 mmol of the silirane; diethylchlorogermane, 0.34 g (1.62 mmol), then was added. No exotherm was noted, but an NMR spectrum of the solution taken after it has been stirred for 2 h at room temperature under nitrogen showed that the starting materials had been consumed. The reaction mixture was trap-to-trap distilled (high vacuum, into a receiver cooled to —78°C) and the distillate was analyzed by GLC (15% SE-30, 160°C). A single product, $Et_2ClGeSiMe_2CMe_2CMe_2H$, n_D^{25} 1.5049, was present in 79% yield. Anal. Found: C, 46.34; H, 9.34. Calcd. for $C_{12}H_{29}ClGeSi$: C, 46.57; H, 9.44%. ^1H NMR (CCl_4): δ 0.31 (s, 6 H, Me_2Si), 0.88 (d, J 7.4 Hz, 6 H, CMe_2H), 0.94 (s, 6 H, CMe_2), 1.17 (s, 10 H, Et_2Ge) and 1.68 ppm (septet, J 7.4 Hz, 1 H, CH).

A similar reaction between 2.0 mmol each of hexamethylsilirane and ethylphenylchlorogermane in THF solution at room temperature for 15 h gave $PhEtClGeSiMe_2CMe_2CMe_2H$, n_D^{25} 1.5439, in 71% yield. Anal. Found: C, 53.20; H, 8.05. Calcd. for $C_{16}H_{29}ClSiGe$: C, 53.75; H, 8.17%. ^1H NMR (CCl_4): δ 0.30 and 0.33 (s, 3 H each, $SiMe_2$), 0.83 (d, J 7.4 Hz, 6 H, CMe_2H), 0.88 (s, 6 H, CMe_2) 1.10—1.37 (m, 5 H, GeEt), 1.50 (septet, 1 H, Me_2H), and 7.10—7.60 ppm (m, 5 H, Ph). The mass spectrum showed the molecular ion at *m/e* 358.

Hexamethylsilirane (3.3 mmol) and diphenylchlorogermane (3.3 mmol) reacted in THF solution at room temperature during 15 h to give $Ph_2ClGeSiMe_2CMe_2CMe_2H$, n_D^{25} 1.5703, in 89% yield. Anal. Found: C, 58.13; H, 6.87. $C_{20}H_{29}ClSiGe$ calcd.: C, 59.23; H, 7.21%. ^1H NMR (CCl_4): δ 0.40 (s, 6 H, Me_2Si), 0.83 (d, J 6.6 Hz, 6 H, CMe_2H), 0.97 (s, 6 H, CMe_2), 1.55 (septet, 1 H, CMe_2H) and 7.10—7.78 ppm (m, 10 H, Ph). The molecular ion was observed in the mass spectrum at *m/e* 406. Since this compound could not be isolated in analytically pure form, two more stable derivatives were prepared by alkylation of the Ge—Cl bond with CH_3MgI in Et_2O and with C_2H_5MgI in Et_2O. In each case, the hexamethylsilirane/Ph_2ClGeH reaction was repeated and then the ethereal Grignard reagent solution was added. After a 5 h reaction period at reflux, the reaction mixture was cooled and hydrolyzed. The organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated. The respective product was isolated by GLC. Prepared in this manner were: $Ph_2MeGeSiMe_2CMe_2CMe_2H$, n_D^{25} 1.5704, in 89% yield. Anal. Found: C, 65.36; H, 8.14. Calcd. for $C_{21}H_{32}SiGe$: C, 65.49; H, 8.37%. ^1H NMR (CCl_4): δ 0.23 (s, 6 H, $SiMe_2$), 0.73 (s, 3 H, GeMe), 0.75 (d, J 6.8 Hz, 6 H, CMe_2H), 0.81 (s, 6 H, CMe_2), 1.60 (septet, 1 H, CMe_2H) and 6.96—7.43 ppm (m, 10 H, Ph). The mass spectrum showed the molecular ion at *m/e* 386. $Ph_2EtGeSiMe_2CMe_2CMe_2H$, n_D^{25} 1.5720, in 82% yield. Anal. Found: C, 65.85; H, 8.59. Calcd. for $C_{22}H_{34}SiGe$: C, 66.19; H, 8.59%. ^1H NMR (CCl_4): δ 0.25 (s, 6 H, $SiMe_2$), 0.75 (d, J 6.6 Hz, 6 H, CMe_2H), 0.76 (s, 6 H, CMe_2). 0.97—1.28 (m, 5 H, GeEt), septet from the EtGe resonance to 1.75 (1 H, CMe_2H) and 7.12—7.55 (m, 5 H, Ph).

In similar fashion, the reaction of 1.62 mmol each of hexamethylsilirane and phenyldichlorogermane in THF for two h at room temperature gave $PhCl_2GeSiMe_2CMe_2CMe_2H$ in 70% yield as determined by NMR spectroscopy. This compound decomposed on attempted analysis or isolation by GLC. A proton NMR spectrum of the concentrated THF solution was consistent with this formulation: δ 0.50 (s, 6 H, Me_2Si), 1.03 (d, J 7.6 Hz, CMe_2H), 1.05 (s, 6 H,

CMe_2) and 7.0—7.97 ppm (m, 5 H, Ph). The methine proton signal was obscured by the THF solvent signals.

(c) Triphenylgermane. A reaction of 3.0 mmol each of hexamethylsilirane and triphenylgermane in THF solution for 15 h at room temperature gave $Ph_3GeSiMe_2CMe_2CMe_2H$, m.p. 61—63°C (GLC sample), in 80% yield. Anal. Found: C, 69.21; H, 7.49. Calcd. for $C_{26}H_{34}SiGe$: C, 69.83; H, 7.66%. ^1H NMR (CCl_4): δ 0.35 (s, 6 H, Me_2Si), 0.75 (d, J 7.6 Hz, CMe_2H), 0.83 (s, 6 H, CMe_2), 1.68 (septet, 1 H, CMe_2H) and 7.07—7.67 ppm (m, 15 H, Ph_3Ge). The mass spectrum showed the molecular ion at *m/e* 448.

Reactions of hexamethylsilirane with tin hydrides

(a) A solution containing 4.16 mmol of hexamethylsilirane (as a THF concentrate) and 2.545 g (8.74 mmol) of tri-n-butyltin hydride in 2.50 ml of dry pentane in a round-bottomed quartz flask was irradiated (under nitrogen) with a 100 W mercury vapor UV lamp for 2 h. Subsequent GLC analysis showed the presence of $n\text{-}Bu_3SnSiMe_2CMe_2CMe_2H$, n_D^{25} 1.4962, in 61% yield (10% UC-W98, 190—250°C). Anal. Found: C, 55.11; H, 10.53. Calcd. for $C_{20}H_{46}SiSn$: C, 55.43; H, 10.70%. ^1H NMR ($CCl_4/CHCl_3$): δ 0.17 (s, 6 H, Me_2Si), 0.85 (d, J 8 Hz, 6 H, CMe_2H), 0.85 (s, 6 H, CMe_2), 0.70—1.80 ppm (m, CMe_2H and Bu_3Sn).

In another experiment, 2.50 ml (large excess) of $n\text{-}Bu_3SnH$ and a THF concentrate containing 2.48 mmol of hexamethylsilirane were heated under nitrogen at 71 ± 3°C for 18 h. This reaction gave the product described above in 60% yield. In both the thermal and the photochemical reactions some hexa-n-butylditin was formed, but its yield was not determined.

(b) Triethyltin hydride. In the standard reaction apparatus, 1.215 g (5.87 mmol) of triethyltin hydride was added dropwise, with stirring and under nitrogen, to a THF concentrate containing 5.20 mmol of hexamethylsilirane. An immediate exothermic reaction with gas evolution was observed. Subsequent GLC examination of the reaction mixture (10% SE-30, 150—200°C) showed the presence of $Et_3SnSiMe_2CMe_2CMe_2H$, n_D^{20} 1.5118, in 61% yield. Anal. Found: C, 47.75; H, 9.72. Calcd. for $C_{14}H_{34}SiSn$: C, 48.15; H, 9.81%. ^1H NMR ($CCl_4/CHCl_3$): δ 0.26 (s, 6 H, Me_2Si), 0.51—1.94 (m, 16 H, CMe_2H and Et_3Sn), 0.90 (d, J 5.5 Hz, 6 H, CMe_2H) and 0.91 ppm (s, 6 H, CMe_2).

Reversed addition (the silirane to triethyltin hydride) resulted in an immediate exothermic reaction, with gas evolution. Large amounts of hexaethylditin were formed which prevented product analysis and isolation.

Acknowledgements

The authors are grateful to the U.S. Air Force Office of Scientific Research (NC)-AFSC for generous support of this research (Grant AF-AFOSR-79-0007). J.E. gratefully acknowledges an NSF/CNRS United States - France Exchange of Scientists Award.

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