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HEXAMETHYLSILIRANE

I. PREPARATION, CHARACTERIZATION AND THERMAL DECOMPOSITION *

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Summary

Hexamethylsilirane has been prepared by the action of magnesium on dimethyl-bis(α-bromoisopropyl)silane in tetrahydrofuran (THF) solution. It was found to be highly reactive toward atmospheric oxygen and moisture and to decompose when heated in solution at 60—75°C. Its decomposition results in the extrusion of dimethylsilylene which may add to the tetramethylethylene produced in the decomposition to regenerate the silirane, insert into the reactive SiC_2 ring of the silirane to give octamethyl-1,2-disilacyclobutane or oligomerize to give $(Me_2Si)_n$ oils.

Dimethyldiisopropyl-, tetraisopropyl- and tert-butyltriisopropylsilane were prepared by catalytic hydrogenation of the corresponding isopropenylsilanes. Bromination of dimethyldiisopropylsilane at 65°C resulted in exclusive formation of dimethyl-bis(α-bromoisopropyl)silane.

Introduction

The first silacyclopropanes (siliranes) were reported from these laboratories in 1972 [1]. These compounds, I, II and III, all were derivatives of the 7-siladispiro[2.0.2.1]heptane ring system. They were found to be very stable thermally but highly reactive, so reactive that inert atmosphere techniques were required at all stages of their synthesis, isolation, handling and storage. Full details of the synthesis [2], structural elucidation [3] and chemical reactivity [4] of these novel compounds have been reported. The study of their chemistry was

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* Dedicated to Professor G.A. Razuvaev on the occasion of his 85th birthday.

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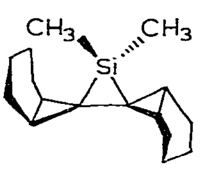

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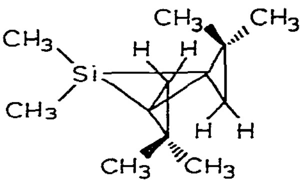

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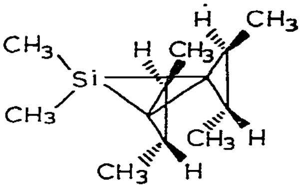

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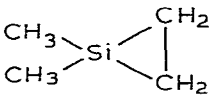
complicated by their relatively high molecular weights, so that the products of their ring-opening reactions were high-boiling liquids whose isolation as pure compounds often was difficult. Furthermore, if the ring-opening of these dispiro systems was a radical process in which the Si—C bond was cleaved, a cyclopropylcarbinyl radical would result and the latter would undergo subsequent rearrangement [5,6]. Thus, in order to develop the chemistry of the silacyclopropane ring system in greater breadth and depth, it was desirable to have available a simpler silirane for these studies. 1,1-Dimethylsilirane, IV, would be the compound of choice for these purposes. This compound, however,



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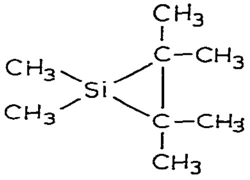
would be expected to be more volatile than tetramethylsilane (bp 26°C) and, perhaps, even would be a gas at room temperature. Another simple silirane is the hexamethyl derivative, V. This compound should be higher boiling than IV and the study of its reactions would avoid the problems of regioselectivity and stereochemistry which would accompany the reactions of siliranes of intermediate degrees of methylation such as compounds VI—IX. Accordingly, we



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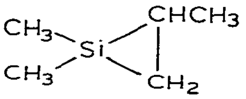

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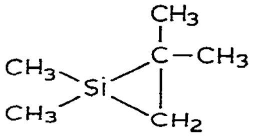

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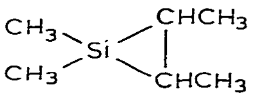

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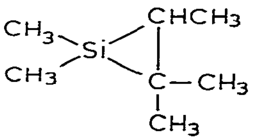


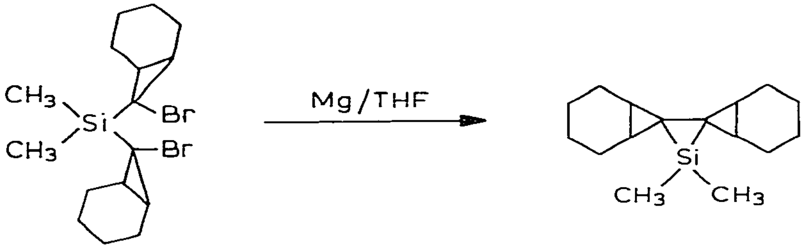
(IX)

concentrated out initial efforts toward the synthesis of hexamethylsilirane, V.

Results and discussion

1) Preparation of starting materials

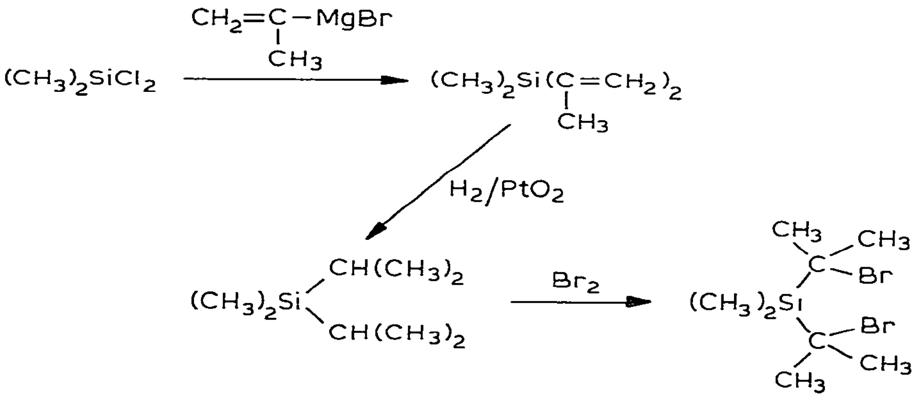
The method of synthesis of siliranes I—III used bromine elimination from the respective 1,3-dibromide for the ring closure reaction, e.g., eq. 1. The application of this procedure to the synthesis of hexamethylsilirane would require the availability of dimethyl-bis(α-bromoisopropyl)silane, X, a compound whose synthesis had not yet been reported. The finding of Cartledge and Jones [7] that dimethylisopropylchlorosilane reacted with molecular bromine to give



(1)

exclusively bromination of the α C—H bond of the isopropyl group suggested that the bromination of dimethyldiisopropylsilane could give the desired X. However, the preparation of dimethyldiisopropylsilane as described in the literature was not satisfactory for the larger quantities of this compound which would be required for our investigation. The reaction of isopropylmagnesium bromide with silicon tetrachloride had been reported to give diisopropyldichlorosilane in 11% yield [8], while, the reaction of isopropylmagnesium chloride with silicon tetrafluoride gave diisopropyldifluorosilane in 27% yield [9]. The methylation of the latter was effected in high yield [9], but the overall yield for the two steps was low. To make possible the preparation of dimethyldiisopropylsilane in larger quantities, we developed a new two-step route to this compound which is shown in Scheme 1. The first step, the reaction of isopropenylmagnesium bromide with dimethyldichlorosilane in tetrahydrofuran gave dimethyldiisopropenylsilane in yields which have ranged between 65 and 85% in most runs. The second step, the catalytic hydrogenation of dimethyldiisopropenylsilane, proceeded readily in a Parr Hydrogenation Apparatus in the presence of platinum(IV) oxide and has given dimethyldiisopropylsilane in yields of

SCHEME 1

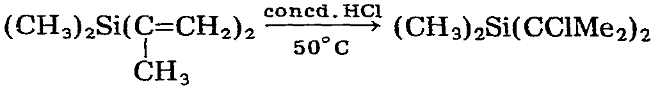


(X)

75—85%. This two-step procedure has also been used to prepare tetraisopropylsilane (step 1, 66% yield; step 2, 63% yield) and tert-butyl-triisopropylsilane (step 1, 33% yield; step 2, 87% yield) and thus appears to be of general applicability.

The bromination of dimethyldiisopropylsilane occurrred readily using neat bromine at 65°C and the reaction was highly regioselective, giving the desired dimethyl-bis(α-bromoisopropyl)silane in 70—80% yield.

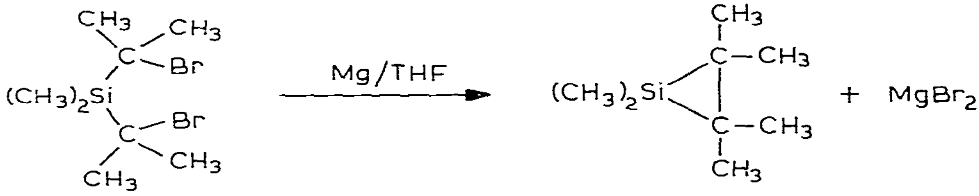
Dimethyl-bis(α-chloroisopropyl)silane also was prepared for evaluation as a hexamethylsilirane precursor. Its synthesis used a method developed by Sommer et al. [10] for the hydrochlorination of trimethylvinylsilane (eq. 2).



$$(CH_3)_2Si(\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2)_2 \xrightarrow[50^\circ C]{\text{concd. HCl}} (CH_3)_2Si(CClMe_2)_2 \qquad (2)$$

2) Preparation and characterization of hexamethylsilirane

The reaction shown in eq. 3 served excellently in the synthesis of hexamethylsilirane. The dibromide X as a ca. 0.5 *M* solution in tetrahydrofuran (THF) was



(3)

added to a 30% excess of magnesium chips in THF. Rigorously dried, freshly distilled,THF was a prerequisite, as was the maintainance of an absolutely air- and moisture-free system. A reaction commenced immediately after a small portion of the dibromide solution had been added. No initiating halide was required. A water bath at 10—20°C served as a heat sink. The remainder of the dibromide solution was added during a period of 2 h and the reaction mixture then was stirred at room temperature for about 10 h. The reaction consumed exactly one molar equivalent of magnesium. The solution was cannulated away from the precipitated magnesium bromide and all volatiles, including the product, were separated by trap-to-trap distillation at 0.02 mmHg. The distillate consisted of a THF solution of hexamethylsilirane together with three minor by-products. The latter were identified as $(CH_3)_2Si(CHMe_2)_2$, $(CH_3)_2Si(CHMe_2)(CMe{=}CH_2)$ and $(CH_3)_2Si(CMe{=}CH_2)_2$. All attempts to isolate hexamethylsilirane as a pure compound by distillation at temperatures as low as 35°C or by gas chromatography (GLC) using columns which had been conditioned by injections of silirane II were unsuccessful, presumable due to the high reactivity and the low thermal stability of hexamethylsilirane. However, in order to study the spectroscopic and the chemical properties of hexamethylsilirane it was not necessary to isolate it as a pure compound. Many of its reactions proceeded well in THF medium so that the trap-to-trap distillate could be used without further processing. If the THF solvent was not desirable (as in the spectroscopic studies and in some reactions), then it could be removed by careful trap-to-trap distillation (room temperature at 65 mmHg) into a receiver cooled to —78°C. This left a distillation residue consisting of hexamethylsilirane and the minor (5—10%) impurities mentioned above. This residue then could be diluted with the solvent of choice.

This ring closure could not be effected in diethyl ether. The action of magnesium on dimethyl-bis(α-bromoisopropyl)silane in this solvent gave a mixture ot elimination and reduction products, $(CH_3)_2Si(CHMe_2)_2$, $(CH_3)_2Si(CHMe_2)(CMe{=}CH_2)$ and $(CH_3)_2Si(CMe{=}CH_2)_2$, in 90% total yield. Dimethyl-bis(α-chloroisopropyl)silane proved to be unsuitable as a starting material for hexamethylsilirane. Its reaction with magnesium in THF did not result in ring closure and also gave instead a mixture of these reduction and elimination products.

The yield of hexamethylsilirane obtained in reaction 3 could be determined by nuclear magnetic resonance spectroscopy using an internal standard (usually benzene). Alternatively, an aliquot of the hexamethylsilirane solution obtained in the trap-to-trap distillation could be treated with methanol and the yield of the ring cleavage product, $(CH_3)_2(MeO)SiCMe_2CHMe_2$, could be determined by GLC. The yields as determined by these procedures usually were comparable. They ranged between 75% and above 90%, based on dibromide X.

Although hexamethylsilirane could not be isolated as a pure compound, it could be characterized thoroughly by nuclear magnetic resonance spectroscopy. The proton magnetic resonance spectrum showed the expected two singlets (at δ 0.133 (Me_2Si) and 1.13 ppm (Me_2C)) in 1 : 2 intensity ratio when the spectrum of a THF solution was measured. In benzene the Me_2C resonance shifted to 1.35 ppm, but the Me_2Si resonance was unchanged. Upon addition of methanol to such a solution a mildly exothermic reaction occurred and the Me_2C resonance changed to a singlet and a doublet, indicative of the presence of the CMe_2CHMe_2 group.

The natural abundance ^{13}C FT NMR spectrum (proton-decoupled) of hexamethylsilirane in concentrated THF solution showed three non-THF resonances at δ_C —9.67, 18.16 and 20.97 ppm *. An off-resonance decoupled spectrum showed the 20.97 ppm line as a quartet, the 18.16 ppm line as a singlet and the —9.67 ppm line also as a quartet, leading to the assignments shown in Figure 1.

As we had found in the case of the 7-siladispiro[2.0.2.1] heptanes, I and II, the ^{29}Si resonance is diagnostic of the silacyclopropane system [1,2]. These siliranes showed their ^{29}Si signals at δ_{Si} 53.21 and 51.78 ppm, respectively, upfield from tetramethylsilane, far from the usual range of ^{29}Si shieldings of both acyclic and cyclic tetraorganosilanes (δ_{Si} 20 to —10 ppm [11]). The decoupled natural abundance ^{29}Si FT NMR spectrum of hexamethylsiliane in concentrated THF solution showed a singlet at 49.31 ppm upfield from tetramethylsilane. A fully coupled spectrum, as expected, consisted of seven lines, with $J(Si{-}C{-}H) = 5$ Hz, centered at —49.31 ppm. Thus all three NMR spectra. ^1H, ^{13}C and ^{29}Si, are in agreement with the structure shown in Figure 1.

An attempt to obtain a low resolution mass spectrum of a concentrated

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* ^{13}C Chemical shifts are referenced to tetramethylsilane. Positive values indicate decreased shielding relative to tetramethylsilane.

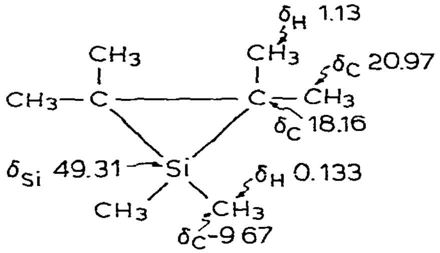


Fig. 1. NMR spectroscopy of hexamethylsilirane in THF solution.

sample of hexamethylsilirane at the normal operating temperature of 160°C was unsuccessful. The only fragment ion which was not derived from THF was observed at *m/e* 84 and assigned to $[Me_4C_2]^+$. However, when the spectrometer heaters were shut down so that a room temperature spectrum could be obtained, the mass spectrum of a sample of neat hexamethylsilirane showed the molecular ion at *m/e* 142. There were no heavier fragment ions observed up to *m/e* 284 ($2M^+$). Fragment ions of high intensity included those with *m/e* 85 and 69, assignable to $[Me_4C_2]^+$ and $[Me_3C_2]^+$. It would appear that the fragmentation of hexamethylsilirane under electron impact occurs with loss of dimethylsilylene.

It must be emphasized that hexamethylsilirane is *extremely* reactive. It reacts with many common reagents toward which acyclic and cyclic tetraorganosilicon compounds (even the strained silacyclobutanes) are completely stable at ambient temperature. (In a recent brief summary [12] we have termed it hyperreactive.) When a bulk sample of hexamethylsilirane is exposed to air, it immediately becomes hot and begins to fume vigorously. It is immediately destroyed by oxygen, water, alcohols and acids, and often these reactions are vigorously exothermic, more so than those of siliranes I, II and III. (These reactions will be discussed in detail in Part II of this series). As a consequence, hexamethylsilirane must be prepared, handled and stored under an inert atmosphere at all times.

3) *Thermolysis of hexamethylsilirane*

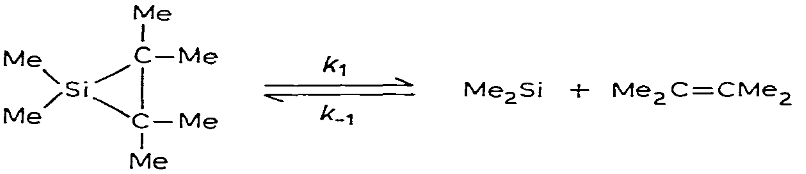
Siliranes I, II and III had been found to be very stable thermally [1,2]. It is not clear what the key factors responsible for their high stability are. Two theoretical studies have attributed the special stability of the 7-siladispiro[2.0.2.1]-heptane system to silicon *d* orbital contributions [3,13], (i.e., interaction of the silicon d_{xy} orbital with the cyclopropane $b_1\sigma$ molecular orbital). Another study [14] explains this stability as due to increased overlap in the σ framework of the silirane ring resulting from increased contributions of the *s* orbitals of the spiro carbon atoms to be bonding. All three studies, however, agree that hexamethylsilirane should be considerably less stable than the dispirosilacyclopropanes, and this is indeed the case.

The half-life of II in THF solution at 63°C is at least 7 days, very likely longer, since a part of the disappearance of II during this prolonged heating time probably was due to slow leakage of air into the system through the rubber septum cap through which samples for analysis were taken by syringe.

A comparable study established a half-life of only about 5 h for hexamethylsilirane in THF solution at 63°C. Its approximate half-life at 37°C was 81 h, at room temperature, greater than 9 days, at 0°C, greater than one month.

An initial experiment in which a solution of hexamethylsilirane in THF was heated at reflux until decomposition was complete gave tetramethylethylene in 46% yield. In an experiment carried out in benzene at 73°C for 15 h its yield was 77%. Although the organosilicon product(s) of this decomposition were not identified at this point, the formation of tetramethylethylene suggested that hexamethylsilirane decomposes thermally by extrusion of dimethylsilylene. Significantly, another experiment showed that hexamethylsilirane was completely stable when heated in tetramethylethylene solution at 63°C for 20 h. Subsequent work, to be described in a later paper of this series, showed that dimethylsilylene from thermolysis of hexamethylsilirane can be intercepted by means of its reactions with silicon hydrides [15], dimethyldimethoxysilane [15], 2,3-dimethyl-1,3-butadiene [15], other olefins [16], and certain acetylenes [17,18]. Further study of its decomposition in the absence of a dimethylsilylene trapping agent revealed that the silirane itself is a good silylene trap. When a solution of hexamethylsilirane in benzene was heated at 70°C for 18 h, two products were formed: tetramethylethylene in 62% yield and the less volatile octamethyl-1,2-disilacyclobutane, XI, in 38% yield. (This product had been left behind with the nonvolatile components in the early experiments).

The thermal decomposition of hexamethylsilirane in benzene solution in the absence of a dimethylsilylene trapping agent then may be pictured as shown in eq. 4 and 5. Reaction 4 is reversible, i.e., dimethylsilylene adds to the C=C bond of tetramethylethylene, as the stability of hexamethylsilirane in tetramethylethylene solution indicated. In a competitive, irreversible process, dimethylsilylene inserts into an Si—C bond of hexamethylsilirane to give XI (reaction 5). In addition, the formation of a nonvolatile, viscous, CH_3—Si-containing (by NMR) oil was noted; this probably is composed of Me_2Si oligomers of higher molecular weight formed in a second, also irreversible process which becomes more important as the concentration of the silirane decreases.



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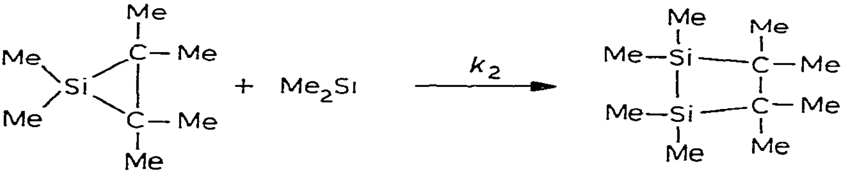
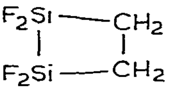


(XI)

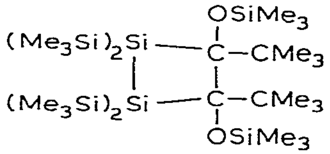
(5)

Only one other example of a 1,2-disilacyclobutane, XII [19], was known at



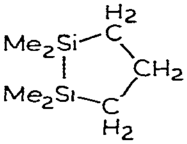
(XII)

the time of our isolation of XI. Subsequently, Brook and Harris [20] reported that head-to-head dimerization of $(Me_3Si)_2Si{=}C(OSiMe_3)CMe_3$, XIII, gives XIV. The latter, however, is not very stable and in solution is in dissociative



(XIV)

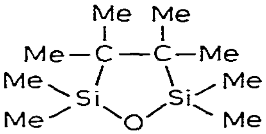
equilibrium with XIII. In contrast, octamethyl-1,2-disilacyclobutane is very stable thermally, surviving a 20 h heating period at 175°C without decomposition *. However, this compound, like other strained cyclic disilanes, e.g., XV



(XV)

[22], is readily oxidized on exposure to air.

In a separate experiment the thermolysis of hexamethylsilirane in benzene medium was followed by exposure of the reaction mixture to air. The product which was isolated was XVI, obtained in 33% yield. Thus, in the present case, as in the case of XV and other strained, reactive disilanes, it is the Si—Si bond which is the site of attack by oxygen.



(XVI)

The availability of hexamethylsilirane by a simple synthesis which may be carried out on a reasonably large laboratory scale (syntheses on a 0.2 mole scale are routine in our laboratories) has allowed a full development of the novel chemistry of this highly reactive compound. The full details of these further investigations will be reported in subsequent papers of this series.

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* A report of the high temperature pyrolysis of octamethyl-1,2-disilacyclobutane has appeared [21].

Experimental

General comments

Infrared spectra were recorded using a Perkin-Elmer Model 457A infrared spectrophotometer, proton magnetic resonance spectra using either a Varian Associates T60, a Perkin Elmer R-20 or a R-22 spectrometer. Chemical shifts are reported in ppm downfield from internal tetramethylsilane. Chloroform and dichloromethane often were used as alternative internal standards. ^{13}C and ^{29}Si FT NMR spectra were obtained using a Bruker HFX-90 spectrometer which was interfaced with a Digilab FTS/NMR-3 computer. Mass spectra were obtained using a Hitachi-Perkin Elmer RMU-6 or a Varian MAT-44 mass spectrometer, both operating at an ionization voltage of 70 eV. Gas-liquid chromatography (GLC) was used routinely for isolation of pure samples, determination of purity of distilled samples and for yield determinations using the internal standard method. F & M Model 700 and 720, Hewlett-Packard Model 5754 and MIT isothermal gas chromatographs were available. All columns were packed on acid-washed, dimethyldichlorosilane-treated Chromosorb W.

All solvents used were rigorously dried. All reactions were carried out under an atmosphere of prepurified nitrogen or argon. All glassware was flame-dried under a stream of nitrogen prior to use. Reactive reagents were transfered by syringe or cannula. The standard apparatus consisted of a three-necked round-bottomed flask of appropriate size which was equipped with a reflux condenser, a thermometer which extended into the reaction mixture, a nitrogen inlet tube, a rubber septum and a magnetic stir-bar.

Preparation of dimethyldiisopropylsilane

A five-liter, round-bottomed, three-necked flask equipped with a mechanical stirrer, a 500 ml pressure-equalizing addition funnel and a reflux condenser topped with an argon inlet tube was charged with 75.38 g (3.10 g atom) of magnesium turnings(Alfa/Ventron, 98%). While stirring, and with a strong argon purge, the entire apparatus was flame-dried and the magnesium heated thoroughly. The flask contents were allowed to cool under a stream of argon and then 500 ml of THF (freshly distilled from sodium benzophenone ketyl) was added.

The addition funnel was charged with 363.2 g (3.00 mol) of isopropenyl bromide (Columbia Organic Chemicals). The reaction was initiated by adding 10—20 ml of the bromide to the magnesium (without stirring). When initiation was apparent, stirring was begun and 2.5 liter of freshly distilled THF was cannulated quickly into the reaction flask while the bromide was added at a rate sufficient to maintain the reaction. The remainder of the isopropenyl bromide was added dropwise at a rate which maintained a gentle reflux. About 4 h was required for the addition. The mixture was stirred until the magnesium was almost consumed.

The addition funnel then was charged with 187.20 g (1.45 mol) of dimethyldichlorosilane (Union Carbide Corp.) and this was added dropwise over a period of 1 h. When the addition had been completed the mixture was stirred and heated at a gentle reflux overnight. Subsequently it was hydrolyzed by addition of saturated ammonium chloride solution to the "dry end point" (about 320 ml was required). The resulting mixture was filtered and the salts were washed with ether. Distillation of the combined organic phases gave 157.18 g (1.12 mol, 77%) of dimethyldiisopropenylsilane, b.p. 128—132°C, n_D^{25} 1.4376. (In a number of such preparations the yield has varied between 65 and 85%). (Anal. Found: C, 68.54; H, 11.64. $C_8H_{16}Si$ calcd.: C, 68.48; H, 11.50%). NMR (CCl_4/$CHCl_3$): δ 0.18 (s, 6 H, Me_2Si), 1.77—1.92 (m, 6 H, C—Me) and 5.20—5.36 and 5.53—5.69 (two m, 2 H each, $=CH_2$). IR (thin film, cm^{-1}): ν(C=C) 1600 w.

A 500 ml heavy-walled centrifuge bottle was charged with 200 ml of glacial acetic acid, 0.2—0.5 g of PtO_2 (Alfa/Ventron) and 40 g of dimethyldiisopropenylsilane. The bottle was attached to a Parr Hydrogenation Apparatus, flushed several times with hydrogen and brought to a hydrogen pressure of 55 psi. The solution was shaken for 18 h at ambient temperature. The hydrogen pressure was raised to 55 psi once again during this time, after which the solution was filtered and diluted with 200 ml of pentane.

This procedure was repeated with new portions of $Me_2Si(CMe=CH_2)_2$ until a total of 118.16 g (0.842 mol) had been brought into reaction. The three solutions were combined, washed with 500 ml of water and extracted with several 150 ml portions of saturated $NaHCO_3$, until the organic phase was free of acetic acid. The aqueous phase was back-extracted with pentane. The combined organic phase was dried ($MgSO_4$), filtered and distilled to give 95.65 g (0.663 mol, 79%) of dimethyldiisopropylsilane, bp 138—141°C, n_D^{25} 1.4181 (lit. [9] n_D^{20} 1.4198). NMR (CCl_4/$CHCl_3$): δ 0.067 (s, 6 H, Me_2Si) and 0.83—1.11 ppm (m, 14 H, Me_2CH).

Yields as high as 90% have been obtained on occasion.

Preparation of dimethyl-bis(α-bromoisopropyl)silane

A 500 ml, three-necked, round-bottomed flask equipped with a reflux condenser topped with an argon inlet tube, a 200 ml pressure-equilizing addition funnel and a magnetic stir-bar was charged with 95.63 g (0.663 mol) of $Me_2Si(CHMe_2)_2$. The flask then was immersed in an oil bath thermostated to 65 ± 5°C and the addition funnel was charged with 213.14 g (1.33 mol) of bromine.

The bromine then was added dropwise at such a rate that in the initial stages (approximately the first third to a half of the addition) the red bromine color is discharged completely between added drops. (Care must be taken that the oil bath temperature does not exceed 70°C at this stage). The bromine was consumed more slowly during the addition of the second half. The total time of addition was about 10 h.

After the addition had been completed, the mixture was stirred at 65°C overnight. (At the end of this time, if bromine still is present it is destroyed by adding sodium sulfite). The reaction mixture was diluted with an equal volume of pentane, filtered, and the filtrate was concentrated at reduced pressure. The yellowish-tan, viscous liquid which remained was distilled at reduced pressure to give 155.53 g (0.515 mol, 78%) of $Me_2Si(CBrMe_2)_2$, bp 114—118°C at 12 mmHg, which was isolated as a waxy, white solid, mp 84—86°C. The product may be sublimed at 28°C and 0.02 mmHg. (Anal. Found: C, 31.76; H, 5.97; Br, 53.11. $C_8H_{18}Br_2Si$ calcd.: C, 31.80; H, 6.00; Br, 52.90%). NMR

($CCl_4/CHCl_3$): δ 0.40 (s, 6 H, Me_2Si) and 1.92 (s, 12 H, Me_2C).

The yields obtained in this bromination reaction are variable but average 70—80%.

Preparation of tetraisopropylsilane

To a one-liter, three-necked, round-bottomed flask equipped with a reflux condenser topped with a nitrogen inlet tube, a mechanical stirrer and a pressure-equalizing addition funnel was added 18.8 g of tetrachlorosilane (0.164 mol) in 100 ml of diethyl ether. The addition funnel was charged with 700 ml of 1.30 *M* isopropenyllithium in diethyl ether. (The reagent had been prepared by reaction of isopropenyl bromide (Columbia Organic Chemicals) with 2 molar equivalents of lithium powder in diethyl ether by the method of Braude [23] and separated from solids by centrifugation). The lithium reagent solution was added to the $SiCl_4$ over a 2 h period. Subsequently, the mixture was stirred at room temperature for 40 h.and then was filtered. The filtrate was washed with water and the organic phase was dried and distilled to give 20.7 g (0.11 mol, 66%) of $(CH_2{=}CMe)_4Si$, bp 111—115°C at 55 mmHg, n_D^{25} 1.4812. (Anal. Found: C, 74.79; H, 10.44. $C_{12}H_{20}Si$ calcd.: C, 74.92; H, 10.48%). ^1H NMR ($CCl_4/CHCl_3$): δ 1.83 (s, 12 H, CH_3) and 5.3—5.8 ppm (m, 8 H, CH_2). IR (thin film, cm^{-1}): ν(C=C) 1615, 1600w.

A 500 ml, heavy-walled centrifuge bottle was charged with 100 ml of glacial acetic acid, 20.7 g (0.11 mol) of $(CH_2{=}CMe)_4Si$ and 0.35 g of PtO_2. The bottle was attached to a Parr Hydrogenation Apparatus and shaken at ambient temperature at an initial hydrogen pressure of 50 psi. After 16 h, 23 psi of hydrogen had been taken up, corresponding to 0.26 mol. At this point the hydrogen pressure was no longer decreasing and the reaction mixture was worked up by filtration, dilution with 200 ml of pentane and washing with three 150 ml portions of saturated $NaHCO_3$ solution. GLC of the organic phase showed that the reaction was not complete, so it was concentrated and returned to the hydrogenation apparatus. Further hydrogenation, as described above, resulted in uptake of an additonal 0.16 mol of hydrogen. Work-up as above gave an organic phase which was concentrated and analyzed by GLC (10% UC-W98 at 115°C). Tetraisopropylsilane, identified by comparison of its IR and ^1H NMR spectra with those reported by Weidenbruch et al. [24], was present in 63% yield.

Preparation of triisopropyl-tert-butylsilane

Using the procedure outlined above, a solution of 153 mmol of isopropenyllithium in 200 ml of diethyl ether was added to 5.0 g (26 mmol) of tert-butyltrichlorosilane (prepared by addition of tert-butyllithium (0.3 mol in 244 ml of pentane) to 0.35 mol of $SiCl_4$ in 200 ml of pentane, followed by filtration, evaporation of volatiles and sublimation of the product) over a period of 2 h. The mixture was stirred at room temperature for 5 h. At this time GLC analysis indicated the presence of a single product. The reaction mixture was trap-to-trap distilled at reduced pressure into a receiver at —196°C. Yield determination by GLC showed the desired product to be present in 33% yield. An analytical sample was isolated by GLC, n_D^{25} 1.4822. (Anal. Found: C, 75.18; H, 11.68. $C_{13}H_{24}Si$ calcd.: C, 74.91; H, 11.61%). NMR ($CCl_4/CHCl_3$): δ 1.12 (s, 9 H, CMe_3), 1.95 (m, 9 H, =CMe) and 5.4—5.8 (m, 6 H, CH_2). IR (thin film, cm^{-1}):

ν(C=C) 1600 w. The distillate was concentrated at reduced pressure.

The hydrogenation of 1.2 g (5.7 mmol) of $Me_3CSi(CMe{=}CH_2)_3$ was carried out as described in the experiment above. After the bomb had been shaken for 16 h, 1.5 psi of hydrogen (about 17 mmol) of hydrogen had been absorbed. Similar work-up gave an organic phase which was examined by GLC (10% Apiezon L, at 130°C). A single product was present in 87% yield. An analytical sample, n_D^{25} 1.4705, was isolated by GLC. (Anal. Found: C, 73.17; H, 14.00. $C_{13}H_{30}Si$ calcd.: C, 72.81; H, 14.10%). NMR ($CCl_4/CHCl_3$): δ 1.07 (s, 9 H, CMe_3) and 1.13—1.20 ppm (m, 22 H, Me_2CH).

Preparation of dimethyl-bis(α-chloroisopropyl)silane

A 500 ml, three-necked, round-bottomed flask equipped with a mechanical stirrer and a reflux condenser topped with a nitrogen inlet was charged with 300 ml of concd. hydrochloric acid and 17.1 (121 mmol) of dimethyldiisopropenylsilane. This mixture was stirred at 50°C for 98 h. Subsequently, 200 ml of hexane was added. The aqueous layer was washed with 400 ml of hexane and the combined organic phases were dried ($MgSO_4$) and concentrated at reduced pressure. The residue was distilled at reduced pressure to give 9.0 g (35%) of the title compound, bp 84—89°C at 12.5 mm, which was isolated as a waxy solid. Two sublimations (room temperature at 0.07 mmHg) gave material of mp 69—72°C. (Anal. Found: C, 45.05; H, 8.46; Cl, 32.82. $C_8H_{18}Cl_2Si$ calcd.: C, 45.06; H, 8.51; Cl, 33.26%). NMR ($CCl_4/CHCl_3$): δ 0.30 (s, 6 H, $SiMe_2$) and 1.66 (s, 12 H, Me_2C).

Preparation of hexamethylsilirane

To a 300 ml, three-necked, round-bottomed flask equipped with a pressure-equalizing addition funnel, a mechanical stirrer and an argon inlet tube was added 1.58 g (65 mg atom, 99.99% purity, from Alfa/Ventron) of magnesium chips. The apparatus was flamed out while argon was passed through it. After it has cooled (still under argon), the magnesium was covered with 10 ml of THF which had been distilled immediately before use and stored under positive argon pressure. The addition funnel was charged with 15.1 g (50 mmol) of dimethly-bis(α-bromoisopropyl)silane in 70 ml of THF. About 5 ml of this solution was added and after about 5 min of stirring at room temperature the reaction commenced, as evidenced by a mild exotherm. A 10—20°C water bath was placed around the reaction vessel to act as a heat sink and the remainder of the dibromo compound was added over a 2 h period. The reaction mixture was stirred at room temperature under argon overnight and then was transferred via cannula under positive argon pressure to a clean, flame-dried, argon-purged flask. The residual magnesium bromide was washed with 50 ml of dry THF and the washings were transferred to the THF solution. The combined THF solutions were trap-to-trap distilled at 25°C and 0.03 mmHg into a tared one-necked flask which was cooled in a liquid nitrogen Dewar flask. Subsequently, a positive pressure of argon was admitted and the flask was stored at 0°C. The yield of hexamethylsilirane was determined by adding a known amount of benzene to an aliquot of the silirane solution and obtaining a proton NMR spectrum. Integration of the benzene signal and the silacyclopropane signals allowed calculation of the yield. In repeated reactions carried out during the past 4 years the yields have ranged between 70 and 95%. An additional check was obtained by treating an aliquot of the hexamethylsilirane/ THF solution with anhydrous methanol and then determining the amount of methanolysis product, $Me_2(MeO)SiCMe_2CHMe_2$, formed by GLC. Calculation of the silirane yield by this procedure required the reasonable assumption that its reaction with methanol is a quantitative process. In general, there was good agreement between the yields determined by the two procedures.

For those reactions in which a solvent other than THF was required the following procedure was used to concentrate and determine the new concentrations of hexamethylsilirane. A standard trap-to-trap apparatus equipped with a 250 ml, one-necked flask as a receiver was flame-dried under an argon flow. The hexamethylsilirane/THF solution, in a 500 ml, one-necked flask, was attached to the trap-to-trap apparatus (all operations in an argon stream) and the THF was removed at room temperature and 65—70 mmHg into the Dry Ice-acetone cooled receiver over a period of at least 4 h. The receiving flask containing the THF was removed from the apparatus under an argon stream and replaced by a tared 50 ml, one-necked flask. The concentrated hexamethylsilirane then was distilled at room temperature and 0.02 mmHg into the receiver at liquid nitrogen temperature. Subsequently, a positive pressure of argon was admitted and the receiving flask was removed, capped with a tared rubber septum and weighed. The septum then was wired on and the flask was flushed and repressurized with argon. An NMR yield determination using an aliquot of the concentrate in benzene solution using toluene as a standard was performed. The concentrated silirane solution was stored under argon at 0°C and portions of this stock solution were removed by syringe for use.

In an alternative procedure, only that amount of hexamethylsilirane which was required for a reaction was concentrated. A 25 ml, one-necked flask equipped with a small magnetic stir-bar was weighed, attached to a standard trap-to-trap apparatus, and flask and apparatus were flame-dried under argon. The flask was cooled and approximately 5—7 ml of the silirane/THF solution was transferred (under argon) to the flask. The THF was removed at room temperature at 65—70 mmHg into a receiver cooled with liquid nitrogen over a period of at least 4 h. The distillation flask, which now contained essentially neat hexamethylsilirane, was capped with a tared rubber septum (positive argon pressure) and weighed. The septum was wired on and the flask was flushed and repressurized with argon. An NMR yield determination was performed on an aliquot using benzene-d_6 as solvent and toluene as standard. Methanol then was added to the NMR sample and the yield of the methanolysis product was determined by GLC. In many cases, the flask containing the neat hexamethylsilirane was used as the reaction vessel, the additional solvents and reagents being added by syringe under the appropriate conditions.

We emphasize again the high reactivity of hexamethylsilirane towards atmospheric oxygen and moisture. All operations involving this compound must be performed with complete exclusion of air in rigorously dried glassware using rigorously dried and degassed reagents and solvents.

Attempted isolation of hexamethylsilirane by GLC was unsuccessful, even when the columns had been preconditioned by injections of silirane II. However, GLC analysis detected the presence of three minor by-products which were isolated and identified (GLC retention times, IR and proton NMR spectra) as dimethyldiisopropenylsilane, dimethyldiisopropylsilane and dimethylisopropenylisopropylsilane. The latter is a new compound: $(CH_3)_2Si(CMe{=}CH_2)$-$(CHMe_2)$, n_D^{25} 1.4275. NMR ($CCl_4/CHCl_3$): δ 0.05 (s, 6 H, $SiMe_2$), 0.68—1.18 (m, 7 H, all $CHMe_2$ protons), 1.65—2.00 (m, 3 H, $=CCH_3$), 5.12—5.33 and 5.45—5.70 ppm (two m, each 1 H, $=CH_2$).

In various preparations these by-products were present in yields ranging from trace to 15%.

The spectroscopic properties of hexamethylsilirane are given in the Results and Discussion section. The complete mass spectrum showed the following fragment ions, *m/e* (relative intensity): 142 (20, M^+), 127 (9), 125 (8), 101 (15), 100 (9), 99 (36), 85 (14), 84 (45), 74 (11), 73 (95), 72 (29), 71 (25), 69 (100), 67 (15), 59 (50), 58 (10), 56 (11), 55 (26), 53 (12), 51 (6), 45 (12) and 43 (35).

Attempted preparation of hexamethylsilirane in diethyl ether solution

The standard apparatus was charged with 1.60 g (66 mg atom) of magnesium and 10 ml of diethyl ether, using the usual precautions to exclude air and moisture. To the magnesium was added 12.65 g (42 mmol) of $Me_2Si(CBrMe_2)_2$ in 80 ml of diethyl ether during the course of 1.5 h at 20°C. The reaction mixture was stirred at room temperature overnight and then all volatiles were removed by trap-to-trap distillation at room temperature and 0.01 mmHg into a receiver cooled to —196°C. Examination of the distillate by proton NMR showed three CH_3—Si resonances of about equal intensity. An aliquot of the distillate was treated with anhydrous methanol and the resulting solution was examined by GLC. Only a trace of the hexamethylsilirane methanolysis product was present, the major products being the minor by-products of the THF reaction: $Me_2Si(CMe{=}CH_2)_2$, $Me_2Si(CHMe_2)_2$ and $Me_2Si(CMe{=}CH_2)(CHMe_2)$. The combined yield of these products, determined by GLC, was 37.6 mmol (90%).

Attempted preparation of hexamethylsilirane from dimethyl-bis(α-chloroisopropyl)silane in THF

The standard ring-closure apparatus was charged with 1.20 g (50 mg atom) of magnesium and 10 ml of THF, using the usual precautions to exclude air and moisture. A 5 ml aliquot of a solution of 7.9 g (37 mmol) of $Me_2Si(CClMe_2)_2$ in 60 ml of THF was added, along with 75 μl of 1,2-dibromoethane to initiate the reaction. Subsequently, the remainder of the dichloro compound solution was added over a period of 1 h. The resulting mixture was stirred at room temperature overnight and then all volatiles were removed by trap-to-trap distillation. A portion of the distillate was treated with anhydrous methanol and examined by GLC. The hexamethylsilirane methanolysis product was not present, the only silicon compounds observed being $Me_2Si(CMe{=}CH_2)_2$, $Me_2Si(CHMe_2)_2$ and $Me_2Si(CMe{=}CH_2)(CHMe_2)$.

Thermal decomposition of hexamethylsilirane in THF medium

A THF solution containing 1.51 mmol of the silirane was heated at reflux (67°C) under argon for 15 h. The resulting solution was trap-to-trap distilled at room temperature and 0.02 mmHg into a receiver cooled with liquid nitrogen. NMR and GLC analysis of the distillate showed the presenceof tetramethylethylene (0.69 mmol, 46%). The distillation residue was a viscous oil whose ^{1}H

NMR spectrum showed only Si—CH_3 and C—CH_3 resonances in about 4 : 1 intensity ratio,

In another experiment, about 6 ml of a hexamethylsilirane solution in THF was heated at 63°C. Aliquots were periodically withdrawn, weighed, added to anhydrous methanol, and then a weighed amount of n-dodecane internal standard was added. The amount of the methanolysis product was determined by GLC and then related to the total solution volume. The initial value was assigned the value of 100% and subsequent values are reported as % of the initial value. The following data were collected: Time in h (amount of hexamethylsilirane present): 0 (100); 1.7 (88); 2.8 (74); 4.1 (58); 5.1 (48); 6.2 (41). Similar experiments were carried out at 37°C; 0 (100); 2 (91); 4.25 (90); 5.5 (92); 23 (76); 30.25 (72); 48.5 (65); 70.75 (59); 95 (47); 119.5 (35); 143.5 (33); 167.5 (30).

Thermal decomposition of hexamethylsilirane in benzene medium

A solution of 1.13 mmol of the silirane in 5 ml of benzene was heated at 73°C under argon for 15 h. The reaction mixture was trap-to-trap distilled at room temperature and 0.02 mmHg into a receiver cooled to —196°C. An NMR spectrum of the distillate showed a singlet at 1.85 ppm. GLC analysis showed the presence of tetramethylethylene in 77% yield. A sample was collected, n_D^{25} 1.4095; lit. [25] n_D^{20} 1.4115.

The decomposition of hexamethylsilirane in benzene-d_6 was monitored by ^1H NMR. An NMR tube was charged with 400 μl of C_6D_6, 15 μl of the silirane and 20 μl of toluene (internal standard), cooled to —96°C, evacuated and sealed. The tube was heated at 60°C. It was cooled and examined by NMR periodically. Heating was discontinued overnight and the tube was stored at 0°C. The decrease of the silirane concentration was monitored by determining the ratio of the silirane to toluene, the initial ratio being given the value of 100. Subsequent values are reported as % of the initial value: Time in h (Amount of hexamethylsilirane, %); 0 (100); 3.5 (79); 8.0 (66); 12.5 (63); 16.0 (43); 19.0 (36); 25.0 (30). During this time the steady growth of the tetramethylethylene resonance and of a singlet at δ 0.28 ppm was noted.

Isolation of octamethyl-1,2-disilacyclobutane

A solution of 4.31 mmol of hexamethylsilirane in 3.0 ml of dry benzene was heated under argon at 70°C for 18 h. GLC analysis showed the presence of tetramethylethylene (62%) and another less volatile compound. The latter was collected by GLC (1.5 ft × 0.25 in column, 20% SE30, MIT isothermal unit, at 117°C) as a colorless solid, mp 71—71.5°C. Its yield was determined by GLC to be 0.82 mmol (38% based on silirane). (Anal. Found: C, 59.67; H, 12.03. $C_{10}H_{24}Si_2$ calcd.: C, 59.91; H, 12.07%).

The results of spectroscopic studies are given below.

IR (cm^{-1}, solid film): 2960(sh), 2955vs, 2930vs, 1890s, 1850vs, 1470(sh), 1465s, 1447m, 1405m, 1375m, 1365m, 1245vs, 1120w, 995(sh), 990w, 925(sh), 915m, 895m, 860(sh), 830s, 805s, 775(sh), 760s, 725m, 690(sh), 675s, 618m cm^{-1}.

Raman (cm^{-1}, capillary): 2951s, 2932(sh), 2902vs, 2869(sh), 2857s, 2742w, 2703w, 1464m, 1435m, 1399w, 1381w, 1353w, 1246w, 1190m, 1170m, 1116m, 1079w, 998w, 938w, 914m, 891w, 856w, 799w, 753w, 715w, 669s, 609w, 533vs, 441w, 416vs, 367s, 325m, 259s, 222s, 154vs cm^{-1}.

NMR (benzene-d_6/benzene): δ 0.29 (s, 12 H, Si—CH_3), 1.07 (s, 12 H, C—CH_3) ppm.

Mass spectrum (m/e, relative intensity) 201 (M^+ + 1, 1.5), 200 (M^+, 6), 142 (1.5), 127 (3), 117 (18), 116 (($Me_2Si{=}SiMe_2)^+$, 100), 101 (17), 85 (6), 73 (80), 59 (27), 58 (8).

^{13}C NMR (benzene-d_6): proton decoupled: singlet, 31.1 ppm downfield from TMS (ring-*C*): singlet, 21.8 ppm downfield from TMS (C—CH_3): singlet, 3.4 ppm upfield from TMS (Si—CH_3).

^{29}Si NMR (benzene-d_6): proton coupled: 3 of the expected 7 lines (considerably broadened) at 11.6 ppm downfield from TMS for the ring-Si.

The preparation of octamethyl-1-oxa-2,5-disilacyclopentane (XVI)

A solution of 5.01 mmol of hexamethylsilirane in 3.0 ml of benzene was heated under argon for 18 h at 70°C. Subsequently, oxygen was bubbled slowly through the solution of 1 h. A strongly exothermic reaction resulted which subsided after the first 15 min. GLC analysis showed the presence of a product which was less volatile than the tetramethylethylene which also was present. This product was isolated as a liquid, n_D^{25} 1.4526, by GLC (conditions as in the experiment above). Its yield, determined by GLC, was 33%, based on the silirane. (Anal. Found: C, 55.40; H, 11.13; $C_{10}H_{24}OSi$ calcd.: C, 55.47; H, 11.18%). NMR (CCl_4, CH_2Cl_2): δ 0.15 (s, 12 H, Me_2Si) and 0.92 ppm (s, 12 H, Me_2C). IR (neat film, cm^{-1}): 2960vs, 2930(sh), 2900(sh), 2860m, 1460s, 1445m, 1405w, 1393m, 1378m, 1365m, 1255vs, 1200w, 1167w, 1125m, 1070w(br), 996m, 935(sh), 922vs(br), 895m, 872w, 842m, 780s, 760(sh), 695s, 685(sh) and 635s. The mass spectrum showed the following fragment ions (*m/e*, relative intensity): 217 (M^+ + 1, 3), 216 (M^+, 14); 201 (M^+ — 15, 1), 202 (5), 174 (2), 173 (1), 147 (6), 135 (7), 134 (14), 133 (100), 118 (6), 117 (43), 116 (1), 103 (2), 73 (30) and 59 (10).

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