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7,7-DIMETHYL-7-SILADISPIRO[2.0.2.1]HEPTANE DERIVATIVES. THE FIRST SILACYCLOPROPANES *

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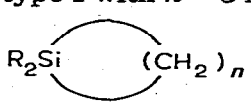
Summary

The preparation of the first silacyclopropanes, all derivatives of 7,7-dimethyl-7-siladispiro[2.0.2.1]heptane, by magnesium-induced ring closure reactions of 1,3-dihalides, is described. Mass spectral and ^{1}H, ^{13}C and ^{29}Si NMR spectral data, as well as the unusually high chemical reactivity of these compounds support the assigned silacyclopropane structures.

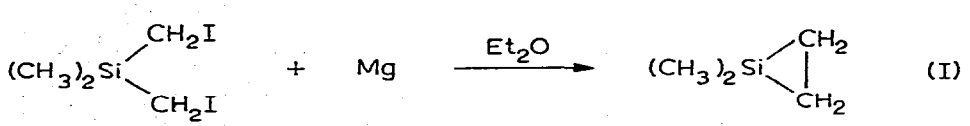
Introduction

At the time the present work was begun in 1972, silacarbocyclic systems of type I with $n = 3$ had been the subject of much research, but silacyclopropanes



(I)

($n = 2$) remained unknown despite the fact that their preparation had been attempted many times during the preceding 20—25 years [2]. One of the procedures tried to effect the synthesis of the SiC_2 ring was an adaptation of the well-known ring closure reaction of an α,ω-dihalide by a divalent metal (magnesium or zinc) (eq. 1) [3]. This reaction gave a polymeric product rather than the

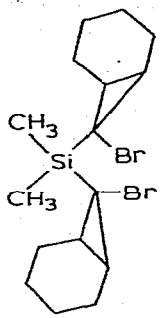


(I)

hoped-for silacyclopropane.

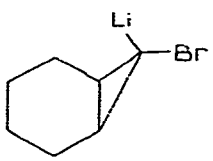
* Preliminary communication, Ref. 1.

During the course of our investigations of the chemistry of α-bromocyclopropyllithium reagents we had occasion to prepare II by reaction of *anti*-7-bromo-*syn*-7-lithionorcarane [4] with dimethyldichlorosilane. The indicated stereochem-



(II)

istry of II is based upon its ^{13}C NMR spectrum which showed that the product had a symmetrical structure. Also, we had developed conditions under which the reaction of n-butyllithium with 7,7-dibromonorcarane gives isomer III, as indicated by the chemical conversions of this reagent, including its reaction with trimethylchlorosilane to give IV.



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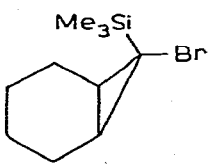
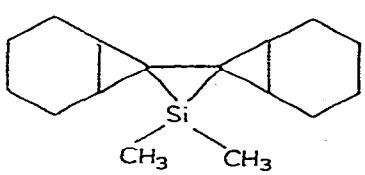


(IV)

Compound II is a 1,3-dibromide; hence its metal-induced ring closure to a silacyclopropane derivative should, in principle, be possible. It was known that the presence of bulky substituents (in most cases, t-butyl groups) could assist in the stabilization of strained, otherwise unstable or poorly stable ring systems such as cyclopropanones [5], oxaziridines [6] and aziridinones [7], and this raised the question if the norcaranylidene substituent might not also have such a stabilizing effect and permit the formation of a stable ring closure product, V,



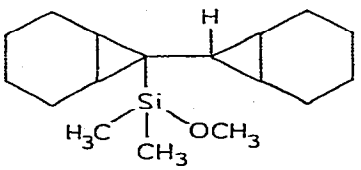
(V)

when II was treated with metallic magnesium. With this idea in mind, we began our studies on silacyclopropanes.

Results and discussion

The precursor silane used in the initial stages of this work was bis(*anti*-7-bromo-*syn*-7-norcaranyl)dimethylsilane (II).

In the first experiment done, compound II was added to an excess of magnesium turnings in dry tetrahydrofuran (THF), under nitrogen, at room temperature. Upon completion of the reaction, the mixture was hydrolyzed by careful addition of saturated ammonium chloride solution to the "dry end point" [8]. Recovery of unreacted magnesium showed that a maximum of 1.18 equivalents had been consumed, which indicated that some process other than formation of a diGrignard reagent had occurred. The organic layer was distilled at reduced pressure to yield a considerable amount of white, crystalline solid, b.p. about 100°C at 0.01 mmHg. This volatility is consistent with a structure such as V with 16 carbon atoms. The solid obtained was very soluble in hexane and extremely air-sensitive. Very brief exposure to the atmosphere converted it irreversibly to a nonvolatile oil. An attempt to precipitate the solid from hexane by adding methanol resulted in a strongly exothermic reaction. Removal of solvents left an oil which could not be induced to crystallize but which could be distilled. Spectroscopic examination and combustion analysis indicated the structure VI for this product. An attempt to measure the proton NMR spectrum of this reactive white solid in carbon tetrachloride solution failed because an exothermic reaction commenced immediately after the solution had been prepared.



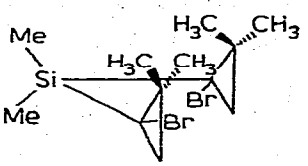
(VI)

It was apparent that the product of the II/Mg reaction was highly reactive, much more reactive than any known silacycloalkane. Since silacyclobutanes are considerably more reactive than higher silacycloalkanes as a result of ring strain [9], it was to be expected that silacyclopropanes would be still more reactive. The initial results thus were encouraging.

Later work showed that V is highly reactive toward water in a homogeneous medium, such as aqueous THF [10]. Although it survived the "dry end point hydrolysis" in the initial experiment (which attests to the truly anhydrous nature of the organic layer obtained when this procedure is carried out correctly), in all subsequent preparations of this and other silacyclopropanes we used a nonhydrolytic work-up, and such a preparation of V is described in the Experimental Section.

The product of the magnesium-induced ring closure reaction of II was characterized as described below. However, the study of its chemistry was complicated by the fact that its reactions gave mostly products which were very high-boiling oils whose isolation and purification by distillation or gas chromatography was difficult if not impossible. For this reason simpler systems were chosen for further study, in particular, the *gem*-dibromocyclopropanes derived from isobutylene and *trans*-2-butene. These formed the respective α-bromocyclopropyllithium reagents at low temperature which reacted with dimethyldichlorosilane to give the expected organosilicon products in 40—50% yield [4]. With these, however, we had the problem of the formation of several isomers. In each of these compounds there are two asymmetric cyclopropane carbon atoms attached

to silicon, so that three possible dibromides, *d*, *l* and *meso*, must be considered: VII, VIII, IX and X, XI, XII respectively.



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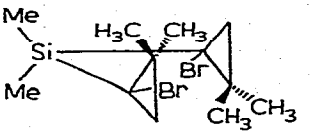

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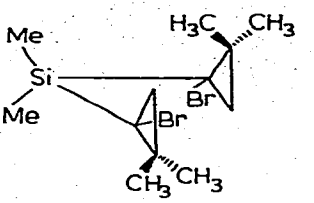

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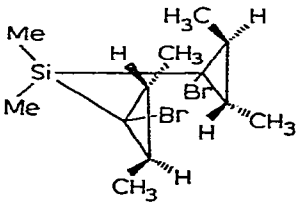

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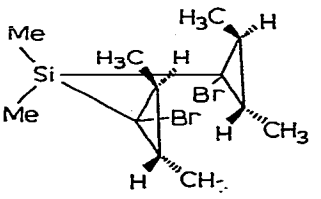

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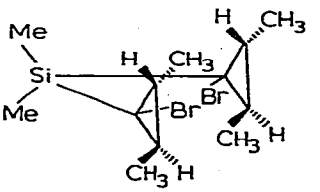
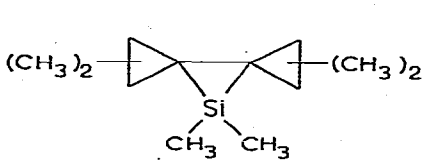


(XII)

The product of the 1-bromo-2,2-dimethylcyclopropyllithium/Me_2SiCl_2 reaction was a liquid which was not sufficiently stable thermally to allow its resolution by GLC. The proton NMR spectrum suggested the presence of all three isomers [4]. On the other hand, the reaction of 1-bromo-*trans*-2,3-dimethylcyclopropyllithium with dimethyldichlorosilane gave a solid product which could be resolved at least partially by fractional crystallization [4].

Treatment of the mixture of isomers of bis(1-bromo-2,2-dimethylcyclopropyl)-dimethylsilane (VII—IX) with magnesium in THF at room temperature produced an air-sensitive, distillable liquid in 45% yield, which also was characterized by its very high reactivity toward many reagents. This was assumed to be XIII and all further data which were collected served to confirm this assignment (see below) In similar fashion, the action of magnesium in THF on bis(1-bromo-*trans*-2,3-dimethylcyclopropyl)dimethylsilane (the isomer of m.p. 95—97° C, believed to be the racemic *d*, *l* mixture) also gave a highly reactive liquid product assumed to be XIV.

Considerable effort was devoted to the thorough characterization of these three compounds in view of the fact that we believed them to be the first three members of the long elusive class of silacyclopropanes to be prepared and isolated. No single piece of data was conclusive by itself (except for the X ray crys-



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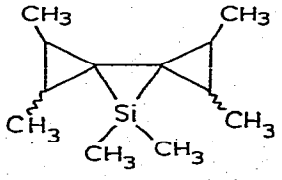


(XIV)

tal structure of V [11], obtained at a later date) but the total accumulated evidence spoke strongly in favor of the assumed silacyclopropane structure. It must be emphasized that the key to the successful handling of these compounds is the absolute maintainance of oxygen- and moisture-free conditions. The compounds are thermally quite stable and survive distillation at about 100°C and gas chromatography with injection port temperatures up to 200°C. The experimental evidence which bears on the structure of these highly reactive organosilicon compounds is as follows.

(1) Combustion analyses. Satisfactory analyses for carbon and hydrogen were obtained for all three products. A silicon analysis was obtained for the solid product of the II/Mg reaction which agreed well with the value calculated for V.

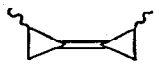
(2) Mass spectra. High resolution mass spectra of all three silacyclopropanes showed the expected molecular ion for the silacyclopropane structures within experimental error. There were no fragment peaks which correspond to $2\,M^+$ or $(2\,M - 15)^+$. This is of importance in that a possible 1,4-disilacyclohexane structure is thus excluded. The most abundant fragment peaks are listed in Table 1, with calculated decimals in parentheses. Of special significance is the fact that fragments corresponding to the respective bicyclopropylidene were abundant in the mass spectra of all three compounds. This gives a good indication that the reactions of magnesium with the bis(α-bromocyclopropyl)dimethylsilanes resulted in C—C bond formation. The $(M + 16)^+$ peaks were variable in relative intensity and may correspond to an oxidation product of the respective silacyclopropanes. Low resolution mass spectra of V provided some indication that this was so. It was found that a sample of V which had a low, broad melting point gave an intense $m/e = 262$ $(m + 16)^+$ peak relative to M^+ $(m/e = 246)$ peak. However, a sample with a high melting point, presumably of higher purity, gave a much less intense m/e 262 peak. When the ionization voltage was reduced as far as the instrument would permit (7.6 eV, uncalibrated), the $m/e = 246$ and 231 $(M - 15)^+$ peaks still were strong, but the m/e 262 peak now was much less intense.

(3) Infrared spectra. The infrared spectra of the three compounds which we believed to be silacyclopropanes showed no remarkable features. Noteworthy is the absence of bands which might be attributed to an Si—O bond.

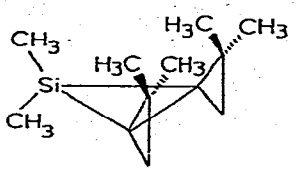
(4) Proton NMR spectra. In all three cases the assumed silacyclopropane products showed only one sharp CH_3—Si resonance in their proton NMR spectrum.

TABLE 1

HIGH RESOLUTION MASS SPECTRAL DATA FOR SILACYCLOPROPANES V, XIII AND XIV

	V	XIII	XIV
M	246.1807 (.1804)	194.1519 (.1491)	194.1525 (.1491)
$M - 15$	231.1570 (.1569)	179.1272 (.1256)	179.1278 (.1256)
$M + 0$	262.1768 (.1753)	210.1440 (.1474)	210.1460 (.1474)
$M + 0 - 15$	247.1518 (.1518)	195.1217 (.1239)	195.1222 (.1239)
	188.1564 (.1565)	136.1250 (.1252)	136.1226 (.1252)
$M - C^{12} + C^{13}$	247.1815 (.1838)	195.1527 (.1524)	195.1538 (.1524)

Of course, we could be dealing with accidental coincidences of chemically different CH_3Si signals. However, it was tempting to conclude that stereospecific processes were occurring and that in the case of XIII and XIV the *meso* isomers



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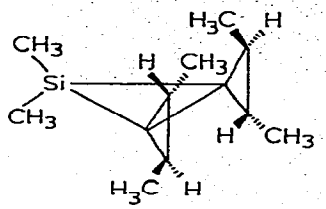
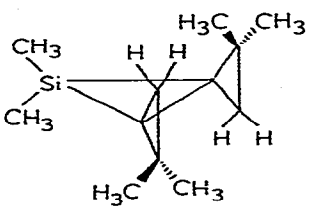


(XVI)

XV and XVI had not been formed. The NMR spectrum of the starting 1,3-dibromide used in the preparation of XIII had CH_3—Si resonances suggestive of a 1 : 1 mixture of isomers, presumably *d, l* (VII, VIII) and *meso* (IX). Considering that a 45% yield of one isomer type, presumably the *d, l* racemic mixture XVII, XVIII, was formed, and none of the *meso*, this would correspond to a 90% yield



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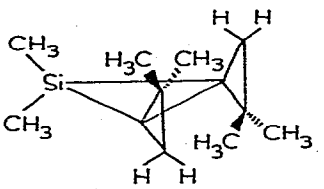


(XVIII)

for the one isomer and 0% for the other if stereospecific closure were occurring. It may be that steric factors prevent the closure to XV, and it is worth noting that the reaction of magnesium with the VII, VIII, IX mixture produces a considerable amount of nonvolatile solid (not characterized) in addition to XIII.

The preparation of XIV proceeded in about 65% isolated yield, acceptably high enough to feel that the starting material probably is the *d, l*, not the *meso* form.

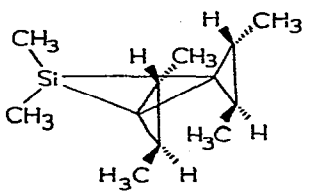
In the proton NMR spectrum of XIII (which is believed to be the XVII, XVIII *d, l* mixture) there were two sharp cyclopropyl—methyl resonances of equal intensity, as well as two discernable cyclopropyl—H resonances which split each other in a typical *AB* pattern with $J = 3.0$ Hz. This spectrum thus is completely consistent with the silacyclopropane structure.

(5) ^{13}C *NMR spectra.* ^{13}C NMR spectra were obtained for all three silacyclopropanes. The structural assignments of the carbon atoms in XIII and XIV was accomplished by several partial decoupling experiments in which only first order splitting by the hydrogen atoms attached directly to the carbon atoms was observed. In this manner, the methyl carbon atoms may appear as quartets, methylene carbon atoms as triplets, methine carbon atoms as doublets and quaternary carbon atoms will remain singlets, compared to the proton-decoupled spectra in which all of the resonances appear as singlets.

The proton-decoupled ^{13}C NMR spectra of silacyclopropanes XIII and XIV

showed six singlets of comparable intensity, consistent with the expectation that each of the compounds has six chemically different carbon atoms which are paired. In the initial ^{13}C experiment with XIII the two quaternary carbons accidentally coincided. It was observed in two succeeding experiments that the two carbon atom signals became resolvable and then readily resolvable. The only systematic difference in these three experiments was that additional hexafluorobenzene (^{19}F internal lock) was added to the sample before the second experiment and even more was added before the third run. The silacyclopropane was the same sample throughout, suggesting that a solvent shift was occurring.

We were able to observe unambiguously the $^{13}C—^{29}Si$ coupling to the methylsilicon carbon atoms and found $J(^{29}Si—^{13}C) = 58 \pm 2$ Hz for both compounds. A value of 51 Hz has been reported for $J(^{29}Si—^{13}C)$ in tetramethylsilane [12]. Figures showing these ^{13}C NMR spectra are available in [13]. All of the proton and ^{13}C NMR data thus are in accord with the formulation of silacyclopropane XIII as the *d,l* pair XVII, XVIII and silacyclopropane XIV as the *d,l* pair XIX, XX.



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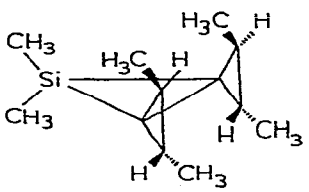
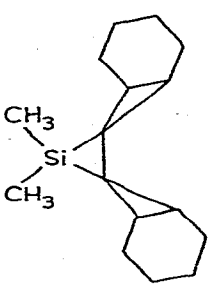


(XX)

The proton-decoupled ^{13}C NMR spectrum of silacyclopropane V in benzene-d_6 showed eight singlets. Our initial assumption had been that the dibromo precursor II would undergo concerted, stereospecific ring closure to give isomer XXI. This, however, did not appear to be the case, since this species would have a ^{13}C proton-decoupled NMR spectrum consisting of only five lines. The ^{13}C NMR spectrum in question is shown in Fig. 1. If one assumes that the signal at 23.2 ppm, whose intensity is markedly greater than those of the others, is due to two sets of carbon atoms, then nine resonances actually are present. A nine line spectrum would be compatible with the requirements of isomer XXII. It is this structure which was established by X ray crystallography for a crystalline sample of V [11].



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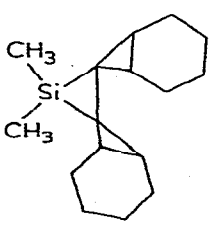


(XXII)

(6) ^{29}Si NMR spectra. More and more information is becoming available concerning the ^{29}Si NMR spectra of organosilicon compounds, and, in particular, the

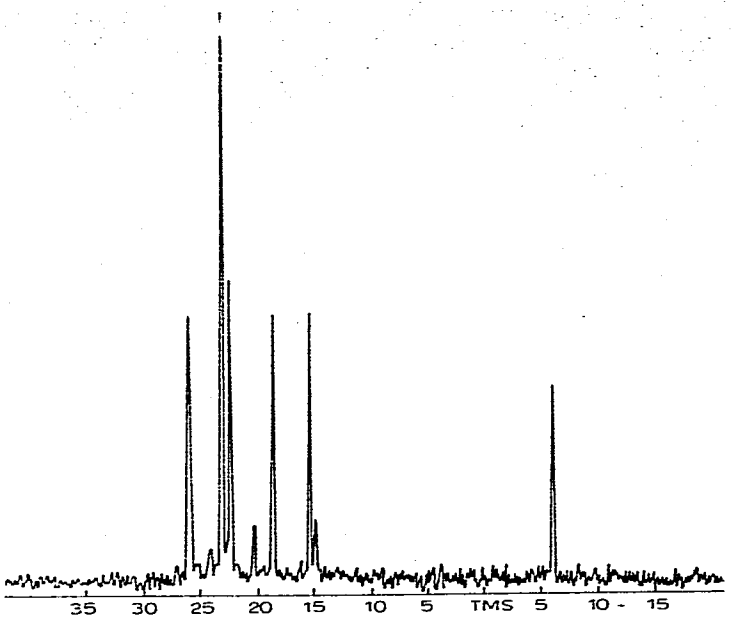


Fig. 1. ^{13}C NMR spectrum of 1,1-dimethyl-2-(syn-7-norcaranylidene)-3-(anti-7-norcaranylidene)-1-silacyclopropane.

surveys of Scholl, Maciel and Musker [14] and of Ernst et al. [15] provide much useful data. All ^{29}Si chemical shifts of acyclic and cyclic tetraalkylsilanes were found between 5 ppm upfield and 20 ppm downfield from tetramethylsilane (TMS). The ^{29}Si resonances of V and XIII were observed as singlets in their proton-decoupled spectra at 53.21 and 51.78 ppm, respectively, upfield from TMS. This indicates that we are dealing with rather atypical organosilicon compounds within the general class of those containing four Si—C bonds. The significance of this large upfield shift becomes apparent when one considers some ^{31}P NMR data. The ^{31}P resonances of most R_3P compounds are found at 20—100 ppm upfield from 85% H_3PO_4, while ^{31}P resonances of 1-methyl- and 1-phenyl-phosphirane were observed at 251 and 234 ppm, respectively, upfield from 85% H_3PO_4 [16]. It would appear that such high upfield shifts are diagnostic for the presence of silicon and of phosphorus in MC_2-type three-membered rings. Hexamethylsilacyclopropane, whose preparation was reported recently [17], showed its ^{29}Si NMR resonance at 49.5 ppm upfield from TMS.

(7) Chemical reactivity. The chemical reactions of XVII/XVIII will be covered in another paper [18], but the exceptionally high reactivity of these three silacyclopropanes provides strong support for the presence of the SiC_2 ring in these compounds. No organosilicon compounds with four Si—C bonds, cyclic or acyclic, have comparable reactivity.

That the magnesium-induced ring closure of II gave XXII, not XXI, was, at first sight somewhat surprising. We had expected that a concerted ring closure would take place with retention of configuration at carbon. Inversion at one of the carbon atoms occurred instead, but the mechanism of this ring closure remains unknown. In any case, we note that it is possible for metal- or organometal-in-

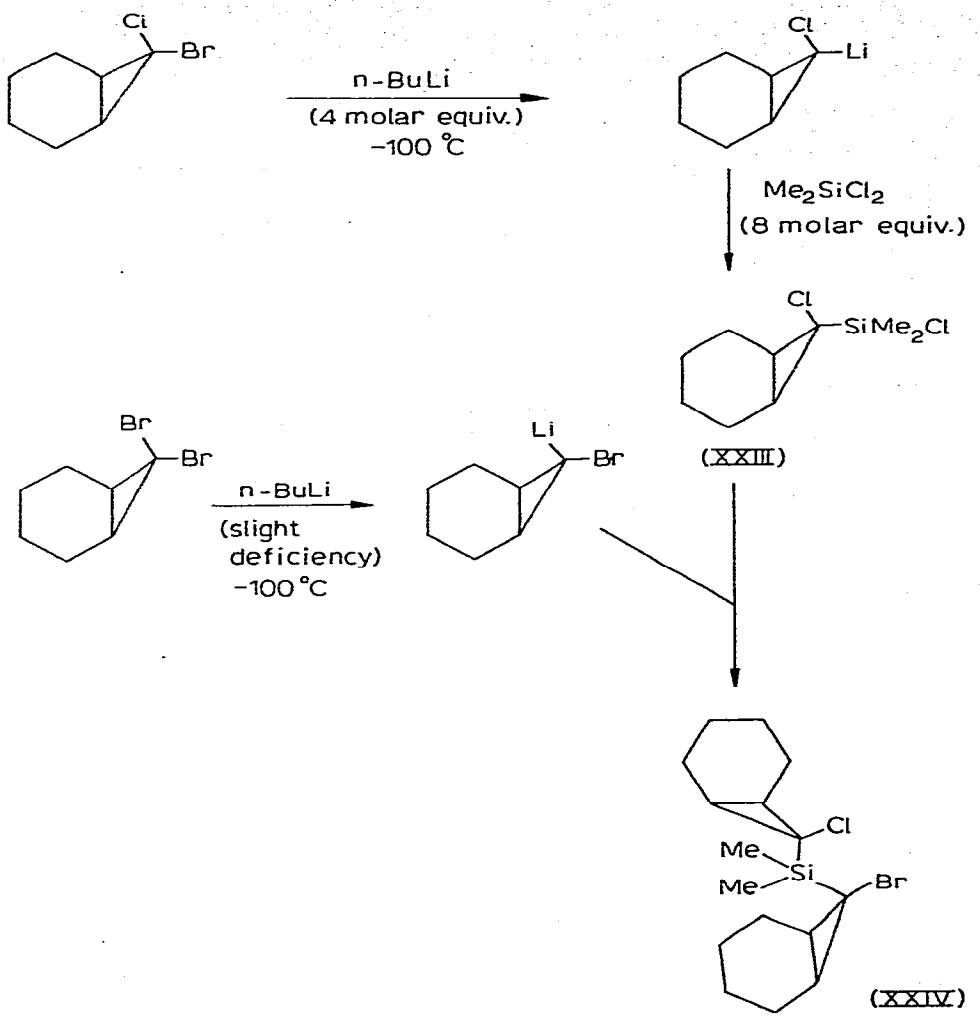
duced ring closure of 1,3-dihalides to give cyclopropanes can proceed with inversion of configuration at carbon [19]. Explanations in terms of orbital symmetry considerations have been given [20].

Since the ^{13}C NMR spectrum of V indicated that the bulk sample of this product (as well as the crystal examined by X ray crystallography [11]) had structure XXII, a stereospecific ring closure must have occurred. Further information bearing on this point was provided by the stereospecific synthesis of another isomer of V, whose structure was not established but which was different from XXII. In the course of our previous studies of α-bromocyclopropyllithium reagents, we prepared by stereospecific reaction isomerically pure *anti*-7-bromo-*syn*-7-chloronorcarane [4]. Reaction of this compound with an excess of n-butyllithium at low temperature formed *anti*-7-lithio-*syn*-7-chloronorcarane whose subsequent reaction with an excess of dimethyldichlorosilane gave the respective *anti*-7-dimethylchlorosilyl derivative, XXIII. Treatment of this product with *anti*-7-bromo-*syn*-7-lithionorcarane gave the required dihalo precursor, XXIV. Scheme 1 illustrates these reactions. The proton NMR spectrum of XXIV showed only one Me—Si resonance which indicated the presence of only one isomer.

Reaction of dihalide XXIV with magnesium in THF proceeded smoothly and gave a solid product, XXV, in 61% yield whose high reactivity was similar to that of the other silacyclopropanes. The physical and spectroscopic properties of XXV were distinctly different from those of XXII. Its melting point was higher (94—96° vs. 72—74°C) and its IR and proton NMR spectra were different from those of XXII. In particular, its proton NMR spectrum showed only one Me—Si resonance at 0.43 ppm (vs. 0.33 ppm for XXII) and in the cyclohexane ring region of the spectrum it had three broad absorptions while that of XXII showed two. The methanolysis of XXV proceeded exothermally at room temperature to give a single product which was spectroscopically very similar to, but distinct from, the methanolysis product of XXII. Thus a different isomeric starting dihalide, XXIII rather than II, results in the formation of a different isomeric 1,1-dimethyl-2,3-di(7'-norcaranylidene)-1-silacyclopropane, XXV, rather than XXII. This is further indication that the ring closure involves a stereospecific process. Unfortunately, a ^{13}C NMR spectrum of XXV was not obtained, so no useful information concerning its structure is available. However, in view of the conversion of II to XXII, it is quite possible that silacyclopropane XXV has structure XXI.

The four silacyclopropanes prepared in this study all are derivatives of 7,7-dimethyl-7-siladispiro[2.0.2.1]heptane. As subsequent theoretical studies showed, we were fortunate in choosing to approach the silacyclopropane problem via silanes II, (VII, VIII, IX) and (X, XI, XII). The spiroannelated cyclopropane rings present in V, XIII and XIV provide a substantial measure of extra stabilization to the ring Si—C bonds by means of d-σ conjugation involving filled cyclopropane Walsh orbitals and vacant silicon 3d orbitals [11,21]. Thus these silacyclopropanes, although so highly reactive that they had to be handled with special precautions to exclude air and moisture, were thermally quite robust. Silacyclopropanes which we prepared during the course of subsequent studies which did not have this special structural feature were much less stable thermally and consequently rather more difficult to handle [17,22]. However, silacy-

SCHEME 1



clopropanes can be prepared and handled provided suitable precautions are taken. It is thus surprising that they as a class are such late arrivals in the area of organosilicon chemistry. Their chemistry is broad in scope and at times rather unusual when compared with that of other silacarbocyclic compounds. The preparation and reactivity of silacyclopropanes promises to be a very interesting field of study.

Experimental

General comments

All reactions were carried out under an atmosphere of dry nitrogen or argon. The apparatus in general was assembled and then flame-dried with a stream of nitrogen passing through it. Transfers involving solutions of air or moisture-sensitive compounds were effected using syringes and/or cannulae. Tetrahydrofuran

was purified by distillation from sodium benzophenone ketyl. The extreme air sensitivity of the silacyclopropanes prepared in this study required the utmost in precautions to maintain an inert atmosphere at all times.

IR spectra were recorded on a Perkin—Elmer 257 or 457A spectrophotometer. For solution spectra of the silacyclopropanes matched cavity cells with no-air stoppers were used. Proton NMR spectra were obtained using a Varian Associates T60 spectrometer. Chemical shifts are given in δ units, ppm downfield from tetramethylsilane. ^{13}C natural abundance NMR spectra were obtained using a Bruker HFX-90 spectrometer interfaced with a Digilab FTS/NMR-3 Fourier transform data system. Samples generally were of 50—70% concentration in a C_6H_6 (internal standard)/C_6F_6 (internal lock) solvent system. Shift values were obtained with proton decoupling. Assignment of structural position was accomplished by varying the degree of proton decoupling, permitting coupling of the ^1H nuclei bonded to the ^{13}C nucleus being observed. ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane. ^{29}Si NMR spectra were obtained at Colorado State University by Professor G.E. Maciel; for experimental details, see ref. 14.

Mass spectra were recorded either on a Hitachi/Perkin—Elmer Model RMU-6D instrument (variable ionization potential, low resolution) or a modified Consolidated Electrodynamics Corp. Model CEC-21-110B (70 ev) instrument by Dr. C. Hignite (high resolution).

Starting materials

Dimethyldichlorosilane was obtained from Union Carbide Corp. The bis-(α-bromocyclopropyl)dimethylsilanes (VII—IX) and (X—XII) used in this study were prepared as described in an earlier paper [4].

Preparation of bis(anti-7-bromonorcaran-7-yl)dimethylsilane (II)

A flamed-out 500 ml standard low temperature reaction apparatus (see ref. 4 for comments on methodology) was charged with 40.0 g (157 mmol) of 7,7-dibromonorcarane and 200 ml of dry THF. The mixture was cooled to —95°C and then 65 ml (150 mmol) of 2.3 *M* n-butyllithium in hexane was added by syringe during a 3 min period. The mixture was stirred at —85°C for 25 min. It then was recooled to —98°C and treated with 9.0 ml (74 mmol) of dimethyldichlorosilane. The reaction mixture was stirred for 2 h and then was allowed to warm to room temperature. Extraction with 100 ml of water (back extraction with 75 ml of hexane) followed, and the combined organic layers were dried over anhydrous sodium sulfate. The solvents were removed at reduced pressure and the residue was recrystallized from hot methanol to give 14.14 g (47%) of white needles, m.p. 114—116°C. (Found: C, 47.39, H, 6.45; Br, 39.25. $C_{16}H_{26}Br_2Si$ calcd.: C, 47.30; H, 6.45; Br, 39.33%.) ^1H NMR (CCl_4, $CHCl_3$): δ 2.2—1.0 (m, 20 H, maxima at 1.80, 1.33) and 0.48 ppm (s, 6 H, Me_2Si).

A saturated deuteriochloroform solution of the product was used to obtain a proton-decoupled ^{13}C NMR spectrum. Five resonances at 3.2, 20.5, 20.7, 26.9 and 37.7 ppm downfield from TMS were observed. This is precisely the expected number of resonances for II, as each of the norcaranylidene groups is equivalent in this arrangement. The observed intensities and field positions of the resonances suggested the assignment of the resonance at 37.7 ppm to be that of the carbon

atom bonded to Br (α to silicon) and the resonance at 3.2 ppm to be that of the CH_3—Si carbon. The remaining resonances then correspond to the methylene carbons and the methine carbon of the norcaranyl group. The other possible symmetrical arrangement with the bromine substituents *syn* is excluded by the method of preparation [4].

This reaction was repeated on a 1 mol scale for a total yield of 96.5 g (48%).

Preparation of the chlorobromide XXIV

A flamed-out 500 ml standard low temperature reaction apparatus [4] was charged with 250 ml of dry THF and cooled to —85° C. n-Butyllithium (125 ml of 1.6 *M* in hexane, 200 mmol) was added and the resulting solution was cooled to —98° C. A solution of 11.0 g (52.6 mmol) of *anti*-7-bromo-*syn*-7-chloronorcarane [4] in 10 ml of dry THF was added rapidly (15 sec) down the wall of the flask. The temperature rose to —86° C momentarily, but the mixture was quickly recooled to —98° C. The reaction mixture was stirred for 10 min and then 50 ml (ca. 400 mmol) of dimethyldichlorosilane was added as quickly as possible. The addition of the first 10—15 ml was rather exothermic and the total addition time was 2 min. The mixture was stirred at —98° C for 1.5 h and then was allowed to warm slowly to room temperature. The lithium salts were allowed to settle and the clear organic layer was transferred via cannula to a nitrogen-flushed 500 ml flask. The organic layer was trap-to-trap distilled (50° C/0.03 mmHg) into a flask cooled with liquid nitrogen. The solvents were removed from the distillate by distillation under nitrogen and the residue was distilled using a short path head, giving two fractions: (1) 33—35° C/0.8 mmHg, probably n-$BuMe_2SiCl$, and (2) 57—59° C/0.8 mmHg, 6.56 g (58%), identified as *syn*-7-chloro-*anti*-7-(dimethylchlorosilyl)norcarane on the basis of its proton NMR spectrum (CCl_4, C_6H_6): δ 2.2—0.7 (m, 10 H, maxima at 1.65 and 2.30) and 0.47 ppm (s, 6 H, Me_2Si).

In a 500 ml standard low temperature reaction apparatus [4] was prepared a solution of *anti*-bromo-*syn*-lithionorcarane in 100 ml of THF from 8.90 g (31.9 mmol) of 7,7-dibromonorcarane and 29.6 mmol of n-butyllithium in hexane as described in ref. 4. To the lithium reagent solution at —95° C was added a solution of 6.50 g (29.1 mmol) of *syn*-7-chloro-*anti*-7-(dimethylchlorosilyl)norcarane in 10 ml of THF. The resulting mixture was stirred for 1.5 h and allowed to warm to room temperature. The reaction mixture was treated with 50 ml of water and the organic layer was separated and dried. Removal of solvents at reduced pressure was followed by distillation of the residue (short path head). The fraction distilling at 105—130° C at 0.01 mmHg was redistilled to give 6.07 g (57%) of a pale yellow liquid, b.p. 119—122° C at 0.01 mm, n_D^{25} 1.5445. (Found: C, 53.15; H, 7.17. $C_{16}H_{26}ClBrSi$ calcd.: C, 53.11; H, 7.24%.) ^{1}H NMR (CCl_4, $CHCl_3$): δ 2.3—0.9 (m, 20 H, maxima at 1.80, 1.32) and 0.22 ppm (s, 6 H, Me_2Si). The presence of a single Me—Si resonance suggests that only one isomer is present. The configurations shown in XXIV follow from the stereospecific reactions of the lithium reagents involved [4].

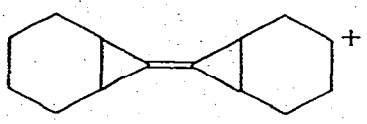
Preparation of dispiro bicyclo[4.1.0]heptane-7,2'-silacyclopropane-3',7''-bicyclo-[4.1.0]heptane (1,1-dimethyl-2,3-di(7'-norcaranylidene)-1-silacyclopropane) (V = XXII)

A 500 ml, three-necked, round-bottom flask equipped with a mechanical stir-

rer, a reflux condenser which was topped with a nitrogen inlet tube and a 250 ml pressure-equalizing addition funnel was charged with 3.10 g (128 mmol) of magnesium turnings (Eastman) and the apparatus was flame-dried while a stream of nitrogen was passed through it. Subsequently, 25 ml of THF (freshly distilled from sodium benzophenone ketyl) was added to the flask and the addition funnel was charged with a solution of 40.5 g (100 mmol) of dibromide II in 200 ml of dry THF. After a few ml of this solution had been added to the magnesium, the reaction was initiated by adding 0.5 ml of 1,2-dibromoethane. The remainder of the solution of II was added dropwise during a 1 h period. During this time the reaction flask was surrounded by an unconnected heating mantle in order to retain the heat generated in the weakly exothermic reaction. The reaction mixture was stirred at room temperature overnight.

The reaction mixture was allowed to settle and the clear upper layer was transfered via cannula into a nitrogen-flushed and stoppered 500 ml flask. The solid residue was washed with 150 ml of dry pentane and the washings were added to the THF solution. The combined organic layer was trap-to-trap distilled (room temperature, 0.02 mm) into a —78°C receiver to remove solvents and the residue was extracted with 150 ml of dry pentane. (All operations under nitrogen throughout). The pentane extracts were trap-to-trap distilled to remove solvent and the residue was dissolved in 50 ml of pentane and transferred via cannula to a 100 ml flask which was attached to a distillation unit. The solvent was removed at room temperature/0.01 mmHg. The solid residue was distilled through a short-path head with no water cooling to give 19.78 g (80%) of clear distillate, b.p. 95—97°C at 0.01 mmHg, which solidified on cooling. (An essentially identical reaction gave 18.42 g (75%) of product by this procedure). A crystalline sample was obtained by recrystallization of the solid from pentane at —50°C, although the distilled material appeared to be of equal purity, as judged by the single CH_3—Si NMR resonance. An analytical sample was prepared by crystallization from pentane, followed by transfer operations in a nitrogen-filled glove bag. Sample purity was found to be of great importance in obtaining a satisfactory ^{13}C NMR spectrum, and for this purpose the isolated product was distilled through a 6 cm Vigreux column at 0.04 mmHg and then sublimed at room temperature/0.02 mmHg during the course of two weeks. (Brief contact with laboratory air served to change the solid product irreversibly into an oil.) (Found: C, 77.91; H, 10.39; Si, 11.17 (Alfred Bernhardt). $C_{16}H_{26}Si$ calcd.: C, 77.97; H, 10.63; Si, 11.40%.) Mass spectrum; low resolution, RMU-6D. Molecular weight of $C_{16}H_{26}Si$ = 246, of $C_{16}H_{26}SiO$ = 262. At 70 eV, different samples showed different *m/e* 246 : 262 ratios. The sample with the highest m.p., 72—74°C, had *m/e* 246 : 262 of 10 : 1. A sample with lower m.p. had *m/e* 246 : 262 of 1 : 1. The sample inlet system available made complete exclusion of air difficult. As the ionization potential was lowered to 7.6 eV (uncalibrated), only *m/e* 246 appeared. High resolution, CEC-21-110B. Observed molecular ion, *m/e* 246.1807; calcd. for $^{12}C_{16}{}^{1}H_{26}{}^{28}Si$, 246.1804. Also observed, inter alia, were the $[M - 15]^+$ species (*m/e* found, 231.1570; calcd., 231.1569) and a fragment ion, $C_{14}H_{20}{}^{+}$ (*m/e* found, 188.1564; calcd., 188.1565). The latter very likely is XXVI. No ions corresponding to a dimeric species, $C_{32}H_{52}Si_2$, or its fragments resulting from methyl group fission were observed.

^1H NMR spectrum (C_6D_6, C_6D_5H): δ 2.3—0.8 (m, 20 H, maxima at 1.90, 1.60



(XXVI)

and 1.40) and 0.33 ppm (s, 6 H, Me_2Si).

^{13}C NMR spectrum (C_6D_6, C_6F_6); proton-decoupled: δ_C 25.9, 23.2, 22.5, 20.5, 18.7, 15.6, 15.0 and —5.8 ppm downfield from TMS (Fig. 1). The —5.8 ppm resonance is due to the methyl groups on silicon and the resonances at 15.0 and 20.5 ppm which are of low intensity no doubt are due to the quaternary carbon atoms. The other signals were not assigned.

^{29}Si NMR spectrum (C_6D_6, Me_4Si), proton-decoupled: 53.21 ppm upfield from TMS.

For subsequent studies of this compound stock solutions in THF or in pentane were prepared in volumetric flasks sealed with no-air stoppers from which aliquot samples could be removed by syringe.

Reaction of 1,1-dimethyl-2,3-di(7'-norcaranylidene)-1-silacyclopropane with methanol

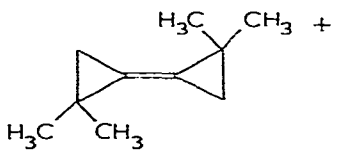
A flamed-out, nitrogen filled 50 ml single-necked flask equipped with a magnetic stirring unit, a no-air stopper and a needle attached to a nitrogen line was charged with 1.60 g (50 mmol) of absolute methanol and 10 ml of freshly distilled THF. To this mixture was added dropwise 25 ml (20.0 mmol) of a 0.80 *M* solution of the silacyclopropane in THF during a 10 min period. An immediate, exothermic reaction was observed and the solution remained clear and colorless. The reaction mixture was stirred for an additional hour and then the solvents were removed by trap-to-trap distillation (room temperature/0.01 mmHg). The pot residue was distilled through a short-path head to give 4.70 g (85%) of a clear, colorless liquid, b.p. 94—96°C/0.01 mmHg, n_D^{25} 1.5100, identified as the methoxysilane VI. (Found: C, 73.25; H, 10.72. $C_{17}H_{30}OSi$ calcd.: C, 73.31; H, 10.86%). NMR (CCl_4, $CHCl_3$): δ 3.40 (s, 3 H, OMe), 2.1—0.4 (m, 20 H, maxima at 1.70, 1.40, 0.83) and 0.28 ppm (s, 6 H, Me_2Si).

Preparation of 1,1-dimethyl-trans-2,3-bis(2',2'-dimethylcyclopropylidene)-1-silacyclopropane (XVII, XVIII)

A 500 ml, three-necked flask equipped as described in the preparation of XXII was flame-dried and charged with 6.3 g (260 mmol) of magnesium turnings and 25 ml of freshly distilled THF. A solution of 70.8 g (200 mmol) of bis-(1-bromo-2,2-dimethylcyclopropyl)dimethylsilane in 200 ml of THF was prepared in the addition funnel and 1 ml of this solution was added to the reaction flask. Subsequently, the reaction was initiated by adding 0.5 ml of 1,2-dibromoethane to the mixture. The flask was kept warm by covering the bottom of the flask with an unconnected heating mantle. The solution of the dibromide was added dropwise over 1.5 h and the reaction mixture was stirred at room temperature overnight. Pentane (100 ml) was added and the precipitated salts were allowed to settle. The clear organic layer was transferred by cannula under nitrogen to a stoppered, nitrogen-flushed 500 ml flask containing a magnetic stir-

ring bar. The solid residue was extracted with two 100 ml portions of pentane. The combined organic layer then was trap-to-trap distilled (40°C/0.02 mmHg) into a receiver cooled with liquid nitrogen. The distillate was concentrated under nitrogen using a 30 cm Vigreux column until almost all of the solvents had been removed. The residue was distilled at reduced pressure through a 20 cm Vigreux column to give 17.65 g (45%) of a clear liquid, b.p. 50—51°C at 3.5 mmHg. A sample for characterization was redistilled at 53.5—54.3°C at 4.0 mmHg and sealed under argon in glass vials. The product fumed on exposure to air as a result of an exothermic reaction with oxygen which caused the flask to become hot. The product was characterized by analysis and by spectroscopic data. (Found: C, 74.08; H, 11.21. $C_{12}H_{22}Si$ calcd.: C, 74.14; H, 11.41%).

High resolution mass spectrum, CEC-21-110B, most abundant species: *m/e* 194.1519 ($^{12}C_{12}{}^{1}H_{22}{}^{28}Si$ molecular ion calcd., 194.1491), 179.1272 ($[M-15]^+$ calcd., 179.1256), 210.1440 ($[M+16]^+$ calcd., 210.1474), 136.1250 ($^{12}C_{10}{}^{1}H_{16}{}^{+}$ calcd., 136.1252), 195.1527 ($[M-{}^{12}C+{}^{13}C]^+$ calcd., 195.1524). The $[C_{10}H_{16}]^+$ fragment should be the bicyclopropylidene, XXVII.



(XXVII)

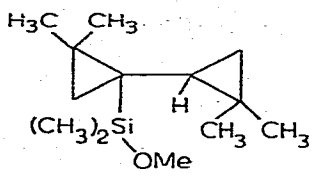
^{1}H NMR spectrum (C_6D_6, C_6D_5H): δ 1.27 (s, 6 H, CH_3—C), 1.24 (s, 6 H, CH_3—C), 1.11 (d, *J* 3.0 Hz, cyclopropyl H), 0.80 (d, *J* 3.0 Hz, cyclopropyl H) and 0.32 ppm (s, 6 H, Me_2Si).

^{13}C NMR spectrum (C_6H_6, C_6F_6): δ_C 29.171 (q, 2 C, CH_3 attached to C), 22.773 (q, 2 C, CH_3 attached to C), 22.604 (s, 2 C, quaternary C), 22.324 (s, 2 C, quaternary C), 20.724 (t, 2 C, cyclopropane CH_2) and —6.185 ppm (q, 2 C, $J(^{29}Si—^{13}C)$ 58 Hz, CH_3—Si).

^{29}Si NMR spectrum (C_6D_6, Me_4Si), proton-decoupled: 51.78 ppm upfield from TMS.

Reaction of 1,1-dimethyl-trans-2,3-bis(2',2'-dimethylcyclopropylidene)-1-silacyclopropane with methanol

The experiment described immediately above was repeated using 10.5 mmol of bis(1-bromo-2,2-dimethylcyclopropyl)dimethylsilane and 20.6 mmol of magnesium. Upon completion of the reaction, all volatiles were trap-to-trap distilled (40°C/0.05 mmHg) into a 50 ml, single-necked flask equipped with a magnetic stirring bar. After the flask was quickly sealed with a no-air stopper and a nitrogen inlet needle had been inserted, 3.0 ml of absolute methanol was added. A moderately exothermic reaction occurred. The reaction mixture subsequently was distilled through a short path head under nitrogen until the head temperature reached 68°C. The pot residue was then distilled at reduced pressure to give 1.12 g (47%) of a clear, colorless liquid, b.p. 33—35°C at 0.2 mmHg, n_D^{25} 1.4576, 1-dimethylmethoxysilyl-2,2,2',2'-tetramethyl-1,1'-bicyclopropyl, XXVIII



(XXVIII)

(Found: C, 69.16; H, 11.64. $C_{13}H_{26}OSi$ calcd.: C, 68.96; H, 11.57%). ^1H NMR (CCl_4, $CHCl_3$): δ 3.42 (s, 3 H, CH_3O), 1.22, 1.18, 1.10, 1.02 (4 s, 12 H, CH_3—C), 0.9 to —0.10 (m, 5 H, cyclopropyl hydrogens) and 0.22 ppm (s, 6 H, Me_2Si).

Preparation of 1,1-dimethyl-anti-2,3-bis(trans-2',3'-dimethylcyclopropylidene)-1-silacyclopropane (XIX, XX)

A 100 ml three-necked flask equipped as described above was charged with 0.90 g (37 mmol) of magnesium turnings and flame-dried. After cooling, 5 ml of freshly distilled THF was added and the addition funnel was charged with 5.50 g (15.5 mmol) of bis(1-bromo-*trans*-2,3-dimethylcyclopropyl)dimethylsilane (the single isomer of m.p. 95—97°C) [4] and 25 ml of THF. A few drops of this solution was added and then the reaction was initiated with 0.10 ml of 1,2-dibromoethane. The rest of the dibromide solution was added dropwise over 1 h and then the reaction mixture was stirred under nitrogen at room temperature overnight. Pentane (25 ml) was added and the solids were allowed to settle. The organic layer was transferred via cannula to a nitrogen-flushed flask equipped with a magnetic stirring bar and a no-air stopper. The remaining solid was washed with pentane. The combined organic layer and pentane washings were trap-to-trap distilled (40°C at 0.02 mmHg). The distillate was concentrated using a 20 cm Vigreux column. The liquid remaining after the solvents had been distilled was distilled through a short path head at reduced pressure to yield 1.87 g (62%) of a clear liquid, b.p. 50—51°C at 2.6 mmHg. (Found: C, 74.81; H, 11.50. $C_{12}H_{22}Si$ calcd.: C, 74.41; H, 11.41%).

High resolution mass spectrum, CEC-21-110B, most abundant species: *m/e* 194.1512 ($^{12}C_{12}{}^1H_{22}{}^{28}Si$ molecular ion calcd., 194.1491), 179.1278 ($[M-15]^+$ calcd., 179.1256), 210.1460 ($[M+16]^+$ calcd., 210.1474), 136.1226 ($^{12}C_{10}{}^1H_{16}{}^+$ calcd., 136.1252; this fragment should be the expected bicyclopropylidene), 195.1538 ($[M-{}^{12}C+{}^{13}C]^+$ calcd., 195.1524).

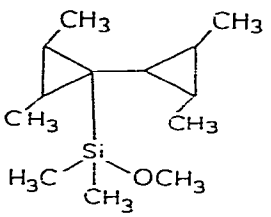
^1H NMR spectrum (C_6D_6, C_6D_5H): δ 1.22 (broad s, 16 H, CH_3—C and cyclopropyl hydrogens) and 0.32 ppm (s, 6 H, Me_2Si).

^{13}C NMR spectrum (C_6H_6, C_6F_6): δ_C 24.429 (q, 2 C, CH_3 attached to C), 22.913 (s, 2 C, quaternary C, apparent $J(^{29}Si—^{13}C)$ 137.5 Hz, $J(^{13}C—^{13}C)$ 123.8 Hz), 21.398 (d, 2 C, cyclopropyl C attached to CH_3), 21.089 (d, 2 C, cyclopropyl C attached to CH_3), 16.235 (q, 2 C, CH_3 attached to C) and —6.213 (q, 2 C, CH_3—Si, $J(^{29}Si—^{13}C)$ 57.5 Hz).

Reaction of 1,1-dimethyl-2,3-bis(trans-2',3'-dimethylcyclopropylidene)-1-silacyclopropane with methanol

A flame-dried, nitrogen-filled 50 ml one-necked flask equipped with a magnetic stirring bar and a no-air stopper with a nitrogen inlet needle was charged

by syringe with a solution of 1.20 g (6.70 mmol) of the silacyclopropane in 15 ml of pentane. Five ml of absolute methanol was added via syringe, resulting in an immediate, exothermic reaction. The mixture was stirred for 1 h. Subsequent distillation at reduced pressure gave 1.20 g (80%) of a clear liquid, b.p. 36—38°C at 0.2 mmHg, n_D^{25} 1.4547, 1-dimethylmethoxysilyl-*trans*-2,3-dimethyl-*trans*-2',3'-dimethyl-1,1'-bicyclopropyl, XXIX (Found: C, 68.78; H, 11.42. $C_{13}H_{26}OSi$ calcd.: C, 68.96; H, 11.57%). ^{1}H NMR (CCl_4, $CHCl_3$): δ 3.35 (s, 3 H, MeO), 1.06, 1.00, 0.96, 0.82 (4 s, 12 H, CH_3—C), 0.8—0.2 (m, 5 H, cyclopropyl H) and 0.10 and 0.07 ppm (2 s, 6 H, Me_2Si).



(XXIX)

Preparation of another isomer of 1,1-dimethyl-2,3-di(7'-norcaranylidene)-1-silacyclopropane

The usual apparatus (100 ml flask) was flamed out and charged with 1.03 g (42 mmol) of magnesium turnings and 5 ml of dry THF under nitrogen. A solution of 5.90 g (16.3 mmol of chlorobromide XXIV in 25 ml of THF was prepared in the addition funnel and 10 drops of this solution was added to the magnesium. 1,2-Dibromoethane (0.1 ml) was used to initiate the reaction. The chlorobromide solution then was added dropwise over 2 h (exothermic reaction). The mixture was stirred under nitrogen at gentle reflux for 2 h. Subsequently, 40 ml of dry pentane was added to precipitate magnesium halide and the mixture was allowed to settle overnight. The clear organic layer was transferred via cannula under nitrogen to another flask and the solvents were removed at 0.02 mmHg. The solid residue was dissolved in a mixture of 30 ml of pentane and 20 ml of hexane and the extracts were transferred by cannula to another flask. Removal of the solvents at reduced pressure was followed by distillation of the residue (about 100°C at 0.01 mmHg) to give 2.40 g (61%) of a solid which was essentially pure, based on the presence of only one Me—Si resonance in its ^{1}H NMR spectrum. The solid was recrystallized from cold pentane and the mother liquor was removed by syringe. The remaining solid was dried (room temperature/0.01 mmHg) to give 1.22 g (31%) of white needles, m.p. 94—96°C, compound XXV. (Found: C, 77.77, 77.83; H, 10.68, 10.48; Si, 11.19, 11.11. $C_{16}H_{26}Si$ calcd.: C, 77.97; H, 10.63; Si, 11.40%.) ^{1}H NMR (C_6D_6, C_6D_5H): δ 2.1—0.8 (m, 20 H, maxima at 1.78, 1.20, 1.05) and 0.43 ppm (s, 6 H, Me_2Si). This compound underwent immediate exothermic reaction with air on exposure, giving an oil.

Reaction of the other isomer of 1,1-dimethyl-2,3-di(7'-norcaranylidene)-1-silacyclopropane with methanol

The dried solid isolated from the experiment above was dissolved under ni-

trogen in 5 ml of pentane and treated with 1.5 ml of absolute methanol. A mildly exothermic reaction ensued. The mixture was stirred overnight and the solvents then were removed at reduced pressure. The residue was distilled using a short path head to give 1.04 g (75%) of clear liquid, b.p. 92—93°C at 0.03 mmHg, n_D^{25} 1.5010. (Found: C, 73.73; H, 10.71. $C_{17}H_{30}OSi$ calcd.: C, 73.31; H, 10.68%). ^1H NMR (CCl_4, $CHCl_3$): δ 3.40 (s, 3 H, MeO), 2.1—0.9 (m, 16 H, maxima at 1.60 and 1.20), 0.7—0.3 (m, 5 H, cyclopropyl H) and 0.24 ppm (s, 6 H, Me_2Si). A mixture of this compound with methoxysilane XXVIII showed a very slight difference of the two MeO and Me—Si proton resonances in the NMR spectra. Each isomer appeared to be free of the other isomer.

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