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THE EXTRAORDINARY REACTIVITY OF THE RING Si—C BONDS IN 1,1-DIMETHYL-*trans*-2,3-BIS(2′,2′-DIMETHYLCYCLOPROPYLIDENE)-1-SILACYCLOPROPANE

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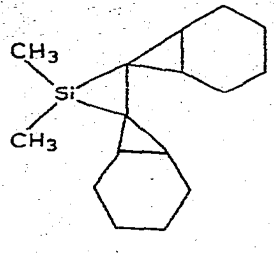
Summary

The reactions of the title silirane with oxygen, water, alcohols, primary and some secondary amines, hydrogen sulfide, carboxylic acids and hydrazoic acid proceeded exothermally at room temperature with opening of the Si—C bond of the SiC_2 ring. Hydrogen chloride reacted rapidly at —78°C, as did methyl- and phenyl-lithium and lithium dialkylamides. Ring cleavage of the silirane also could be effected with acetyl chloride, boron trichloride and lithium aluminum hydride. A comparison of the reactivity of the title silirane with that of 1,1-dimethyl-1-silacyclobutane shows the dramatic effect of the high ring strain in the former, which results in hyper-reactive ring Si—C bonds.

Introduction

The first stable, isolable silacyclopropanes (siliranes) to be prepared were I, II and III, whose isolation we reported in 1972 [1]. Full details of their preparation and characterization have been provided [2]. Our early work [3] showed these compounds to be highly reactive, indeed hyper-reactive, compared to all other organosilanes containing four Si—C bonds. Thus these siliranes reacted exothermally with the oxygen in the air, with water, with methanol, and with carbon tetrachloride [1—3]. Their hydrolysis and methanolysis reactions were shown to proceed with cleavage of the SiC_2 ring to give substituted bicyclopropylsilicon compounds.

Subsequent work was directed to a more thorough development of the chemistry of the SiC_2 ring and an assessment of its reactivity relative to larger silacarbocyclic compounds. Calculations, which were later confirmed by the results of an X-ray diffraction study of I [4], indicated that this ring system is highly strained, with a C—Si—C angle of about 48°. Hence the high reactivity of these



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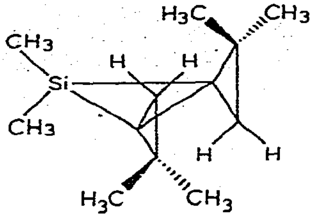

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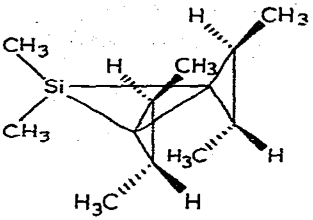


(III)

compounds toward the limited number of reagents examined initially was expected to be a general phenomenon.

Although I was a crystalline solid, the few of its reactions which we studied all gave products which were oils. These were very high-boiling and thus were difficult to isolate in pure form. For this reason, we focussed our attention on II, which is a distillable, highly reactive liquid and which proton and ^{13}C NMR spectroscopy had shown to be the isomer indicated [1,2]. We report here concerning the chemistry of the SiC_2 ring of II.

Results

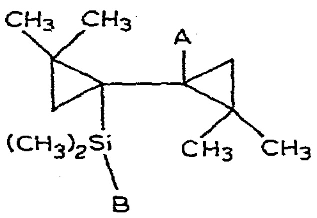
Since the siliranes I, II and III are extremely air- and water-sensitive, we turn our attention to their reactions with these reagents first and consider their reactions with other classes of compounds (e.g., alcohols, thiols, amines, etc.) afterwards.

Oxidation

As noted previously, I, a crystalline solid, was converted rapidly and irreversibly to an oil upon exposure to the atmosphere. Compounds II and III, as the neat liquids, fumed profusely and became hot when they were exposed to air. When dry oxygen was passed over a hexane solution of II, a strong exotherm reaction was noted. Removal of the hexane left a viscous, nonvolatile oil which appeared to be a peroxide. In acetic acid medium it oxidized iodide ion to iodine and it converted triphenylphosphine to triphenylphosphine oxide. A quantitative study of the former reaction showed that 3.1 mmol of the silirane on oxidation developed a peroxide value sufficient to form 2.77 mmol of iodine on treatment with sodium iodide in acetic acid. This corresponds to a yield of 89% if one assumes a 1/1 stoichiometry for the reaction of II with oxygen. The nature of the nonvolatile peroxide remains obscure. Its proton NMR spectrum is not very revealing and its IR spectrum shows a strong absorption in the carbonyl region at 1730 cm^{-1}.

Hydrolysis and alcoholysis

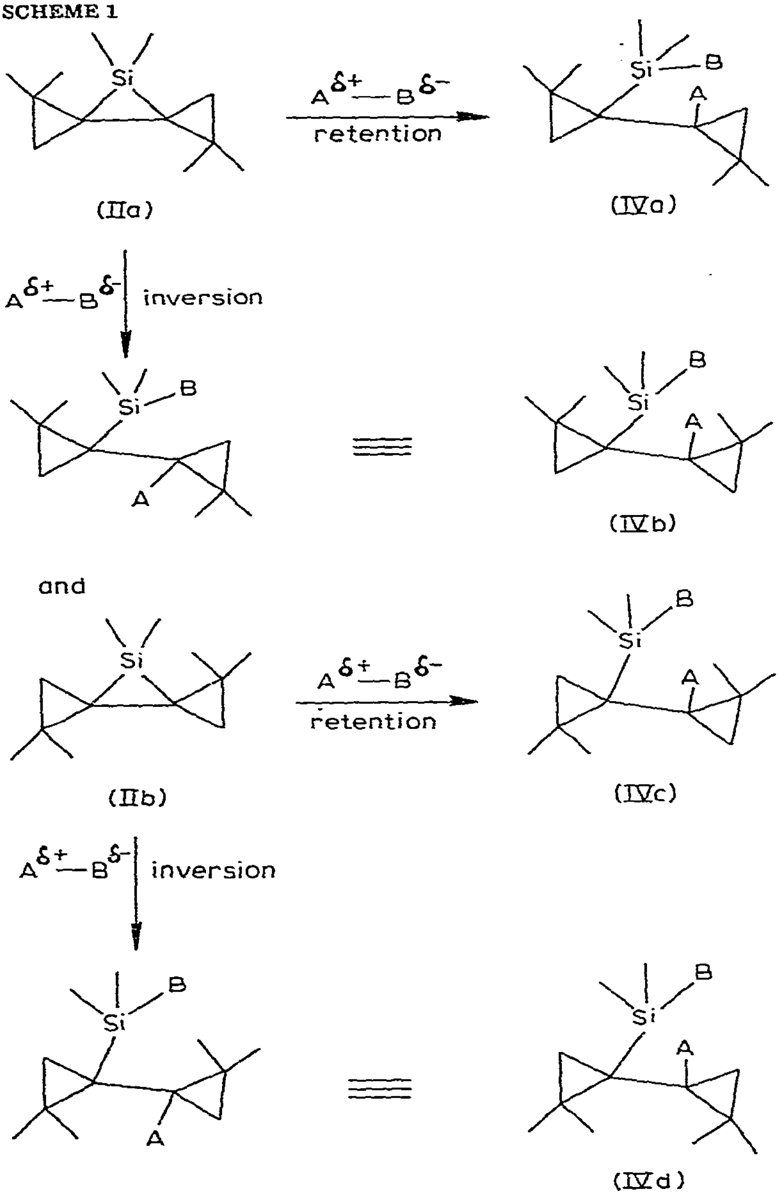
Silirane II is obtained with the structure shown, which implies the formation of a *d,l* pair, IIa, IIb, in the ring closure reaction [1,2]. Reaction of a polar reagent, $A^{\delta+}—B^{\delta-}$, with II would be expected to occur at the polar $Si^{\delta+}—C^{\delta-}$ bond to give the ring-opening product, IV. This reaction could occur with retention or inversion of configuration at silicon, but both processes would lead to formation of the same isomer. However, retention and inversion of configura-



(IV)

tion at carbon in these reactions would give different products, as shown in Scheme 1. Isomers IVa and IVc, which are formed in the retention process, form an enantiomeric pair which are diastereotopic with respect to IVb and IVd,

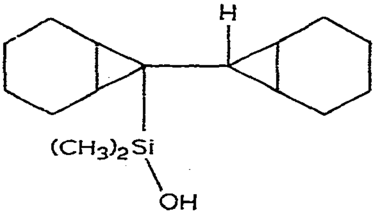
SCHEME 1



another enantiomeric pair resulting from an inversion process. Thus, if both retention and inversion pathways occur, two distinct products should be observed. In the hydrolysis and alcoholysis reactions of II only one isomer is formed within the limits of detection by GLC and NMR. The substituents in these systems do not allow the complete assignment of structure with respect to the configuration at the cyclopropyl carbon atom, and so it is not possible to determine whether these reactions are proceeding with retention or inversion at carbon.

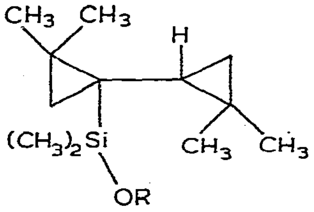
Silirane II, in THF solution, reacted exothermally with water to give 2,2,2',2'-tetramethyl-1,1'-bicycloprop-1-yldimethylsilanol (Va) in 70% yield. This product survived distillation and GLC collection without condensing to the siloxane, no doubt as a result of the steric hindrance to the bimolecular condensation process [5] offered by the bulky tetramethylbicyclopropyl substituent.

An exothermic reaction also occurred when an excess of water was added to a THF solution of silirane I, giving silanol VI, a low-melting solid. In this compound hindrance to condensation to the disiloxane should be even more severe than in Va.



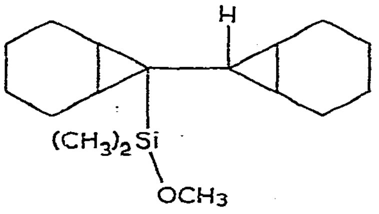
(VI)

All alcohols examined, even hindered alcohols such as t-butanol, reacted exothermally with silirane II in benzene solution, giving the respective 2,2,2',2'-tetramethyl-1,1'-bicycloprop-1-yldimethylalkoxysilane (Vb—Ve). Phenol reacted analogously to give phenoxysilane Vf.

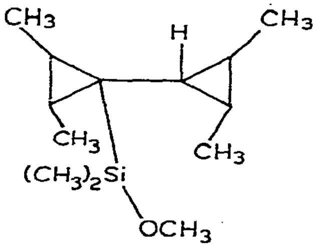


(Va) R = H (70%)
(Vb) R = Me (47%)
(Vc) R = Et (81%)
(Vd) R = i-Pr (76%)
(Ve) R = t-Bu (80%)
(Vf) R = Ph (83%)

Silirane I and silirane III also reacted exothermally with methanol, giving in each case the expected methoxysilane, VIIa and VIIb, respectively.



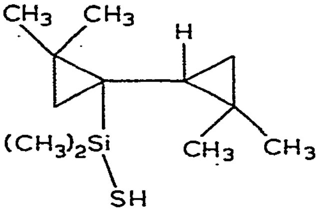
(VIIa)



(VIIb)

Thiolysis

When gaseous hydrogen sulfide was bubbled through a THF solution of II, an exothermic reaction gave 2,2,2′,2′-tetramethyl-1,1′-bicycloprop-1-yldimethylsilanethiol (VIIIa), which survived distillation and GLC collection without apparent condensation to the disilthiane.

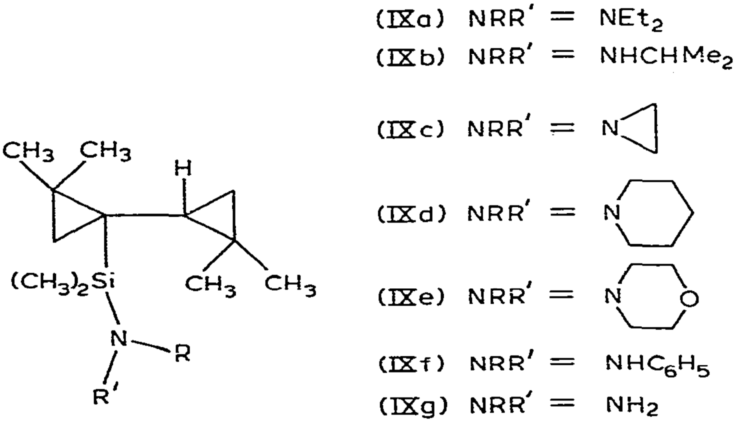


(VIII)

Aminolysis

Silirane II is considerably less reactive toward amines. Diisopropylamine failed to react with II in benzene solution during a reaction time of 20 h at 65°C. A reaction of diethylamine with II at 65°C for 6 h gave the expected 2,2,2′,2′-tetramethyl-1,1′-bicycloprop-1-yldimethyl(diethylamino)silane (IXa) in 57% yield, and isopropylamine gave IXb in 62% yield after 3 h at 55°C. Less hindered amines, aziridine, piperidine, morpholine, and aniline, reacted readily with II in reactions which often were mildly exothermic, giving IXc—IXf as products. The reaction with gaseous ammonia also was exothermic. The product was aminosilane IXg in 56% yield, which like the silanol and silanethiol, could be purified by distillation and gas chromatography without undergoing condensation to the disilazane.

In view of the considerably less than quantitative yields of products formed in the reactions of II with amines, and the failure of the bulky diisopropylamine to react at all, we investigated the reactions of lithium amides with II. When II was treated with lithium diethylamide in THF containing one molar equivalent of diethylamine at —78°C and the reaction mixture was allowed to warm slowly to room temperature, a bright orange color appeared at about —15°C. A non-aqueous work-up was required since the expected silylamine product would be hydrolyzed to the silanol in aqueous medium. Instead, the reaction mixture was treated with solid ammonium chloride, which served to discharge the orange



(IXa) $NRR' = NEt_2$

(IXb) $NRR' = NHCHMe_2$

(IXc) $NRR' =$

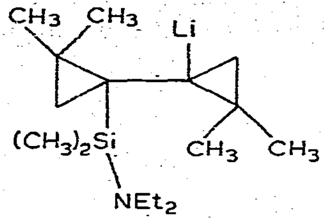
(IXd) $NRR' =$

(IXe) $NRR' =$

(IXf) $NRR' = NHC_6H_5$

(IXg) $NRR' = NH_2$

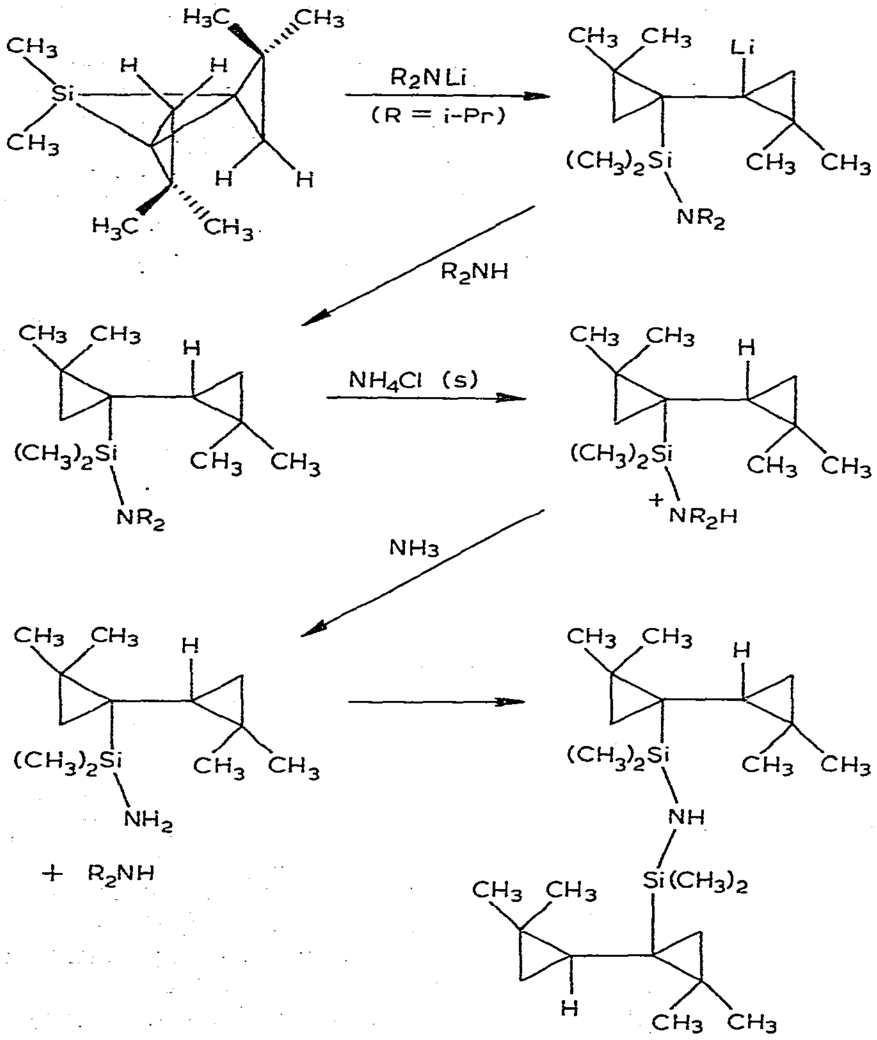
color, which very likely was due to the organolithium intermediate X. The product, obtained in 67% yield, was identical in all respects to that of the Et_2NH/



(X)

II reaction. A similar reaction of II with lithium diisopropylamide/diisopropylamine, in which an NH_4Cl work-up also was used, took a different course. The expected diisopropylaminosilane was not formed. The product which was isolated instead had an IR spectrum which showed absorptions attributable to

SCHEME 2

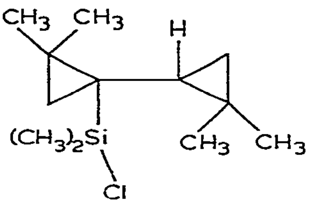


(XI)

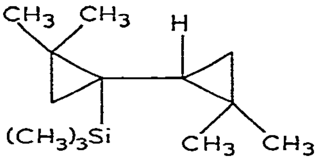
an N—H bond (ν(NH) 3384 cm^{-1}) [6] and the Si—N—Si moiety (922 cm^{-1}) [7]. Mass spectral and elemental analysis demonstrated that the disilazane XI had been isolated. It is likely that the transamination shown in Scheme 2 had occurred

Acidolysis

Anhydrous acids of various kinds will cleave the SiC_2 ring of II. Reaction with anhydrous hydrogen chloride in pentane at —78°C gave the chlorosilane XII which was identified spectroscopically and then treated with methanolic sodium methoxide. The product obtained was identical in all respects with the reaction product of II and methanol. Chlorosilane XII also was converted to the trimethylsilyl derivative XIII by treatment with methyllithium in diethyl ether.

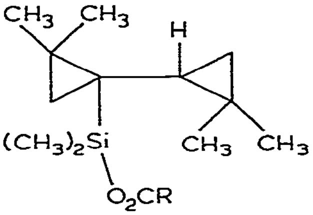


(XII)



(XIII)

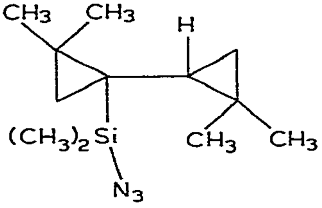
Carboxylic acids such as acetic and pivalic acids reacted exothermally with II in hexane solution, giving the expected silyl carboxylates, XIVa and XIVb, respectively, in high yield. An exothermic reaction also occurred when II was added to a solution of hydrazoic acid in benzene, producing the ring-opened



(XIVa) $R = CH_3$

(XIVb) $R = C(CH_3)_3$

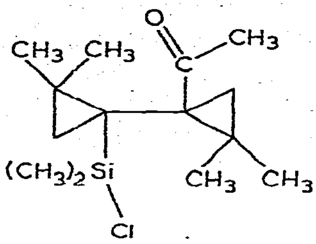
product XV. This compound, like other silyl azides [8], was very stable and could be distilled at reduced pressure and passed through a gas chromatograph without decomposition.



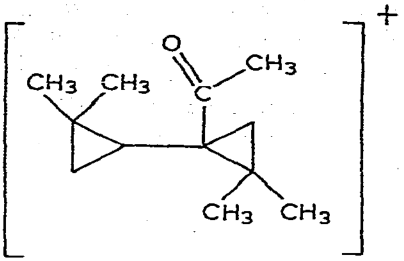
(XV)

Reactions with acid halides

The SiC_2 ring of II was cleaved when it was heated in refluxing hexane with acetyl chloride. The product, which was not stable to attempted gas-chromatographic purification, was assigned structure XVI on the basis of its infrared spectrum (ν(CO) at 1640 cm^{-1} and an Si—Cl absorption [7] at 588 cm^{-1}), and its mass spectrum showed the molecular ion as well as fragments corresponding to Me_2SiCl^+ and XVII. The 1640 cm^{-1} band is at lower frequency than usually observed for cyclopropyl ketones (Bellamy [9] quotes the range 1704—1686 cm^{-1}), but further lowering of $\nu(CO)$ in a bicyclopropyl system is not unreasonable.



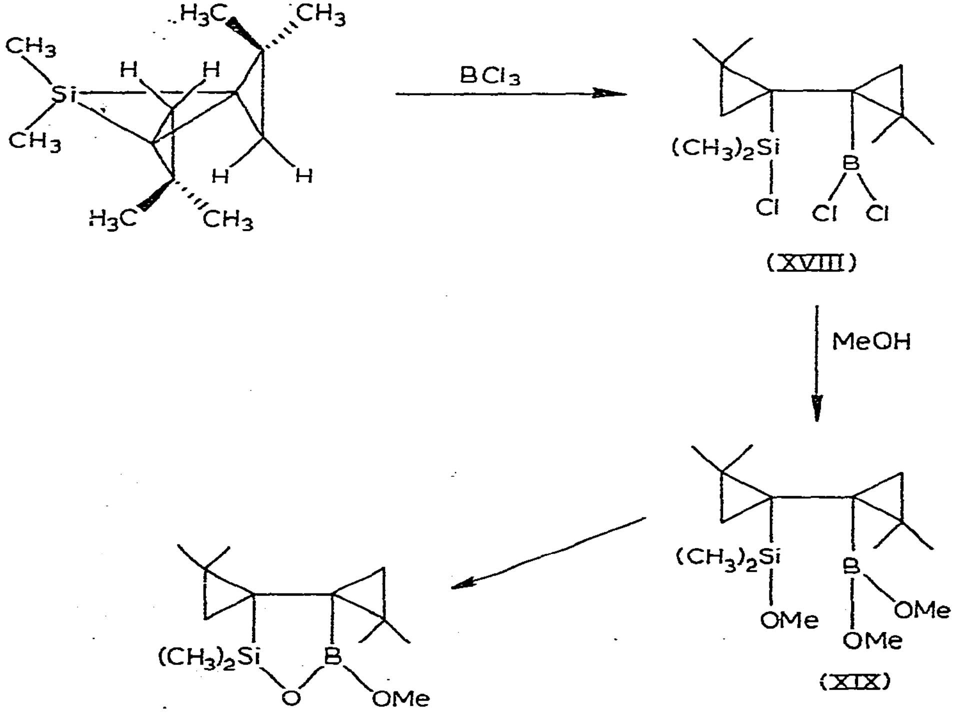
(XVI)



(XVII)

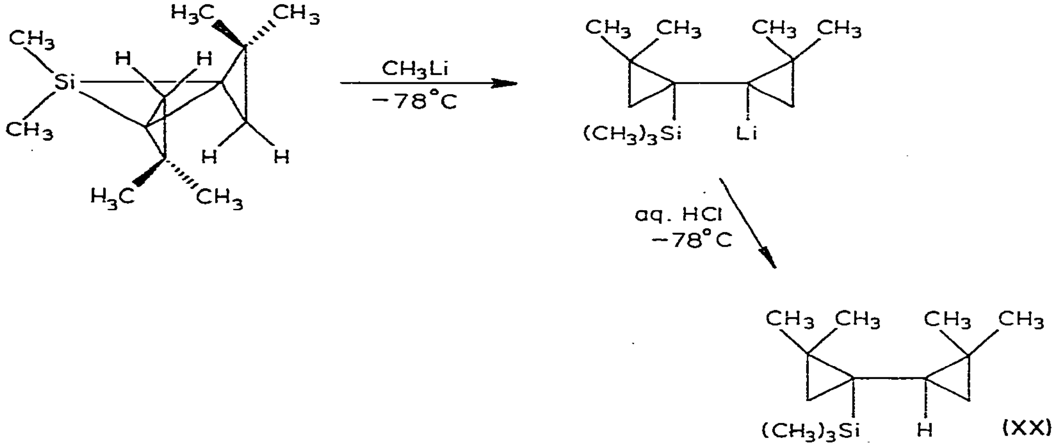
Inorganic acid halides also react with II. Thus an exothermic reaction occurred between II and boron trichloride in hexane. Since the most likely product, XVIII, was expected to contain both reactive B—Cl and Si—Cl bonds, the reaction mixture was quenched with methanol. The infrared spectrum of the product of this treatment showed both Si—O [7] and B—O stretches at 1170 and 1318 cm^{-1}, respectively. However, its NMR spectrum showed only a single methoxy resonance. These data, as well as its mass spectrum, which showed the molecular ion, and its C/H analysis, suggested that the product which had been isolated was XIX. Its mode of formation is indicated in Scheme 3.

SCHEME 3



Reactions with organometallic reagents

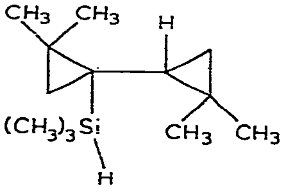
Silirane II underwent ring opening on treatment with methyllithium in diethyl ether/THF. Acid hydrolysis at —78°C of the yellow-orange solution which resulted when these reactants were mixed at —78°C gave a 2,2,2′,2′-tetramethyl-1,1′-bicycloprop-1-yltrimethylsilane which was different from the isomer of this compound which had been obtained by methylation of the product of the II/HCl reaction. The latter was believed to have structure XIII. If this is correct, then the product of the II/MeLi(H_3O^+) reaction must be XX, i.e., the reaction must have proceeded with inversion at carbon (eq. 1). However, when the hydrolysis of the reaction mixture was performed at 0°C rather than at —78°C, a 58% yield of the isomer believed to be XIII and a 17% yield of the supposed XX was obtained instead. Similar observations were made in the case of the reaction of silirane II with phenyllithium at —78°C. Hydrolysis of the reaction mixture at —78° resulted in isolation of one isomer of 2,2,2′,2′-tetramethyl-1,1′-bicycloprop-1-yldimethylphenylsilane, while hydrolysis after the reaction mixture had been allowed to warm to 0°C produced another isomeric product. A reasonable explanation for these results is that the initially formed bicyclopropyllithium species is not configurationally stable. Grignard reagents such as methylmagnesium iodide in diethyl ether and isopropylmagnesium chloride in THF did not react with silirane II, the latter reagent even at 65°C.



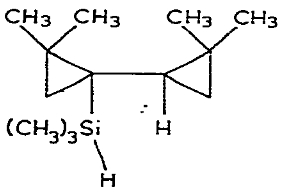
(XX)

(1)

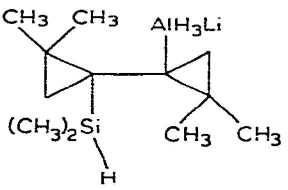
Treatment of silirane II with lithium aluminum hydride in THF at room temperature resulted in a mildly exothermic reaction. Upon aqueous work-up, two isomers of the reduction product, XXIa and XXIb, were obtained in 43% yield. An organometallic intermediate, XXII, may be discussed.



(XXIa)



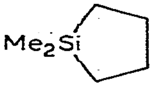
(XXIb)



(XXII)

Discussion

It is clear from the results presented in the previous section that the silacyclopropanes, as judged by the chemical properties of silirane II, are the most reactive tetraorganosilicon compounds known *. Tetraalkylsilanes are characterized by their lack of reactivity toward air, water, alcohols, acid and bases under nonforcing conditions [14]. Incorporation of a silicon atom into a carbocyclic ring, e.g., XXIII or XXIV, gives equally unreactive systems, but in the case of a somewhat strained silacarbocyclic system, the silacyclobutanes, enhanced reactivity of the endocyclic Si—C bond is observed. This was recognized immediately by Sommer and Baum [15], who prepared the first silacyclobutane, and Nametkin and Vdovin and their coworkers later developed the chemistry of this class of compounds, especially their ring-opening reactions, in some detail [16].



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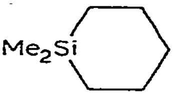
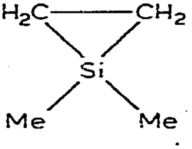


(XXIV)

As mentioned in the introduction, the silacyclopropanes are highly strained, much more so than the silacyclobutanes, and so their polarized $Si^{\delta+}$—$C^{\delta-}$ bonds should be more highly reactive toward their polar reagents than those of the silacyclobutanes. Furthermore, the hybridization of the silicon and carbon atoms of the SiC_2 ring will be an important factor. In cyclobutane, the C—C bonds have 76% *p* character, while in cyclopropane they have 80% *p* character [17]. A similar increase in %*p* character can be expected in the SiC_2 ring bonds when compared with the larger SiC_n cyclics ($n \geqslant 3$). This also should result in enhanced reactivity.

A comparison of the reactivity of the ring Si—C bonds of a silacyclopropane and the comparably-substituted silacyclobutane would be instructive. In the silacyclobutane series, most studies of the reactivity of the ring have been carried out with 1,1-dimethyl-1-silacyclobutane [16]. The comparable silacyclopropane, XXV, has not been isolated, although evidence for its transitory existence has been reported [18]. Accordingly, we present here a comparison of the reactivities of silirane II and 1,1-dimethyl-1-silacyclobutane (Table 1). In every reaction for which the basis for a comparison exists, it is the silirane which is decisively and often spectacularly more reactive. This enhanced reactivity is seen with electrophilic as well as with nucleophilic reagents. Enhanced reactivity



(XXV)

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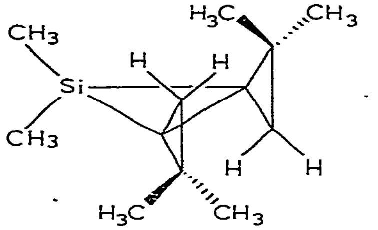
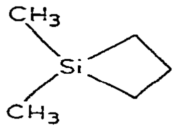
* In the meantime, the preparation of the first silacyclopropenes in these laboratories [11] and in others [12] has provided a still more reactive class of tetraorganosilicon compounds, as limited comparative studies have shown [11,13].

TABLE 1

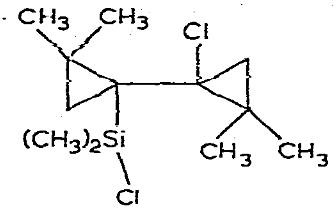
COMPARISON OF THE REACTIVITY OF 1,1-DIMETHYL-*trans*-2,3-BIS(2′,2′-DIMETHYLCYCLOPROPYLIDENE)-1-SILACYCLOPROPANE AND 1,1-DIMETHYL-1-SILACYCLOBUTANE TOWARD VARIOUS REAGENTS

Reagent		
O_2	Vigorous, exothermic reaction at room temperature.	Stable toward oxygen.
H_2O	Reaction exothermic and complete at room temperature in THF solution.	10% yield of $Me_2(n\text{-}C_3H_7)SiOH$ after 8 h at reflux [19].
Cl_2	Rapid reaction at —130° C; very vigorous reaction above —75°C.	Reaction above —40°C [20].
Br_2	Rapid reaction at —100°C.	Rapid reaction at room temperature.
$HCl(g)$	Rapid and complete reaction at —78°C.	60% yield of $Me_2(n\text{-}C_3H_7)SiCl$ after 8 h at 20°C [19].
ROH	Reaction exothermic and complete at room temperature.	58% yield of $Me_2(n\text{-}C_3H_7)SiOR$ after 11 h at 180°C ($R = n\text{-}C_6H_{13}$) [19].
HOAc	Reaction exothermic and complete at room temperature.	65% yield of $Me_2(n\text{-}C_3H_7)SiOAc$ after 8 h at 160—180°C [19].
Et_2NH	57% yield of ring-opened product after 6 h at 65°C.	No reaction at reflux or at 150°C in a sealed tube [19].
RLi [a]	Rapid and complete reaction at —70°C (R = Me).	75% yield of $Me_2(n\text{-}C_3H_7)SiR$ after 5 h at reflux in Et_2O (R = Ph) [21].
CCl_4	Exothermic reaction at room temperature.	No reaction at room temperature.

[a] With subsequent hydrolysis of the reaction mixture.

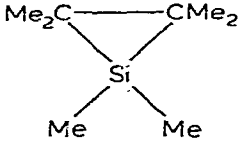
on going from a four-membered to the analogous, more highly strained three-membered ring is known for the cyclobutane vs. cyclopropane systems, but since nonpolar C—C bonds rather than polar Si—C bonds are involved, the baseline reactivity of the C_4 ring and the degree of its enhancement in the C_3 ring are much less than those of the comparable SiC_3/SiC_2 system.

The question of the mechanism and stereochemistry of these ring-opening reactions of siliranes remains an open one. With simple nucleophiles, initial attack at silicon seems reasonable. In the case of ring cleavage by acids, one must consider not only initial attack at a ring carbon atom by the electrophile, but also edge attack at the Si—C bond. It was apparent that alcohols are more reactive toward silirane II than amines. With secondary amines steric factors no doubt are important, but steric factors do not explain why t-butanol appears to be more reactive toward II than isopropylamine. Clearly, other factors are operative. Some reagents, e.g., carbon tetrachloride, appear to react by a radical pathway (hexachloroethane was formed). Other reagents reacted readily to give a multiplicity of products (e.g., bromine). Still others reacted readily to give unexpected and sometimes not readily rationalizable products. For instance, the low temperature reaction of chlorine with II in carbon disulfide gave XII rather than the expected XXVI (or decomposition products of the latter).



(XXVI)

We have developed the chemistry of the siliranes further during our investigations of the reactivity of hexamethylsilirane XXVII. The results of these



(XXVII)

studies have been presented in several preliminary communications [13,22]. Noteworthy are the one- and two-atom insertion reactions which this compound undergoes with aldehydes, ketones, arylolefins, 1,3-dienes, terminal acetylenes and dimethylsilylene, reactions which find no parallel in silacyclobutane chemistry.

Experimental

General comments

Infrared spectra were recorded using a Perkin—Elmer Model 257 or 457A infrared spectrophotometer, NMR spectra using a Varian Associates T60 or a Perkin—Elmer/Hitachi R-20B spectrometer. Chemical shifts are reported in δ units, ppm downfield from internal tetramethylsilane. Chloroform (δ 7.27 ppm) and dichloromethane (δ 5.30 ppm) often were used as alternative internal standards. Mass spectra were obtained using a Hitachi/Perkin—Elmer RMU-6 mass spectrometer operating at an ionizing voltage of 70 eV.

Gas-liquid chromatography (GLC) was used for isolation of pure samples, determination of purity of distilled samples and for yield determinations by the internal standard method. F & M Model 700 and 720, Hewlett—Packard Model 5754 and M.I.T. isothermal gas chromatographs were used. All columns used were packed with acid-washed, dimethyldichlorosilane-treated Chromosorb W.

All solvents were rigorously dried, usually by distillation from sodium benzophenone ketyl. 1,1-Dimethyl-*trans*-2,3-bis(2′,2′-dimethylcyclopropylidene)-1-silacyclopropane was prepared as described previously [2]. All transfers of this extremely oxygen and moisture-sensitive compound were effected using a syringe under a positive pressure of nitrogen.

In general, reactions of this silirane were carried out in a 50 ml, three-necked, round-bottomed flask which was equipped with a reflux condenser, a thermometer which extended into the reaction solution, a rubber septum and nitrogen inlet tube. The apparatus was flame-dried under a brisk stream of dry nitrogen. In most cases, the silirane was added slowly to a solution of the reagent in an appropriate solvent while monitoring the temperature of the mixture, If required, the reaction mixture was heated at reflux for several hours. Upon completion of the reaction, the mixture was transferred by a glass tube under nitrogen pressure to a 50 ml, single-necked, round-bottomed flask. A short path distillation head was attached and the solution was degassed. The low boiling components were trap-to-trap distilled at reduced pressure (0.05—0.1 mmHg) through the short-path head into a liquid nitrogen-cooled 100 ml receiver; the distillation pot was not heated during this process. Subsequently, the higher-boiling components were vacuum-distilled into another receiver. The yields which are reported represent the amount of isolated material, corrected for product purity on the basis of GLC analysis. Since most of the compounds prepared in this study were more or less hydrolytically unstable, all operations were carried out with a minimum exposure of the products to air.

Characterizing data for new compounds prepared in this study are given in Table 2.

Oxidation of silirane II

Oxygen gas, dried by passing it through a drying tower filled with KOH and P_2O_5, was passed over the surface of a solution of 0.6 g (3.1 mmol) of the silirane in 10 ml of hexane. An exothermic reaction occurred, with a 10°C temperature rise. The hexane was removed at reduced pressure and, following the procedure of Johnson and Siddiqi [23] the oily residue was dissolved in 50 ml of freshly boiled acetic acid, and 6 g of sodium iodide was added. After the mixture had been heated for 20 min at reflux, it showed the deep red-brown color of iodine. (A blank solution remained colorless.) The mixture was diluted to 100.00 ml with freshly boiled water, and aliquots were withdrawn and titrated with 0.04827 *M* sodium thiosulfate. It was determined that 2.77 mmol of iodine had been formed, which respresents an 89% conversion of iodide to iodine, based on the amount of starting silirane.

In another experiment, 1.26 g (6.5 mmol) of the silirane was converted to its oxidation product. The solvent was removed at reduced pressure and the oily residue was dissolved in 10 ml of toluene. Then 3.92 g of triphenylphosphine was added. An identical blank solution was prepared from 3.92 g of Ph_3P and 10 ml of toluene. Both solutions were heated at reflux for 24 h, cooled to room temperature, treated with 4 ml of iodomethane, and left to stand overnight [24]. The precipitated $Ph_3MeP^+I^-$ was filtered from each solution. The solution containing the silirane oxidation product yielded 5.12 g (12.4 mmol) of the phosphonium iodide, while the blank solution yielded 6.1 g (15.1 mmol). The filtrate from the solution of the silirane oxidation product thus treated was evaporated at reduced pressure. Pentane was added to the residue; filtration gave 0.70 g (2.5 mmol) of triphenylphosphine oxide, m.p. 152—153°C (lit. [25] m.p. 153°C). (No Ph_3PO was present in the blank solution.) Based on 6.5 mmol of starting silirane, this represents a 39% conversion of Ph_3P to the oxide.

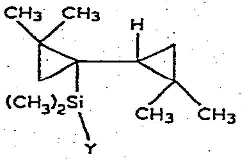
Hydrolysis of siliranes I and II.

Silirane I. To a solution of 1.85 g (7.5 mmol) of silirane I, prepared as described in ref. 2, in 30 ml of THF was added 0.13 ml of distilled water. The reaction

(continued on p. 146)

TABLE 2

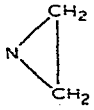
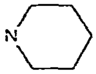
CHARACTERIZATION[a] OF COMPOUNDS OF TYPE



Y	Distillation temperature, (°C/mmHg)	n_D^{25}	Analysis (found (calcd.) (%))			Proton NMR spectrum[c]
			C	H	N	
OH	41—44/0.02	1.4745	67.61 (67.85)	11.35 (11.39)		0.20 (s, 6H, Me_2Si), —0.30 to 0.90 (m, 5H, cyclopropyl H), 1.05, 1.10, 1.17, 1.21 (four s, 3H each, C—CH_3), 1.78 (s, 1H, SiOH)
OCH_3	33—35/0.2	1.4576	69.16 (68.96)	11.64 (11.57)		0.22 (s, 6H, Me_2Si), —0.10 to 0.9 (m, 5H, cyclopropyl H), 1.02, 1.10, 1.18, 1.22 (four s, 3H each, C—CH_3), 3.42 (s, 3H, OCH_3)
OC_2H_5	41—43/0.02	1.4538	69.96 (69.92)	11.74 (11.74)		0.22 (s, 6H, Me_2Si), 0.00—0.86 (m, 5H, cyclopropyl H), 1.04, 1.10, 1.18, 1.23 (four s, 3H each, C—CH_3), 1.20 (t, J 7 Hz, 3H, CH_3 of Et), 3.74 (q, J 7 Hz, 2H, CH_2)
$OCHMe_2$	41—42/0.02	1.4519	70.67 (70.78)	11.81 (11.88)		0.23 (s, 6H, Me_2Si), —0.10—0.63 (m, 5H, cyclopropyl H), 1.03, 1.13, 1.18, 1.27 (four s, 3H each, C—CH_3), 1.18 (d, J 6 Hz, 6H, CMe_2 of i-Pr), 4.00 (heptet, 1H, OCH)
$OCMe_3$	50/0.04	1.4538	71.48 (71.56)	11.84 (12.01)		0.33 (s, 6H, Me_2Si), 0.02—0.75 (m, 5H, cyclopropyl H), 1.12, 1.18, 1.25, 1.35 (four s, 3H each, C—CH_3), 1.37 (s, 9H, CMe_3)
OC_6H_5	92—97/0.03	1.5070	74.63 (74.91)	9.76 (9.81)		0.33 (s, 6H, Me_2Si), —0.06—0.92 (m, 5H, cyclopropyl H), 1.07, 1.10, 1.20, 1.30 (four s, 3H each, C—CH_3), 6.66—7.20 (m, 5H, C_6H_5)
SH	45/0.02					0.40 (s, 6H, Me_2Si), —0.35—0.9 (m, 5H, cyclopropyl H), 0.99, 1.05, 1.15, 1.21 (four s, 3H each, C—CH_3), 1.10 (s, 1H, SH)
NH_2	43/0.05	1.4718	68.04 (68.17)	11.70 (11.92)		0.13 (s, 6H, Me_2Si), —0.10—0.90 (m, 5H, cyclopropyl H), 1.00, 1.10, 1.16, 1.22 (four s, 3H each, C—CH_3)
$NHCHMe_2$	57—59/0.03	1.4643	70.88 (71.06)	12.07 (12.33)	5.25 (5.61)	0.12 (s, 6H, Me_2Si), —0.18—0.85 (m, 5H, cyclopropyl H), 1.03, 1.07, 1.10, 1.13, 1.18 (apparent s, CH_3)

continued

TABLE 2 (continued)

Y	Distillation temperature, (°C/mmHg)	n_D^{25}	Analysis (found (calcd.) (%))			Proton NMR spectrum ^{c}
			C	H	N	
NHC_6H_5	114—115/0.01	1.5300	74.90 (75.19)	10.44 (10.17)	4.74 (4.87)	0.37 (s, 6H, Me$_2$Si), —0.07—0.70 (m, 5H, cyclopropyl H), 1.13, 1.17, 1.20, 1.27 (four s, 3H each, C—CH$_3$), 3.30 (s, 1H, NH), 6.40—7.20 (m, 5H, C$_6$H$_5$).
	90—92/2.5	1.4789	70.10 (70.80)	11.48 (11.46)	5.52 (5.90)	—0.03 and 0.17 (two s, 3H each, Me$_2$Si), 0.17—0.94 (m, 5H, cyclopropyl H), 1.04, 1.07, 1.18, 1.32 (four s, 3H each, C—CH$_3$), 1.63 (s, 4H, NCH$_2$)
$N(C_2H_5)_2$	62—64/0.03	1.4709	71.82 (71.84)	12.38 (12.43)	5.02 (5.24)	0.17 and 0.25 (two s, 3H each, Me$_2$Si), —0.10—0.86 (m, 5H, cyclopropyl H), 1.05 (t, J 7 Hz, 6H, CH$_3$ of Et), 1.06, 1.14, 1.22, 1.23 (four s, 3H each, C—CH$_3$), 2.86 (q, J 7 Hz, 4H, NCH$_2$)
	114—117/0.01	1.4875	72.85 (73.04)	11.93 (11.90)	5.08 (5.01)	0.10 and 0.15 (two s, 3H each, Me$_2$Si), —0.20—0.91 (m, 5H, cyclopropyl H), 1.02, 1.07, 1.15, 1.18 (four s, 3H each, C—CH$_3$), 1.50 (broad m, 6H, pip H), 2.76 (broad m, 4H, pip H)
	80—82/0.02	1.4883	68.20 (68.26)	11.22 (11.10)	4.94 (4.98)	0.10 and 0.15 (two s, 3H each, Me$_2$Si), —0.07—0.77 (m, 5H, cyclopropyl H), 1.00, 1.07, 1.13, 1.18 (four s, 3H each, C—CH$_3$), 2.75 (t, J 4 Hz), 4H, N—CH$_2$), 3.45 (t, J 4 Hz, 4H, OCH$_2$)
$NC_{12}H_{24}Si$ (disilazane XI)	110/0.05	1.4890	70.86 (71.02)	11.66 (11.67)		0.12 and 0.17 (two s, 6H each, Me$_2$Si), —0.20—0.83 (m, 10H, cyclopropyl H), 0.97, 1.07, 1.13, 1.20 (four s, 6H each, C—CH$_3$)
O_2CCH_3	60—62/0.05	1.4592	66.08 (66.08)	10.30 (10.30)		0.27 and 0.38 (two s, 3H each Me$_2$Si), —0.15—0.75 (m, 5H, cyclopropyl H), 0.98, 1.10, (two s, 3H each, C—CH$_3$), 1.14 (s, 6H, C—CH$_3$), 2.02 (s, 3H, CH$_3$C(O))
$O_2CC(CH_3)_3$	77—79/0.04	1.4543	68.65 (68.85)	10.93 (10.88)		0.28 and 0.47 (two s, 3H each, Me$_2$Si), —0.12—0.72 (m, 5H, cyclopropyl H), 1.02, 1.12, 1.15, 1.17 (four s, 3H each, C—CH$_3$), 1.17 (s, 9H, Me$_3$C)

continued

TABLE 2 (continued)

Y	Distillation temperature, (°C/mmHg)	n_D^{25}	Analysis (found (calcd.) (%))			Proton NMR spectrum [a]
			C	H	N	
N_3	41—43/0.01	1.4850	60.57 (60.70)	10.11 (9.77)	17.28 (17.70)	0.33 (6H, Me_2Si), —0.16—0.85 (m, 5H, cyclopropyl H), 1.00, 1.10, 1.18, 1.22 (four s, 3H each, C—CH_3)
H (52% abundant isomer)	55/3.3 [b]	1.4470	73.56 [c] (73.38)	12.22 (12.31)		0.08 (d, J 3 Hz, 6H, Me_2Si), 0.68—1.00 (m, 5H, cyclopropyl H), 1.17 (s, 12H, C—CH_3), 3.90 (m, 1H, SiH)
H (48% abundant isomer)		1.4566				0.15 (d, J 4 Hz, 6H, Me_2Si), 0.30—0.92 (m, 5H, cyclopropyl H), 1.02, 1.07 (two s, 3H each, C—CH_3), 1.17 (s, 6H, C—CH_3), 4.00 (m, 1H, SiH)
CH_3 (isomer from II/MeLi reaction, H_2O work-up)	50—54/4.0	1.4302	74.40 (74.20)	12.54 (12.45)		0.16 (s, 9H, Me_3Si), 0.82 (s, 2H, cyclopropyl CH_2), 1.17 (s, 9H, C—CH_3 and cyclopropyl H), 1.20 (s, 6H, C—CH_3)
CH_3 (isomer from XII/MeLi reaction)		1.4332	74.05 (74.20)	12.35 (12.45)		0.05 (s, 9H, Me_3Si), —0.10—0.8 (m, 5H, cyclopropyl H), 0.92 and 1.02 (two s, 3H, each, C—CH_3), 1.11 (s, 6H, C—CH_3)
C_6H_5 (isomer from II/PhLi reaction: low temp. hydrolysis)	77—79/0.01	1.5189	79.25 (79.33)	10.45 (10.36)		0.33 and 0.40 (two s, 3H each, Me_2Si), —0.10—0.50 (m, 5H, cyclopropyl H), 0.93, 1.17 (two s, 3H each, C—CH_3), 1.02 (s, 6H, C—CH_3), 7.10—7.60 (m, 5H, C_6H_5)
C_6H_5 (isomer from II/PhLi reaction; 0°C hydrolysis)	74—78/0.01	1.4925	78.99 (79.33)	10.37 (10.36)		—0.42 (s, 6H, Me_2Si), 1.05—1.33 (m, 5H, cyclopropyl H), 1.18 (s, 6H, C—CH_3), 1.22 (s, 6H, C—CH_3), 7.15—7.60 (m, 5H, C_6H_5)

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[a] Infrared spectra and mass spectra are listed in the Ph.D. theses (M.I.T.) of C.K.H., R.L.L. and D.C.A. The 70 eV mass spectra of these compounds in almost all cases showed the expected molecular ion. NMR spectra were determined in carbon tetrachloride solution with chloroform as the internal standard. [b] Distillation temperature of the mixture of both isomers. [c] Analysis of the mixture of both isomers.

mixture was heated at reflux for 3 h and then was chromatographed on a 35 X 5 cm column packed with 100 mesh silicic acid. Elution with hexane removed trace impurities and elution with dichloromethane gave the silanol VI as an oil which could be crystallized from methanol at 0°C. An analytical sample, m.p. 43.5—46.5°C, was prepared by sublimation (room temperature at 0.02 mmHg). Found: C, 72.47; H, 10.66. $C_{16}H_{28}OSi$ calcd.: C, 72.66; H, 10.67%. IR (Nujol):

3700m, 3440m (OH), 1255s, 1175w, 1135w, 1110w, 1040m, 1005w, 965m, 955m, 915m, 860s, 835s, 775s and 665s, cm^{-1}. The mass spectrum showed the molecular ion at *m/e* 264.

When this reaction was repeated using 1.45 g (5.9 mmol) of silirane I in 10 ml of THF and an excess of water, the yield of silanol VI was 0.95 g (60%). Under these conditions the reaction is exothermic and external heating is not required.

Silirane II. To a solution of 1.05 g (5.4 mmol) of II in 10 ml of THF was added 0.2 ml of distilled water, resulting in an exothermic reaction (15°C temperature rise). The mixture was stirred for 2.5 h at room temperature and then the solvent was removed in vacuum. Short-path distillation gave 0.80 g (70%) of silanol Va. An analytical sample was collected by GLC (20% UC-W98 silicone rubber gum, 140°C).

Alcoholysis reactions of silirane II

The reaction of II with t-butanol is typical. To a solution of 3 ml (30 mmol) of t-butanol in 8 ml of benzene was added 0.83 g (4.3 mmol) of silirane II. An exothermic reaction (15°C temperature rise) resulted. The mixture was stirred at room temperature for 2 h and then the solvent and excess t-butanol was removed by trap-to-trap distillation (room temperature at 0.04 mmHg). The residue was distilled (50°C at 0.04 mmHg) to give 0.91 g (99% pure by GLC, 80% yield) of t-butoxysilane Ve. Samples for analysis and spectroscopic measurements were collected by GLC (20% UC-W98, 160°C).

Reactions of silirane II with other alcohols and with phenol are summarized in Table 3.

Methanolysis of silirane I

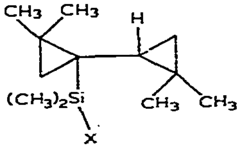
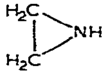
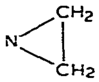
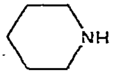
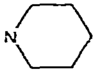
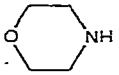
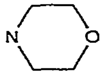
To a mixture of 1.60 g (50 mmol) of absolute methanol in 10 ml of THF under nitrogen was added dropwise with stirring 25 ml of a 0.80 *M* solution of silirane I (20.0 mmol) in THF during a 10 min period. There was an immediate exothermic reaction, and the solution remained clear and colorless. The reaction mixture was stirred at room temperature for 1 h and then the THF and excess methanol were removed at reduced pressure. The residue was short-path distilled to give 4.70 g (85%) of VIIa, a clear, colorless liquid, b.p. 94—96°C at 0.01 mmHg. An analytical sample was redistilled, b.p. 85—86°C at 0.01 mmHg, n_D^{25} 1.5100. 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 0.28 (s, 6H, Me_2Si), 0.4—2.1 (m, 20 H, maxima at 1.70, 1.40, 0.83) and 3.40 ppm (s, 3H, OCH_3).

Methanolysis of silirane III

To a solution of 1.20 g (6.70 mmol) of silirane III in 15 ml of pentane under nitrogen was added, with stirring, 2 ml of absolute methanol in 5 ml of pentane. After the exothermic reaction had subsided, the reaction mixture was stirred at room temperature under nitrogen for 1 h. Subsequent distillation at reduced pressure gave 1.20 g (80%) of clear liquid, b.p. 36—38°C at 0.2 mmHg, methoxysilane VIIb. An analytical sample was collected by GLC (20% UC-W98, 160°C), n_D^{25} 1.4547. (Found: C, 68.78; H, 11.42. $C_{13}H_{26}OSi$ calcd.: C, 68.96; H, 11.57%.) NMR (CCl_4, $CHCl_3$): δ 0.07 and 0.1 (two s, 3H each, Me_2Si), 0.2—0.8 (m, 5H, cyclopropyl H), 0.82, 0.96, 1.00, 1.06 (four s, 3H each, C—CH_3) and 3.35 ppm (s, 3H, OCH_3).

TABLE 3

REACTIONS OF 1,1-DIMETHYL-*trans*-2,3-BIS(2′,2′-DIMETHYLCYCLOPROPYLIDENE)-1-SILACYCLOPROPANE (SILIRANE II)

Silirane II (mmol)	Substrate (mmol)	Reaction conditions		Product 	
		Time (h)	Temperature (°C)	X	Yield (%)
4.73	CH_3OH (30)	1	room temp. ^{a}	OCH_3	90
3.6	C_2H_5OH (20)	1	room temp. ^{a}	OC_2H_5	81
4.1	Me_2CHOH (18)	1	room temp. ^{a}	$OCHMe_2$	76
4.3	Me_3COH (30) ^{b}	2	room temp. ^{a}	$OCMe_3$	80
3.68	C_6H_5OH (10.7) ^{b}	0.5	room temp. ^{a}	OC_6H_5	83
5.4	H_2O (11) ^{c}	2.5	room temp. ^{a}	OH	70
5.15	H_2S(g)(excess)	3	room temp.	SH	40
3.25	NH_3(g) (excess) ^{c}	5	8	NH_2	56
4.2	Me_2CHNH_2 (27) ^{b}	3	55	$NHCHMe_2$	62
6.0	Et_2NH (48) ^{b}	6	65	NEt_2	57
4.4	 (12) ^{d}	3	room temp. ^{a}		68
5.7	 (21)	1.5 2	room temp. ^{a}, 84		64
5.2	 (20)	1.5 2	room temp. ^{a}, 85		64
5.15	$PhNH_2$ (18)	2	room temp. ^{a}	NHPh	66
4.6	HN_3 (9.0)	2	room temp. ^{a}	N_3	45
4.45	CH_3CO_2H (50)	0.33	room temp. ^{a}	O_2CCH_3	88
55.15	$(CH_3)_3CCO_2H$ (36)	0.25	room temp.	$O_2CC(CH_3)_3$	87
22.5	HCl(g)		−78	Cl	77

[a] Exothermic reaction upon mixing the reactants at room temperature. [b] Reaction carried out in benzene solution. [c] Reaction carried out in tetrahydrofuran solution. [d] Reaction carried out in hexane solution.

Thiolysis of silirane II

With hydrogen sulfide. The standard apparatus was modified so that one neck of the flask was sealed with a no-air stopper. Through this stopper was inserted a 15 gauge stainless steel needle which reached nearly to the bottom of the flask and which was connected to a tank of gaseous hydrogen sulfide (Matheson Co.). The apparatus was charged with a solution of 1.0 g (5.15 mmol) of silirane II in 10 ml of THF. The condenser was replaced with a Dry-Ice condenser and then hydrogen sulfide was bubbled through the solution. An exotherm (7°C temperature rise) was observed. The H_2S was allowed to reflux for 3 h at the rate of one drop/min. The reaction mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure and the residue was distilled, giving 0.47 g (40%) of thiol VIII, b.p. 45°C at 0.02 mmHg. A sample was collected by GLC (20% UC-W98, 175°C). Its NMR spectrum (Table 2) was consistent with its formulation as VIIIa and its mass spectrum showed the molecular ion at *m/e* 228, but a satisfactory combustion analysis could not be obtained.

Aminolysis of silirane II

With ammonia. A solution of 0.63 g (3.25 mmol) of silirane II in 10 ml of THF was prepared in a 50 ml flask equipped with a Dry-Ice condenser, a thermometer and a no-air stopper through which a 15 gauge needle, which was connected to a tank of ammonia, had been inserted. Ammonia was bubbled through the solution until it refluxed from the cold finger. The solution was stirred for 5 h (8°C solution temperature). The solvent was removed at room temperature at 0.05 mmHg and subsequent distillation gave 0.35 g (98% pure; 56% yield) of aminosilane IXg.

With diethylamine. A solution of 1.17 g (6.0 mmol) of silirane II, 5 ml of diethylamine (48 mmol, dried over Linde 3A molecular sieves) and 5 ml of benzene was heated at reflux (65°C) with stirring for 6 h. During this time the solution turned dark yellow. After removal of benzene and unreacted diethylamine at reduced pressure, short path distillation of the residue gave 0.90 g (98% pure, 57% yield) of aminosilane IXa. An analytical sample was collected by GLC (10% Carbowax 20M at 160°C).

A similar procedure was used in the reaction of silirane II with isopropylamine in benzene (3 h at reflux), but when a solution of 36 mmol of diisopropylamine and 6.76 mmol of silirane II in benzene was heated at reflux for 20 h, no reaction occurred.

The reactions of piperidine and morpholine with silirane II in benzene solution were mildly exothermic (ca. 3°C temperature rise on mixing). In each case, the reaction mixture was stirred at room temperature for 1.5 h and then was heated at reflux for another 2 h. The reaction of silirane II with aniline in benzene solution and with aziridine in hexane were more exothermic (10—20°C temperature rise on mixing) and a 2 h reaction time at room temperature sufficed to give equivalent product yields.

Reaction of silirane II with lithium dialkylamides

Lithium diethylamide. To 0.88 g (11 mmol) of diethylamine in 8 ml of THF cooled to 0°C (under nitrogen) was added 2.5 ml of 2.2 *M* n-butyllithium (5.5 mmol). The resulting light-yellow solution was stirred for 30 min at 0°C and then was cooled to —78°C. To the Et_2NLi/Et_2NH solution was added 0.79 g (4.08 mmol) of silirane II over a 5 min period. After it had been stirred at —78°C for 30 min, the reaction mixture was allowed to warm slowly to 15°C. During this time a color change to orange was observed. Solid ammonium chloride (0.3 g, 5.7 mmol) was added in one portion. After the resulting mixture had been stirred for 10 min, the orange color was discharged. The reaction mixture was filtered under nitrogen and the residue was washed with pentane. The filtrate and combined washings were distilled at reduced pressure to give 0.72 g (99% pure, 67% yield) of aminosilane IXa. The IR and NMR spectra of the product were identical with those of the Et_2NH/silirane II reaction product.

Lithium diisopropylamide. To the $i\text{-}Pr_2NLi/i\text{-}Pr_2NH$ reagent solution prepared by reaction of 5.5 mmol of n-butyllithium with 9.2 mmol of diisopropylamine in 8 ml of THF at 5°C was added, at —78°C under nitrogen, 0.78 g (4.0 mmol) of silirane II. A procedure as described in the experiment above gave a dark orange solution which was treated with 5.6 mmol of solid ammonium chloride at room temperature. Filtration, followed by distillation of the filtrate gave 0.48 g (60%) of disilazane XI. An analytical sample was collected by GLC (10% Carbowax 20M at 200°C).

Acidolysis of silirane II

With hydrogen chloride. A solution of 22.5 mmol of silirane II in 25 ml of pentane under nitrogen was cooled to −78°C and then dry gaseous hydrogen chloride was bubbled through the mixture for 10 min. An NMR spectrum taken at that point showed that all of the silirane had been consumed. The mixture was stirred and allowed to warm slowly to room temperature and then was distilled under nitrogen to remove the pentane and subsequently at reduced pressure. A pale yellow liquid (3.98 g, 77%), b.p. 58—60°C at 1.0 mmHg, was obtained. GLC analysis indicated a purity of about 90%. The NMR spectrum was consistent with structure XII. NMR (CCl_4, $CHCl_3$): δ 0.51 (s, 6H, Me_2Si), 0.90 to −0.05 (m, 5H, cyclopropyl H), 1.01, 1.10, 1.19, 1.27 (four s, 12H, CH_3) ppm.

A 0.86 g (3.7 mmol) sample of this product was added by syringe to a solution of sodium methoxide in methanol prepared from 0.26 g (11 mmol) of sodium metal and 20 ml of methanol. The reaction mixture was stirred at room temperature for 4 h, treated with 0.65 ml of Me_3SiCl to consume unreacted sodium methoxide and stirred for another 3 h. The solids were allowed to settle and the organic layer was transferred to a single-necked flask. Distillation at reduced pressure (short path head) gave 0.70 g (84%) of methoxysilane Vb, b.p. 42—43°C at 0.4 mmHg, whose IR and NMR spectra were identical with those of the silirane II/methanol product.

Another 0.92 g (4.0 mmol) of chlorosilane XII in 10 ml of diethyl ether was treated with 4.0 ml of a solution of 1.6 *M* methyllithium (6.4 mmol) in diethyl ether under nitrogen. The reaction mixture was stirred at room temperature for 2 h and then was hydrolyzed by careful addition of 1 ml of water. The ether layer was separated and trap-to-trap distilled at 50°C and 0.01 mmHg. The distillate was redistilled to remove solvent. The less volatile residue was analyzed by GLC (10% UC-W98, 130°C) and found to contain trimethylsilyl derivative XIII (77% yield). An analytical sample was collected by GLC (10% Apiezon L, 200°C).

With acetic acid. To a solution of 3 ml (50 mmol) of glacial acetic acid in 8 ml of benzene was added 0.86 g (4.45 mmol) of silirane II, dropwise with stirring. A temperature rise of 15° C was observed. The mixture was stirred at room temperature for 20 min and then was distilled. The product (XIVa, 0.95 g, 98% pure, 88%) was collected at 60—62° C at 0.05 mmHg. An analytical sample was collected by GLC (10% Carbowax 20 M, 160° C). The ν(C=O) of the product was observed at 1710 cm^{-1} (neat film).

A similar reaction between 36 mmol of pivalic acid and 5.15 mmol of silirane II in 10 ml of benzene at room temperature gave the silyl carboxylate XIVb, 1.32 g, 97% pure, 87% yield; ν(C=O) 1709 cm^{-1} (neat film).

With hydrazoic acid. To a solution of 10 ml of 1.8 *M* HN_3 in benzene under nitrogen was added slowly with stirring 0.90 g (4.6 mmol) of silirane II; an exothermic reaction with a 10°C temperature rise resulted. The mixture was stirred at room temperature for 2 h and then was distilled to give 0.50 g (45%) of azidosilane XV, b.p. 41—43°C at 0.01 mmHg. An analytical sample was collected by GLC (20% UC-W98 at 150°C).

Reaction of silirane II with acetyl chloride

A solution of 0.84 g (4.3 mmol) of silirane II and 1.00 ml (15 mmol) of freshly distilled acetyl chloride in 15 ml of hexane was heated at reflux and stirred under nitrogen for 4 h. After removal of the solvent and excess acetyl chloride at reduced pressure, the product, chlorosilane XVI was distilled at 67—73°C at 0.05 mmHg and obtained in 60% yield. Attempts to further purify this material by GLC (10 or 15% Carbowax 20M or 10% DC-200) were unsuccessful, and an acceptable combustion analysis was not obtained. The proton NMR and the mass spectrum, however, supported its formulation as XVI. (Found: C, 62.40, H, 9.38; Cl, 11.68. $C_{14}H_{25}OClSi$ calcd.: C, 61.61; H, 9.23; Cl, 12.99%). NMR ($CCl_4/CHCl_3$): δ 0.20 (s, 6H, Me_2Si), 1.10 and 1.20 (two s, 3H each, $C—CH_3$), 1.53 (s, 6H, $C—CH_3$), 1.86 (s, 3H, CH_3CO) ppm. The mass spectrum (70 eV) showed the molecular ion at *m/e* 272.

Reaction of silirane II with boron trichloride

A 50 ml, three-necked flask equipped with a no-air stopper through which a disposable pipet connected to a boron trichloride cylinder was inserted, a mechanical stirrer, a thermometer and a nitrogen inlet tube was charged with 0.83 g (4.3 mmol) of silirane II in 15 ml of hexane and treated with boron trichloride (in short bursts) at room temperature, until no further exotherm was noted on addition. Subsequently, the orange solution which resulted was treated with 1 ml of dry methanol. The colorless solution which was formed was distilled to remove solvents (room temperature at 0.05 mmHg). Further distillation gave the product, b.p. 80°C at 0.05 mmHg, in 60% yield, based on Scheme 3. A sample of the product burned with a green flame, confirming the presence of boron. An analytical sample was collected by GLC (10% Carbowax 20M, 175°C), n_D^{25} 1.4701. (Found: C, 62.09; H, 10.18. $C_{13}H_{25}O_2BSi$ calcd.: C, 61.89; H, 9.99%). NMR ($CCl_4/CHCl_3$): δ 0.53 (s, 6H, Me_2Si), 0.17—0.75 (m, 5H, cyclopropyl H), 1.03 (s, 3H, $C—CH_3$), 1.13 (s, 3H, $C—CH_3$), 1.25 (s, 3H, $C—CH_3$), 1.36 (s, 3H, $C—CH_3$) and 3.52 (s, 3H, OCH_3) ppm. The 70 eV mass spectrum showed, inter alia, the molecular ion at *m/e* 252, (relative intensity 1), as well as fragment ions with *m/e* 136 and 121, which are characteristic of the tetramethylbicyclopropyl moiety (see below). IR (neat film) (cm^{-1}): 3060w, 2990m, 2958m, 2935s, 2877m, 1450m, 1420 (sh), 1408w, 1378m, 1318m (br), 1253s, 1170w (br), 1120m (br), 1088w, 1032w, 953w, 922w, 868m, 844s, 821m, 809s, 783s and 678m.

Reaction of silirane II with methyllithium

A solution of 2.40 g (12.4 mmol) of silirane II in 10 ml each of pentane and THF, under nitrogen, was cooled to —78°C (Dry-Ice/acetone bath) and 10 ml of 1.62 *M* methyllithium in diethyl ether (16.3 mmol) was added dropwise with stirring over 5 min to produce an orange solution. The reaction mixture was stirred at —78°C for 30 min and then was treated carefully with 2.0 ml (25 mmol) of concentrated hydrochloric acid. The mixture was allowed to warm to room temperature, was stirred for another 2 h and the the organic layer was separated. The solvents were removed by distillation through a short path head and the residue was distilled at reduced pressure to give 2.08 g of clear liquid, b.p. 50—54°C at 4.0 mmHg. The distillate was analyzed by GLC (10% UC-W98 at 140°C) and found to contain several components. The major component was collected by GLC and characterized as an isomer of 1-trimethylsilyl-2,2,2′,2′-tetramethyl-1,1′-bicyclopropyl. GLC yield determination showed that this compound was present in 56% yield.

Reaction of silirane II with phenyllithium

A solution of 0.93 g (4.80 mmol) of silirane II in 10 ml of THF was cooled to —78°C and 7 ml of 1.2 *M* phenyllithium in diethyl ether was added, under nitrogen with stirring, during 5 min. The solution was stirred at —78°C for 1 h and then 1 ml of concentrated hydrochloric acid was added dropwise. The resulting mixture was diluted with 5 ml of water and the organic layer was separated and dried. Removal of solvents at reduced pressure was followed by distillation of the product, 0.4 g (32%), b.p. 77—79°C at 0.01 mmHg. An analytical sample was collected by GLC (20% UC-W98, 185°C).

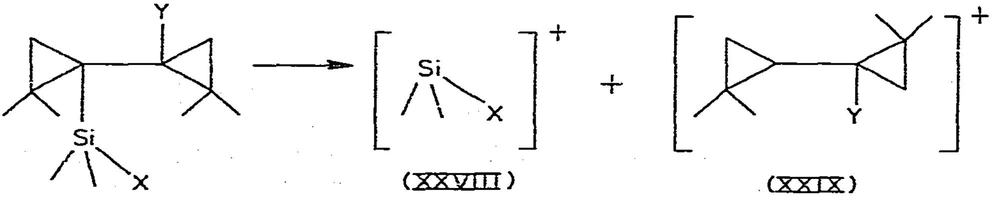
In another such reaction, carried out with 4.90 mmol of silirane II and 8 mmol of phenyllithium at —78°C, the reaction mixture was allowed to warm to 0°C before the hydrochloric acid was added. Subsequent work-up was identical to that in the experiment above and gave 0.60 g (45%) of product, b.p. 74—78°C at 0.01 mmHg.

Reaction of silirane II with lithium aluminum hydride

To 0.10 g (2.6 mmol) of lithium aluminum hydride in 20 ml of THF under nitrogen was added 1.03 g (5.5 mmol) of silirane II. A small rise in temperature was observed. The mixture was stirred at 40°C for 2 h and then 1 ml of acetone and subsequently 1 ml of water were added. The reaction mixture was filtered through Celite and solvents were removed from the filtrate by distillation at atmospheric pressure. GLC analysis of the residue showed the presence of two components which were collected by GLC (10% Carbowax 20M, 130°C) and characterized as isomers XXIa and XXIb. These showed ν(Si—H) at 2108 and 2110 cm^{-1}, respectively (neat film).

Mass spectroscopy of products derived from silirane II

Mass spectra have proved quite useful in establishing the structures of compounds prepared in this study. In the ring opened structures, a principle mode of fragmentation involves the breaking of the silicon—bicyclopropyl bond (eq. 2).



(2)

(XXVIII)

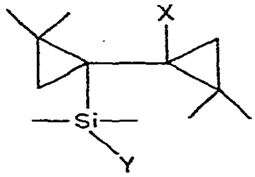
m/e 58 + X

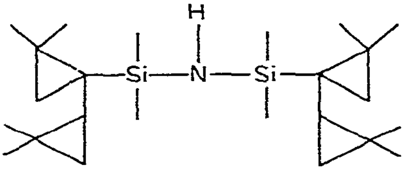
(XXIX)

m/e 136 + Y

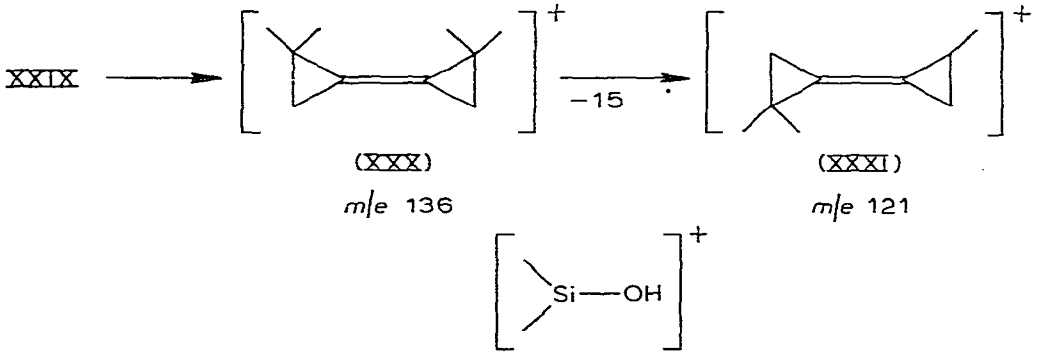
TABLE 4

MASS SPECTRA: % ABUNDANCE OF IONS



Y	X	M^{+} (m/e)	136 + X (m/e)	136	121	[$>$Si—Y]$^+$ (m/e)	75	Other ions (m/e, identity)
OMe	H	2 (226)	7 (137)	6	3	100 (89)	27	76 (58, Me_2SiH^+)
OEt	H	2 (240)	5 (137)	5	2	100 (103)	43	
OH	H	71 (212)	10 (137)		22	100 (75)		
NHPr-i	H	1 (253)	5 (137)	5	3	6 (58)	100	
NEt_2	H	0.2 (257)	8 (137)	4	6	16 (131)	68	36 (73, $HNEt_2$) 100 (58, $HNEt_2$-15)
H	H	4.5 (228)	14 (137)		21	85 (91)	45	
CH_3COO	H	254 (2)	11 (137)	2	6	94 (192)	100	33 (60, CH_3COOH), 24 (59, CH_2COOH^+)
Cl	H	2 (230)	14 (137)	5	8	100 (93)	5	
CH_3	H	2 (210)	5 (137)	11	4	100 (73)	6	11 (59, Me_2SiH^+)
H	H	2 (196)	12 (137)	3	11	100 (59)	4	83 (73, Me_3Si^+)
Cl	$\underset{\underset{O}{\Vert}}{C}CH_3$	1 (272)	7 (179)	12	10	30 (93)	65	100 (43, $CH_3\underset{\underset{O}{\Vert}}{C^+}$)
		0.2 (405)	20(137)	10	10		100	

The bicyclopropyl ion in turn leads to the bicyclopropylidene XXX which loses a methyl group to give XXXI. In view of the hydrolytic instability of com-



(XXX)
m/e 136

(XXXI)
m/e 121

(XXXII)
m/e 75

pounds containing SiN, SiS and SiCl bonds it is not surprising that hydrolysis often occurs in the mass spectrometer. A large fragment seen at *m/e* 75, XXXII, is in accord with this process.

A summary of these processes is included in Table 4.

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