Reactions of Fluoride Ion Sources with Haloalkyl Derivatives of Phenazasilines and Phenoxasilins

Joyce Y. Corey,* Eugene R. Corey, Vincent H. T. Chang, Michael A. Hauser, Mark A. Leiber, Thomas E. Reinsel, and Mark E. Riva

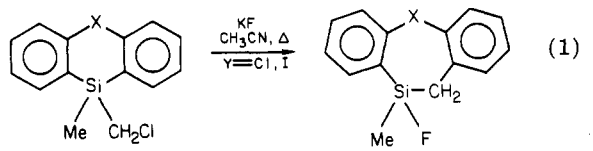
Department of Chemistry, University of Missouri—St. Louis, St. Louis, Missouri 63121

Received January 4, 1984

The reaction of haloalkyl derivatives of phenazasilines and phenoxasilins with fluoride sources under both heterogeneous and homogeneous conditions has been examined. Halomethyl derivatives undergo a rearrangement reaction that results in ring enlargement to dihydrodibenzazasilepine and dihydrodibenzoxasilepin. The rate of the reaction follows the order $Bu_4N^+F^-$ > CsF > KF sources [KF(tech), $KF\cdot 2H_2O$, KF·HF]. Use of anhydrous KF results in cleavage of the Si–Ar bonds. Rearrangement followed by rapid cleavage of the silicon–benzyl bond occurs with α-chloroethyl derivatives under both heterogeneous and homogeneous conditions. Fluoride causes elimination of β-chloroethyl substituents. No reaction with γ-chloropropyl derivatives occurs under heterogeneous conditions, and silicon–aryl cleavage occurs under homogeneous conditions with isolated products a function of the water content in the latter case. Reaction of γ-iodopropyl derivatives with $Bu_4N^+F^-$ gave products of substitution at the C–I bond. Other salts also react with chloromethyl derivatives to give products of substitution at carbon (KOAc, KI), cleavage of the chloromethyl group (KCN), or ring expansion followed by rapid ring cleavage (KOH). The molecular structure of 2,8-dibromo-5,10-dimethyl-10-fluoro-10,11-dihydro-5*H*-dibenz[*b*,*f*][1,4]azasilepine, VI, has been determined by X-ray diffraction methods. The crystal data are as follows: monoclinic, $P2_1/c$, a = 8.869 (2) Å, b = 9.934 (5) Å, c = 18.392 (8) Å; β = 98.75°; Z = 4; 1121 data > 3σ yielded a final R value of 0.042 by least-squares refinement. Molecules of VI assume a folded boat conformation with a dihedral angle between benzo group planes of 112°. The sum of angles about the nitrogen atom is 348°.

Introduction

We have shown that fluoride ion induces phenyl migration in tricyclic silicon heterocycles to produce ring-expanded products (eq 1) and have utilized this reaction



(1)

I, X = –, CH_2, CH_2CH_2
II, X = NMe[a]
III, X = O
IV, X = OCH_2

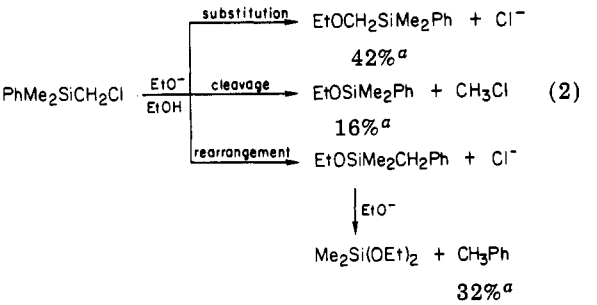
V, X = –, CH_2, CH_2CH_2[1b]
VI, X = NMe[1c]
VII, X = O[1d]
VIII, X = OCH_2[1e]

[a] 2,8-Dibromo derivative.

to synthesize silepins [V (X = CH_2), VI, VII] in which the silicon heteroatom is part of a two-atom bridge between the two benzo groups.[1] Occasional byproducts arise from cleavage of Si–Ar and Si–CH_2Ar bonds, but yields of ring expansion products are generally high. The development of this rearrangement reaction is part of a program to prepare and examine the structures of silicon analogues of psychotropic drugs.

A study was initiated to determine the influence of the fluoride ion source on the reaction shown in eq 1, to determine whether other anions would promote the rearrangement process, and to determine whether fluoride ion could induce a ring expansion by two or three carbon atom units. We wish to report here the results of the reactions of II and III with various fluoride sources as well as other potassium salts. In addition, the reaction of F^- with derivatives of II in which the halomethyl group has been replaced by an α-chloroethyl or a β-chloroethyl substituent and of III where halomethyl was replaced by a γ-halopropyl substituent have been investigated.

Previous studies have shown that (halomethyl)organosilanes react with anionic reagents to provide products that result from attack at the silicon center and at the carbon center of the chloromethyl group. An early investigation of the reaction of sodium ethoxide with (chloromethyl)silanes $ClCH_2Me_2SiAr$[2] showed that there were three principal reaction pathways as summarized in eq 2 (for Ar = Ph): substitution at the carbon of the chloromethyl



(2)

[a] Isolated product.

substituent, 1,2 migration of phenyl from silicon to carbon, and elimination of the chloromethyl group. Anion-induced rearrangement of both alkyl and hydride groups from silicon to the carbon of a chloromethyl substituent on silicon have also been reported.[3,4] The reactions reported here for II and III also exhibit the three pathways shown in eq 2.

In addition to the general synthetic program the structures of several tricyclic silicon heterocycles have been previously determined and a set of parameters have been developed to describe the features of these molecules.[5] In

(1) (a) Corey, J. Y.; Chang, V. H. T. *J. Organomet. Chem.* **1979**, *174*, C15. (b) Corey, J. Y.; Francis, E. A.; Bursten, M. S.; Kunz, J. C. *Ibid.* **1981**, *210*, 149. (c) Corey, J. Y.; Janoski, H. M.; Vermont, D. F.; Paton, J. P.; Chang, V. H. T. *Ibid.* **1980**, *194*, 15. (d) Chang, V. H. T.; Corey, J. Y. *Ibid.* **1980**, *190*, 217. (e) Corey, J. Y.; Chang, V. H. T. *Organometallics* **1982**, *1*, 645.

(2) Eaborn, C.; Jeffrey, J. C. *J. Chem. Soc.* **1957**, 137.

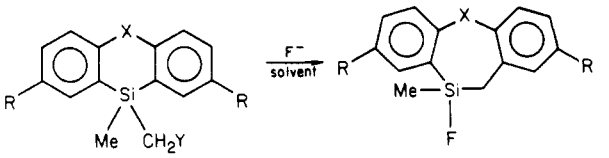
(3) Voronkov, M. G.; Kirpichencko, S. V.; Keiko, V. V.; Pestunovich, V. A.; Tsetlina, E. O.; Khvalovskii, V.; Vchelak, Ya. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1975**, 2052.

(4) Tacke, R.; Lange, H.; Atlar-Bashi, M. T. *Justus Liebigs Ann. Chem.* **1982**, 1946.

(5) Corey, E. R.; Corey, J. Y.; Glick, M. D. *J. Organomet. Chem.* **1975**, *101*, 177.

0276-7333/84/2303-1051$01.50/0

Table I. Ring Expansion as a Function of Fluoride Ion Source



IIa, X = NMe, R = Br, Y = Cl
IIb, X = NMe, R = Br, Y = I
IIIa, X = O, R = H, Y = Cl
IIIb, X = O, R = H, Y = I

VI, X = NMe, R = Br
VII, X = O, R = H

	IIa		IIIa	
F^- source	conditns,[a] h	% VI[b]	conditns,[c] h	% VII[d]
KF(tech)[e]	15 (15.5)[f]	60 (100)[f]	18 (10)[f]	64 (73)[f]
KF(tech, dried)	15[g]	45	18[h]	33
$KF \cdot 2H_2O$	18	80	18	43
KF·HF	15	54	18	50
KF(anhyd)	15	0[i]	18	0[i]
KF(tech) (Soxhlet)[j]	170	0[k]		
KF/KI = 8/1	3	46		
	5.5	75		
CsF	2	58		
$Bu_4N^+F^-$	0.15[l]	~100		

[a] Ratio $II/F^- = 1$; 0.10-0.12 M silane in acetonitrile; number of hours of reflux (see Experimental Section). [b] % VI determined from average of integration ratio of NMe (II)/NMe (II + VI) and SiMe (II)/SiMe (II + VI). [c] Ratio $III/F^- = 1$; 0.10 M silane in acetonitrile; number of hours of reflux (see Experimental Section). [d] % VII determined from average of integration ratio of SiMe (III)/SiMe (III + VII). [e] KF(tech) = $KF \cdot 0.6H_2O$. [f] Value for IIb and IIIb in parentheses. [g] KF(tech) dried for 24 h. [h] KF(tech) dried for 4 h at 110 °C. [i] Cleavage products only. [j] KF in extraction thimble; 0.026 M in II. [k] Starting material recovered. [l] THF solvent, room temperature.

all the derivatives studied thus far where the central ring contains six or seven atoms the silicon atom has been a one-atom bridge between the two benzo groups. The structure of VI has been determined as the first example of a derivative in which silicon is part of a two-atom bridge.

Results

(Halomethyl)silanes and Fluoride Sources. The usual fluoride source employed in our initial studies was technical grade KF. Samples were normally dried overnight before use but prolonged drying caused erratic reaction results, and therefore a variety of fluoride sources were examined for effectiveness in the promotion of the reaction shown in eq 1. The samples of technical grade KF were found to be hydrated and of approximate composition $KF \cdot 0.6H_2O$ as determined by drying samples to constant weight. Other fluoride sources examined were $KF \cdot 2H_2O$, KF·HF, CsF, and $Bu_4N^+F^-$. Comparisons of the reactions of these various fluoride sources with II and III are summarized in Table I. The ratio of II or III to F^- was taken as one in all cases to minimize possible cleavage of the ring-expanded products. The values shown in Table I were reproduced in independent runs. The potassium salts, KF(tech) = $KF \cdot 0.6H_2O$, $KF \cdot 2H_2O$, and KF·HF, are all effective in promoting the ring expansion reaction shown in eq 1. Prolonged heating of KF(tech) is required to obtain anhydrous KF as shown in Figure 1. When anhydrous samples are employed, only cleavage products of both II (III) and VI (VII) are obtained. Prior drying of KF·HF had no effect on the rate of conversion of II and III to ring-expanded products. Potassium fluoride is negligibly soluble in CH_3CN as was demonstrated by an attempted Soxhlet extraction of KF where no detectable reaction of II occurred in 1 week.

As an additional comparison the first entry in Table I includes data for the reaction of the iodomethyl derivative of II (III). The iodide ion is a more effective leaving group as indicated by the more rapid conversion to VI (VII). The substitution of chloride for iodide occurs more rapidly than ring expansion (see Experimental Section), and the combination KF/KI provides an "in situ" preparation of the iodomethyl derivative that ring expands to VI. Cesium fluoride, which is slightly soluble in acetonitrile, is more effective than the potassium salts in promoting the rate of the ring expansion reaction.[6] Under the homogeneous conditions provided by $Bu_4N^+F^-$/THF conversion of II to

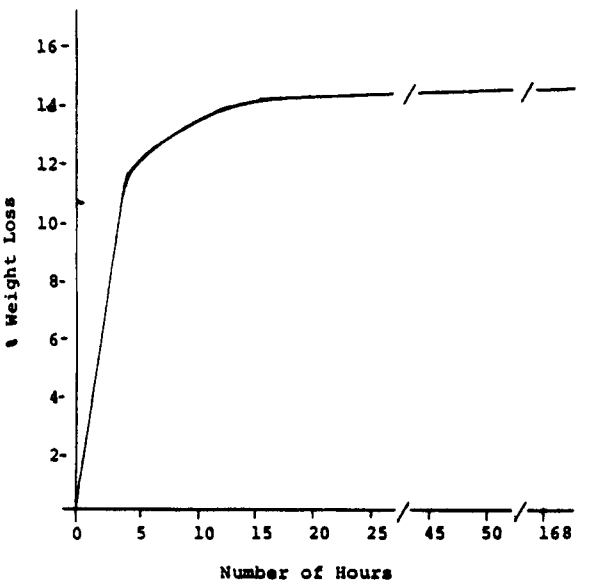
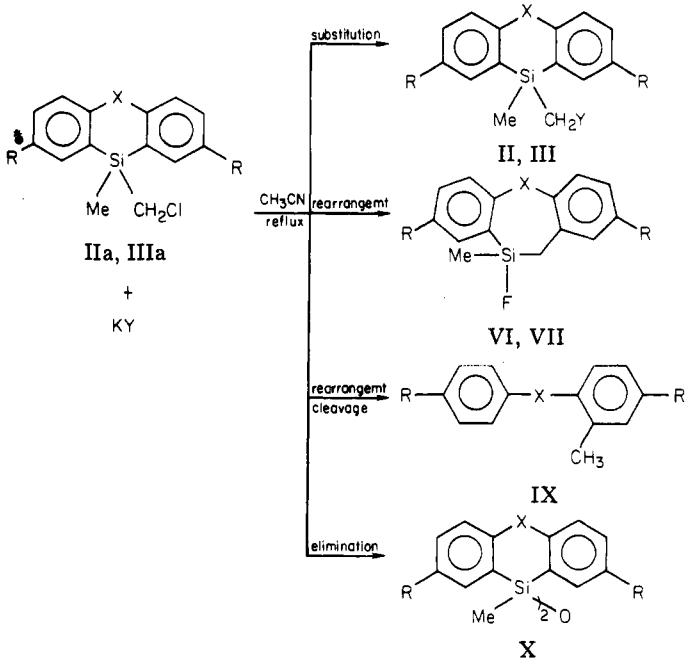


Figure 1. Weight loss on heating technical grade KF at 110 °C.

(6) When reaction is performed with CsF in an extraction thimble, about 33% conversion of II to VI occurs in 4 days.

Table II. Reactions of IIa and IIIa with Potassium Salts

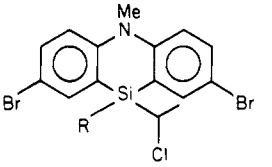


IIa, IIIa[a]	salt[b]	hours reflux	product (yield, %)[c]
NMe		170	IIa (100)
O	KCl	60	IIIa (100)
NMe	KI	15	IIb (54) (Y = I)
O	KI	5	IIb (70) (Y = I)
O	KOAc[d]	44	IIIb (67) (Y = OAc)
O	KOH[d]	1	IX (77)
O	KF[d]	23	VI (28), IX (31)[e]
NMe	KCN	8	Xa (82)[f]
O	KCN	4	Xb (94)[f]

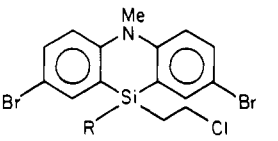
[a] IIa (R = Br); IIIa (R = H). [b] Ratio of salt/silane = 2. [c] Isolated product unless otherwise specified. [d] 18-Crown-6 added. [e] Residue, bp >240 °C (0.02 mmHg). [f] Crude product.

VI is complete in minutes rather than hours.

(Chloromethyl)silanes and Potassium Salts. The reactions of other potassium salts with III were investigated to determine whether the rearrangement reaction could be initiated by other anions. The results are outlined in Table II. The salts investigated were KCl, KI, KOAc, KOH, and KCN. In each case there appears to be one principal reaction product. No reaction occurs on heating IIa in the absence of any salt, and refluxing with KCl produces no overall change. Both KI and KOAc cause substitution at the carbon atom of the chloromethyl group to give IIb (IIIb) (Y = I) and IIIc (Y = OAc), respectively. Reaction of IIIa and KOH occurs rapidly to give phenyl *o*-tolyl ether, IX (X = O), as the only isolated product. This product would arise from rearrangement, followed by cleavage of the ring-expanded product VII by excess hydroxide. When the reaction of IIIa with KOH was carried out in a 1:1 ratio, a high boiling residue was obtained that was not identified. Such rearrangement/cleavage processes were sometimes observed particularly with II (X = SO_2, Y = Cl) where both rearrangement products and cleavage products were observed during the course of the consumption of starting material.[1a] Prolonged heating of IIIa with KF also results in destruction of ring-expanded product particularly in the presence of the phase-transfer catalyst 18-crown-6. The salt KCN causes elimination of the chloromethyl group to give siloxane product X. No substitution or rearrangement products were observed although conversion of Et_3SiCH_2Cl to Et_3SiCH_2CN in 50% yield is claimed with KCN.[7]



XIa, R = Cl
b, R = Me

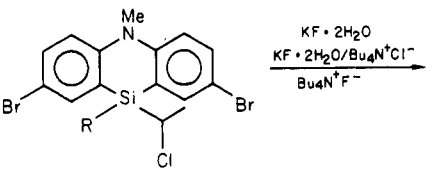


XIIa, R = Cl
b, R = Me

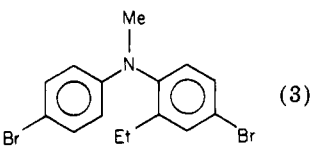
Figure 2.

The reaction of the α-functional methyl derivatives IIIc (Y = OAc) and IIId (Y = OH) with KF was briefly explored to determine the effect of leaving group at the α-carbon atom on the reaction pathway. About 75% decomposition of the hydroxymethyl derivative occurs within 2 h to form primarily a high boiling product that was not identified as well as a minor amount of IX. The acetate derivative does not undergo appreciable reaction after 24 h. When 18-crown-6 was added and the mixture heated for 27 h, only the ether IX was observed in addition to unreacted starting material. When IIId was treated with Yaravenko reagent, rearrangement to VII occurred in 90% yield.

α-Chloroethyl and β-Chloroethyl Groups. To determine the effect of substituents at the α-carbon atom and also to access the possibility of ring expansion by two carbon atoms, the reactions of XIb and XIIb with fluoride sources was examined (Figure 2). Both XI and XII were prepared from the reaction of $(2,4\text{-}LiBrC_6H_4)_2NMe$ with $Cl_3SiCHClCH_3$ and $Cl_3SiCH_2CH_2Cl$ to give XIa and XIIa, respectively. Conversion to XIb and XIIb was accomplished by reaction of the chlorosilanes with MeLi. An attempt to generate XIIb directly from $(2,4\text{-}LiBrC_6H_4)_2NMe$ with commercially available $Me(ClCH_2CH_2)SiCl_2$ gave Xa as the only isolated product. The reaction of XIb and $KF\cdot2H_2O$, $KF\cdot2H_2O$/KI, and $KF\cdot2H_2O/Bu_4N^+Cl^-$ gave XIII (from ring expansion/cleavage) as the only identified volatile product in about 60% yield (eq 3). An exothermic reaction occurred when



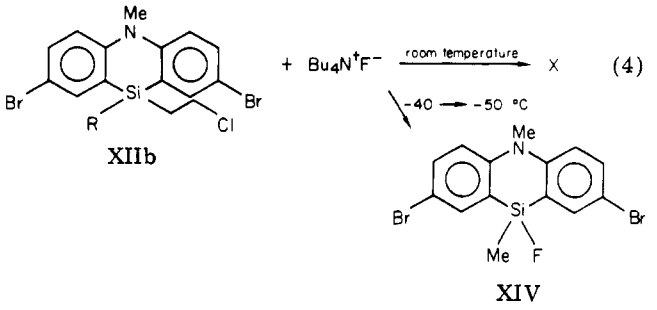
XIb



XIII (3)

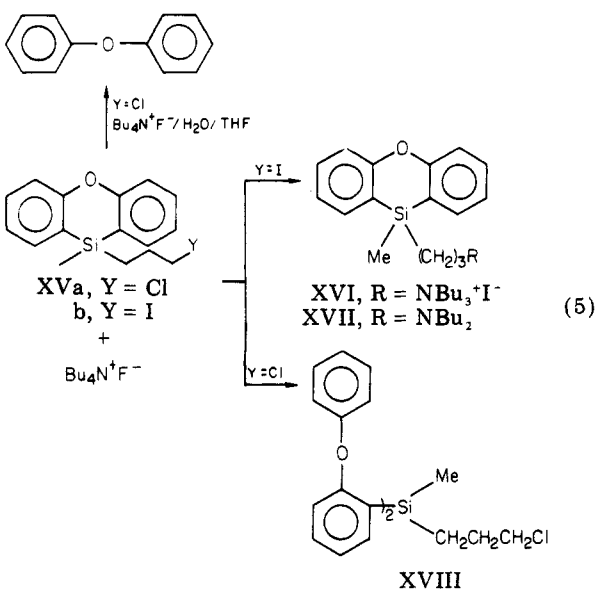
$Bu_4N^+F^-$/THF was added to a THF solution of XIb at room temperature, and the results were similar to those obtained with the potassium fluoride salts. When $Bu_4N^+F^-$/THF was added to XII at room temperature, gas evolution occurred immediately. The product isolated contains ether-insoluble X and an ether-soluble portion that contains at least three products. When the reaction was performed at low temperature, a crude sample of the fluoro derivative XIV, which would be derived from displacement of the β-chloroethyl group by F^-, was detected in low yield (eq 4).

(7) Brodskaya, E. I.; Belousova, L. I.; Kruglaya, O. A.; Vyazankin, N. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1980**, 1640.



XIIb XIV

γ-Halopropyl Groups. The phenoxasilin XVa, 10-methyl-10-(γ-chloropropyl)phenoxasilin was prepared from the reaction of *o,o'*-dilithiodiphenyl ether and methyl(γ-chloropropyl)dichlorosilane. Heating XVa with potassium iodide in acetonitrile produced the γ-iodopropyl derivative XVb. Unlike II, III, XI, and XII, XV does not react with KF(tech) after a 24-h reflux period in acetonitrile. The reaction of CsF with XVb produced diphenyl ether as the only identified product. Under homogenous conditions with $Bu_4N^+F^-$/THF, the iodomethyl derivative undergoes substitution at the γ-carbon atom to give the tributylammonium salt XVI and the dibutylamine XVII (eq 5).



XVIII

This represents the only reaction observed that involves the cationic portion of the fluoride source. The same products were obtained whether the reaction in THF was conducted at room temperature or at reflux. Even more unusual was the product observed from the chloropropyl derivative XVa and $Bu_4N^+F^-$ when conducted in untreated HPLC grade tetrahydrofuran. The solid product, isolated in 80% yield, exhibited resonances associated with an unreacted chloropropyl group but considerably enhanced intensity for the aromatic protons relative to the sum of the alkyl resonances. The ^1H and ^{13}C NMR spectra, mass spectrum, and analytical data all support the assignment of bis(*o*-phenoxyphenyl)methyl(γ-chloropropyl)silane, XVIII, to this product. When the reaction was conducted in dried THF to which had been added 2.5 equiv of water, diphenyl ether and somewhat impure starting material were recovered in 68% and 27% yields, respectively. The reactions of XV are summarized in eq 5.

Acyclic (Halomethyl)silanes. An appropriate acyclic model for the tricyclic systems whose chemistry is described in the previous sections is $Ph_2MeSiCH_2Cl$ (XIXa), which was prepared by addition of phenyllithium to Me-$(ClCH_2)SiCl_2$. Surprisingly, XIXa did not react with KF in refluxing CH_3CN up to 72 h even in the presence of

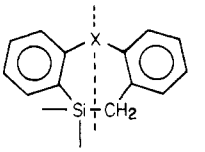


Figure 3.

18-crown-6 nor was any reaction observed when XIXa was refluxed with KF in DMF for 5 h. However, when 18-crown-6 was added to the solutions of XIX in DMFA with KF, the starting silane was consumed but several products were obtained as indicated by the NMR spectrum of the crude reaction residue. The iodomethyl derivative XIXb, prepared from XIXa and KI in CH_3CN, also did not react with KF/18-crown-6 in refluxing acetonitrile (48 h) but did react with KF in refluxing DMF. However, the reaction residue appears to be identical with that obtained from XIXa and KF/crown in DMF. When XIXb is treated with $Bu_4N^+F^-$ in THF, $Ph(Me)Si(F)CH_2Ph$, XX, was obtained in 50–60% crude yield.

Discussion

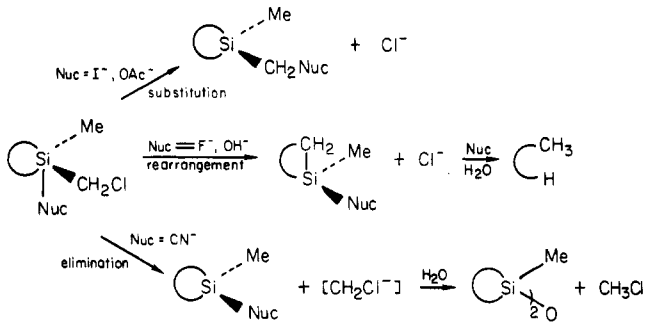
The original motivation for the exploration of the reaction of fluoride sources with (chloromethyl)silanes was to develop a synthetic method for the generation of tricyclic systems that contain a silicon–carbon bridge between the two benzo groups (Figure 3). Such systems are not readily available from organolithium or organomagnesium precursors. Previously we had demonstrated a Lewis acid catalyzed ring expansion of chloromethyl-substituted silacarbocycles (central 5-, 6-, and 7-membered rings) to produce 6-, 7-, and 8-membered ring systems, but when additional heteroatoms such as N or O are present in the central ring of the chloromethyl precursor (IIa or IIIa), the Lewis acid complexed to the heteroatom and even an excess of a stoichiometric amount of the acid did not result in any further reaction. Thus, the possibility of initiating ring enlargement by attack at silicon rather than at carbon seemed an attractive alternative.

Since reporting our initial work on the fluoride ion induced ring enlargement of silicon heterocycles with exocyclic chloromethyl substituents,[1a] we observed that the time required for reaction to take place seemed to vary from 24 to 48 h with the same starting materials and with the same scale. Occasionally none of the expected products were obtained. The origin of this variation in results was traced to the water content in the technical grade KF that had been used. Although samples of KF(tech) were usually dried overnight, the drying periods were variable. Some water content is necessary since anhydrous KF caused ring cleavage. The observation that KF·HF was effective in the promotion of the rearrangement reaction was surprising as presumably no free fluoride ion is present in this salt. The fact that water appears to be a necessary coreactant and that KF·HF is also an effective fluoride source suggests the possibility of electrophilic assistance of the chloride leaving group in the transition state.[8] Of the potassium fluoride salts, the use of KF·HF seems to provide fewer byproducts.

The rate of cleavage of the rearranged products V–VIII in some cases approaches the rate of ring expansion of the precursor and thus precludes isolation of ring-expanded product especially under heterogeneous conditions. This was readily apparent in the case of the reaction of KF with 10-(chloromethyl)-10-methylphenothiasilin 5,5-dioxide[1a] and with one of the 8-membered ring isomers produced

(8) We thank Dr. Thomas J. Barton for this suggestion.

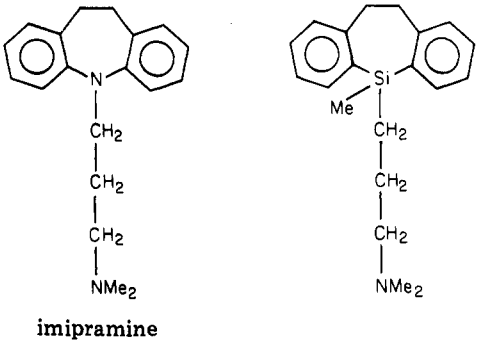
Scheme I



from 11-(halomethyl)-11-methyl-5,11-dihydrodibenz[*b*,*e*][1,4]oxasilepin.[1e] However, VI, produced from IIa, is decomposed slowly by KF sources and 18-crown-6 is required before approximately 50% decomposition to IX occurs in a 24-h period at reflux. When the chloromethyl substituent of IIIa is replaced by an acetoxymethyl group, reaction with KF (in the presence of 18-crown-6) produced the ring expansion/cleavage product. The rate of ring expansion followed by cleavage occurs rapidly when KOH is used as the nucleophile (IX is produced from IIIa in less than 2 h). When one of the C–H bonds in the CH_2Cl substituent of IIa is replaced by a Me group to give XIa (α-chloroethyl substituent), the only identified product obtained under both heterogeneous and homogeneous conditions (slow and fast reaction conditions) was the ring expansion/cleavage product.

The more usual reactions exhibited by haloalkyl substituents at silicon are substitution at carbon or displacement of the substituent. Substitution at the carbon center of the chloromethyl substituent of II and III occurs with KI or KOAc. Displacement in the heterocyclic systems that are the subject of this report occurred when either II or III were treated with KCN although prior substitution at the chloromethyl group followed by elimination cannot be precluded. Silanes with β-chloroethyl substituents are known to be unstable, and XII, which eliminates ethylene on addition of a solution of $Bu_4N^+F^-$, is no exeption.

Anion-induced rearrangements of groups from silicon to carbon are not common. Earlier cases have been summarized by Eaborn[9] and since then a few more examples have appeared and these include hydride migration (HMe_2SiCH_2Cl and KOBu-*t*),[10] benzyl migration [MePh($PhCH_2$)–$SiCH_2Cl$ and KOPh],[11] phenyl migration ($Me_2PhSiCH_2Cl$ and KOAc),[12] and fluorenyl migration [$FlMe_2SiCH_2Cl$ (Fl = fluorenyl) and BuLi].[13] Substitution at the carbon center of the chloromethyl substituent has recently been employed to produce (hydroxymethyl)silanes. Treatment of the chloromethyl derivative with $NaOAc/Bu_4N^+Cl^-$ in CCl_4[14] or with $AcOH/NEt_3$ in toluene[15] were followed by reduction in both cases with $LiAlH_4$. Both of these routes were published after our original work on the synthesis of IIId. The conversion of Me_3SiCH_2Cl to Me_3SiCH_2X (X = Br, I) by NaX in H_2O in the presence of the phase-transfer catalyst $Bu_4N^+X^-$ has also been described, but 11 days at reflux are required when X = Br.[14]



imipramine

Figure 4.

It is not clear which of these three reaction pathways, substitution, cleavage, or rearrangement, will occur with a particular combination of (chloromethyl)silane, nucleophile, and solvent. It is possible that the common intermediate in all these processes is a pentacovalent silicon intermediate as suggested by Eaborn[9] and summarized in Scheme I for the tricyclic system described in this study. Since the acyclic analogue $Ph_2MeSiCH_2Cl$ does not react with F^- under heterogeneous conditions and gives a maximum of 50% rearranged product under homogeneous conditions ($Bu_4N^+F^-$/THF), either the pentacoordinate intermediate is formed with more difficulty in the acyclic case or there is an electronic influence on the rate of the reaction by the N or O heteroatom in the cyclic systems II and III.

Alternatively, the course of the reaction in halomethylsilanes may be related to the hardness or softness of the nucleophile. Reaction of the hard nucleophile $LiOCH_2CH_2NMe_2$ with $Ph_2Si(H)CH_2X$ gives the rearrangement product $Ph_2(Me)SiOCH_2CH_2NMe_2$ (86–92%), whereas reaction of the same substrate with the soft nucleophile $-SCH_2CH_2NMe_2$ provides the substitution product $Ph_2(H)SiCH_2SCH_2CH_2NMe_2$ (76%).[4] A change from retention to inversion of configuration in substitution reactions at silicon centers has been reported and summarized by Corriu and co-workers[16] and correlation with the hardness or softness of the nucleophile has been suggested. Hard nucleophiles react with retention of configuration at silicon whereas soft nucleophiles react with inversion. A theoretical study also shows that hard nucleophiles promote retention of configuration in an S_N2 reaction.[17] If a similar frontier orbital process governs the reactions of (halomethyl)silanes then hard nucleophiles would be expected to react at silicon and soft nucleophiles at carbon. However, such a correlation should be viewed as tentative.

Although the reactions exhibited by chloromethyl-, α-chloroethyl-, and β-chloroethyl substituents seem to follow interrelated patterns, no obvious correlation exists with the γ-halopropyl group. No anionic rearrangement of an aryl group in the tricyclic derivatives XVa and XVb occurred in the presence of fluoride. Instead either cleavage of one or both of the aryl–silicon bonds occurred in XVa or substitution of iodide in XVb. With the exception of diphenyl ether the products shown in eq 5 are not easily rationalized. The products produced from XVa are probably a function of the water content of the solvent, but the origin of XVIII is certainly obscure. It is probable

(9) Eaborn, C.; Bott, R. W. "Organometallic Compounds of the Group IV Elements: The Bond to Carbon"; MacDiarmid, A. G., Ed.; Marcel Dekker: New York, 1968; pp 448–450.
(10) Hopper, S. P.; Tremelling, M. J.; Ginsberg, R. J.; Mendelowitz, P. C. *J. Organomet. Chem.* **1977**, *134*, 173.
(11) Petrov, K. A.; Chauzov, V. A.; Pastukhova, I. V.; Pazhitova, N. V. *J. Gen. Chem. USSR (Engl. Transl.)* **1978**, *41*, 1261.
(12) Pola, J.; Papouskova, Z.; Chvalovsky, V. *Collect. Czech. Chem. Commun.* **1973**, *38*, 1522.
(13) Peddle, G. J. D. *J. Organomet. Chem.* **1967**, *9*, 171.
(14) Ambashi, S.; Chiu, S. K.; Peterson, P. E.; Queen, J. *Sythesis* **1980**, 318.
(15) Tacke, R.; Lange, H.; Bentlage, A. *Chem. Ber.* **1982**, *115*, 3673.
(16) Corriu, R. J. P.; Guerin, C. *J. Organomet. Chem.* **1980**, *198*, 231.
(17) Anh, N. T.; Minot, C. *J. Am. Chem. Soc.* **1980**, *102*, 103.

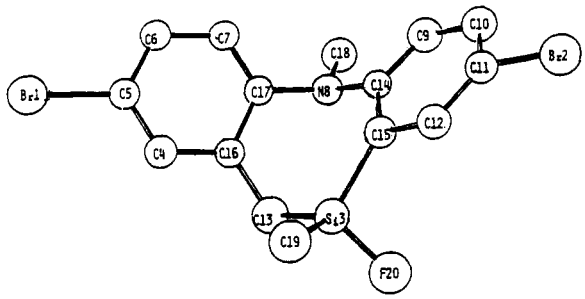


Figure 5. A perspective view of VI with atom labels (hydrogen atoms ommitted).

that the migrating aryl group bears a significant negative charge but the transfer of an intact *o*-phenoxyphenyl from one silicon center to a second silicon center is unusual. In one previously reported case an aryl group that has been displaced by nucleophilic attack at silicon has been trapped by addition of CO_2 and formation of the carboxylic acid.[13]

The synthetic applications of the ring expansion reaction and the chemistry of the new heterocyclic systems were developed as part of a program to prepare and to determine the structures of silicon analogues of tricyclic derivatives that are CNS agents.[1] The framework of the azasilepine VI is related to that of the antidepressant imipramine through replacement of a $-CH_2-$ group in the ethano bridge by a $Si(CH_3)_2$ moiety (Figure 4). The solid-state structure of VI is the first reported for this ring system and has been determined to provide a comparison of the structural parameters of the azasilepine tricyclic framework to those of imipramine and to silipramine in which $Si(CH_3)_2$ replaces the central ring N atom of imipramine.

Interatomic bond distances and angles with estimated standard deviations are included with the supplementary material. Mean values for Br–C, Si–C, N–C, and the benzo C–C distances are 1.904 Å [1.903 (9) and 1.905 (10) Å], 1.845 Å [range 1.822 (13)–1.862 (10) Å], 1.446 Å [range 1.420 (10)–1.472 (13) Å], and 1.384 Å [range 1.373 (13)–1.411 (10) Å]; the Si–F bond length is 1.615 (6) Å. All hydrogen atoms were located in the electron density map and were refined with fixed isotropic thermal parameters of 5.0 Å^2. The mean C–H distance is 0.94 (11) Å (range 0.78–1.03 Å). A perspective view of the molecular structure is presented in Figure 5 with the atom labels that have been used. The sum of the bond angles about the nitrogen atom is 348.5°. The C–Si–F angles are all smaller than the C–Si–C angles (mean values 106.5 and 112.3°, respectively) as would be expected due to the greater electronegativity of fluorine. A comparison of dibenzotricyclic structural parameters for silipramine, imipramine, and azasilepine frameworks is presented in Table III. These four structural parameters have been compared for related dibenzoheteroepins in a previous report.[5,18] There are no intermolecular contacts less than van der Waals distances.

As summarized in Table III, the result of silicon substitution for nitrogen is to flatten the tricyclic framework relative to imipramine. However, replacement of silicon for carbon in the ethano bridge results in a more bent framework. The bromine substituents in the 2,8-positions of VI may exert an electronic effect that results in a contribution to the decrease of the bend angle. Such an apparent effect on the decrease in bend angle of phenazasiline upon bromine substitution in the 2,8-positions has been observed.[19]

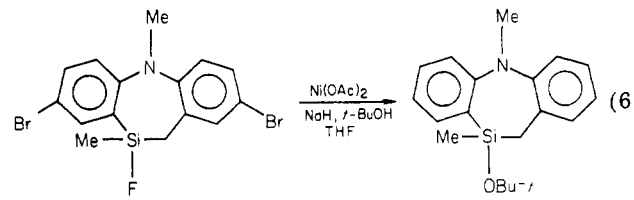
(18) Corey, E. R.; Corey, J. Y.; Glick, M. D. *Acta Crystallogr., Sect. B* **1976**, *B32*, 2025.

Table III. Comparison of Dibenzotricyclic Structural Parameters of Silipramine, Imipramine, and Azasilepine

	silipramine[a]	imipramine[b]		azasilepine
bend angle, deg	141.8	130.3	123.0	112.3
dist between benzo centers, Å	5.56	4.96	4.79	4.79
skew dist,[c] Å	0.31	0.67	0.61	0.82
twist angle[d]	22.9	17.2	8.4	21.6

[a] Reference 18. [b] Post, M. L.; Kennard, O.; Horn, A. S. *Acta Crystallogr., Sect. B* **1975**, *B31*, 1008. [c] Difference in nonbonded central ring benzo C···C distances (i.e., C15···C16 and C14···C17). [d] Average torsion angle about the nonbonded vectors C15···C16 and C14···C17.

The presence of the bromine substituents in VI is primarily due to the synthetic convenicnce in the ease of preparation of 2,2′,4,4′-tetrabromomethyldiphenylamine, which is the precursor to the phenazasiline framework. Although 2,8-dibromophenazasiline can be debrominated by addition of excess BuLi followed by an aqueous quench,[20] the same method cannot be used to remove the Br substituents in VI without simultaneous conversion of SiF to SiBu that would result in the removal of functionality at the silicon center. An alternate route using the reducing system $Ni(OAc)_2/NaH/ROH$[21] in THF was found to be a simple method for conversion of VI to the debrominated derivative XXI (eq 6). The determination of the



VI XXI (6)

structure of XXI may provide an indication of electronic effects of bromine substituents in VI on the bend angle of the silazepine framework.

Experimental Section

General Data. All reactions that involved organolithium reagents, chlorosilanes, and Grignard reagents were carried out under an atmosphere of dry N_2 in flame-dried glassware.

All potassium salts, *n*-$Bu_4N^+Cl^-$, *n*-$Bu_4N^+F^-$ [1 M in THF (<5 wt % H_2O)], 18-crown-6, chlorosilanes, and diphenyl ether were commercial reagents and used as supplied.

The following reagents were prepared by literature methods: 2,2′,4,4′-tetrabromo-*N*-methyldiphenylamine,[20] 2,8-dibromo-5,10-dimethyl-10-(chloromethyl)-5,10-dihydrophenazasiline, IIa,[1c] 10-methyl-10-(chloromethyl)phenoxasilin, IIIa,[1d] Yarovenko reagent,[22] $Cl_3SiCHClCH_3$, and $Cl_3SiCH_2CH_2Cl$].[23]

Tetrahydrofuran (Fischer, certified grade) was dried over $LiAlH_4$ or by addition of BuLi followed by distillation.[24] Anhydrous ether was used as supplied, and CH_3CN was dried over molecular sieves for a minimum of 25 h before use.

Proton NMR were recorded on a Varian T-60 spectrometer, and a JEOL FX-100 multinuclear spectrometer was used to obtain the ^{13}C data (internal Me_4Si as reference unless otherwise specified). Mass spectral data were collected at 70 eV on an AEI MS-1201 B or an HP 5985A GC/MS mass spectrometer. The

(19) Belsky, V. K.; Saratov, I. E.; Reikhsfeld, V. O.; Simonenko, A. A. *J. Organomet. Chem.* **1983**, *258*, 283.
(20) Corey, J. Y.; Paton, J. P.; Rankin, D. M. *J. Organomet. Chem.* **1977**, *139*, 1.
(21) Brunet, J. J.; Vanderesse, R.; Caubere, P. *J. Organomet. Chem.* **1978**, *157*, 125.
(22) Yarovenko, N. N.; Raksha, M. A. *J. Gen. Chem. USSR (Engl. Trans.)* **1959**, *29*, 2125.
(23) Sommer, L. H.; Whitmore, F. C. *J. Am. Chem. Soc.* **1946**, *68*, 485.
(24) Purdum, W. R.; Barling, G. J. *J. Chem. Educ.* **1975**, *52*, 120.

Kugelrohr distillation method was employed in all vacuum distillations. Melting points are uncorrected and are obtained on a Thomas-Hoover capillary melting point apparatus.

Analyses were performed by Galbraith Laboratories, Inc., and by Miles Laboratories.

Reaction of IIa and IIIa with Fluoride Sources. Mixtures of IIa (0.50 g, 1.2 mmol) and the fluoride salt (1.2 mmol) in CH_3CN (10 mL) or of IIIa (0.26 g, 1.0 mmol) and the fluoride salt (1.0 mmol) in CH_3CN (10 mL) were heated at reflux for the time periods indicated in Table I. The solvent was removed, $CDCl_3$ was added to the residue, and spectra were recorded for the filtered solutions.

Determination of Water Content of Technical KF Samples. Samples of technical KF were dried in a weighing bottle in an oven held at 110–120 °C. The samples were removed periodically, cooled in a dessicator, and reweighed. A sample weighing 14.3146 g initially gave the following weights at the time periods indicated: 14.2586 g (0.5 h); 13.4691 g (2 h); 12.6399 g (4 h); 12.4791 g (9 h); 12.2550 g (22 h); 12.2263 g (48 h); 12.2148 g (168 h). An 11.0737-g sample weighed 9.6535 g after 4 months at 110–120 °C or 14.87 % of the sample is lost as water. The composition of the technical KF used in this study was $KF\cdot 0.56H_2O$ or approximately $KF\cdot 0.6H_2O$.

Synthesis of 2,8-Dibromo-5,10-dimethyl-10-(iodomethyl)-5,10-dihydrophenazasiline, IIb. A slurry of IIa (3.99 g, 9.24 mmol) and KI (1.53 g, 9.24 mmol) in CH_3CN (75 mL) was heated at reflux for 15 h. After removal of the solvent the solid was treated with Et_2O/H_2O and the organic layer dried over Na_2SO_4. Removal of the volatile material gave a solid with a broad melting point range (133–150 °C). Recrystallization of a 2.18-g sample from heptane provided purified IIa as pale yellow crystals: mp 171–173 °C; 1.43 g (54%). A second recrystallization provided IIa; mp 173–175 °C; ^1H NMR ($CDCl_3$) δ 6.8–7.7 (m, 5.8, arom), 3.5 (s, 3.1, NCH_3), 2.0 (s, 1.9, $SiCH_2I$), 0.77 (s, 3.2, $SiCH_3$); *m/e* 521 (M^+ based on ^{79}Br). Anal. Calcd for $C_{15}H_{14}Br_2NiSi$: C, 35.45; H, 2.68. Found: 35.21; H, 2.89.

Synthesis of 10-Methyl-10-(iodomethyl)phenoxasilin, IIIb. A mixture of IIIa (3.16 g, 12.1 mmol) and KI (2.02 g, 12.2 mmol) in acetonitrile (40 mL) was refluxed for 5 h after which ether/water was added, the organic layer was dried over Na_2SO_4, and the volatiles were removed. Distillation of the residue provided crude IIIb as a pale yellow oil: bp 148–161 °C (0.3 mmHg); 3.0 g (70%); ^1H NMR δ 6.6–7.6 (m, 8.9, arom), 2.1 (s, 1.6, $SiCH_2I$), 0.70 (s, 2.5, $SiCH_3$); *m/e* 352 (M^+). A purified sample was prepared by elution over silica gel with chloroform/hexanes = 1/4. Anal. Calcd for $C_{14}H_{13}IOSi$: C, 47.74; H, 3.62. Found: C, 48.15; H, 3.62.

Reaction of IIIa with KOAc. Formation of 10-(Acetoxymethyl)-10-methylphenoxasilin, IIIc. A mixture of IIIa (6.5 g, 25 mmol), KOAc (4.9 g, 50 mmol), and 18-crown-6 (0.16 g) in acetonitrile (50 mL) was heated at reflux for 44 h. The reaction mixture was treated with ether/water, the organic layer was dried, and volatiles were removed. Distillation of the residue provided IIIc as a colorless oil; bp 110–166 °C (0.4 mmHg); 4.7 g, which contained about 15% IIIa (NMR); ^1H NMR ($CDCl_3$) δ 6.9–7.7 (m, 8.7, arom), 4.0 (s, 1.6, $SiCH_2OAc$), 2.0 (s, 2.7, O_2CH_3), 0.53 (s, 2.6, $SiCH_3$). Additional resonances at δ 1.7 and 0.67 are consistent with those of the starting material. The crude reaction product was used for the synthesis of IIId. An analytical sample was prepared by elution over silica gel with chloroform/hexanes = 1/4. Anal. Calcd for $C_{16}H_{16}O_3Si$: C, 67.61; H, 5.63. Found: C, 67.67; H, 5.64.

When IIIa was heated for a sufficient period to consume starting material as indicated by an NMR spectrum of the reaction mixture, ring cleavage products contaminated the products.

No reaction (<5%) occurs in absence of 18-crown-6 during the same time period.

Synthesis of 10-Methyl-10-(hydroxymethyl)phenoxasilin, IIId. Crude IIIc (1.7 g, 6.0 mmol) and $LiAlH_4$ (1.0 g, 26 mmol) were added to ether (50 mL), and the mixture was heated at reflux for 2 h. Excess $LiAlH_4$ was removed by filtration and the filtrate hydrolyzed with saturated aqueous NH_4Cl. The solution was extracted with ether and the organic layer dried over Na_2SO_4 prior to removal of the volatiles. Kugelrohr distillation of the residue provided IIId: bp 135–150 °C (0.1 mmHg); 1.04 g (70%), which solidified. Recrystallization from hexane gave a white solid: mp 63–64 °C; ^1H NMR ($CDCl_3$) δ 7.1–8.0 (m, 8.0, arom), 3.8 (s, 1.9, $SiCH_2OH$), 1.2 (br s, 1.0, OH), 0.6 (s, 3.1, $SiCH_3$); *m/e* 242 (M^+). Anal. Calcd for $C_{14}H_{14}O_2Si$: C, 69.42; H, 5.79. Found: C, 69.88; H, 6.28.

Reaction of IIa with KCN. Formation of Xa. A mixture of IIa (1.90 g, 4.4 mmol) and KCN (0.38 g, 5.9 mmol) in CH_3CN (50 mL) was heated at reflux for 8 h. The reaction mixture was cooled and filtered and the solid extracted with water. The resultant insoluble material was Xa, 1.4 g (82%). Recrystallization from toluene provided an analytical sample of IIa as a colorless solid, mp 275–278 °C. Anal. Calcd for $C_{28}H_{28}Br_4N_2OSi_2$: C, 43.04; H, 3.23. Found: C, 43.88; H, 3.09. Samples of Xa are insufficiently soluble or volatile enough to obtain either NMR or mass spectral data. An IR spectrum of the solid (Nujol mull) exhibited a broad band at 1020–1100 cm^{-1} characteristic of a siloxane.

Reaction of IIIa with KCN. Formation of Xb. A mixture of IIIa (1.02 g, 4.39 mmol) and KCN (0.319 g, 4.91 mmol) in acetonitrile (50 mL) was heated at reflux for 4 h. After addition of water the solution was filtered to remove the salts. Removal of the volatile material from the organic layer gave Xb, 0.75 g, which was contaminated with IIIa. Trituration of the oil with hexanes gave a solid that was recrystallized from EtOH to give pure Xb as a colorless solid: mp 121.5–123 °C; ^1H NMR (CCl_4) δ 6.5–7.6 (m, 8.1, arom), 0.52 (s, 2.9, $SiCH_3$); IR 1030–1100 (SiOSi). Anal. Calcd for $C_{26}H_{22}O_3Si_2$: C, 71.17; H, 5.06. Found: C, 71.49; H, 5.08.

Reaction of IIIc with KF. A mixture of IIc (0.55 g) and KF·tech (0.11 g) in CH_3CN (10 mL) was heated at reflux for 24 h. An NMR spectrum of an aliquot showed some formation of the ring expansion/cleavage ether IXb (singlet at δ 2.3). Addition of 18-crown-6 (20 mg) and continued heating for 27 h resulted in the increase of formation of IXb but no other observable product.

Reaction of IIId and KF. A mixture of hydroxymethyl derivative, IIId (0.47 g, 1.9 mmol), and KF·tech (0.22 g) in CH_3CN (10 mL) was heated at reflux for 2 h. After the usual workup distillation provided 0.17 g of volatile material, bp 100–168 °C (0.2 mmHg), which contained some unreacted starting material. The residue did not distill up to 240 °C (0.2 mmHg).

Reaction of IIIa with KF in the Presence of 18-Crown-6. A mixture of IIIa (3.3 g, 13 mmol), KF·tech (1.45 g), and 18-crown-6 (0.23 g) in CH_3CN (50 mL) was heated at reflux for 23 h. After hydrolytic workup distillation provided a volatile portion, 1.56 g [bp 110–158 °C (0.1 mmHg)], which contained IX and VII and a nonvolatile residue, 1.23 g [bp >220 °C (0.1 mmHg)].

Reaction of IIIa and KOH. A solution of IIIa (1.1 g, 4.2 mmol) and KOH (0.47 g) in CH_3CN (20 mL) was stirred at room temperature for 2 h. After removal of solvent and the usual workup, distillation of the oil produced gave 2-methylphenyl phenyl ether, 0.60 g (78%) [bp 85–100 °C (0.1 mmHg)], identical with an authentic sample [lit.[25] bp 267 °C (738.5 mmHg]: ^1H NMR ($CDCl_3$) δ 6.8–7.5 (m, 9.3, arom), 2.3 (s, 2.7, CH_3Ph); *m/e* 184 (M^+).

Reaction of IIIe with Yarovenko Reagent. Excess Yarovenko reagent, 2-chloro-1,1,2-trifluoroethylamine[22] (2.8 g), in ether (25 mL) was added dropwise to a solution of IIIe (0.50 g, 2.1 mmol) in ether (25 mL). The reaction mixture was heated at reflux for 1.5 h. After removal of the solvent, Kugelrohr distillation of the residue provided an oil, 0.46 g (92%) [b.p. 110–140 °C (0.2 mmHg)], which was identical with an authentic sample of VII.

Synthesis of 10-(1-Chloroethyl)-5,10-dimethylphenazasiline, XIb. The dilithium precursor was prepared from 2,2′,4,4′-tetrabromomethyldiphenylamine (30 g, 60 mmol) and BuLi (2.4 M, 50 mL) according to the procedure described for IIa[1c] and added simultaneously with a same volume of $Cl_3SiCHClCH_3$ [12 g (bp 130–142 °C)] to about 100 mL of ether, and the mixture was stirred overnight. After the usual workup, Kugelrohr distillation provided a viscous oil: bp 210–240 °C (0.35 mmHg); 15.5 g. Trituration of the oil provided crude XIa, 7.5 g, and distillation of the oil obtained from the filtrate provided an additional 3.6 g of XIa (40% combined yield). Samples were usually contaminated with varying amounts of XIIb.

To a solution of XIa (7.4 g, 16 mmol) in ether (100 mL) was added MeLi·LiBr (1.3 M, 13 mL), and the mixture was stirred

(25) Ullman; Sponagel *Justus Liebigs Ann. Chem.* **1906**, *350*, 87.

for 2.5 h followed by 2.5 h at reflux. After hydrolysis and the usual workup, removal of the ether gave a solid. Recrystallization from EtOH provided XIb as a white solid: mp 121–123 °C; 5.5 g (77%); ^{1}H NMR ($CDCl_3$) δ 6.9–7.7 (m, 6.3, arom), 3.4–3.6 (overlapping s + q, 4.3, $SiCHClCH_3$ + NCH_3), 1.3–1.4 (d, 2.3, CCH_3), 0.7 (s, 3.0, $SiCH_3$).

Samples of XIb prepared from chlorinated $EtSiCl_3$ usually contained either XIIb or 10-ethyl-5,10-dimethylphenazasiline, mp 128–129 °C. Therefore, an analytical sample of XIb was prepared from commercial $Cl_3Si(CHClCH_3)$ according to the above procedure; mp 149–150.5 °C. Anal. Calcd for $C_{16}H_{16}ClBr_2NSi$: C, 43.12; H, 3.62. Found: C, 43.16; H, 3.72.

Preparation of 10-(2-Chloroethyl)-5,10-dimethylphenazasiline, XIIb. The dilithio precursor was prepared from 2,2′,4,4′-tetrabromomethyldiphenylamine (20 g, 40 mmol) and *n*-BuLi (2.4 M, 38 mL) according to the described procedure for IIa[1c] and added simultaneously with a same volume of $Cl_3SiCH_2CH_2Cl$ (7.92 g, 40 mmol) to about 100 mL of ether, and the mixture was stirred overnight at room temperature. The solvent was removed and the residual oil extracted with a mixture of Skelly B/Et_2O and then Et_2O. The combined extracts were stripped, and the residual oil was distilled to give a viscous liquid: bp 220–250 °C (0.6 mmHg); 9.6 g. The oil was triturated with hexanes whereupon crude, solid XIIa was obtained; 7.2 g (39%).

To a slurry of XIIa (4.46 g, 9.6 mmol) in ether was added MeLi (1.7 M, 5.6 mL), and the mixture was stirred at room temperature for 2 h. After aqueous workup, the organic layer was dried over Na_2SO_4. Removal of the volatiles provided crude XIIb, 3.40 g (79%). Recrystallization from ethanol provided a white solid: mp 127–128 °C; ^{1}H NMR ($CDCl_3$) δ 6.6–7.5 (m, 6.2, arom), 3.2–3.6 (overlapping s + t, 4.8, $SiCH_2CH_2Cl$ + NCH_3), 1.6–2.0 (m, 2.0, $SiCH_2CH_2Cl$), 0.60 (s, 3.0, $SiCH_3$). An analytical sample could not be obtained by recrystallization.

When commercial samples of $Me(ClCH_2CH_2)SiCl_2$ were added to the dilithium reagent generated from 2,2′,4,4′-tetrabromomethyldiphenylamine, the only reaction product that could be identified was Xa which would result from the elimination of the β-chloroethyl group.

Reaction of XIb with F^- Sources. A mixture of XIb (contaminated with XIIb; 3.1 g, 7.0 mmol), $Bu_4N^+Cl^-$ (3.9 g, 14 mmol), and $KF{\cdot}2H_2O$ (1.3 g, 14 mmol) in CH_3CN (40 mL) was heated at reflux for 24 h. The solvent was removed and the residue hydrolyzed with Et_2O/H_2O. An insoluble portion remained, 1.0 g, identified as siloxane Xa. Removal of the solvent from the dried ether layer gave an oil, 0.94 g [bp 128–140 °C (0.2 mmHg)], and an unidentified nonvolatile residue (0.42 g). The properties of the distilled material are consistent with the ring expansion/cleavage product XIII: *m/e* 366 (M^+ based on ^{79}Br); ^{1}H NMR ($CDCl_3$) δ 6.2–7.6 (m, 7.1, arom), 3.2 (s, 3.0, NCH_3), 2.4–2.7 (q, 1.6, CH_2CH_3), 1.1–1.3 (t, 3.2, CH_2CH_3). The yield of XIII based on XIb in the original sample (1.9 g) is 60%. Attempts to prepare an analytical sample of XIII by redistillation or chromatography over silica gel failed.

Reaction of XIb with $KF{\cdot}2H_2O$ in CH_3CN or with $Bu_4N^+F^-$ in THF produced similar results.

Reaction of XIIb with $Bu_4N^+F^-$ in THF. To a stirred solution of XIIb (0.95 g, 2.1 mmol) in THF was added $Bu_4N^+F^-$ (1 M, 3.5 mL, 3.5 mmol) at room temperature. Gas evolution occurred immediately. After 0.5 h the THF was removed and the residue treated with a mixture of ether/water. The insoluble portion weighed 0.57 g and did not depress the melting point of an authentic sample of the siloxane Xa. The ether layer gave an oil, 0.44 g, with a complex NMR spectrum (at least three resonances in the N–Me region).

When the reaction was run by addition of $Bu_4N^+F^-$ in THF (1.0 M, 7.3 mL) to XIIb (? 18 g, 4.9 mmol) in THF in a bath held at −50 to −40 °C, the p[illegible]ts were Xa (1.27 g, 66%) identified by comparison to an authentic sample and an oil, 0.55 g, whose NMR spectrum is consistent with the presence of 2,8-dibromo-5,10-dimethyl-10-fluoro-5,10-dihydro-phenazasiline, XIV, on the basis of a characteristic doublet centered at δ 0.8 [$J(HCSiF)$ = 7.2 Hz].

Synthesis of 10-(3-Chloropropyl)-10-methylphenoxasilin, XVa. The dilithio precursor was prepared according to the procedure published for IIIa[1d] from diphenyl ether (13.6 g, 80 mmol) in THF/ether (120 mL/280 mL) and BuLi (120 mL, 1.55 M in hexane). A solution of (3-chloropropyl)methyldichlorosilane (15.4 g, 80 mmol) in THF and the organolithium solution were added simultaneously, dropwise to about 100 mL of THF. After addition was complete, the mixture was heated at reflux for 18 h. After aqueous workup the reaction mixture was eluted over silica gel with hexanes/chloroform = 5/1 to give slightly impure XVa: 10.5 g (45%); ^{1}H NMR ($CDCl_3$) δ 6.8–7.8 (m, 7.7, arom), 3.2–3.4 (t, 1.9, CH_2Cl), 0.8–2.0 (br m, 5.2, $SiCH_2CH_2$), 0.47 (s, 2.2, $SiCH_3$). Anal. Calcd for $C_{16}H_{17}ClOSi$: C, 66.53; H, 5.93. Found: C, 65.74; H, 6.05.

When the synthesis was performed on the same scale as above, distillation of the oil obtained after workup gave a fraction, bp 160–180 °C (0.05 mmHg), of impure XVa, 17.1 g. Redistillation gave a fraction, 13.6 g, [bp 120–140 °C (0.05 mmHg)], of XVa with the same impurities. Elution of twice distilled oil (2.45 g) over silica gel (44 g) with chloroform/hexanes = 1/4 provided purified XVa (1.54 g).

Synthesis of 10-(3-Iodopropyl)-10-methylphenoxasilin, XVb. A slurry of XVa (1.5 g, 5.2 mmol) and KI (2.0 g, 12 mmol) in acetonitrile (25 mL) was heated at reflux for 40 h. After removal of the solvent, the residue was extracted with $CHCl_3/H_2O$. The organic layer was dried over Na_2SO_4. Evaporation of the solvent provided crude XVb, 1.7 g (86%), which showed no indication of the presence of XVa and was used directly for reaction studies: ^{1}H NMR ($CDCl_3$) δ 6.8–7.8 (m, 7.3, arom), 2.9–3.1 (t, 2.1, CH_2I), 0.73–2.0 (br m, 4.6, $SiCH_2CH_2$), 0.45 (s, 3.1, $SiCH_3$).

Reaction of XVa with KF. A mixture of XVa (2.0 g, 6.9 mmol) and KF (0.40 g, 6.9 mmol) in acetonitrile (25 mL) was heated at reflux for 18 h. An NMR spectrum of an aliquot showed no change from that of XVa. A small amount of KI was added and the mixture heated an additional 20 h. The solvent was removed, the residue treated with ether/water, and the organic layer dried over Na_2SO_4. An NMR spectrum of the residue obtained after removal of the ether showed only XVa and a trace of XVb.

Reaction of XVa with $Bu_4N^+F^-$ in HPLC Grade THF. To a solution of XVa (1.4 g, 4.8 mmol) in HPLC grade THF (5 mL, minimum H_2O content, 0.02%) was added $Bu_4N^+F^-$ (1 M, 4.9 mL), and the mixture was stirred at room temperature for 16 h. After workup, the residual oil slowly crystallized. Recrystallization from hexane provided 0.88 g of a solid, mp 58–59 °C, that was identified as XVIII on the basis of the following spectroscopic information: *m/e* 458 (M^+, based on ^{35}Cl), 380 ($M^+ - C_3H_7Cl$), 365 ($M^+ - C_3H_7Cl$ − Me), 287 ($M^+ - C_3H_7Cl - C_6H_5O$), 271, 211 (B^+); ^{1}H NMR ($CDCl_3$) δ 6.6–7.5 (m, 17.5, arom), 3.2–3.5 (t, 1.6, CH_2Cl), 0.92–1.7 (br m, 5.0, CH_2CH_2), 0.55 (s, 3.0, $SiCH_3$); ^{13}C NMR ($CDCl_3$) δ 161.7, 156.7, 136.5, 130.9, 129.5, 127.1, 123.9, 122.8, 118.7, 117.0, 47.7, 27.8, 11.9, −3.8. Anal. Calcd for $C_{28}H_{27}ClO_2Si$: C, 73.26; H, 5.93. Found: C, 73.80; H, 6.03. The percent yield, based on the original aromatic grouping, is 80%.

Reaction of XVa with $Bu_4N^+F^-$ and H_2O in THF. To a solution of XVa (1.33 g, 4.6 mmol) in dried THF (15 mL) was added $Bu_4N^+F^-$ (1 M, 4.8 mL) and H_2O (0.205 g, 11.4 mmol), and the mixture was stirred at room temperature for 22 h. The volatiles were removed, and the residue was extracted with ether/water. The organic layer was dried and the ether removed. Distillation of the residue provided a fraction, 0.53 g [bp 80–85 °C (0.1 mmHg)], a second fraction, 0.36 g [bp 120–135 °C (0.05 mmHg)], and a residue (0.34 g). The lower boiling fraction solidified and was identified as diphenyl ether (69% based on initial XVa) by spectroscopic comparison to an authentic sample and mixed melting point. The higher boiling fraction was XVa contaminated with some of the residue that contained only a trace of an aromatic moiety.

Reaction of XVb with $Bu_4N^+F^-$ in THF. A solution of XVb (1.0 g, 2.6 mmol) and $Bu_4N^+F^-$ (1 M, 2.7 mL) in THF (25 mL) was refluxed for 18 h. The solvent was removed and the residue slowly solidified. After recrystallization from EtOAc/MeOH a solid, mp 132–135 °C (0.50 g), was obtained that was identified as the tributylammonium iodide salt XVI on the basis of spectroscopic properties and chemical analysis (34% yield); *m/e* 381 (M^+ of free amine); ^{1}H NMR ($CDCl_3$) δ 6.7–7.4 (m, 7.5, arom), 2.8–3.2 (broad featureless multiplet, 7.8, $N(CH_2R)_4$), 0.58–2.3 (br m, 26, $SiCH_2CH_2CH_2N(/CH_2CH_2CH_2CH_3)_3$), 0.55 (s, 2.7, $SiCH_3$). Anal. Calcd for $C_{23}H_{34}INOSi$: C, 61.10; H, 7.52; N, 2.37. Found: C, 59.89; H, 8.15; N, 2.45.

5,10-Dimethyl-10-*tert*-butoxy-10,11-dihydro-5*H*-dibenz[*b*,*f*][1,4]azasilepine, XXI. The combined reducing agent was prepared by the literature method.[21] To NaH (1.50 g, 50% in mineral oil, washed 3 times with THF) in THF (10 mL) was added $Ni(OAc)_2$ (0.90 g, 5.1 mmol; prepared by drying $Ni(OAc)_2 \cdot H_2O$ at 95–100 °C for 15 h), and the slurry was heated to reflux before addition of *t*-BuOH (0.74 g, 100 mmol) in THF (5 mL). The reflux was continued for 45 min, a solution of VIa (1.0 g, 2.4 mmol) in THF (7 mL) added, and heating continued for 10 min. Ether/water was added to the cooled reaction mixture and the mixture gravity filtered from the black gummy residue. The ether layer was separated and dried over Na_2SO_4, and the volatiles were removed. Kugelrohr distillation provided crude XXI, 0.44 g [bp 120–128 °C (0.1 mmHg)], which slowly solidified. Recrystallization from EtOH provided the analytical sample as a white solid: mp 78–79.5 °C; ^1H NMR ($CDCl_3$) δ 6.5–7.5 (m, 7.8, arom), 3.2 (s, 2.6, NCH_3), 2.1–3.1 (q, 2.4, $SiCH_2$ arom), 1.8 (s, 9.2, $C(CH_3)_3$), 0.13 (s, 3.0, $SiCH_3$); *m/e* 311 (M^+). Anal. Calcd for $C_{19}H_{25}NOSi$: C, 73.26; H, 8.09. Found: C, 73.04; H, 8.10.

Preparation of (Chloromethyl)methyldiphenylsilane, XIXa. A solution of PhLi in ether (1.0 L) was prepared from bromobenzene (157 g, 1.0 mol) and lithium metal (14.0 g, 2.0 mol) and added dropwise to $Me(ClCH_2)SiCl_2$ (63 mL, 0.50 mol) in ether (300 mL). After the addition was complete, the reaction mixture was heated at reflux for 1 h. The cooled reaction mixture was hydrolyzed with water and the ether layer dried over Na_2SO_4. After removal of the volatiles the residue was distilled to give slightly impure XIXa: bp 115–130 °C (0.2 mmHg) [lit.[26] 152–153 °C (4.5 mmHg)]; 166 g (67%); ^1H NMR ($CDCl_3$) δ 7.3–7.8 (m, 10.3, arom), 3.2 (s, 1.8, CH_2Cl), 0.67 (s, 2.9, CH_3); *m/e* 246 (M^+ based on ^{35}Cl).

Synthesis of (Iodomethyl)methyldiphenylsilane, XIXb. A modification of the literature method was used to prepare XIXb.[26] A slurry of XIXa (19.9 g, 81.1 mmol) and KI (13.5 g, 81.1 mmol) in CH_3CN (50 mL) was heated at reflux for 48 h. After aqueous workup the residue was extracted with ether and the ether layer dried over Na_2SO_4. The volatiles were removed from the organic layer to give XIXb (17.1 g, 63%) which showed no traces of XIXb (NMR spectrum). The product was used directly for reaction studies: ^1H NMR ($CDCl_3$) δ 7.3–7.8 (m, 10.1, arom), 2.4 (s, 1.9, CH_2I), 0.72 (s, 3.0, CH_3); *m/e* 338 (M^+).

Attempted Reactions of XIX with KF Sources. a. A slurry of XIXa (5.0 g, 20 mmol) and KF·HF (3.2 g, 41 mmol) in CH_3CN were heated at reflux for 48 h. After removal of the solvent, an NMR spectrum of the residue showed only starting material. The mixture was redissolved in CH_3CN, 18-crown-6 added (about 50 mg), and the slurry heated at reflux for 50 h. After workup there was no evidence for reaction. Similar results were obtained when KF(tech) was used instead of KF·HF.

b. A mixture of XIXa (1.0 g, 4.1 mmol) and KF(tech) (0.47 g) in dimethylformamide (30 mL) was heated at reflux for 5 h. The DMF was distilled (atmospheric pressure), and an NMR spectrum of the residue showed that no reaction had taken place. Fresh DMF was added to the residue and 18-crown-6 added (about 50 mg) and the mixture heated at reflux for 5 h. The majority of the DMF was removed at atmospheric pressure and the residue treated with water. Extraction with ether and removal of the solvent from the organic layer gave an oil. Distillation of the residue provided a small quantity of material, bp 140 °C (0.1 mmHg), whose NMR spectrum suggested a mixture of products.

c. A mixture of XIXb (2.0 g, 5.9 mmol) and KF(tech) (0.48 g) and 18-crown-6 (about 50 mg) was heated at reflux in CH_3CN (50 mL) for 48 h. After workup the residue contained unreacted XIXb and the crown ether.

d. A mixture of XIXb (2.0 g, 5.9 mmol) and KF(tech) (0.49 g) in DMF (20 mL) was heated at reflux for 8 h. After removal of DMF the residue was hydrolyzed with water and extracted with ether. Evaporation of the ether layer provided an oil whose NMR spectrum was consistent with several products in addition to XIXb.

Reaction of XIXb with $Bu_4N^+F^-$ in THF. To a solution of XIXb (4.38 g, 13 mmol) in THF (50 mL) was added $Bu_4N^+F^-$ (1.0 M in THF, 15 mL, 15 mmol) rapidly from a syringe. The solution was stirred for 1 h during which a precipitate of Bu_4NI forms. The solvent was evaporated and ether added to the residue, and the resultant slurry filtered. After removal of the ether the oil residue was distilled to give crude XX: bp 90–100 °C (0.10 mmHg); 1.60 g;[27] ^1H NMR ($CDCl_3$) δ 6.9–7.8 (m, 10.7, arom),

(26) Huang, C. T.; Wang, P.-J. *Acta Chimic Sinica* **1959**, *25*, 341; *Chem. Abstr.* **1960** *54*, 16413.

Table IV. Crystal Data and Summary of Intensity Data and Structure Refinement

compd	$C_{15}H_{14}Br_2FNSi$ (VI)
mol wt	415.2
space group	$P2_1/c$
cell constants	
a, Å	8.869 (2)
b, Å	9.934 (5)
c, Å	18.392 (8)
β, deg	98.75 (3)
vol, Å^3	1602 (1)
d(calcd), g cm^{-3}	1.72
d(obsd), g cm^{-3}	1.71 (2)
μ(calcd), cm^{-1}	50.8
cryst dimens	seven well-developed faces with edges 0.02–0.37 mm in length
absorptn	analytical correction applied (av correction 2.90; max 3.87; min 2.27)
radiatn	Mo Kα, 0.710 69 Å
2θ scan range	$2\theta(\text{Mo K}\alpha_1) - 1.0$ to $2\theta(\text{Mo K}\alpha_2) + 1.0$
no. of reflectns scanned	2574
no. of data > 3σ	1121
no. of parameters varied	133
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.042
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma wF_o^2]^{1/2}$	0.053

Table V. Final Positional Parameters for 2,8-Dibromo-5,10-dimethyl-10-fluoro-10,11-dihydro-5*H*-dibenz[*b*,*f*][1,4]azasilepine (VI)[a]

atom	*x*	*y*	*z*
Br(1)	−0.07455 (13)	0.93190 (13)	0.09917 (8)
Br(2)	0.72497 (12)	0.22500 (14)	0.00439 (6)
Si(3)	0.50048 (30)	0.56402 (32)	0.20374 (15)
C(4)	0.1367 (10)	0.7429 (11)	0.1754 (5)
C(5)	0.0120 (10)	0.7585 (11)	0.1214 (5)
C(6)	−0.0551 (10)	0.6484 (11)	0.0830 (5)
C(7)	0.0100 (10)	0.5228 (10)	0.0980 (5)
N(8)	0.1988 (7)	0.3756 (8)	0.1669 (4)
C(9)	0.3218 (10)	0.2194 (11)	0.0912 (5)
C(10)	0.4376 (11)	0.1865 (12)	0.0545 (6)
C(11)	0.5614 (9)	0.2700 (11)	0.0559 (5)
C(12)	0.5700 (10)	0.3864 (11)	0.0973 (5)
C(13)	0.3356 (12)	0.6016 (13)	0.2513 (6)
C(14)	0.3229 (9)	0.3401 (10)	0.1303 (5)
C(15)	0.4528 (10)	0.4238 (10)	0.1370 (5)
C(16)	0.1977 (9)	0.6177 (10)	0.1926 (5)
C(17)	0.1347 (9)	0.5081 (10)	0.1517 (5)
C(18)	0.0856 (12)	0.2707 (13)	0.1755 (7)
C(19)	0.5742 (13)	0.7144 (14)	0.1647 (7)
F(20)	0.6361 (6)	0.5038 (7)	0.2634 (3)
H(21)	0.174 (12)	0.815 (12)	0.201 (6)
H(22)	−0.124 (12)	0.663 (11)	0.045 (6)
H(23)	−0.037 (11)	0.452 (12)	0.070 (6)
H(24)	0.241 (11)	0.154 (11)	0.091 (5)
H(25)	0.460 (12)	0.114 (12)	0.025 (6)
H(26)	0.645 (12)	0.429 (12)	0.102 (6)
H(27)	0.342 (12)	0.683 (12)	0.284 (6)
H(28)	0.323 (12)	0.527 (12)	0.274 (6)
H(29)	0.141 (12)	0.187 (12)	0.199 (6)
H(30)	0.027 (12)	0.249 (11)	0.127 (6)
H(31)	0.025 (12)	0.311 (11)	0.214 (6)
H(32)	0.660 (12)	0.766 (12)	0.197 (6)
H(33)	0.490 (12)	0.754 (12)	0.131 (6)
H(34)	0.638 (13)	0.691 (12)	0.138 (6)

[a] Estimated standard deviations of least significant figure(s) in parentheses.

2.3–2.6 (br m, 1.6, $SiCH_2$), 0.33–0.46 (d, 2.6, $FSiCH_3$). A higher boiling fraction contained XIXb (0.49 g).

X-ray Structure Analysis of VI. A crystal of 2,8-dibromo-5,10-dimethyl-10-fluoro-10,11-dihydro-5*H*-dibenz[*b*,*f*][1,4]azasilepine with well-developed faces was attached to a glass fiber. Pertinent crystal and intensity data are given in Table IV. Systematic absences of *h*0*l*, *l* odd, and 0*k*0, *k* odd, uniquely determine the space group $P2_1/c$. Thirteen reflections with $2\theta > 15°$ were centered with a programmed centering routine; cell parameters were obtained by least-squares refinement of these angles. The intensities of three standard reflections were measured every 97 reflections and decreased in intensity approximately 22% during the data collection. A linear correction for loss of intensity was applied during the data reduction. The data were reduced to F^2 and $\sigma(F^2)$ by procedures similar to those described previously.[29] Standard deviations were assigned as follows: $\sigma(I) = [\sigma_{counter}(I)^2 + (0.05I)^2]^{1/2}$, where $\sigma_{counter} = (I + K^2B)^{1/2}$, I = net intensity, B = total background count, and K = ratio of scan time to background time.

The structure was solved by an iterative application of the Σ_2 relationship with 129 normalized structure factors of magnitude 1.3 or greater. An E map based on the set of phases for the solution with the largest consistency index (0.98) gave the positions of the non-hydrogen atoms of the structure. Least-squares refinement of the non-hydrogen atoms with isotropic thermal parameters gave a discrepancy factors $R = 0.052$ and $R_w = 0.066$; all hydrogen atoms were located in an electron density difference map ($R = 0.060$) and included in the final refinement with thermal parameters fixed at 5.0 Å^2. Final positional parameters with estimated standard deviations are given in Table V. Atomic scattering factors and real and imaginary anomalous dispersion corrections for Br and Si were taken from ref 30. The highest residual electron density in the final difference map was 0.60 e A^{-3} near the region of Br(1).

Acknowledgment. M.A.L. and T.E.R. acknowledge support through the National Science Foundation Undergraduate Research Participation Program (1979). A portion of this work was supported by the Graduate School of the University of Missouri—St. Louis through the Summer Fellowship Program (J.Y.C.) and the Weldon Spring Fund (E.R.C.). The generous use of the facilities of the University of Wisconsin—Madison (J.Y.C.) and of the Miles Laboratories, Inc. (V.H.T.C.) for a part of the investigation is gratefully acknowledged.

Registry No. IIa, 75482-82-5; IIb, 89889-26-9; IIIa, 71445-82-4; IIIb, 89889-27-0; IIIc, 89889-28-1; IIId, 89889-29-2; VI, 75499-01-3; VII, 71445-86-8; IX, 3991-61-5; Xa, 89889-30-5; Xb, 89889-31-6; XIa, 89889-32-7; XIb, 89908-12-3; XIIa, 89921-98-2; XIIb, 89889-33-8; XIII, 89889-34-9; XIV, 89889-35-0; XVa, 89889-36-1; XVb, 89889-37-2; XVI, 89889-38-3; XVIII, 89889-39-4; XIXa, 18407-40-4; XIXb, 18407-42-6; XX, 27977-42-0; XXI, 89889-40-7; KCN, 151-50-8; KF, 7789-23-3; KOH, 1310-58-3; $Cl_3SiCHClCH_3$, 7787-82-8; $Me(ClCH_2CH_2)SiCl_2$, 7787-85-1; $Bu_4N^+F^-$, 429-41-4; $Me(ClCH_2)SiCl_2$, 1558-33-4; 2-methylphenyl phenyl ether, 3991-61-5; 2-chloro-1,1,2-trifluoroethylamine, 40062-89-3; 2,2′,4,4′-tetrabromomethyldiphenylamine, 3666-95-3; (3-chloropropyl)methyldichlorosilane, 7787-93-1; diphenyl ether, 101-84-8.

Supplementary Material Available: Tables of anisotropic thermal parameters for the bromine atoms and isotropic thermal parameters for non-hydrogen atoms, bond distances and angles, and structure factor amplitudes and a stereoscopic packing diagram (11 pages). Ordering information is given on any current masthead.

(27) The synthesis of $PhSi(Me)CH_2C_6H_5F$ has been reported but the boiling point was given without the pressure.[28]

(28) Drozdov, V. A.; Kreshkov, A. P.; Romanova, A. D. *Zh. Obsch. Khim.* **1970**, *40*, 104.

(29) See program references in: Corey, E. R.; Paton, W. F.; Corey, J. Y. *J. Organomet. Chem.* **1979**, *179*, 241. Bellavance, P. L.; Corey, E. R.; Corey, J. Y.; Hey, G. W. *Inorg. Chem.* **1977**, *16*, 462.

(30) "International Tables of X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974.

^{29}Si NMR Access to Stereochemistry of Molecules. 2. (Trimethylsilyl)cyclopropyl Compounds

Micheline Grignon-Dubois*

Laboratoire de Chimie du Silicium et de l'Etain associé au CNRS (LA 35), Université de Bordeaux I, 33405 Talence Cédex, France

Michel Laguerre

ERA 890, Université de Bordeaux II, Faculté de Pharmacie, 33000 Bordeaux, France

Bernard Barbe and Michel Petraud

CESAMO, Université de Bordeaux I, 33405 Talence Cédex, France

Received November 22, 1983

^{29}Si NMR spectra of cyclopropylsilanes were recorded by using the SPI technique. The variation of $^{29}Si-^{1}H$ coupling constants with stereochemistry was studied. Our results confirm the dependence of ^3J on the relative position of the Me_3Si group and also the unexpected zero value for $^2J'$ (H_α to the silicon). As far as chemical shifts are concerned, the additivity rule seems to exist.

In a previous paper[1] we were able to show for the first time that $^{29}Si-^{1}H$ long-range coupling constants can be used to determine the stereochemistry of organosilicon synthons of the bicyclo[*n*.1.0]alkane type A. In particular we have shown that the magnitude of the coupling constants $^3J(^{29}Si\cdots^{1}H)$ across the cyclopropane ring is a function of the dihedral angle between the C–H and the C–Si bonds. This suggests a Karplus type relationship.

In order to verify the generality of this relationship, we

(1) Grignon-Dubois, M.; Laguerre, M.; Barbe, B.; Pétraud, M. *Organometallics* **1984**, *3*, 359.

0276-7333/84/2303-1060$01.50/0