

sodium hydroxide solution maintained at 0°. The alkaline solution was extracted several times with methylene chloride, and the combined organic extracts were dried (Na₂CO₃) and evaporated, to yield 3.8 g of a yellow oil which solidified. The crude precipitate was dissolved in ether; pentane was added until no more crystallization took place, to yield 3.7 g (95%) of a white solid: mp 66.0–67.5°; [α]_D –24.0° (c 1, acetone); ir (KBr) 3250, 1200, 970, 880, 810 cm⁻¹; nmr (CDCl₃) δ 8.0–7.2 (q, 4, tolyl), 2.7 (s, 1, NH), 2.5 (s, 3, *p*-CH₃), 2.8–2.3 (m, 1, CH), 1.5–0.6 (m, 4, CH₂CH₂).

(+)-(R)-(Dimethylamino)cyclopropyl-*p*-tolylsulfonium Fluoroborate (27). To a solution of 3.0 g (0.0154 mol) of (–)-*S*-cyclopropyl-*S*-(*p*-tolyl)sulfoximine (16), [α]_D –24.0° (c 1, acetone), in 20 ml of methylene chloride was added 2.5 g (0.017 mol) of trimethylxonium fluoroborate. The reaction, initially at 0°, was allowed to warm to 25° and was stirred for 1 hr. The excess alkylating agent was filtered and 10% sodium hydroxide was added until the mixture was alkaline. The organic portion was drawn off and the aqueous layer extracted several times with methylene chloride. The combined extracts were dried (Na₂CO₃) and the volume was reduced to 20 ml. The above procedure was repeated twice. After removal of solvent, the residue was dissolved in ethanol and ether was added until no further precipitation occurred, to yield 4.6 g (95%) of yellowish solid. All attempts to obtain a constant, narrow range melting point were futile. The solids with various melting points were triturated to yield 3.8 g (80%) of a white solid: mp 101–115°; [α]_D²⁵ +61.8° (c 1, acetone); ir (Nujol) and nmr (CDCl₃) are identical with the authentic racemic compound.

(+)-(S)-*N*-Methyl-*S*-cyclopropyl-*S*-phenylsulfoximine (29). To a cooled (15°) solution of 0.25 g (1.5 mmol) of (+)-(S)-*N*,*S*-dimethyl-*S*-phenylsulfoximine, [α]_D +178° (c 1, acetone, 97% optically pure), in 3 ml of DMSO was added dropwise 0.98 g (1.5 mmol) of *n*-butyllithium (1.6 M in hexane).⁹ To the orange solution was added 0.50 g (0.030 mol) of trimethylvinylammonium bromide¹⁸ at once as a solid, whereupon a moderately exothermic reaction took place. (On a larger scale the sulfoximine anion should be cooled to 0° to minimize frothing.) The reaction mixture was allowed to stir for 72 hr at 25°. The deep orange solution was poured into 20 ml of a saturated sodium chloride solution and ex-

tracted four times with 20 ml each of ether. The combined ether extracts were washed twice with a small amount of water to remove DMSO. The organic phase was dried (Na₂CO₃) and evaporated, yielding 200 mg of a dark orange oil which was decolorized with Norit. The desired product was separated from other components by elution chromatography on alumina using an ether–chloroform solvent mixture (3:2). The product was further purified by sublimation, 55° (0.25 mm), and finally by recrystallization from pentane, to yield 84 mg (28%) of a white solid: mp 70.0–71.5°; [α]_D +118° (c 1, acetone); ir (melt) 1240, 1140, 855, 720, 690 cm⁻¹; nmr (CDCl₃) δ 8.0–7.4 (m, 5, C₆H₅), 2.75 (s, 3, NCH₃), 2.7–2.3 (m, 1, CH), 1.7–0.5 (m, 4, CH₂CH₂).

A major difficulty in purification of the desired cyclopropylsulfoximine was the presence of a product resulting from the addition of the cyclopropyl anion to another mole of vinyltrimethylammonium bromide. The resultant *N*-methyl-*S*-phenyl-*S*-(1-vinylcyclopropyl)sulfoximine (30) was isolated as an oil (~10% yield): ir (neat) 1640, 1240, 1140, 860 cm⁻¹; nmr (CDCl₃) δ 8.0–7.4 (m, 5, C₆H₅), 6.7–6.2 (m, 1, CH=C), 5.3–4.8 (m, 2, CCH₂), 2.9 (s, 3, NCH₃), 2.2–0.8 (m, 4, CH₂CH₂).

(–)-(S)-(Dimethylamino)cyclopropylphenyloxosulfonium Fluoroborate (31). The optically active salt was prepared from the corresponding *N*-methylsulfoximine, [α]_D +118° (c 1, acetone), by the usual alkylation procedure. Recrystallization from methylene chloride–ether gave in 87% yield a white solid: mp 139–141°; [α]_D +49.2° (c 1, acetone); the spectral properties were identical with those of the racemic salt. Reactions of the chiral ylide 32 derived from the salt are reported in Table II.

Supplementary Material Available. A table of microanalytical data will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-73-7692.

Reactivity Studies of Bridgehead Organosilicon Compounds with Nucleophilic Reagents

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Abstract: The reactivity of 1-chloro-1-silabicyclo[2.2.1]heptane (IIa), a highly angle-strained bridgehead organosilicon chloride, 1-chloro-3,5,7-trimethyl-1,3,5,7-tetrasilaadamantane (Ib), a relatively unstrained bridgehead organosilicon chloride, and tris(trimethylsilylmethyl)chlorosilane (IIIa), the acyclic analog of Ib, toward a variety of nucleophilic reagents was investigated. Both IIa and IIIa were found to be much more reactive than Ib. Most of the results for nucleophilic displacement at bridgehead silicon in both Ib and IIa are best accounted for by an S_N2-Si mechanism involving substantial d-orbital participation and proceeding with *retention* of configuration.

The relative reactivity of bridgehead carbon compounds has been extensively studied and several excellent reviews are available.^{1–3} Knowledge gained from these studies has played an important part in the fundamental understanding of reaction mechanisms at carbon centers. Similar studies for analogous bridgehead organosilicon compounds have been quite limited in comparison.

(1) R. C. Fort, Jr., and P. v. R. Schleyer, *Advan. Alicyclic Chem.*, **1**, 283 (1966).

(2) R. C. Fort, Jr., and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).

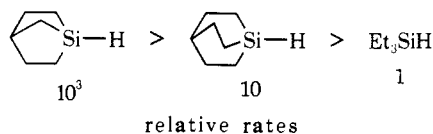
(3) R. C. Bingham and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 3189 (1971).

The initial work in this area was reported by Sommer and Bennett in 1957.⁴ They synthesized 1-chloro-1-silabicyclo[2.2.1]heptane, IIa, and found that this silicon chloride, in sharp contrast to relatively inert structurally analogous angle-strained bridgehead carbon compounds, was highly reactive toward both hydrolysis and reduction by LiAlH₄. A similar reactivity was also found for 1-chloro-1-silabicyclo[2.2.2]octane.⁵ A quantitative comparison reported for these two sys-

(4) L. H. Sommer and O. F. Bennett, *J. Amer. Chem. Soc.*, **79**, 1008 (1957).

(5) L. H. Sommer and O. F. Bennett, *J. Amer. Chem. Soc.*, **81**, 251 (1959).

tems showed that 1-silabicyclo[2.2.1]heptane, IId, was more reactive than 1-silabicyclo[2.2.2]octane toward base-catalyzed solvolysis in 95% ethanol which gives H_2 and $Si-OH$.⁶ Indeed (see below), both bridgehead compounds are more reactive than Et_3SiH .



In 1961 Smith and Clark⁷ reported the fortuitous preparation of 1,3,5,7-tetrachloro-1,3,5,7-tetrasiladamantane, Ia, and found, contrary to the behavior of the above bridgehead systems, that it was highly resistant to hydrolysis and coupling with CH_3MgCl . In 1970 Frye and coworkers⁸ reported a facile synthesis of 1,3,5,7-tetrasiladamantanes which included the preparation of the monofunctional 1-chloro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ib), hereafter referred to as Me_3AdCl .⁹ This material was inert to hydrolysis in moist acetone containing triethylamine for a period of 1 month and was very sluggish in its reduction with $LiAlH_4$. Furthermore, a silylamine derivative of this system was found to be sufficiently stable to aqueous hydrochloric acid to be recovered from solution with the Si-N bond still intact,⁹ a situation unique in organosilicon chemistry.

This highly unusual lack of reactivity of Me_3AdCl and Ia, $AdCl_4$, toward nucleophiles such as water and ethereal $LiAlH_4$ (most chlorosilanes react virtually instantaneously with these reagents) was attributed to the relatively rigid and strain-free ground-state geometry of these systems.⁸⁻¹⁰

In contrast to the above prior reports, we have recently found the first facile reactions of Me_3AdCl with nucleophilic reagents¹¹ which clearly demonstrate that this system is not universally unreactive toward nucleophilic attack at silicon in spite of its unique ground-state geometry.

This paper reports a much more detailed study of the relative reactivities of bridgehead organosilicon compounds. This work was undertaken because of our conviction that for silicon, as well as for carbon, the unique geometry of bridgehead compounds can lead to a clearer and more securely based understanding of reaction mechanisms.

Results

The data in this paper concern primarily three basic systems: the tetrasiladamantanes (I), the 1-silabicyclo[2.2.1]heptanes (II), and the tris(trimethylsilylmethyl)silanes (III); see below.

The tetrasiladamantane system has four bridgehead silicon atoms whose angles should resist distortion

(6) L. H. Sommer, O. F. Bennett, P. G. Campbell, and D. R. Weyenberg, *J. Amer. Chem. Soc.*, **79**, 3295 (1957).

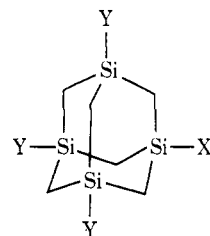
(7) A. L. Smith and H. A. Clark, *J. Amer. Chem. Soc.*, **83**, 3345 (1961).

(8) C. L. Frye, J. M. Klosowski, and D. R. Weyenberg, *J. Amer. Chem. Soc.*, **92**, 6379 (1970).

(9) C. L. Frye and J. M. Klosowski, *J. Amer. Chem. Soc.*, **94**, 7186 (1972). This reference used Ad to represent tetrasiladamantyl and we have followed this precedent. For convenience in discussion some such symbol is needed.

(10) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965, Chapter 9.

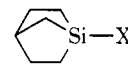
(11) G. D. Homer and L. H. Sommer, *J. Organometal. Chem.*, **49**, C13 (1973).



- Ia, Y = X = Cl
 b, Y = CH_3 ; X = Cl
 c, Y = CH_3 ; X = Br
 d, Y = CH_3 ; X = H
 e, Y = CH_3 ; X = OCH_3
 f, Y = X = CH_3
 g, Y = CH_3 ; X = C_6H_5
 h, Y = CH_3 ; X = F

from the tetrahedral because of the nature of the ring system which is virtually free from angle strain and from conformational strain as indicated by accurate molecular models.^{8,10}

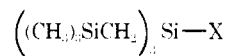
The 1-silabicyclo[2.2.1]heptane system, in contrast to



- IIa, X = Cl
 b, X = F
 c, X = $-O-Si$ (with a cyclohexane ring)
 d, X = H
 e, X = C_6H_5

the tetrasiladamantane system, contains bridgehead silicon in a highly strained geometry. Accurate molecular models of this system indicate that the C-Si-C bond angles probably lie in the 90 to 95° range when the carbon atoms of the ring system maintain tetrahedral geometry.¹⁰

The tris(trimethylsilylmethyl)silane system¹² serves







- IIIa, X = Cl
 b, X = F
 c, X = OCH_3
 d, X = OH
 e, X = H
 f, X = CH_3

as an acyclic analog to the tetrasiladamantanes. It contains four silicon atoms arranged in the $Si-CH_2-Si$ structure characteristic of the tetrasiladamantanes. However, unlike the tetrasiladamantanes, this system is not confined to a relatively rigid cage structure. It seemed important to establish the reactivity pattern for the tris(trimethylsilylmethyl)silanes in order to determine if any unusual effects are engendered by the $Si-CH_2-Si$ structure. Thus a more meaningful comparison could be made between strained 1-silabicyclo[2.2.1]heptanes and the relatively unstrained tetrasiladamantanes.

Reactions with a given reagent were carried out under essentially the same conditions with each substrate. All the reactions reported in this paper are clean and virtually free of side reactions. Reaction rates are expressed in terms of approximate half-lives as de-



(12) L. H. Sommer, R. M. Murch, and F. A. Mitch, *J. Amer. Chem. Soc.*, **76**, 1619 (1954).

Table I. Reduction^a

Reaction no.	Substrate	Reagent	Approximate half-life	Product	Yield, %
1	Me ₃ AdCl	LiAlH ₄	100 hr	Me ₃ AdH	100 ^b
2	Me ₃ AdBr	LiAlH ₄	10 hr	Me ₃ AdH	75
3	(Me ₃ SiCH ₂) ₃ SiCl	LiAlH ₄	Inst ^c	(Me ₃ SiCH ₂) ₃ SiH	90
4		LiAlH ₄	Inst ^c		56
5	Me ₃ AdCl	(<i>i</i> -Bu) ₂ AlH/TMEDA ^d	No reaction ^e		
6	(Me ₃ SiCH ₂) ₃ SiCl	(<i>i</i> -Bu) ₂ AlH/TMEDA ^d	5 min	(Me ₃ SiCH ₂) ₃ SiH	74
7		(<i>i</i> -Bu) ₂ AlH	Inst ^c		55
8	Me ₃ AdOCH ₃	(<i>i</i> -Bu) ₂ AlH	30 min	Me ₃ AdH	86
9	(Me ₃ SiCH ₂) ₃ SiOCH ₃	(<i>i</i> -Bu) ₂ AlH	80 hr	(Me ₃ SiCH ₂) ₃ SiH	100 ^b

^a All reactions were run in anhydrous ethyl ether at 25°. ^b Glc yield. ^c Instantaneous and exothermic reaction. ^d *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) was added in equimolar amounts relative to (*i*-Bu)₂AlH in order to accelerate the reaction. ^e No reaction detected over a 55-hr period. Starting material was recovered.

Table II. Coupling Reactions with Alkyl- and Aryllithium Reagents^a

Reaction no.	Substrate	Reagent	Approximate half-life	Product	Yield, %
10	Me ₃ AdCl	CH ₃ Li ^b	5 min	Me ₄ Ad	70
11	Me ₃ AdBr	CH ₃ Li ^b	5 min	Me ₄ Ad	76
12	Me ₃ AdCl	C ₆ H ₅ Li	12 min	Me ₃ AdC ₆ H ₅	83
13		C ₆ H ₅ Li	Inst ^c		86
14	(Me ₃ SiCH ₂) ₃ SiCl	CH ₃ Li ^b	Inst ^c	(Me ₃ SiCH ₂) ₃ SiCH ₃	75

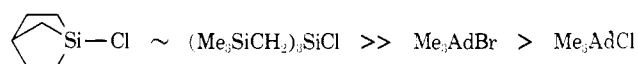
^a All reactions were run in anhydrous ethyl ether at 25°. ^b The reaction was carried out in the presence of an equimolar amount of TMEDA relative to CH₃Li. The reaction is very slow in the absence of TMEDA. ^c Instantaneous and exothermic reaction.

terminated by periodic glc analysis of the reaction mixtures. Reported yields are isolated yields unless otherwise noted. The low yields reported for a few reactions were due to separation problems. All new compounds were characterized by ir, nmr, mass spectroscopy, and elemental analysis.

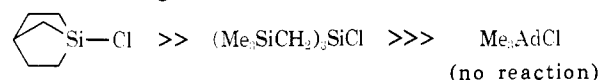
Rate data in Tables I-IV are given in terms of approximate half-lives instead of precise rate constants for a number of reasons. In 16 out of the 34 studies reported in these tables rates were too fast to measure by convenient ordinary techniques and the use of special techniques seemed to us unwarranted in terms of our objective of discerning general reactivity trends. Because of the latter objective, plus the accuracy limitations of using a glc technique which makes it difficult to obtain precise rate data, approximate half-lives for reactions of moderate speed seemed to us to be quite appropriate for these reactions. Also, in certain cases scarcity of difficult to obtain materials effectively blocked any attempt to obtain precise rate data by glc monitoring and also made impossible any adequate studies leading to determination of reaction order.

The reduction of functionally substituted organosilanes with reagents like LiAlH₄ and diisobutylaluminum hydride, (*i*-Bu)₂AlH, is fundamental in organosilicon chemistry. The data concerning the reactions of the subject compounds with these reagents are shown in Table I.

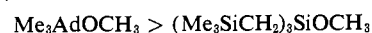
The results in Table I clearly show that both IIa and IIIa are considerably more reactive toward reduction with LiAlH₄ than either Me₃AdCl or Me₂AdBr (reactions 1-4). The relative order of reactivity is shown below.



When the reducing agent is (*i*-Bu)₂AlH some changes are observed. Me₂AdCl is now inert to reduction even when TMEDA is present as an activator (reaction 5). Reduction of IIIa, the acyclic analog of Me₃AdCl, is very slow unless TMEDA is present (reaction 6), while IIa is reduced with ease in the absence of TMEDA (reaction 7). Thus, a slightly different reactivity pattern is observed for (*i*-Bu)₂AlH as compared with LiAlH₄, although the relative order remains the same.



A more dramatic change in the reactivity pattern is observed when the leaving group is changed from Cl to OCH₃ (reactions 8 and 9). Now the tetrasilaadamantyl methoxide (Ie), Me₃AdOCH₃, is actually more reactive than its acyclic analog IIIc. This result is discussed later.





Another fundamental reaction in organosilicon chemistry is the coupling reaction of chlorosilanes with alkyl- and aryllithium and magnesium reagents. Due to the known low reactivity of the tetrasilaadamantane system toward Grignard reagents,⁷ the more reactive lithium reagents were used in this study. The results are shown in Table II.

The results in Table II show that both Me₃AdCl and Me₃AdBr are less reactive than IIIa toward CH₃Li (reactions 10, 11, and 14). All three of these reactions required activation by TMEDA in order to obtain reasonable reaction rates. When C₆H₅Li was used TMEDA was not required. This is presumably due to a lesser degree of association of C₆H₅Li in ethyl ether.¹³

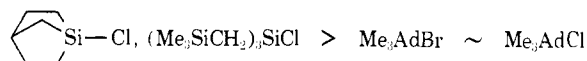
(13) G. Wittig, F. J. Meyer, and G. Lange, *Justus Liebigs Ann. Chem.*, 571, 167 (1951).

Table III. Hydrolysis and Methanolysis^a

Reaction no.	Substrate	Reagent	Approximate half-life	Product	Yield, %
15	Me ₃ AdCl	H ₂ O ^b	No reaction ^c
16	 -Cl	H ₂ O ^b	Inst ^d		94
17	(Me ₃ SiCH ₂) ₃ SiCl	H ₂ O ^b	Inst ^d	(Me ₃ SiCH ₂) ₃ SiOH	92
18	Me ₃ AdCl	CH ₃ OH	No reaction ^c
19	Me ₃ AdBr	CH ₃ OH	No reaction ^c
20	Me ₃ AdCl	CH ₃ OH/PhCH ₂ N ⁺ Et ₃ ClO ₄ ^{-e}	No reaction ^f
21	(Me ₃ SiCH ₂) ₃ SiCl	CH ₃ OH	Inst ^d	(Me ₃ SiCH ₂) ₃ SiOCH ₃	70
22	Me ₃ AdCl	NaOCH ₃ /CH ₃ OH	1 min	Me ₃ AdOCH ₃	86
23	Me ₃ AdBr	NaOCH ₃ /CH ₃ OH	Inst ^d	Me ₃ AdOCH ₃	90
24	Me ₃ AdCl	Triton B/CH ₃ OH ^g	1 min	Me ₃ AdOCH ₃ ^h	92
25	(Me ₃ SiCH ₂) ₃ SiCl	NaOCH ₃ /CH ₃ OH	Inst ^d	(Me ₃ SiCH ₂) ₃ SiOCH ₃	40

^a All the reactions were run at 25°. ^b The reaction was run in ethyl ether containing a slight excess of triethylamine as an HCl acceptor. ^c No reaction detected over a 24-hr period. Starting material was recovered. ^d Instantaneous and exothermic reaction. ^e Two equivalents of benzyltriethylammonium perchlorate were present in order to increase the ionic strength of the medium. ^f No reaction detected over a 72-hr period. Starting material was recovered. ^g Triton B is a methanol solution of benzyltrimethylammonium hydroxide. ^h Me₃AdOCH₃ was virtually the only product. A small peak, <1% of the total, was detected by glc in addition to the Me₃AdOCH₃ peak. This peak was presumably the silanol, Me₃AdOH.

Reactions 12 and 13 clearly show that IIa is more reactive than Me₃AdCl toward coupling with C₆H₅Li. Unfortunately, the reaction of C₆H₅Li with IIIa was not clean and therefore it is not included in Table II. The results from Table II do not allow a comparison between IIa and IIIa; however, it is clear that both of these compounds are more reactive than Me₃AdCl.



The first two tables show the results with representative hydride and carbanion nucleophiles. Another important class of nucleophilic reagents in organosilicon chemistry is the oxygen nucleophiles. The simplest of these are water and methanol and their respective anions. The results for the hydrolysis and methanolysis of the subject organosilicon halides are shown in Table III.

The results from Table III show that Me₃AdCl and Me₃AdBr are inert to water and methanol under conditions that normally lead to rapid hydrolysis and methanolysis of simple acyclic organosilicon halides¹⁴ (reactions 15, 18, and 19). Me₃AdCl is inert to methanolysis even when the ionic strength of the medium is increased by added inert salt (reaction 20). In contrast, both IIa and IIIa undergo facile hydrolysis with water (reactions 16 and 17). A dramatic increase in rate is observed for the methanolysis of Me₃AdCl and Me₃AdBr when NaOCH₃ is used instead of CH₃OH alone (reactions 22 and 23). In fact, the relative rates of displacement for Me₃AdBr and IIIa (reactions 23 and 25) become indistinguishable under these conditions. In the case of reaction 24 an equilibrium between the ammonium hydroxide and the ammonium methoxide in methanol solution must exist with the rate of formation of Me₃AdOCH₃ greatly exceeding the rate of formation of Me₃AdOH under these conditions. It is also interesting to note that a change in the cation from Na⁺ to C₆H₅CH₂N⁺(CH₃)₃ has no significant effect on the rate of formation of Me₃AdOCH₃ (re-

actions 22 and 24), thus indicating the primary importance of the nucleophilic portion of the reagent.

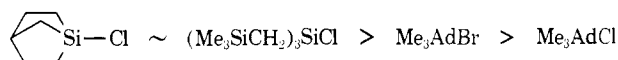
A careful comparison of the reactions in Table III shows the following trend in reactivity.



In actual fact, the rate for IIa probably greatly exceeds that for IIIa, but both reactions are so fast that the order of reactivity is difficult to discern.

Organosilicon halides are readily converted to the fluorides by inorganic and organic fluoride salts in inert solvents.¹⁵ This conversion of the subject compounds was investigated using two organic fluoride salts in chloroform solvent. The chloroform was purified by extraction with concentrated H₂SO₄ followed by chromatography on silica gel just prior to use. The results are shown in Table IV.

When the primary ammonium fluoride, *c*-C₆H₁₁-NH₃F, is the fluoride reagent the relative ease of reaction is readily seen as indicated by reactions 26, 28, 29, and 30. The reactivity order is shown below.



Reactions 26 and 27 show the importance of bulk solvent polarity. Me₃AdCl reacts much faster in CH₃OH than in CHCl₃.

When the primary ammonium fluoride is replaced with the quaternary ammonium fluoride, (C₂H₅)₄NF, as the fluoride reagent a leveling effect is observed (reactions 31–34). That is, all four compounds now react so fast that the relative reactivity order is not discernible under these conditions. This large difference in reactivity for the two salts, especially evident in the comparison of reactions 26 and 31, is very important from a mechanistic point of view. This aspect will be discussed in greater detail below.





Discussion

All the data from Tables I–IV, taken together, clearly

(15) Reference 14, Chapter 5.

(14) C. Eaborn, "Organosilicon Compounds," Butterworths, London, England, 1960, Chapters 8 and 9.

Table IV. Conversion to Fluorides^a

Reaction no.	Substrate	Reagent	Approximate half-life	Product	Yield, %
26	Me ₃ AdCl	c-C ₆ H ₁₁ NH ₂ F	1 hr	Me ₃ AdF	89
27	Me ₃ AdCl ^b	c-C ₆ H ₁₁ NH ₂ F	10 min	Me ₃ AdF	90
28	Me ₃ AdBr	c-C ₆ H ₁₁ NH ₂ F	6 min	Me ₃ AdF	95
29		c-C ₆ H ₁₁ NH ₂ F	Inst ^c		81
30	(Me ₃ SiCH ₂) ₃ SiCl	c-C ₆ H ₁₁ NH ₂ F	Inst ^c	(Me ₃ SiCH ₂) ₃ SiF	84
31	Me ₃ AdCl	(C ₂ H ₅) ₄ NF	Inst ^c	Me ₃ AdF	95
32	Me ₃ AdBr	(C ₂ H ₅) ₄ NF	Inst ^c	Me ₃ AdF	92
33		(C ₂ H ₅) ₄ NF	Inst ^c		64
34	(Me ₃ SiCH ₂) ₃ SiCl	(C ₂ H ₅) ₄ NF	Inst ^c	(Me ₃ SiCH ₂) ₃ SiF	96

^a All the reactions were run in ethanol-free chloroform at 25° unless otherwise noted. ^b This reaction was run in anhydrous methanol at 25°. ^c Instantaneous and exothermic reaction.

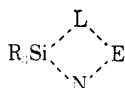
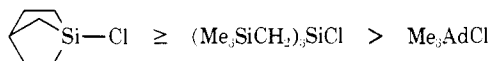


Figure 1. S_N1-Si transition state or intermediate: L = leaving group (OR); N = entering nucleophile (H); and E = electrophilic portion of the reagent (Al).

indicate a general trend in the reactivity of the three systems toward nucleophilic displacement at silicon. This general trend is shown below.



Substitution of Br for Cl in Me₃AdCl leads to increased reactivity, but in general the tetrasiladamantane system is still the least reactive of the systems studied.

It is interesting to note that the reduced reactivity of the tetrasiladamantanes relative to the 1-silabicyclo[2.2.1]heptane system is in dramatic contrast to the reactivity pattern observed for the corresponding carbon compounds. For example, the 1-substituted adamantanes are about 10¹⁰ times more reactive than the analogously 1-substituted bicyclo[2.2.1]heptanes under solvolysis conditions.^{2,3} However, the bridgehead carbon compounds are known to react by an ionization (S_N1) mechanism^{2,3} while it is more likely that the analogous bridgehead silicon compounds react by a nonionization mechanism involving nucleophilic substitution at silicon.^{4,6}

In general, IIIa, the acyclic analog of Me₃AdCl, shows no unusual reactivity which might be attributed to the Si-CH₂-Si structure. It appears to behave like a typical acyclic triorganosilicon chloride substituted with relatively bulky organic groups. Thus, small reagents such as H₂O, CH₃OH, NaOCH₃, hydride (from LiAlH₄), and F⁻ give rapid reaction. Reagents with larger steric requirements such as (*i*-Bu)₂AlH and CH₃Li, which is highly associated in ethyl ether,¹³ require activation by TMEDA in order to bring about facile reactions. The dramatic change in relative reactivity for the (*i*-Bu)₂AlH reductions of IIIc and Me₃AdOCH₃ (reactions 8 and 9) can also be attributed to steric effects. An S_N1-Si mechanism¹⁶ is very likely operating for these reactions since stereochemical and rate studies have shown that this mechanism is favored for (*i*-Bu)₂AlH

(16) Reference 10, Chapter 11.

reductions of other alkoxysilanes.^{17,18} This mechanism requires a relatively compact four-centered transition state as shown in Figure 1. The appropriate groups are shown in parentheses for the specific case of (*i*-Bu)₂AlH reductions of alkoxysilanes. It is reasonable to postulate considerable steric interaction between the bulky isobutyl groups of (*i*-Bu)₂AlH and the bulky trimethylsilylmethyl groups of IIIc, thus retarding the reaction rate. This type of steric interaction would be greatly reduced for Me₃AdOCH₃ where the nonreacting groups on silicon are "tied back" by the cage structure.

Since IIIa appears to behave like a typical acyclic triorganosilicon chloride, it is a reasonable assumption that the large differences in reactivity observed for the two bridgehead organosilicon chlorides, IIa and Me₃AdCl, result from differences in ground-state geometry and not unusual effects engendered by the Si-CH₂-Si structure of Me₃AdCl. The differences in ground-state geometry are profound. Me₃AdCl contains bridgehead silicon in a virtually strain-free tetrahedral geometry while IIa contains bridgehead silicon in a highly strained geometry with C-Si-C bond angles of about 90-95°.¹⁰ Evidently, this highly strained ground-state geometry leads to greatly enhanced reactivity toward nucleophilic displacement at silicon as indicated by the results from Tables I-IV where IIa is much more reactive than Me₃AdCl in all the reactions investigated.

The rate-enhancing effects of angle-strained ground-state geometry in IIa have previously been attributed to a combination of geometrical- and orbital-hybridization factors.¹⁰ Thus, IIa has the requisite geometry for retention of configuration "built in" the ground state, and the effects of angle strain on orbital hybridization at bridgehead silicon should make such a silicon center a more effective target for nucleophilic attack.¹⁰ Results of the present work are in accord with these postulates.

Perhaps the most significant results in this paper from a mechanistic standpoint are those which show that a quaternary ammonium hydroxide (Table III) as well as a quaternary ammonium fluoride (Table IV) give very fast rates with Me₃AdCl and with IIa. Because of the very weak electrophilic character of quaternary nitrogen these reagents should be functioning es-

(17) L. H. Sommer, J. McLick, and C. M. Golino, *J. Amer. Chem. Soc.*, **94**, 669 (1972).

(18) L. H. Sommer, C. M. Golino, D. N. Roark, and R. D. Bush, *J. Organometal. Chem.*, **49**, C3 (1973).

entially as nucleophiles. Thus, their high reactivity provides substantial evidence that the bridgehead silicon atoms in both IIa and Me_3AdCl can undergo nucleophilic attack by an $\text{S}_{\text{N}}2\text{-Si}$ mechanism proceeding with *retention* of configuration, a mechanism previously proposed as a possible reaction path in special cases.¹⁹ We believe that the present work strongly supports this earlier hypothesis.

Experimental Section

General. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points were determined on a Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were taken on a Beckman IR8 spectrophotometer. Nmr spectra were obtained with the Varian A-60A spectrometer; chemical shifts are reported in parts per million relative to external tetramethylsilane. Mass spectra were obtained on a Varian M66 at 70 eV. Preparative glc was carried out on an Aerograph P-90; analytical glc was carried out on a Hewlett-Packard 7620A with flame ionization detector.

1-Chloro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ib). This compound was prepared by the method of Frye⁹ and isolated by preparative glc (20 ft \times $\frac{3}{8}$ in., 20% SE-30 on 45-60 Chromosorb W): mp 136-137°; nmr (CCl_4) τ 9.8 (9 H, s, SiCH_3), 9.7 (6 H, s, SiCH_2SiCl), 10.2 (6 H, s, SiCH_2Si); ir (CCl_4) 1250 (SiCH_3) and 1030 cm^{-1} (SiCH_2Si); the mass spectrum gave a small parent peak m/e 276 (4) with a P - CH_3 m/e 261 (100) base peak.

Anal. Calcd for $\text{C}_9\text{H}_{21}\text{ClSi}_4$: C, 39.01; H, 7.64; Cl, 12.80. Found: C, 38.87; H, 7.79; Cl, 12.77.

1-Chloro-1-silabicyclo[2.2.1]heptane (IIa). This compound was available in this laboratory from a previous synthesis by Bennett.^{4,20} The infrared spectrum (CCl_4) was identical with the reported spectrum of authentic material.²⁰ The mass spectrum gave a large parent peak m/e 146 (74) and two peaks of nearly equal intensity for P - C_2H_4 m/e 118 (99) and P - C_2H_5 m/e 117 (100).

Tris(trimethylsilylmethyl)chlorosilane (IIIa). This compound was prepared by the method of Sommer:¹² bp 84-86° (0.8 mm); n_D^{25} 1.4595 (lit.¹² n_D^{20} 1.4600); neutralization equivalent was 333 g/mol (calcd 324 g/mol); the mass spectrum was complex. The parent peak was not detected, but peaks for P - CH_3 m/e 309 (67) and P - $(\text{CH}_2\text{Si}(\text{CH}_3))$ m/e 237 (3) were detected. The base peak was m/e 201 (100).

1-Bromo-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ic). 3,5,7-Trimethyl-1,3,5,7-tetrasiladamantane (Id), 100 mg (0.41 mmol), was dissolved in 5 ml of carbon tetrachloride in a 25-ml suction flask. The solution was treated in a dropwise manner with a solution of bromine in carbon tetrachloride. The red bromine color disappeared at once in a slightly exothermic reaction. When the addition was complete, the solvent was removed by aspiration and the residue was chromatographed on silica gel with pentane eluent: yield = 120 mg (91%); mp 150-152°; nmr (CCl_4) τ 9.7 (9 H, s, SiCH_3), 9.5 (6 H, s, SiCH_2SiBr), 10.1 (6 H, s, SiCH_2Si); ir (CCl_4) 1250 (SiCH_3) and 1030 cm^{-1} (SiCH_2Si); the mass spectrum did not show the parent peak m/e 320 but gave a base peak for P - CH_3 m/e 305 (100) and a small peak for P - Br m/e 241 (1).

Anal. Calcd for $\text{C}_9\text{H}_{21}\text{BrSi}_4$: C, 33.62; H, 6.58. Found: C, 33.75; H, 6.68.

Reduction. General Procedure. The substrate silane was added all at once to a mixture of the reducing agent, lithium aluminum hydride or diisobutylaluminum hydride, and ether solvent in a round-bottomed flask equipped with thermometer, magnetic stirrer, and condenser. The reaction was run at room temperature and under an atmosphere of nitrogen. The progress of the reaction was followed by periodic glc analysis of the reaction mixture. When the reaction was complete it was carefully added to a mixture of concentrated HCl, cracked ice, and pentane. The organic layer was then separated and washed with water until neutral to litmus and then dried over anhydrous Na_2SO_4 . Filtration and removal of the solvent by aspiration gave the crude product which was then purified by standard methods.

Reduction of 1-Bromo-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ic) with LiAlH_4 . This reaction was carried out with 234 mg (0.73 mmol) of 1-bromo-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane, 120

mg (3.0 mmol) of lithium aluminum hydride, and 10 ml of ether. The reaction required 3 days to go to completion. The product was identified as 3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Id): yield = 133 mg (75%); mp 33-35°; nmr (CCl_4) τ 9.8 (9 H, s, SiCH_3), 10.1 (12 H, s, SiCH_2SiH and SiCH_2Si), 5.3 (1 H, m, SiH); ir (CCl_4) 2110 cm^{-1} (SiH); the mass spectrum gave a small parent peak m/e 242 (7) with a P - CH_3 m/e 227 (100) base peak.

Anal. Calcd for $\text{C}_9\text{H}_{22}\text{Si}_4$: C, 44.55; H, 9.14. Found: C, 44.67; H, 9.00.

Reduction of 1-Chloro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ib) with LiAlH_4 . This reaction was carried out with 200 mg (0.73 mmol) of 1-chloro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane, 120 mg (3.0 mmol) of lithium aluminum hydride, and 10 ml of ether. The reaction required 22 days to go to completion. The product was identified as 3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Id) by melting point and infrared. An isolated yield was not determined due to excessive material loss during glc sampling over the 22-day period.

Reduction of 1-Chloro-1-silabicyclo[2.2.1]heptane (IIa) with LiAlH_4 . This reaction was carried out with 624 mg (4.3 mmol) of 1-chloro-1-silabicyclo[2.2.1]heptane, 330 mg (8.6 mmol) of lithium aluminum hydride, and 10 ml of ether. The reaction was complete in less than 5 min after mixing. The product was identified as 1-silabicyclo[2.2.1]heptane (IIc) by comparison of the melting point and infrared with authentic material: yield = 270 mg (56%); mp 58-61° (lit.²⁰ mp 62-63°).

Reduction of Tris(trimethylsilylmethyl)chlorosilane (IIIa) with LiAlH_4 . This reaction was carried out with 1.0 g (3.08 mmol) of tris(trimethylsilylmethyl)chlorosilane, 230 mg (6.0 mmol) of lithium aluminum hydride, and 20 ml of ether. The reaction was complete in less than 10 min after mixing. The product was identified as tris(trimethylsilylmethyl)silane (IIIc): yield = 800 mg (90%); nmr (CCl_4) τ 9.8 (27 H, s, SiCH_3), 10.1 (6 H, d, SiCH_2Si), 5.8 (1 H, m, SiH); ir (CCl_4) 2120 cm^{-1} (SiH); the mass spectrum gave a base peak for P - CH_3 m/e 275 (100) and a relatively large P - $\text{CH}_2\text{Si}(\text{CH}_3)_2$ peak m/e 203 (35).

Anal. Calcd for $\text{C}_{12}\text{H}_{34}\text{Si}_4$: C, 49.57; H, 11.79. Found: C, 49.67; H, 11.77.

Reduction of 1-Chloro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ib) with $(i\text{-Bu})_2\text{AlH}$. This reaction was carried out with 200 mg (0.73 mmol) of 1-chloro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane, 1.0 ml (\sim 5.4 mmol) of diisobutylaluminum hydride, and 10 ml of ether. No reaction was detected after 1 hour by glc analysis. N,N,N',N' -Tetramethylethylenediamine, 0.75 ml (\sim 5.4 mmol), was then added as an activator. No reaction was detected by glc after 55 hr. Work-up in the usual manner gave the starting material which was identified by melting point (133-136°) and infrared.

Reduction of 1-Methoxy-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ie) with $(i\text{-Bu})_2\text{AlH}$. This reaction was carried out with 133 mg (0.49 mmol) of 1-methoxy-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane, 0.27 ml (\sim 1.47 mmol) of diisobutylaluminum hydride, and 5.0 ml of ether. This reaction required 4 hr to go to completion. The product was identified as 3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Id) by melting point and infrared; yield = 103 mg (86%).

Reduction of Tris(trimethylsilylmethyl)chlorosilane (IIIa) with $(i\text{-Bu})_2\text{AlH}$. This reaction was carried out with 1.0 g (3.08 mmol) of tris(trimethylsilylmethyl)chlorosilane, 3.0 ml (\sim 16.2 mmol) of diisobutylaluminum hydride, and 20 ml of ether. About 5% reaction was detected by glc after 24 hr. N,N,N',N' -Tetramethylethylenediamine, 2.0 ml (\sim 16.2 mmol), was then added as an activator. The reaction was now complete after 1 hr. The product was identified as tris(trimethylsilylmethyl)silane (IIIc) by infrared; yield = 660 mg (74%).

Reduction of Tris(trimethylsilylmethyl)methoxysilane (IIIc) with $(i\text{-Bu})_2\text{AlH}$. This reaction was carried out with 280 mg (0.88 mmol) of tris(trimethylsilylmethyl)methoxysilane, 0.5 ml (\sim 2.7 mmol) of diisobutylaluminum hydride, and 10 ml of ether. After 24 hr the reaction was only 5% complete by glc analysis. It was 50% complete in about 6 days and required nearly 3 weeks to go to completion. The product was identified as tris(trimethylsilylmethyl)silane (IIIc) by infrared. An isolated yield was not determined due to excessive material loss during glc sampling over the 3-week period.

Reduction of 1-Chloro-1-silabicyclo[2.2.1]heptane (IIa) with $(i\text{-Bu})_2\text{AlH}$. Diisobutylaluminum hydride, 1.0 ml (\sim 5.4 mmol), was added to 10 ml of ether in a 25-ml round-bottomed flask equipped with thermometer and magnetic stirrer and kept under an atmosphere of dry nitrogen. A small sample of this solution was transferred by syringe to a 0.1-mm infrared cell and the spectrum

(19) Reference 10, p 155.

(20) O. F. Bennett, Ph.D. Thesis, The Pennsylvania State University, 1958.

was recorded. A strong broad band for Al-H²¹ was observed at 1760 cm⁻¹. 1-Chloro-1-silabicyclo[2.2.1]heptane, 619 mg (4.3 mmol), was added to the ether solution all at once and the infrared spectrum was recorded as before. The total elapsed time after mixing for the analysis was about 5 min. A strong band for Si-H at 2160 cm⁻¹ was now present and the Al-H band at 1760 cm⁻¹ was greatly reduced. This spectrum remained unchanged after an additional 45 min. Work-up in the usual manner gave 250 mg (55%) of 1-silabicyclo[2.2.1]heptane (II_d), which was identified by melting point and infrared.

Coupling with Alkyl/Aryl Lithiums. General Procedure. The substrate silane was added all at once to an ether solution of the organolithium reagent, methylolithium or phenyllithium, in a round-bottomed flask equipped with thermometer, magnetic stirrer, and condenser. The reaction was run at room temperature and under an atmosphere of nitrogen. The progress of the reaction was followed by periodic glc analysis of the reaction mixture. When the reaction was complete it was carefully added to a mixture of concentrated HCl, cracked ice, and pentane. The organic layer was then separated and washed with water until neutral to litmus and then dried over anhydrous Na₂SO₄. Filtration and removal of the solvent by aspiration gave the crude product which was then purified by standard methods.

Coupling of 1-Chloro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ib) with CH₃Li. This reaction was carried out with 200 mg (0.73 mmol) of 1-chloro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane, 2.2 ml (~3.0 mmol) of 1.5 M CH₃Li in ether (Foote Mineral Co.), and 10 ml of ether. Little or no reaction was detected after 1 hr. *N,N,N',N'*-Tetramethylethylenediamine, 0.40 ml (~3.0 mmol), was then added as an activator. The reaction now required 30 min to go to completion. The product was identified as 1,3,5,7-tetramethyl-1,3,5,7-tetrasiladamantane (I_f): yield = 130 mg (70%); mp 118–120° (recrystallized from pentane); nmr (CCl₄) τ 9.8 (12 H, s, SiCH₃), 10.2 (12 H, s, SiCH₂Si); ir (CCl₄) 1250 (SiCH₃) and 1030 cm⁻¹ (SiCH₂Si); the mass spectrum gave a detectable parent peak *m/e* 256 (1) and a P - CH₃ *m/e* 241 (100) base peak.

Anal. Calcd for C₁₀H₂₄Si₄: C, 46.80; H, 9.42. Found: C, 46.80; H, 9.22.

Coupling of 1-Bromo-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ic) with CH₃Li. This reaction was carried out with 234 mg (0.73 mmol) of 1-bromo-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane, 2.2 ml (~3.0 mmol) of 1.5 M CH₃Li in ether (Foote Mineral Co.), 0.40 ml (~3.0 mmol) of *N,N,N',N'*-tetramethylethylenediamine, and 10 ml of ether. The reaction required about 30 min to go to completion. The product was identified as 1,3,5,7-tetramethyl-1,3,5,7-tetrasiladamantane (I_f) by melting point and infrared; yield = 140 mg (76%).

Coupling of Tris(trimethylsilylmethyl)chlorosilane (IIIa) with CH₃Li. This reaction was carried out with 1.0 g (3.08 mmol) of tris(trimethylsilylmethyl)chlorosilane, 6.7 ml (~10 mmol) of 1.5 M CH₃Li in ether (Foote Mineral Co.), 1.5 ml (~10 mmol) of *N,N,N',N'*-tetramethylethylenediamine, and 20 ml of ether. The reaction was complete in less than 10 min after mixing. The product was identified as tris(trimethylsilylmethyl)methylsilane (III_f): yield = 690 mg (75%); nmr (CCl₄) τ 9.8 (30 H, s, SiCH₃), 10.1 (6 H, s, SiCH₂Si); ir (CCl₄) 1250 (SiCH₃) and 1060 cm⁻¹ (SiCH₂Si); the mass spectrum did not show a parent peak but did give a P - CH₃ *m/e* 289 (10) and P - CH₂Si(CH₃)₃ *m/e* 217 (100) base peak.

Anal. Calcd for C₁₃H₃₄Si₄: C, 51.23; H, 11.91. Found: C, 51.19; H, 11.83.

Coupling of 1-Chloro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ib) with Phenyllithium. This reaction was carried out with 500 mg (1.83 mmol) of 1-chloro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane, about 2.40 mmol of phenyllithium prepared from 380 mg (2.40 mmol) of bromobenzene, 2.60 mmol of *n*-butyllithium (Foote Mineral Co.) in the usual manner, and 15 ml of ether. The reaction required 4 hr to go to completion. The product was identified as 1-phenyl-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (I_g): yield = 480 mg (83%); nmr (CCl₄) τ 2.6 (5 H, m, PhH), 9.8 (9 H, s, SiCH₃), 10.0 (6 H, s, SiCH₂SiPh), 10.2 (6 H, s, SiCH₂Si); ir (CCl₄) 3060 (PhH), 1429 and 1110 cm⁻¹ (SiPh); the mass spectrum gave a small parent peak *m/e* 318 (6), P - Ph peak *m/e* 241 (2), and a P - CH₃ *m/e* 303 (100) base peak.

Anal. Calcd for C₁₁H₂₈Si₄: C, 56.52; H, 8.22. Found: C, 56.43; H, 8.24.

Coupling of 1-Chloro-1-silabicyclo[2.2.1]heptane (IIa) with Phenyl-

lithium. This reaction was carried out with 884 mg (6.1 mmol) of 1-chloro-1-silabicyclo[2.2.1]heptane, about 8.70 mmol of phenyllithium prepared from 1.37 g (8.7 mmol) of bromobenzene and 9.00 mmol of *n*-butyllithium (Foote Mineral Co.) in the usual manner, and 20 ml of ether. This reaction was complete in less than 5 min after mixing. The product was identified as 1-phenyl-1-silabicyclo[2.2.1]heptane (II_e): yield = 990 mg (86%); nmr (CCl₄) τ 2.6 (5 H, m, PhH), 7.6 (1 H, m, >CH), 8.2 (4 H, m, CH₂CH₂), 9.3 (6 H, m, SiCH₂); ir (CCl₄) 3060 (PhH), 1415 and 1105 cm⁻¹ (SiPh); the mass spectrum gave a large parent peak *m/e* 188 (67), P - C₂H₅ *m/e* 159 (33), and a P - C₂H₄ *m/e* 160 (100) base peak.

Anal. Calcd for C₁₂H₁₆Si: C, 76.55; H, 8.57. Found: C, 76.45; H, 8.60.

Hydrolysis. General Procedure. The substrate silane was added all at once to a rapidly stirred mixture of ether, water, and triethylamine at room temperature. The progress of the reaction was followed by periodic glc analysis of the reaction mixture. When the reaction was complete it was added to a mixture of dilute HCl and pentane. The organic layer was then separated and washed with water until neutral to litmus and then dried over anhydrous Na₂SO₄. Filtration and removal of the solvent by aspiration gave the crude product which was then purified by standard methods.

Hydrolysis of 1-Chloro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ib). This reaction was carried out with 100 mg (0.37 mmol) of 1-chloro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane, 1.0 ml of water, 180 mg (1.8 mmol) of triethylamine, and 5.0 ml of ether. After 22 hr no reaction could be detected by glc. The starting material was recovered and identified by melting point and infrared.

Hydrolysis of Tris(trimethylsilylmethyl)chlorosilane (IIIa). This reaction was carried out with 2.0 g (6.16 mmol) of tris(trimethylsilylmethyl)chlorosilane, 5.0 ml of water, 3.03 g (30 mmol) of triethylamine, and 40 ml of ether. The reaction was complete in less than 5 min after mixing. The product was identified as tris(trimethylsilylmethyl)silanol (III_d): yield = 1.75 g (92%); ir (CCl₄) 3700 (free OH), 3500 (H-bonded OH), and 1090 cm⁻¹ (SiO); the mass spectrum did not give a parent peak but did give a P - CH₃ *m/e* 291 (31) peak and the base peak was *m/e* 203 (100).

Anal. Calcd for C₁₂H₃₄O₃Si₄: C, 46.98; H, 11.17. Found: C, 47.08; H, 11.09.

Hydrolysis of 1-Chloro-silabicyclo[2.2.1]heptane (IIa). This reaction was carried out with 434 mg (2.98 mmol) of 1-chloro-1-silabicyclo[2.2.1]heptane, 1.0 ml of water, 303 mg (3.0 mmol) of triethylamine, and 10 ml of ether. The reaction was complete in less than 5 min after mixing. The product was identified as bis-(1-silabicyclo[2.2.1]heptyl)oxide (II_c): yield = 332 mg (94%); mp 72–75° (lit.^{4,20} mp 74.5–76°); the infrared spectrum was identical with the spectrum of the authentic material.

Methanolysis. General Procedure. The substrate silane was added all at once to a methanol solution of the reagent, Na⁺OCH₃⁻ or C₆H₅CH₂N⁺(CH₃)₃OH⁻, in a round-bottomed flask equipped with thermometer and magnetic stirrer. The reaction was run at room temperature and was protected from atmospheric moisture by a CaCl₂ drying tube. The progress of the reaction was followed by periodic glc analysis. When the reaction was complete the solvent was removed on an aspirator. The residue was then taken up in hot pentane and filtered to remove the salts. Removal of the pentane by aspiration then gave the crude product which was purified by standard methods.

Reaction of 1-Chloro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ib) with CH₃OH. This reaction was carried out with 200 mg (0.73 mmol) of 1-chloro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane and 15 ml of anhydrous methanol. No reaction could be detected after 24 hr and the starting material was recovered and identified by melting point and infrared.

Reaction of 1-Bromo-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ic) with CH₃OH. This reaction was carried out with 234 mg (0.73 mmol) of 1-bromo-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane and 15 ml of anhydrous methanol. No reaction could be detected after 24 hr and the starting material was recovered and identified by melting point and infrared.

Reaction of Tris(trimethylsilylmethyl)chlorosilane (IIIa) with CH₃OH. This reaction was carried out with 1.0 g (3.08 mmol) of tris(trimethylsilylmethyl)chlorosilane and 15 ml of anhydrous methanol. The reaction was complete in less than 8 min after mixing. The product was identified as tris(trimethylsilylmethyl)methoxysilane (III_c): yield = 700 mg (70%); nmr (CCl₄) τ 6.5 (3 H, s, OCH₃), 9.8 (27 H, s, SiCH₃), 10.1 (6 H, s, SiCH₂Si); ir (CCl₄) 1100 cm⁻¹ (SiOC); the mass spectrum gave no detectable parent peak but did give a large P - CH₃ *m/e* 305 (87) and a base peak for P - CH₂Si(CH₃)₃ *m/e* 233 (100).

(21) E. G. Hoffman and G. Schomburg, *Z. Elektrochem.*, **61**, 1101 (1957).

Anal. Calcd for $C_{13}H_{36}OSi_4$: C, 48.68; H, 11.31. Found: C, 48.79; H, 11.43.

Reaction of 1-Chloro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ib) with $NaOCH_3-CH_3OH$. This reaction was carried out with 200 mg (0.73 mmol) of 1-chloro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane, 110 mg (2.0 mmol) of $NaOCH_3$, and 15 ml of anhydrous methanol. The reaction required 15 min to go to completion. The product was identified as 1-methoxy-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ie): yield = 172 mg (86%); mp 63–64°; nmr (CCl_4) τ 6.5 (3 H, s, OCH_3), 9.8 (9 H, s, $SiCH_3$), 9.9 (6 H, s, $SiCH_2SiOCH_3$), 10.2 (6 H, s, $SiCH_2Si$); ir (CCl_4) 1090 ($SiOC$) and 1035 cm^{-1} ($SiCH_2Si$); the mass spectrum gave a detectable parent peak m/e 272 (~ 1) and a $P - CH_3$ m/e 257 (100) base peak.

Anal. Calcd for $C_{10}H_{24}OSi_4$: C, 44.05; H, 8.87. Found: C, 44.18; H, 8.95.

Reaction of 1-Bromo-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ic) with $NaOCH_3-CH_3OH$. This reaction was carried out with 234 mg (0.73 mmol) of 1-bromo-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane, 110 mg (2.0 mmol) of $NaOCH_3$, and 15 ml of anhydrous methanol. The reaction was complete in less than 2 min after mixing. The product was identified as 1-methoxy-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ie) by melting point and nmr; yield = 180 mg (90%).

Reaction of Tris(trimethylsilylmethyl)chlorosilane (IIIa) with $NaOCH_3-CH_3OH$. This reaction was carried out with 1.0 g (3.08 mmol) of tris(trimethylsilylmethyl)chlorosilane, 220 mg (4.0 mmol) of $NaOCH_3$, and 10 ml of anhydrous methanol. The reaction was complete in less than 5 min after mixing. The product was identified as tris(trimethylsilylmethyl)methoxysilane (IIIc) by infrared and nmr; yield = 400 mg (40%).

Reaction of 1-Chloro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ib) with $C_6H_5CH_2N(CH_3)_3OH-CH_3OH$. This reaction was carried out with 200 mg (0.73 mmol) of 1-chloro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane, about 2.0 mmol of $C_6H_5CH_2N(CH_3)_3OH$ from 835 mg of a 40% solution in methanol, and 15 ml of anhydrous methanol. The reaction required 15 min to go to completion. The product was identified as 1-methoxy-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ie) by infrared and nmr. It was shown to be about 99% pure by glc analysis. Presumably the small impurity was the silanol; yield = 183 mg (92%).

Reaction of 1-Chloro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ib) with CH_3OH Containing $C_6H_5CH_2N(C_2H_5)_3ClO_4$. This reaction was carried out with 200 mg (0.73 mmol) of 1-chloro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane, 407 mg (1.40 mmol) of $C_6H_5CH_2N(C_2H_5)_3ClO_4$, and 15 ml of anhydrous methanol. No reaction could be detected after 72 hr at room temperature. The starting material was recovered and identified by melting point and infrared.

Reaction with Fluoride. General Procedure. The substrate silane was added all at once to a solution of the fluoride reagent, $c-C_6H_{11}NH_3F$ or $(C_2H_5)_4NF$, in chloroform in a round-bottomed flask equipped with thermometer and magnetic stirrer. The reaction was run at room temperature and was protected from atmospheric moisture by a $CaCl_2$ drying tube. The progress of the reaction was followed by periodic glc analysis of the reaction mixture. When the reaction was complete the solvent was removed on an aspirator. The residue was then taken up in hot pentane and filtered to remove the salts. Removal of the pentane by aspiration then gave the crude product which was purified by standard methods.

Reaction of 1-Chloro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ib) with $c-C_6H_{11}NH_3F-CHCl_3$. This reaction was carried out with 200 mg (0.73 mmol) of 1-chloro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane, 210 mg (1.8 mmol) of $c-C_6H_{11}NH_3F$, and 10 ml of chloroform. The reaction required 12 hr to go to completion. The product was identified as 1-fluoro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ih): yield = 169 mg (89%); mp 70–71° (recrystallized from pentane); nmr (CCl_4) τ 9.7 (9 H, s, $SiCH_3$), 9.8 (6 H, s, $SiCH_2SiF$), 10.1 (6 H, s, $SiCH_2Si$); ir (CCl_4) 1250 ($SiCH_2SiF$) and 1035 cm^{-1} ($SiCH_2Si$); the mass spectrum gave no detectable parent peak but did give a $P - CH_3$ m/e 245 (100) base peak.

Anal. Calcd for $C_9H_{21}FSi_4$: C, 41.47; H, 8.12. Found: C, 41.62; H, 8.04.

Reaction of 1-Chloro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ib) with $c-C_6H_{11}NH_3F-CH_3OH$. This reaction was carried out

with 200 mg (0.73 mmol) of 1-chloro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane, 210 mg (1.80 mmol) of $c-C_6H_{11}NH_3F$, and 15 ml of anhydrous methanol instead of chloroform. The reaction required 90 min to go to completion. The product was identified as 1-fluoro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ih) by melting point, infrared, and nmr; yield = 170 mg (90%).

Reaction of 1-Chloro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ib) with $(C_2H_5)_4NF-CHCl_3$. This reaction was carried out with 200 mg (0.73 mmol) of 1-chloro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane, 268 mg (1.80 mmol) of $(C_2H_5)_4NF$, and 10 ml of chloroform. The reaction was complete in less than 5 min after mixing. The product was identified as 1-fluoro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ih) by melting point, infrared, and nmr; yield = 180 mg (95%).

Reaction of 1-Bromo-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ic) with $c-C_6H_{11}NH_3F-CHCl_3$. This reaction was carried out with 234 mg (0.73 mmol) of 1-bromo-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane, 210 mg (1.80 mmol) of $c-C_6H_{11}NH_3F$, and 10 ml of chloroform. The reaction required 45 min to go to completion. The product was identified as 1-fluoro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ih) by melting point, infrared, and nmr; yield = 180 mg (95%).

Reaction of 1-Bromo-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ic) with $(C_2H_5)_4NF-CHCl_3$. This reaction was carried out with 234 mg (0.73 mmol) of 1-bromo-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane, 268 mg (1.80 mmol) of $(C_2H_5)_4NF$, and 10 ml of chloroform. The reaction was complete in less than 5 min after mixing. The product was identified as 1-fluoro-3,5,7-trimethyl-1,3,5,7-tetrasiladamantane (Ih) by melting point, infrared, and nmr; yield = 175 mg (92%).

Reaction of 1-Chloro-1-silabicyclo[2.2.1]heptane (IIa) with $c-C_6H_{11}NH_3F-CHCl_3$. This reaction was carried out with 537 mg (3.72 mmol) of 1-chloro-1-silabicyclo[2.2.1]heptane, 470 mg (4.00 mmol) of $c-C_6H_{11}NH_3F$, and 20 ml of chloroform. The reaction was complete in less than 2 min after mixing. The product was identified as 1-fluoro-1-silabicyclo[2.2.1]heptane (IIb): yield = 390 mg (81%); mp 64–67° (lit.²² mp 68–69°); the infrared spectrum was identical with the spectrum of authentic material.

Reaction of 1-Chloro-1-silabicyclo[2.2.1]heptane (IIa) with $(C_2H_5)_4NF-CHCl_3$. This reaction was carried out with 495 mg (3.44 mmol) of 1-chloro-1-silabicyclo[2.2.1]heptane, 595 mg (4.00 mmol) of $(C_2H_5)_4NF$, and 20 ml of $CHCl_3$. The reaction was complete in less than 2 min after mixing. The product was identified as 1-fluoro-1-silabicyclo[2.2.1]heptane (IIb) by melting point and infrared; yield = 285 mg (64%).

Reaction of Tris(trimethylsilylmethyl)chlorosilane (IIIa) with $c-C_6H_{11}NH_3F-CHCl_3$. This reaction was carried out with 1.0 g (3.08 mmol) of tris(trimethylsilylmethyl)chlorosilane, 410 mg (3.50 mmol) of $c-C_6H_{11}NH_3F$, and 15 ml of chloroform. The reaction was complete in less than 10 min after mixing. The product was identified as tris(trimethylsilylmethyl)fluorosilane (IIIb): yield = 800 mg (84%); mp 35–37° (recrystallized from pentane); nmr (CCl_4) τ 9.9 (27 H, s, $SiCH_3$), 10.1 (6 H, s, $SiCH_2Si$); ir (CCl_4) 860 cm^{-1} (SiF); the mass spectrum gave no detectable parent peak, but peaks for $P - CH_3$ m/e 293 (87) and $P - CH_2Si(CH_3)_3$ m/e 221 (3) were detected, and the base peak was m/e 201 (100).

Anal. Calcd for $C_{12}H_{33}FSi_4$: C, 46.68; H, 10.77. Found: C, 46.60; H, 10.88.

Reaction of Tris(trimethylsilylmethyl)chlorosilane (IIIa) with $(C_2H_5)_4NF-CHCl_3$. This reaction was carried out with 475 mg (1.46 mmol) of tris(trimethylsilylmethyl)chlorosilane, 536 mg (3.60 mmol) of $(C_2H_5)_4NF$, and 20 ml of chloroform. The reaction was complete in less than 2 min after mixing. The product was identified as tris(trimethylsilylmethyl)fluorosilane (IIIb) by melting point, infrared, and nmr; yield = 430 mg (96%).

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(22) M. C. Musolf, Ph.D. Thesis, The Pennsylvania State University, 1960.