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Silicon Effects. III. Rates and Products for Solvolysis of α-(Pentamethyldisilanyl)benzyl Halides and 1,1,2,2-Tetramethyl-1,2-disilaindan-3-yl Chloride. Structure and Stability of α-(Pentamethyldisilanyl)benzyl Cation in Solution[1,2]

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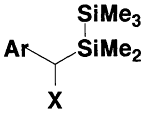
Detailed kinetic and product studies have been made on solvolysis of α-(pentamethyldisilanyl)benzyl halides (**1a-X**; X=Cl and Br) and 1,1,2,2-tetramethyl-1,2-disilaindan-3-yl chloride (**2-Cl**) in various solvents. The solvolysis of **1a-X** at 25 °C is characterized by (1) a complete 1,2-$SiMe_3$ rearrangement in the products, (2) m (sensitivity to the solvent ionizing power Y_X) values of 0.98 (X=Cl) and 0.91 (X=Br) for the solvolyses in aq acetone, (3) α-deuterium isotope effects of 1.167 and 1.163 for **1a-Cl** in 97% aq 2,2,2-trifluoroethanol (TFE) and 40% aq ethanol respectively, and (4) substituent effect expressed by a Yukawa–Tsuno LArSR equation: $\log k/k^{H} = -3.71\,(\sigma^{\circ} + 1.16\,\Delta\bar{\sigma}_R^{+})$ for the solvolysis of **1a-Cl** and the p-Me, m-Me, p-Cl, and m-Cl derivatives in 40% aq ethanol. These findings are consistent with k_c mechanism. The relative rates for **1a-Br**, α-(trimethylsilyl)benzyl bromide, and α-(t-butyldimethylsilyl)benzyl bromide are $1.07\times10^5 : 0.54 : 1.0$ in 97% aq TFE at 25 °C indicating solvolytic generation of α-(pentamethyldisilanyl)benzyl cation to be ca. 7 kcal mol^{-1} energetically more favorable than that of the corresponding α-(trialkylsilyl)benzyl cations. In contrast, **2-Cl** solvolyzes 0.209 times less rapidly than does 2,2-dimethyl-2-silaindan-1-yl chloride in 97% aq TFE indicating that a β-Si–Si σ bond orthogonal to the leaving group does not enhance the rate of ionization at all.

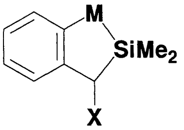
Silicon–silicon single bonds possess unusual low ionization potentials[3] and are capable of interacting with π-systems intermolecularly as well as intramolecularly.[4–6]

The Si–Si bonds are expected to interact strongly with neighboring electron-deficient centers. Eaborn and coworkers[7] have shown that p-disilanyl groups $[(Me_3Si)_nSiMe_{3-n}]$ exert small and additive rate-acceleration effects in the protodestannylation of aryltrimethyltins indicative of inductive and hyperconjugative electron release from the Si–Si bonds. Kumada and coworkers[8] have reported several cationoid reactions of (halomethyl)disilanes undergoing a 1,2-silyl rearrangement from the silicon to the carbenium carbon suggestive of neighboring group participation of the Si–Si σ bond in ionization of the adjacent carbon–halogen bonds. However, neither precise mechanism for the solvolysis of the (halomethyl)disilanes nor structures of carbocations bearing α-disilanyl groups have been elucidated.

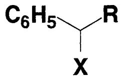
The α and β-silicon effects on stability of carbocations have received considerable mechanistic[9–11] and theoretical interests[12,13] in recent years. Previously,[1,14] we estimated the α- and β-silicon effects in the benzylic k_c solvolysis and it is of interest to compare the β-silicon effects in two benzylic cation systems, $PhHC^{+}\text{–Si–}SiMe_3$ and $PhHC^{+}\text{–C–}SiMe_3$. In order to estimate the β-silicon effect in the former system, we selected the solvolysis of α-(pentamethyldisilanyl)benzyl halides (**1a-X**; X=Br and Cl) and compared their solvolysis rates with those for structurally related α-(trialkylsilyl)benzyl halides.[14] In this paper we describe detailed kinetic and product studies on the solvolysis of **1a-X** and its cyclic analogue, 1,1,2,2-tetramethyl-1,2-disilaindan-3-yl chloride (**2-Cl**), in which the Si–Si bond is orthogonal to the leaving group, and discuss mechanistic implications on the β-silicon effects of the disilanyl groups.



1a; Ar=C_6H_5
b; Ar=p-MeC_6H_4
c; Ar=m-MeC_6H_4
d; Ar=p-ClC_6H_4
e; Ar=m-ClC_6H_4



2; M=$SiMe_2$
3; M=CH_2

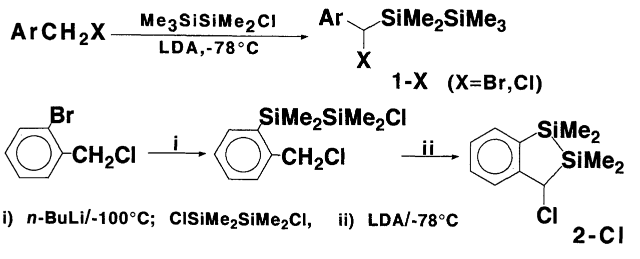


4; R=Me
5; R=$SiMe_2CMe_3$
6; R=$SiMe_3$
7; R=CH_2SiMe_3
8; R=CH_2CMe_3

Results

Synthesis. The bromide **1a-Br** was prepared by treatment of benzyl bromide with LDA at −78 °C in the presence of chloropentamethyldisilane.[14] The chloride **1a-Cl** and the p-Me, m-Me, p-Cl, and m-Cl derivatives (**1b-Cl-1e-Cl**) were prepared in a similar procedure. The cyclic chloride, **2-Cl**, was synthesized from o-bromobenzyl chloride via o-lithiation, a coupling reaction with 1,2-dichlorotetramethyldisilane, and ring closure of the resulting o-(2-chlorotetramethyldisilanyl)benzyl chloride by use of LDA, as shown in Scheme 1. 2,2-Dimethyl-2-silaindan-1-yl chloride (**3-Cl**), a reference standard for **2-Cl**, was prepared by chlorination of 2,2-dimethyl-2-silaindan with sulfuryl chloride.

Kinetic Studies. The rates of solvolysis of the halides



Scheme 1.

1-X, **2-Cl**, and **3-Cl** were determined UV spectrometrically in various solvents including 80/20 to 30/70 (v/v) ethanol–water (E series), 80/20 to 30/70 (v/v) acetone–water (A series), and 97/3 (w/w) to 40/60 (v/v) 2,2,2-trifluoroethanol (TFE)–water (T series) binary solvent mixtures by measuring either decrease in the reactant or increase in acid formed as its acridinium salt by using (0.1—1.0)$\times10^{-4}$ M (M= mol dm^{-3}) solutions in the presence or absence of 2—3 equiv acridine.[14] The rates were reproducible within ±3% in the both measurements and the first-order rate constants determined at 25.0±0.05 °C for **1a-Br**, **1a-Cl**, **2-Cl**, and **3-Cl** were given in Tables 1 and 2. Table 1 includes rate data for 1-phenylethyl bromide (**4-Br**) for comparison.

The solvolysis of **2-Cl** in 97% aq TFE (97T) in the presence of 2 equiv acridine also followed excellent first-order kinetics (correlation coefficient R=0.99998). Unexpectedly, however, the solvolyses in aq ethanol and aq acetone did not follow the first-order kinetics probably due to occurrence of a side reaction (vide infra) and we could not measure the rates in these solvents.

Table 3 compares the solvolysis rates of **1a-Br** in 97T and 30% aq acetone (30A) with those of its β-alkyl reference standards, α-(t-butyldimethylsilyl)benzyl and α-(trimethylsilyl)benzyl bromides[14] (**5-Br** and **6-Br** respectively), and the rate of solvolysis of **2-Cl** in 97T with

Table 1. Solvolysis Rates for **1a-Br**, **1a-Cl**, and **4-Br**[a)]

Solvent[b)]	$10^5\times k/\mathrm{s}^{-1}$ [a)]		
	1a-Br	**1a-Cl**	**4a-Br**
97T	6200[c)]	775 ±2.1[e)]	515 ±0.12
80T	4400±26[d)]	501 ±0.25	893 ±0.2
50T	5020±71[d)]	500 ±4.8[d)]	
30T	5590±52[d)]		
30A	2060±24[d)]	165 ±0.26	3100±30[d)]
40A	489 ±0.3	35.5 ±0.02	876 ±0.23
50A	96.7 ±0.17	5.20 ±0.002	232 ±0.06
60A	21.8 ±0.03	0.987±0.0006	50.9 ±0.017
70A	4.30 ±0.016		12.6 ±0.001
80A	1.08 ±0.0004		
30E		437 ±0.65	
40E	668 ±1.7	59.6 ±0.51[e)]	
50E	139 ±0.2	10.4 ±0.009	
60E	44.1 ±0.10	3.58 ±0.003	
70E	15.4 ±0.10		
80E	4.75 ±0.007		
90E	1.44 ±0.007		

a) At 25.0±0.05 °C. b) A: acetone–water (v/v), E: ethanol–water (v/v), and T: 2,2,2-trifluoroethanol–water (v/v) binary solvent mixtures except for 97T which is a mixture in weight percent. c) Extrapolated from other temperatures. d) Average of two runs. e) Average of three runs.

Table 2. Solvolysis Rates for **2-Cl** and **3-Cl**[a)]

Solvent	$10^5\times k/\mathrm{s}^{-1}$	
	2-Cl	**3-Cl**
97T	38.6±0.03	184±0.08
30A		189±0.11
40A		40.5±0.02
50A		6.72±0.001
40E		87.3±0.04

a) At 25±0.05 °C.

Table 3. β-Silicon Effects[a)]

Substrate	β-Group	Solvent	k/s^{-1}	Relative rate
1a-Br	SiMe$_3$	97T	6.20×10^{-2} [b)]	1.07×10^5
5-Br	CMe$_3$		5.79×10^{-7} [c,d)]	1.0
6-Br	Me		3.13×10^{-7} [c)]	0.54
1a-Br	SiMe$_3$	30A	2.06×10^{-2}	3.38×10^4
5-Br	CMe$_3$		6.10×10^{-7} [c,e)]	1.0
6-Br	Me		1.02×10^{-6} [c)]	1.67
2-Cl	SiMe$_2$	97T	3.86×10^{-4}	0.209
3-Cl	CH$_2$		1.84×10^{-3}	1.0
7-OTFA[f)]	SiMe$_3$	30D[g)]	4.01×10 [h)]	2.99×10^5
8-OTFA[f)]	CMe$_3$	30D[g)]	1.23×10^{-4} [h)]	1.0
4-OTFA[f)]	H	30D[g)]	3.49×10^{-4} [h)]	2.84

a) At 25 °C. b) Extrapolated value from other temperatures. c) Data taken from Ref. 14. d) Estimated from k(**6-Br**) and a k(**5-OTs**)/k(**6-OTs**) rate ratio of 1.85 in 97T (Ref. 14). e) Estimated from k(**6-Br**) and a k(**5-OTs**)/k(**6-OTs**) rate ratio of 0.598 in 30A (Ref. 14). f) Trifluoroacetates. g) In 30% aq dioxane. h) Data taken from Ref. 1.

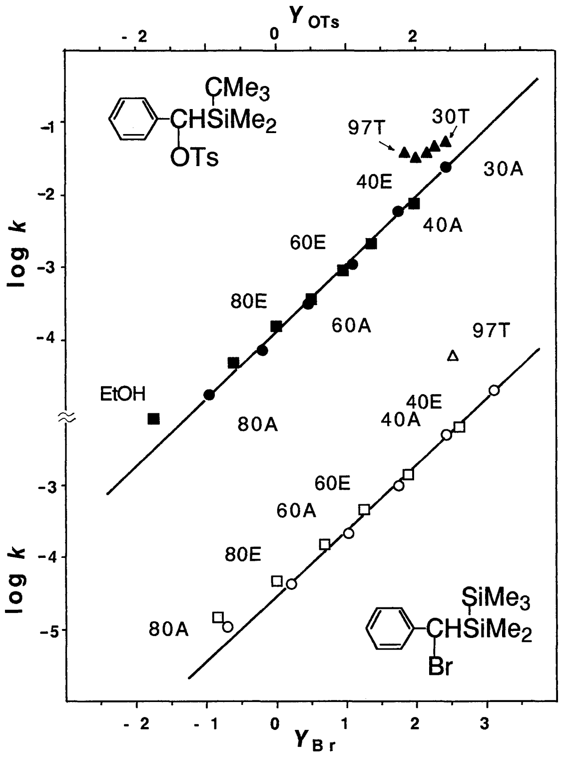


Fig. 1. Plot of log k vs. Y_{Br} for **1a-Br** (open marks) and log k vs. Y_{OTs} for **5-OTs** (closed marks) for aq acetone (circles), aq ethanol (squares), and aq TFE (triangles).

that of its standard compound **3-Cl**. Rate data[1)] for 1-phenylethyl trifluoroacetate (**4-OTFA**), 1-phenyl-2-(trimethylsilyl)ethyl trifluoroacetate (**7-OTFA**), and 3,3-dimethyl-1-phenylbutyl trifluoroacetate (**8-OTFA**) were also included in Table 3 for comparison.

Figure 1 represents dependence of the solvolysis rates (log k) of **1a-Br** on solvent ionizing power Y_{Br}.[15)] A separate mY plot for α-(t-butyldimethylsilyl)benzyl p-toluenesulfonate (**5-OTs**) against Y_{OTs}[16)] is included for comparison. A plot of log k for **1a-Cl** vs. Y_{Cl}[15)] exhibited a very similar mY plot pattern to that for **1a-Br** for the A, E, and T solvent series. Table 4 compares m values for the five different substrates, **1a-Cl**, **1a-Br**, **3-Cl**, **4-Br**, and **5-OTs**, determined from the linear correlation observed in acetone–water binary solvent mixtures.

Table 5 shows α-deuterium kinetic isotope effects (α-KIE) for the solvolysis of **1a-Cl** in 40% aq ethanol (40E) and in 97T at 25 °C.

Table 6 shows the solvolysis rates for **1a-Cl**—**1e-Cl** measured in 40E at 25 °C. The substituent effect was linearly expressed by the Yukawa-Tsuno LArSR equation (Eq. 1)[17)] with an r value of 1.16 and a ρ value of −3.71 (n=5, R=0.998, SD=0.066).

$$\log k/k^{\mathrm{H}} = \rho(\sigma^{\circ} + r\Delta\bar{\sigma}_{\mathrm{R}}^{+}) \quad (1)$$

Table 7 shows salt effects on the solvolysis of **1a-Cl** in 40E. Neither common ion rate depression nor special salt effect was significant, indicative of unimportance of return processes. Activation parameters for the solvolyses of **1a-Br** and **1a-Cl** are given in Table 8.

Table 4. Solvent Effect

Substrate	$m^{\mathrm{a,b)}}$
1a-Br	0.91 (n=5, R=0.996)
1a-Cl	0.98 (n=4, R=0.994)
3-Cl	0.98 (n=3, R=0.998)
5-OTs	0.94 (n=6, R=0.999)[c)]
4-Br	0.87 (n=5, R=0.998)

a) Sensitivity to the solvent ionizing power; Y_{Br}, Y_{Cl} (Ref. 15), and Y_{OTs} (Ref. 16) were used for chlorides, bromides, and tosylates respectively. b) Determined from the rates in 80/20 to 30/70 (v/v) acetone/water binary mixtures. c) Data taken from Ref. 14.

Table 5. α-Deuterium Kinetic Isotope Effects[a)]

Substrate	Solvent	$10^5 \times k/\mathrm{s}^{-1}$	$k_{\mathrm{H}}/k_{\mathrm{D}}$
1a-Cl	97T	769.3 ±8.4[b)]	
1a-Cl-α-d_1	97T	659.3 ±5.6[c)]	1.167±0.023
1a-Cl	40E	59.61±0.50[c)]	
1a-Cl-α-d_1	40E	51.27±0.50[c)]	1.163±0.021

a) At 25 °C. b) Average of three runs. c) Average of two runs.

Table 6. Substituent Effect on the Solvolysis of **1-Cl**[a)]

Substrate	$10^5 \times k/\mathrm{s}^{-1}$	$r^{\mathrm{b)}}$	ρ
1b-Cl	1100		
1c-Cl	85.2		
1a-Cl	59.6	1.16	−3.71[c)]
1d-Cl	23.6		
1e-Cl	1.91		

a) In 40% aq ethanol at 25 °C. b) Resonance parameter in the Yukawa-Tsuno equation (Ref. 17). c) R=0.998; SD=0.067.

Table 7. Salt Effects on the Solvolysis of **1a-Cl**[a)]

Salt	[Salt]/M	$10^5 \times k/\mathrm{s}^{-1}$	k_{rel}
None		59.6	1.0
LiCl	0.100	62.8	1.05
LiBr	0.100	65.1	1.11
$\mathrm{LiClO_4}$	0.040	65.6	1.11

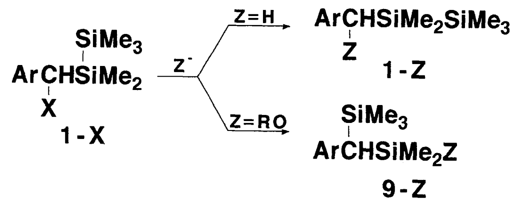
a) In 40% aq ethanol at 25 °C.

Product Studies. Reductive dehalogenation of **1a-Br** and **2-Cl** with $\mathrm{LiAlH_4}$ cleanly gave the corresponding reduction products, benzylpentamethyldisilane (**1a-H**) and 2,2-dimethyl-2-silaindan (**2-H**), suggestive of structural conservation in $\mathrm{S_N2}$-type reactions. In contrast, a solvolytic reaction of **1a-Br** with ethanol in the presence or absence of a buffer base quantitatively gave a 1,2-$\mathrm{SiMe_3}$ rearranged compound, an ethoxysilane **9a-OEt** (Scheme 2). We could not detect the formation of a structure-retained product **1a-OEt**. Similarly, buffered

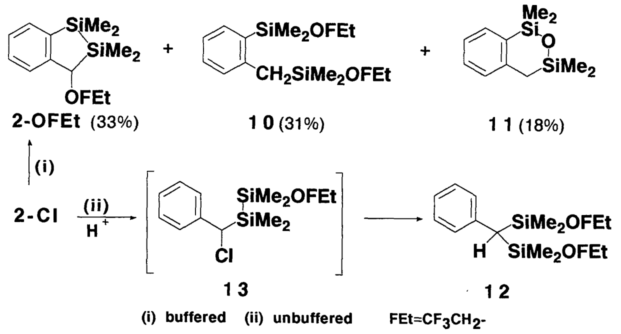
Table 8. Activation Parameters

Substrate	Solvent	Temp	$10^5 \times k$	$\Delta H^{\ddagger}_{298}$	$\Delta S^{\ddagger}_{298}$
		°C	s^{-1}	kcal mol^{-1}	cal K^{-1} mol^{-1}
1a-Br	97T	25.0	6200[a]	14.5	−15.5
		20.5	4180		
		11.7	1900		
		3.7	871		
	40E	33.5	1610		
		25.0	668	17.1	−9.0
		16.0	252		
		11.7	163		
1a-Cl	40E	46.2	486		
		33.5	144		
		25.0	59.6	18.1	−12.5

a) Extrapolated value.



Scheme 2.



Scheme 3.

solvolyses in TFE and in 50% aq acetone respectively gave rearranged compounds, a (2,2,2-trifluoroethoxy)silane **9a-OFEt** (FEt=CH_2CF_3) and a silanol **9a-OH**, as a single product in each case. The same was true for the chlorides **1a-Cl** and **1b-Cl**. The 1,2-$SiMe_3$ migration must be directly associated with the ionization of the C–X bond of the halides **1-X**. The 1,2-silyl rearrangement has already been observed in several cationoid reactions of (halomethyl)disilanes.[8] A related 1,2-alkyl shift from the α-silicon to a carbenium carbon has also been reported by Apeloig and Stanger in the solvolysis of 2-trimethylsilyl-2-adamantyl *p*-nitrobenzoate.[18]

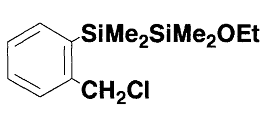
The solvolysis of **1b-Cl** in TFE in the presence of 1 M sodium cyanotrihydroborate gave a mixture of two rearranged products, **9b-OFEt** and a silane **9b-H**, in a ratio of 95:5, while the solvolysis in ethanol in the presence of 1 M sodium cyanotrihydroborate afforded a mixture of **9b-OEt** and a reduction product **1b-H** in the ratio 98:2. Apparently, an $\mathrm{S_N}2$ reduction by the hydroborate can compete with the $\mathrm{S_N}1$ solvolysis in ethanol of low ionizing power, but not in a strong ionizing solvent, TFE ($Y_{\mathrm{OTs}}=-1.75$ and 1.80 for ethanol and TFE respectively). On the other hand, the hydroborate can attack a solvolysis intermediate in competition with solvent in a weakly nucleophilic solvent TFE but not in a strongly nucleophilic solvent ethanol ($N_{\mathrm{OTs}}=-3.0$ and 0.0 for TFE and ethanol respectively[16]).

The halides **1-X** underwent the skeletal rearrangement thermally as well; for example, **1a-Cl** quantitatively gave a chorosilane **9a-Cl** on heating at 150 °C. We also examined a silver(I)-assisted reaction of **1a-Br**; it reacted instantaneously with silver perchlorate in THF at −78 °C and gave **9a-OEt** when ethanol was added to the mixture. Since **1a-Br** did not react with ethanol at this temperature, a precursory species must be a silyl perchlorate **9a-OClO$_3$**.

The cyclic halide **3-Cl** solvolyzed in aq acetone cleanly to give an expected alcohol **3-OH**, as does the bromide **3-Br**.[14] On the other hand, solvolytic reactions of **2-Cl** were complicated. A buffered reaction of **2-Cl** with TFE gave two solvolysis products, a structure-retained ether **2-OFEt** (33%) and an open compound **10** (31%), together with a cyclic disiloxane **11** (18%) which was presumably formed from **10** during isolation processes (Scheme 3). The result is consistent with the observed good first-order kinetics for the buffered solvolysis in 97T.

On the other hand, an unbuffered reaction with TFE led to the formation of a completely different compound, α,α-bis[dimethyl(2,2,2-trifluoroethoxy)silyl]toluene **12**. Initial protodesilylation of **2-Cl** accounts for this; as soon as hydrogen chloride is liberated on solvolysis, it must catalyze a ring opening of **2-Cl** to an α-(disilanyl)benzyl chloride **13** which would give **12** upon solvolysis (Scheme 3).

Furthermore, a buffered reaction of **2-Cl** with ethanol at 25 °C did not give solvolysis products; instead, *o*-(2-ethoxytetramethyldisilanyl)benzyl chloride **14** was obtained as the major product. Although precise mechanism for the formation of **14** is not clear at present, **2-Cl** appears to undergo solvolysis only in strongly ionizing but weakly nucleophilic media like TFE; a strongly nucleophilic solvent like ethanol prefers attack on the α-silicon rather than it promotes ionization of the C–Cl bond. Oxidation of the Si–Si bond in **2-Cl** occurred predominantly at higher temperatures. For example, an attempted solvolysis in 70% aq acetone at 70 °C led to the formation of a cyclic disiloxane **15** as the major product. Compound **2-Cl** was rapidly oxidized to **15** when heated in carbon tetrachloride in the air.



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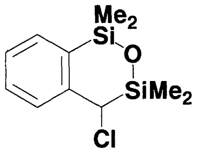

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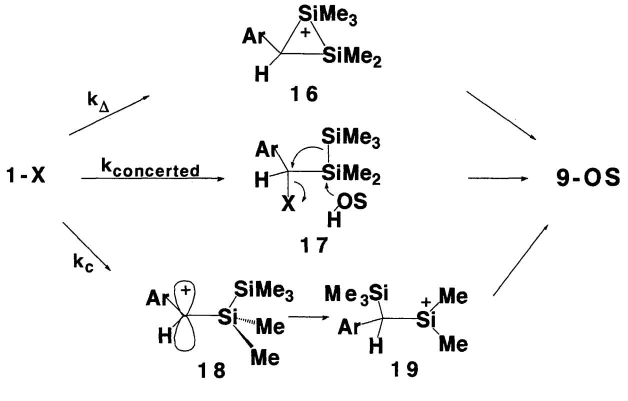
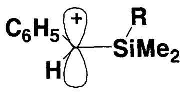
Discussion

Mechanism. Two observations characterizing the solvolysis of **1a-X** are a marked rate acceleration of $(0.34—1.1)\times10^5$ by the α-SiMe$_2$SiMe$_3$ group relative to the structurally related SiMe$_2$(*t*-Bu) group (Table 3) and the clean formation of the rearranged product via a 1,2-SiMe$_3$ shift. The accelerated rate coupled with the skeletal rearrangement is a general feature suggestive of neighboring group participation[19] and hence a σ-participation mechanism (k_Δ) via a bridged siliconium ion intermediate **16** is seemingly operative. However, these findings can also be accounted for by two other mechanisms. They are a concerted pathway[8] involving simultaneous solvent attack on the α-silicon, migration of an SiMe$_3$ group from the silicon to the benzylic carbon, and cleavage of the C–X bond as illustrated by the structure **17** and a simple ionization mechanism (k_c) via rate-determining formation of an open α-(pentamethyldisilanyl)benzyl cation **18** which rapidly decays to the rearranged product most likely via a silylenium ion **19** (Scheme 4).

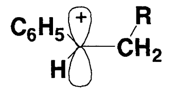


Scheme 4.

On the precise mechanism the following findings are instructive. First, the halides **1a-X** exhibit high sensitivities to the solvent ionizing power for their solvolyses in acetone–water binary solvent mixtures (Table 4), i.e., m=0.91 and 0.98 for the bromide and chloride respectively, supporting an unassisted ionization. Noteworthy is a striking resemblane in the mY plot for **1a-Br** to that for the solvolysis of the structurally related α-trialkylsilyl compound **5-OTs** (Fig. 1) indicative of a close similarity in the mechanism between the two solvolysis reactions. We have proposed the k_c mechanism for the solvolysis of **5-OTs** via a benzylic cation **20**.[14] Thus, the solvent effect is obviously more in accord with the k_c mechanism via **18** than the k_Δ and concerted mechanisms. Aq ethanol of low water content (80E and 90E) deviates upward from the aq acetone correlation line; however, this is not a result of nucleophilic solvent assistance because such interaction should lead to significant downward deviations for T solvents which are much less nucleophilic than aq acetone against the observation. The upward deviation for 97T by about one log k unit is striking but this is not associated with the 1,2-SiMe$_3$ rearrangement either because a similar large deviation of 97T is also observed for **5-OTs** which does not undergo a skeletal rearrangement. The diverging mY plot instead of a single linear correlation for A, E, and T solvent series does not mean a mechanistic shift from the k_c solvolysis but probably arises from the different responses to the ionizing power between the present benzylic derivatives and the standard adamantyl compounds.[14]



20; R=*t*-Bu



21; R=SiMe$_3$
22; R=*t*-Bu

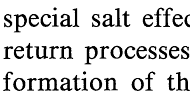
Second, the α-KIEs (k_H/k_D) of 1.16—1.17 (Table 5) for the solvolysis of the chloride **1a-Cl** are comparable with those (1.15—1.16) for the related 1-arylethyl chlorides which undergo S$_N$1 solvolysis.[20] The result suggests that **1a-Cl** solvolyzes via a transition state structurally close to the cation **18**.

Thirdly, the LArSR analysis reveals that the transition state of the solvolysis of **1-Cl** requires a rather high resonance demand $r>1$ (Table 6). This is obviously incompatible with the k_Δ and concerted mechanisms and is most reasonably accommodated with the k_c mechanism. Noteworthy is a marked reduction in ρ value (−3.7) as compared to typical values around −5.5 for the S$_N$1 solvolysis of structurally related α-alkylbenzyl compounds.[21,22] This is undoubtedly associated with low ionization potentials of the Si–Si σ bonds.[3] The positive charge on the benzylic carbon must be significantly delocalized to the Si–Si bond mainly through hyperconjugation.[23]

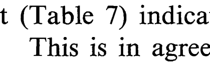
Thus, the combined results lead us to conclude the k_c mechanism for the solvolysis of α-(pentamethyldisilanyl-)benzyl halides. It is worth stating that 1-phenyl-2-(trimethylsilyl)ethyl trifluoroacetate **7-OTFA** has been shown to solvolyze also by the k_c mechanism via an open benzylic cation **21**.[1] The k_c solvolysis for these benzylic systems is in agreement with recent experimental[10] and theoretical[12] results that an open bisected structure of 2-silylalkyl cations is more stable than a bridged form except for the primary cation where a bridged form is slightly more favorable than an open structure.

The absence of the common ion rate depression and special salt effect (Table 7) indicates unimportance of return processes. This is in agreement with the clean formation of the rearranged products suggestive of a rapid decay of the cation **18** to the products via a 1,2-$SiMe_3$ shift. It is of interest whether the silylenium ion **19** is really involved in the product-forming step. We have no compelling evidence for the formation of **19** but the rearrangement of **18** to **19** appears energetically favorable.[24,25]

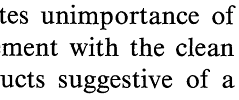
Previously,[14] we showed the S_N1 solvolysis of 2,2-dimethyl-2-silaindan-1-yl bromide (**3-Br**). The same mechanism would probably be operative in the solvolysis of the chloride **3-Cl**. The *m* value of 0.98 (Table 4) strongly supports this. Judging from a structural similarity, we can assume the k_c solvolysis of the related chloride **2-Cl** in 97T. The formation of **2-OFEt** and **10** is compatible with intervention of 1,1,2,2-tetramethyl-1,2-disilaindan-3-yl cation **23**; the cation gives either **2-OFEt** directly or **10** after cleavage of the Si–Si bond presumably via a silene **24** or a silacyclobutene **25**.



23



24



25

β-Silicon Effect. The $SiMe_2SiMe_3$ group exerts α- and β-silicon effects on the stability of the adjacent carbocations. The β-silicon effect can be estimated by comparing the rates of the α-(pentamethyldisilanyl)benzyl and the structurally related α-(trialkylsilyl)benzyl compounds. Although the rates of solvolysis of α-alkylbenzyl compounds are subjected to the steric effect of the α-alkyl group,[26] we have shown that there is little difference in the steric effect between the two α-trialkylsilyl groups, $SiMe_3$ and $SiMe_2$(*t*-Bu), in the benzylic k_c solvolysis.[14] This suggests that the steric effect of the α-$SiMe_2SiMe_3$ group is practically the same as that of $SiMe_2$(*t*-Bu) or $SiMe_3$. Thus, the *k*(**1a-Br**)/*k*(**5-Br**) rate ratios of $(0.34—1.1)\times10^5$ (Table 3) provide a reasonable estimate for the β-silicon effect of the pentamethydisilanyl group indicating the solvolytic generation of **18** to be 6.2—6.8 kcal mol^{-1} (1 kcal=4.18 kJ) energetically more favorable than that of **20**. A similar β-silicon effect has also been observed in the related k_c solvolysis of α-alkylbenzyl derivatives (Table 3); **7-OTFA** solvolyzes 2.99×10^5 times more rapidly than **8-OTFA** suggesting the formation of the cation **21** to be 7.5 kcal mol^{-1} more favorable than that of the corresponding β-alkyl cation **22**.[1]

It is worth stating that despite the huge β-silicon effect of the $SiMe_2SiMe_3$ group relative to $SiMe_2$(*t*-Bu), the overall effect is comparable to that of methyl (Table 1). This arises from the fact that an α-silyl group exerts a marked deactivating effect in the benzylic solvolysis. For example, **6-Br** solvolyzes $(1.6—3.3)\times10^4$ times less rapidly than **4-Br** due to the electronic and steric effects of the trimethylsilyl group relative to methyl.[14]

Noteworthy is the fact that **2-Cl** solvolyzes slightly less rapidly than **3-Cl** (Table 3). This means that the Si–Si bond orthogonal to the leaving group does not enhance the ionization of the adjacent C–Cl bond at all. The result not only shows a striking conformational dependence of the β-silicon effect but also indicates unimportance of the inductive electron release from the β-silicon. The observed small inverse rate ratio, *k*(**2-Cl**)/*k*(**3-Cl**)=0.209, can be attributed to differences in the electronic effects and/or the steric effects between the silyl group and the alkyl group at the ortho position (*A*-value, σ_I, and $\sigma_\mathrm{R}{}^\circ$ are ca. 2.5, −0.10, and 0.12 for $SiMe_3$ and 1.70, −0.01, and −0.16 for CH_3.[27,28]).

The β-silicon effect depends on the electronic demands of the carbenium carbon of the parent cation.[10,12] For example, a theoretical study indicates that the stabilization energy of a cation $R^1R^2C^+–CH_2R^3$ afforded by replacement of R^3 from hydrogen to SiH_3 increases from 15.9 kcal mol^{-1} for *t*-butyl cation (R^1=R^2=Me) to 22.1 kcal mol^{-1} for 1-methylethyl cation (R^1=Me, R^2=H) which is 18 kcal mol^{-1} less stable than *t*-butyl cation.[12] Therefore, in order to compare the β-silicon effect in the two benzylic cation systems, $PhHC^+–SiMe_2–R$ and $PhHC^+–CH_2–R$ (R=$SiMe_3$ and *t*-Bu), we must consider the stabilities of the parent cations (R=*t*-Bu) in the two systems, i.e., **20** and **22**. We can assume **22** to be 3—4 kcal mol^{-1} more stable than **20** in view of the fact that the solvolytic generation of 2,2-dimethyl-1-indanyl cation is 3—4 kcal mol^{-1} more favorable than that of 2,2-dimethyl-2-silaindan-1-yl cation.[14] Consequently, a more pronounced β-silicon effect than the observed value of 7.5 kcal mol^{-1} is expected in the $PhHC^+–CH_2R$ system if **22** exhibits the same electronic demand as that of **20**; a value of more than 8.5 kcal mol^{-1} can be evaluated if we simply assume that the difference in stability between *t*-butyl cation and 1-methylethyl cation by 18 kcal mol^{-1} causes a change in the β-silicon effect by about 6 kcal mol^{-1}. Thus, it is concluded that the hyperconjugative interaction of the Si–Si bonds with the empty 2p orbital of the benzylic cation is 1—2 kcal mol^{-1} less effective than that of the corresponding C–Si bonds in agreement with the earlier suggestion that π–σ(Si–Si) conjugation is weaker than π–σ(C–Si) conjugation.[23,29]

Finally, we must point out that a direct comparison of the solvolysis rates of the two α-disilanyl compounds, **1a-Cl** and **2-Cl**, may lead to an erroneous conclusion; a k(**1a-Cl**)/k(**2-Cl**) rate ratio of 20 would suggest a very small rate enhancement by the Si–Si bond through hyperconjugation contrary to the rate enhancement of 10^5 mentioned earlier. This is obviously not justified. Since there is a marked intrinsic difference in reactivity between 1-indanyl ring system and the corresponding open benzylic system,[14,30] the k(**1a-Cl**)/k(**2-Cl**) rate ratio itself tells us nothing about the effect of the Si–Si bonds. It should be noted that a cyclic bromide **3-Br** is 7.1×10^3 times as reactive as an open compound **6-Br**.[14] If we take this rate factor as an effect of the indanyl ring system, we can estimate the rate (k_{calcd}) of solvolysis of **2-Cl** from 7.1×10^3 times k(**1a-Cl**), i.e., $k_{\text{calcd}}=56\ \text{s}^{-1}$ in 97T; however, **2-Cl** in fact solvolyzes with a rate constant of $k_{\text{obsd}}=3.86\times10^{-4}\ \text{s}^{-1}$ which is 1.5×10^5 times smaller than the expected one. The actual low reactivity of **2-Cl** undoubtedly arises from the orthogonal alignment of the Si–Si bond to the empty p-orbital of the carbenium carbon incapable of hyperconjugation. Thus, the $k_{\text{calcd}}/k_{\text{obsd}}$ rate ratio of ca. 10^5 corresponds to a rate enhancement by the Si–Si bond mainly through hyperconjugation in the open system in good agreement with the earlier discussion.

Experimental

IR spectra were recorded on a Hitachi R-215 spectrophotometer. NMR spectra were recorded on a Hitachi R-20B spectrometer in carbon tetrachloride. Mass spectra were recorded on a Hitachi M-60 mass spectrometer. Kinetic measurements were performed with a Hitachi 220A spectrophotometer equipped with a programmed data printer. GLC analysis was performed with a Hitachi 163 gas chromatograph by using glass columns (6 mm×1.5 and 2.0 m) packed with 10% Silicone DC 550 on Chamelite CS (Column A) and 25% Apiezon grease L on Chromosorb W (Column B).

Materials. α-(Pentamethyldisilanyl)benzyl Bromide (**1a-Br**), α-(pentamethyldisilanyl)benzyl chloride (**1a-Cl**), its *p*-Me, *m*-Me, *p*-Cl, and *m*-Cl derivatives (**1b-Cl—1e-Cl**), and α-deuterio-α-(pentamethyldisilanyl)benzyl chloride (**1a-Cl-d_1**) were prepared by in situ coupling reaction of the corresponding benzyl halides with chloropentamethyldisilane in the presence of LDA. The following procedure for preparation of **1a-Br** is representative.

Into a stirred solution of LDA prepared from butyllithium (20 cm^3, 1.7 M in hexane) and diisopropylamine (3.5 g) in THF (25 cm^3) was added dropwise a solution of chloropentamethyldisilane (5.1 g) in THF (5 cm^3) at −78 °C and subsequently a solution of benzyl bromide (5.2 g) in THF (5 cm^3) over a period of 15 min at −78 °C. The resulting mixture was stirred overnight at that temperature. Pentane (75 cm^3) was added, the mixture poured into water, and separated. Water layer was extracted with pentane (50 cm^3). A combined organic layer was washed with 10% sulfuric acid, aq $NaHCO_3$, aq NaCl, and dried ($MgSO_4$). Solvent was removed on a rotary evaporator and the residual oil was distilled to give 5.32 g (58%) of **1a-Br** as a colorless oil, bp 98—99 °C (1 Torr; 1 Torr=133.3 Pa): IR 1600, 1245, 835, 800, 695 cm^{-1}; ^{1}H NMR δ=0.0 (9H, s), 0.13 (3H, s), 0.19 (3H, s), 4.32 (1H, s), 7.20 (5H, almost s). Found: C, 48.01; H, 6.96%. Calcd for $C_{12}H_{21}BrSi_2$: C, 47.83; H, 7.02%.

1a-Cl: Bp 94—95 °C (3 Torr); IR 1595, 1245, 1065, 1025, 830, 800 cm^{-1}; UV (95% EtOH) $\lambda_{\max}$ (log ε) 207 (4.16), 229 (4.01); ^{1}H NMR δ=0.02 (9H, s), 0.07 (3H, s), 0.13 (3H, s), 4.38 (1H, s), 7.19 (5H, almost s). Found: C, 55.90; H, 8.17%. Calcd for $C_{12}H_{21}ClSi_2$: C, 56.10; H, 8.24%.

1a-Cl-d_1: Bp 87—88 °C (1 Torr); IR 1245, 950, 830, 795 cm^{-1}; ^{1}H NMR δ=0.02 (9H, s), 0.07 (3H, s), 0.13 (3H, s), 7.19 (5H, almost s). Found: C, 55.88; H, 8.28%. Calcd for $C_{12}H_{20}DClSi_2$: C, 55.88; H, 8.22%. ^{1}H NMR analysis indicated isotopic purity of more than 99%.

1b-Cl: Bp 106—107 °C (1 Torr); IR 1245, 1105, 830, 795 cm^{-1}; ^{1}H NMR δ=0.02 (9H, s), 0.06 (3H, s), 0.11 (3H, s), 4.33 (1H, s), 7.03 (4H, almost s). Found: C, 57.43; H, 8.42%. Calcd for $C_{13}H_{23}ClSi_2$: C, 57.63; H, 8.56%.

1c-Cl: Bp 107—108 °C (1 Torr); IR 1245, 1120, 865, 830, 800 cm^{-1}; ^{1}H NMR δ=0.02 (9H, s), 0.07 (3H, s), 0.11 (3H, s), 2.31 (3H, s), 4.33 (1H, s), 6.8—7.2 (4H, m). Found: C, 57.41; H, 8.43%. Calcd for $C_{13}H_{23}ClSi_2$: C, 57.63; H, 8.56%.

1d-Cl: Bp 92—93 °C (0.5 Torr); IR 1245, 1120, 1090, 1010, 830, 790 cm^{-1}; ^{1}H NMR δ=0.05 (12H, s), 0.11 (3H, s), 4.35 (1H, s), 7.18 (4H, A_2B_2, J=9.0 Hz). Found: C, 49.19; H, 6.86%. Calcd for $C_{12}H_{20}Cl_2Si_2$: C, 49.47; H, 6.92%.

1e-Cl: Bp 105—106 °C (1 Torr); IR 1245, 1110, 1090, 1075, 880, 830, 800 cm^{-1}; ^{1}H NMR δ=0.05 (9H, s), 0.08 (3H, s), 0.13 (3H, s), 4.34 (1H, s), 7.14 (4H, m). Found: C, 49.27; H, 6.92%. Calcd for $C_{12}H_{20}Cl_2Si_2$: C, 49.47; H, 6.92%.

1,1,2,2-Tetramethyl-1,2-disilaindan-3-yl Chloride (2-Cl): Into a solution of *o*-bromobenzyl chloride (7.65 g, 37.2 mmol) in a mixture of THF (130 cm^3) and hexane (40 cm^3) was added butyllithium (25 cm^3, 1.6 M in hexane) at temperature around −100 °C and the mixture was stirred for 10 min at −100 °C under argon. A solution of 1,2-dichlorotetramethyldisilane (7.0 g) in THF (15 cm^3) was added at such a rate as to maintain the temperature of the solution below −90 °C. The bath was removed and the mixture was allowed to warm to room temperature. Solvent was removed by distillation under reduced pressure. Dry pentane (150 cm^3) was added to the residue and decanted. Pentane was removed on a rotary evaporator and the residue was distilled to give 7.02 g (68%) of *o*-(2-chlorotetramethyldisilanyl)benzyl chloride: Bp 124—125 °C (2.5 Torr); ^{1}H NMR δ=0.45 (6H, s), 0.56 (6H, s), 4.57 (2H, s), 7.18—7.56 (4H, m). Into a solution of LDA (23 mmol) in THF (20 cm^3) was added a solution of this compound in THF (5 cm^3) at −78 °C and the mixture was stirred for 2 h at −78 °C. Usual workup gave 2.90 g (57%) of **2-Cl** as a colorless oil: Bp 80—80.5 °C (0.5 Torr); IR 1585, 1250, 1130, 995, 860, 830, 735 m^{-1}; UV(CH_3CN) $\lambda_{\max}$ (log ε) 208 (4.22), 220 (shoulder, 3.92), 265 (shoulder, 2.85) 280 nm (2.55); ^{1}H NMR δ=0.20 (3H, s), 0.31 (3H, s), 0.35 (3H, s), 0.41 (3H, s), 4.46 (1H, s), 7.08—7.65 (4H, m). Found: C, 54.80; H, 7.12%. Calcd for $C_{11}H_{17}ClSi_2$: C, 54.86; H, 7.12%.

2,2-Dimethyl-2-silaindan-1-yl Chloride (3-Cl): A solution of 2,2-dimethyl-2-silaindan (3.24 g, 20 mmol),[14] sulfuryl chloride (1.35 g), and benzoyl peroxide (24 mg) in carbon tetrachloride (5 cm^3) was heated under reflux for 30 min. Usual workup gave 1.2 g of **3-Cl:** Bp 86—87 °C (4 Torr); IR 1600, 1255, 1130, 1115, 850, 830, 820 cm^{-1}; UV (CH_3CN) $\lambda_{\max}$ (log ε) 203 (4.39), 225 (3.76), 2.77 nm (2.92); ^{1}H NMR δ=0.22

(3H, s), 0.40 (3H, s), 1.94 (1H, d, J=17.4 Hz), 2.22 (1H, d, J=17.4 Hz), 4.30 (1H, s), 6.95—7.56 (4H, m). Found: C; 60.95; H, 6.61%. Calcd for $C_{10}H_{16}ClSi$: C, 61.05; H, 6.66%.

Kinetics. Purification of solvents and kinetic procedure for rate measurements have been described elsewhere.[14] All the solvolysis reactions were followed UV spectrometrically by measuring either decrease in a reactant [243 nm for **1a-Br** and **1a-Cl** to **1e-Cl**, 245 nm for **2-Cl**, and 240 nm for **3-Cl**] or increase in a produced acid at 402.5 nm as its acridinium salt. The solvolyses followed excellent first-order kinetics over 3 to 4 half-lives (correlation coefficient R>0.9999).

Product Studies. Solvolysis of 1-X: Solvolytic reactions of **1a-Br**, **1a-Cl**, and **1b-Cl** in TFE, ethanol, and aq acetone were carried out by using 0.01—0.1 M solutions containing equimolar amounts of 2,6-dimethylpyridine at 25 °C and higher temperatures in some cases. In all cases, a single product was formed almost quantitatively and the following products were characterized.

2-Ethoxy-2,4-dimethyl-3-phenyl-2,4-disilapentane (9a-OEt): IR 1250, 1200, 1105, 1080, 1030, 940, 905, 840, 780 cm^{-1}; ^{1}H NMR δ=0.02 (12H, s), 0.06 (3H, s), 1.15 (3H, t, J=7.2 Hz), 1.52 (1H, s), 3.61 (2H, q, J=7.2 Hz), 6.6—7.3 (5H, m). Found: C, 62.80; H, 9.71%. Calcd for $C_{14}H_{26}OSi_2$: C, 63.09; H, 9.83.

2,4-Dimethyl-3-phenyl-2,4-disilapentan-2-ol (9a-OH): IR 3400, 1600, 1250, 1200, 1030, 845 cm^{-1}; ^{1}H NMR δ=0.03 (12H, s), 0.12 (3H, s), 1.35 (1H, s, disappeared on addition of D_2O), 1.51 (1H, s), 6.8—7.3 (5H, m); MS m/z 238 (M$^+$, 10), 223 (23), 148 (60), 147 (100), 73 (30). Found: C, 60.17; H, 9.31%. Calcd for $C_{12}H_{22}OSi_2$: C, 60.45; H, 9.30%.

2,4-Dimethyl-3-phenyl-2-(2,2,2-trifluoroethoxy)-2,4-disilapentane (9a-OFEt): IR 1600, 1300, 1285, 1255, 1160, 1030, 960, 850, 695 cm^{-1}; ^{1}H NMR δ=0.02 (9H, s), 0.09 (3H, s), 0.14 (3H, s), 1.55 (1H, s), 3.80 (2H, q, J=8.6 Hz), 6.7—7.2 (5H, m). Pure sample was obtained by GLC. Found: C, 52.80; H, 7.44%. Calcd for $C_{14}H_{23}F_3OSi_2$: C, 52.47; H, 7.23%.

2,4-Dimethyl-3-(4-methylphenyl)-2,4-disilapentan-2-ol (9b-OH): IR 3390, 1600, 1245, 1215, 1195, 1030, 850, 770 cm^{-1}; ^{1}H NMR δ=0.02 (9H, s), 0.04 (3H, s), 0.10 (3H, s), 1.47 (1H, s), 1.78 (1H, disappeared on addition of D_2O), 2.26 (3H, s), 6.88 (4H, AA′BB′, J=9.0 Hz).

2-Ethoxy-2,4-dimethyl-3-(4-methylphenyl)-2,4-disilapentane (9b-OEt): IR 1605, 1250, 1080, 1030, 945, 860, 835, 780 cm^{-1}; ^{1}H NMR δ=0.0 (12H, s), 0.03 (3H, s), 1.14 (3H, t, J=7.0 Hz), 1.44 (1H, s), 2.25 (3H, s), 3.59 (2H, q, J=7.0 Hz), 6.83 (4H, AA′BB′, J=9.0 Hz). Found: C, 71.10; H, 11.01%. Calcd for $C_{15}H_{28}OSi_2$: C, 71.37; H, 11.18%.

3-(4-Methylphenyl)-2-(2,2,2-trifluoroethoxy)-2,4,4-trimethyl-2,4-disilapentane (9b-OFEt): ^{1}H NMR δ=0.0 (9H, s), 0.07 (3H, s), 0.13 (3H, s), 1.62 (1H, s), 2.25 (3H, s), 3.81 (2H, q, J=9.0 Hz), 6.68 (4H, A_2B_2).

Solvolysis of 2-Cl: Compound **2-Cl** (399 mg) was dissolved in TFE (15 cm^3) containing acetone (1.0 cm^3) and 2,6-dimethylpyridine (182 mg) and the solution was allowed to stand for 3 d at 25 °C. A crude oil (464 mg) obtained after usual workup was shown to be a mixture of four compounds in the ratio 20:38:36:4 by GLC [Column A, 180 °C; retention time (t_R):4.0, 6.4, 13.2, and 18.4 min, respectively]. The first three components were isolated by GLC and were respectively assinged to 1,1,3,3-tetramethyl-1,3-disilaisochroman (**11**), 1,1,2,2-tetramethyl-3-(2,2,2-trifluoroethoxy)-1,2-disilaindan (**2-OFEt**), and α,o-bis[dimethyl(2,2,2-trifluoroethoxy)silyl]toluene (**10**) from the following spectral data.

2-OFEt: IR 1590, 1300, 1280, 1250, 1160, 1115, 965, 830, 670 cm^{-1}; ^{1}H NMR δ=0.04 (3H, s), 0.31 (3H, s), 0.35 (6H, s), 3.61 (2H, q, J=8.9 Hz), 4.31 (1H, s), 6.91—7.77 (4H, m). Found: C, 51.02; H, 6.30%. Calcd for $C_{13}H_{19}F_3OSi_2$: C, 51.29; H, 6.29%.

10: IR 1590, 1305, 1290, 1260, 1170, 965, 850, 840 cm^{-1}; ^{1}H NMR δ=0.14 (6H, s), 0.44 (6H, s), 2.42 (2H, s), 3.74 (2H, q, J=8.4 Hz), 3.88 (2H, q, J=8.4 Hz), 6.90—7.53 (4H, m). Found: C, 44.69; H, 5.69%. Calcd for $C_{15}H_{22}F_6O_2Si_2$: C, 44.54; H, 5.48%.

11: ^{1}H NMR δ=0.09 (6H, s), 0.31 (6H, s), 2.08 (2H, s), 6.9—7.4 (4H, m). Found: C, 59.38; H, 8.15%. Calcd for $C_{11}H_{18}OSi_2$: C, 59.41; H, 8.16%.

A solution of **2-Cl** (50 mg) in TFE (5 cm^3) was allowed to stand for 3 d at 25 °C. A crude oil (55 mg) obtained after usual workup was shown to be a mixture of 2,4-dimethyl-2,4-bis(2,2,2-trifluoroethoxy)-3-phenyl-2,4-disilapentane (**12**) and other two unidentified compounds in the GLC area ratio of 8:1:1.

12: ^{1}H NMR δ=0.13 (6H, s), 0.17 (6H, s), 1.73 (1H, s), 3.82 (4H, q, J=8.4 Hz), 6.82—7.32 (5H, m). Found: C, 45.01; H, 5.78%. Calcd for $C_{15}H_{22}F_6O_2Si_2$: C, 44.54; H, 5.48%.

The chloride **2-Cl** (420 mg) was heated in ethanol (25 cm^3) in the presence of triethylamine (185 mg) at 60 °C for 3 d. A crude oil obtained after usual workup was subjected to bulb-to-bulb distillation (130 °C, 3 Torr) to give 406 mg (81%) of 1-ethoxy-2-[o-(chloromethyl)phenyl]-1,1,2,2-tetramethyldisilane (**14**): IR 1250, 1105, 1075, 945, 830, 790, 765, 735 cm^{-1}; ^{1}H NMR δ=0.18 (6H, s), 0.44 (6H, s), 1.10 (3H, t, J=7.2 Hz), 3.54 (2H, q, J=7.2 Hz), 4.63 (1H, s), 7.04—7.56 (4H, m). Found: C, 54.72; H, 8.15%. Calcd for $C_{13}H_{23}ClOSi_2$: C, 54.42; H, 8.08%.

The chloride **2-Cl** (60 mg) was heated in 70% aq acetone (25 cm^3) at 70 °C for 4 d. A crude oil obtained after workup was subjected to chromatography over silica gel eluting with benzene to give 26 mg (40%) of 4-chloro-1,1,3,3-tetramethyl-1,3-disilaisochroman (**15**): Mp 77—78 °C; IR 1595, 1255, 1330, 1075, 990, 880, 855, 825, 790, 740 cm^{-1}; ^{1}H NMR δ=0.12 (3H, s), 0.33 (3H, s), 0.40 (3H, s), 4.18 (1H, s), 7.08—7.50 (4H, m). Found: C, 51.44; H, 6.61%. Calcd for $C_{11}H_{17}ClOSi_2$: C, 51.44; H, 6.67%.

Reactions of 1a-Br, 1b-Cl, and 2-Cl with $LiAlH_4$: A reaction of **1a-Br** (1.10 g) with $LiAlH_4$ (0.3 g) in THF (25 cm^3) (room temperature, 1 h) gave 672 mg (82%) of benzylpentamethyldisilane (**1a-H**): Bp 125—126 °C (22 Torr); IR 1600, 1250, 835, 805, 785, 695 cm^{-1}; ^{1}H NMR δ=0.0 (15H, almost s), 2.11 (2H, s), 6.75—7.30 (5H, s). Found: C, 64.77; H, 9.91%. Calcd for $C_{12}H_{22}Si_2$: C, 64.80; H, 9.97%. A reaction of **1b-Cl** with $LiAlH_4$ in THF cleanly gave **1b-H:** ^{1}H NMR δ=0.0 (15H, s), 2.06 (2H, s), 2.27 (3H, s), 6.67—7.14 (4H, m). Found: C, 65.80; H, 10.03%. Calcd for $C_{13}H_{24}Si$: C, 66.02; H, 10.23%.

A reaction of **2-Cl** (471 mg) with $LiAlH_4$ (100 mg) in THF (5 cm^3) gave 1,1,2,2-tetramethyl-1,2-disilaindan (**2-H**)[6] (353 mg, 87%).

Oxidation of 2-Cl: A solution of **2-Cl** (150 mg) in carbon tetrachloride (20 cm^3) was heated at 70 °C for 2 h, while a slow stream of oxygen being bubbled into the solution. Solvent was removed and the residue was recrystallized from pentane to give 123 mg (83%) of **15**.

Thermolysis of 1-Cl: **1a-Cl** was heated to 150 °C for 1 h in a glass ampoule. ^{1}H NMR analysis indicated clean formation of 1-chloro-2,4-dimethyl-3-phenyl-2,4-disilapentane (**9a-Cl**):

IR 1250, 1200, 1030, 840, 800, 700 cm^{-1}; ^{1}H NMR δ=0.07 (9H, s), 0.35 (6H, s), 1.73 (1H, s), 6.86—7.24 (5H, m). Similarly, **1e-Cl** cleanly gave **9e-Cl** on heating to 150 °C: IR 1250, 1190, 1030, 860, 830, 800, 780 cm^{-1}; ^{1}H NMR δ=0.06 (9H, s), 0.34 (6H, s), 1.67 (1H, s), 2.27 (3H, s), 6.72—7.05 (4H, m). Reduction of **9b-Cl** with $LiAlH_4$ in ether gave the corresponding hydrosilane **9b-H:** IR 2110, 1250, 1030, 890, 850, 830 cm^{-1}; ^{1}H NMR δ=0.04 (3H, s, J=3.6 Hz), 0.0 (9H, s), 0.05 (3H, d, J=3.6 Hz), 1.39 (1H, d, J=3.6 Hz), 2.23 (3H, s), 3.87—4.23 (1H, m), 6.61—7.04 (4H, m). Found: C, 65.55; H, 10.17%. Calcd for $C_{12}H_{24}Si_2$: C, 66.02; H, 10.23%.

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