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Silicon Effects. IV.[1] Solvolysis of 1-(Pentamethyldisilanyl)-2-phenylcyclopropyl Bromide in 2,2,2-Trifluoroethanol via σ(CC)-Assisted and -Unassisted Ionization Processes

Nobujiro Shimizu,* Fumie Hayakawa, and Yuho Tsuno
Department of Chemistry, Faculty of Science, Kyushu University,
Hakozaki, Fukuoka 812

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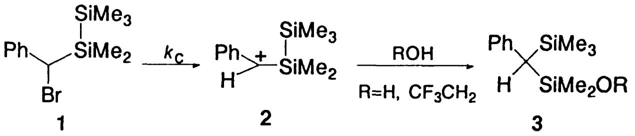
The rates of solvolysis of 1-(pentamethyldisilanyl)-, 1-trimethylsilyl-, and 1-methyl-substituted 2-phenylcyclopropyl bromides (**4a**, **4b**, and **4c**) were measured in 2,2,2-trifluoroethanol at 100 °C: The relative rates for *trans*-**4a**, *trans*-**4b**, and *trans*-**4c** were 3.48 : 1.0 : 10.7, respectively; the trans/cis isomeric rate ratios (k^t/k^c), which were determined by competition experiments, were 2.99 for **4a** and 1.70 for **4b**. The solvolysis of *trans*-**4b** yielded only open allylic ethers, consistent with a σ-assisted mechanism (k_Δ); the *trans*-**4a** predominantly, however, gave a cyclopropyl ring-retained compound, dimethyl[*trans*-2-phenyl-1-(trimethylsilyl)cyclopropyl](2,2,2-trifluoroethoxy)silane, indicative of σ-unassisted (k_c) solvolysis.

Cyclopropyl compounds may undergo solvolysis by two different ionization mechanisms: One involves a σ-assisted ionization (k_Δ) via a concerted disrotatory ring opening to form the corresponding allylic cations; the other involves a simple ionization (k_c) to cyclopropyl cations without any ring opening.[2—9] The k_c process is energetically much less favorable than is the k_Δ process in a secondary cyclopropyl system. Acceleration by the σ-participation in the solvolysis of the parent cyclopropyl compounds has been estimated to be in the range $10^{4.6-7}$[2] to 10^{12}.[3]

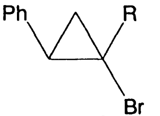
When a strongly electron-supplying group is present at the α-position, the k_c process may take place in competition with the k_Δ process.[3—6] Such a substituent includes aryl,[3,4] cyclopropyl,[5] and alkylthio[6] groups. A change in the mechanism from the k_Δ to the k_c processes has been verified by Brown and his co-workers in the solvolysis of 1-arylcyclopropyl 3,5-dinitrobenzoates in 80% aqueous acetone.[3] For example, although a *p*-methylphenyl derivative predominantly undergoes k_Δ solvolysis, a *p*-dimethylaminophenyl derivative solvolyzes exclusively by the k_c mechanism.

A β-silicon group is another class of substituents capable of stabilizing carbocations.[10—15] We previously showed that α-(pentamethyldisilanyl)benzyl bromide (**1**) undergoes k_c solvolysis via the α-(pentamethyldisilanyl)benzyl cation (**2**) to give a 1,2-silyl rearranged product **3** and that **1** solvolyzes $10^{4.3-5.3}$ times more rapidly than does a reference standard, α-(trimethylsilyl)benzyl bromide, suggesting a marked stabilization of the carbocation by the adjacent Si–Si single bond.[1,15]

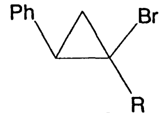
It is interesting to see how an α-disilanyl group affects ionization of the cyclopropyl compounds. If the β-silicon effect operates in harmony with σ(CC)-participation, an enhanced k_Δ reactivity would result; however, if it works independently of σ(CC)-participation, the k_c ionization would occur in competition with k_Δ ionization. This paper describes both kinetic and product studies concerning the solvolysis of 1-(pentamethyldisilanyl)-2-phenylcyclopropyl bromide (**4a**) and two reference standards, 1-(trimethylsilyl)- and 1-methyl-substituted derivatives **4b** and **4c**. It also discusses the effect of the α-disilanyl group on ionization of the cyclopropyl system.



1 **2** **3**



trans-**4**



cis-**4**

a; R=$SiMe_2SiMe_3$, b; R=$SiMe_3$, c; R=CH_3

Results

Stereochemically pure *trans*-**4a** was prepared according to a method described in the literature for the synthesis of *trans*-**4b** and *trans*-**4c**[16] by a treatment of 1,1-dibromo-2-phenylcyclopropane with butyllithium at −100 °C, followed by the addition of chloropentamethyldisilane. The corresponding *cis*-**4a** was obtained as a 1.34 : 1 mixture of cis and trans isomers by a reaction of 1,1-dibromo-2-phenylcyclopropane with magnesium in HMPA in the presence of chloropentamethyldisilane.[17]

Solvolysis. The rates of solvolysis for a trans series of **4a**—**4c** were determined in 2,2,2-trifluoroethanol (TFE) at 100±0.05 °C by a sealed ampoule technique using 0.003 mol dm^{-3} solutions. The decrease of the reactant was followed by GLC using diphenylmethane as an internal standard; the first-order rate constants (correlation coefficient $r > 0.999$) for these compounds are given in Table 1. The solvolysis rates for the corresponding cis isomers were determined for **4a** and **4b** by

Table 1. Rates of Trifluoroethanolysis for **4a**—**4c**[a]

Substrate	$10^5k/\mathrm{s}^{-1}$ (k_rel)			
	k_obsd		k_Δ	k_c
trans-**4a**	6.75±0.06	(3.48)	3.10 (1.60)[b]	3.65[b]
trans-**4b**	1.94±0.03	(1.0)	1.94 (1.0)	
trans-**4c**	20.8±0.1	(10.7)	20.8 (10.7)	
cis-**4a**	2.26[c,d]	(1.16)		
cis-**4b**	1.14[c,e]	(0.59)		

a) At 100±0.05 °C using 0.003 mol dm^{-3} solutions. b) Calculated from k_obsd and a **5a**-**OFEt**/**7**-**OFEt** ratio of 0.85. c) Determined by competition experiments. d) Calculated from a *trans*-**4a**/*cis*-**4a** rate ratio of 2.99. e) Calculated from a *trans*-**4b**/*cis*-**4b** rate ratio of 1.70.

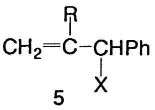
Table 2. Comparison of the Reactivities between **4a** and **4b**

Conditions	k(**4a**)/k(**4b**)		$k^\mathrm{t}/k^\mathrm{c}$ [a]	
	trans	cis	**4a**	**4b**
TFE, 100 °C	3.48	1.98[b]	2.99[c]	1.70[c]
TFE/AgClO$_4$, 80 °C[d]	8.2[c]			

a) Isomeric trans/cis rate ratio. b) Calculated from a k(*trans*-**4a**)/k(*trans*-**4b**) ratio of 3.48 and $k^\mathrm{t}/k^\mathrm{c}$ ratios for **4a** and **4b**. c) Determined by competition experiments. d) In the presence of 1.5 equiv AgClO$_4$ and 1.5 equiv 2,6-lutidine.

a competition experiment technique. Table 2 compares the solvolytic reactivities between **4a** and **4b** and between the trans and cis stereoisomers for these two bromides.

Product Studies. The products of solvolysis of *trans*-**4a** and *trans*-**4b** were determined in buffered TFE. The latter bromide afforded two allylic ethers, **5b**-**OFEt** (FEt=CH$_2$CF$_3$) and its regioisomer **6b**-**OFEt**, at a ratio of 95 : 5 in 84% isolated yield. The former bromide gave an allylic ether **5a**-**OFEt** and two cyclopropyl ring-retained compounds, a trifluoroethoxysilane **7**-**OFEt** and a silanol **7**-**OH**, in the ratio 46 : 21 : 3 in 80% combined yield. The last compound was formed from **7**-**OFEt** during isolation processes.


$$\mathrm{CH_2{=}\overset{R}{\underset{}{C}}{-}\underset{X}{CHPh}}$$

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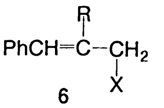
$$\mathrm{PhCH{=}\overset{R}{C}{-}\underset{X}{CH_2}}$$

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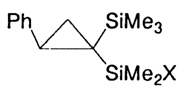

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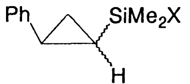

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X; OCH$_2$CF$_3$ (OFEt), OMe, OH, H

A silver perchlorate-induced reaction of *trans*-**4a** in TFE exclusively gave **7**-**OFEt**. We also examined the products of silver perchlorate-induced methanolysis. Both *trans*-**4b** and *trans*-**4c** gave corresponding allylic ethers as mixtures of the two regioisomers, **5**-**OMe** and **6**-**OMe**. In contrast, *trans*-**4a** afforded two cyclopropane derivatives, **7**-**OMe** and **8**-**OMe**, which were isolated as the corresponding trisubstituted silanes, **7**-**H** and **8**-**H**, after reduction with LiAlH$_4$. The results are summarized in Table 3.

The formation of **7**-**OFEt** and **7**-**OMe** was highly stereoselective: NMR analyses suggested an exclusive formation of the trans isomer. On the other hand, **8**-**OMe** was formed as a 1.2 : 1 mixture of the two stereoisomers.

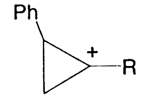
Discussion

The solvolysis of 1-methylcyclopropyl tosylate (*p*-toluenesulfonate) proceeds exclusively by the k_Δ mechanism;[2,18] the presence of a phenyl group at the 2-position in the cyclopropyl system promotes more effectively k_Δ ionization than k_c ionization.[19,20] Accordingly, the cyclopropyl bromide **4c**, which possesses 1-methyl and 2-phenyl substituents, must solvolyze exclusively by the k_Δ mechanism. An α-SiMe$_3$ group is less effective in stabilizing the adjacent carbocation than is an α-methyl group;[21,22] hence, the k_c process via the cyclopropyl cation **9** should be less favorable for **4b** than for **4c**. Therefore, the k_Δ mechanism must also be operative in the solvolysis of **4b**. Various product studies (Table 3) support the k_Δ solvolysis for **4b** and **4c**: Both *trans*-**4b** and *trans*-**4c** only gave the open allylic compounds, **5** and **6**, as expected from σ-assisted ionization via the allyl cation *cis*-**10** in the solvolysis in TFE, as well as in the Ag(I)-induced methanolysis; we could not detect the formation of any cyclopropyl ring-retained compounds.

Table 3. Solvolysis Products

Substrate	Conditions	Yield/%[a]	Products (ratio)
trans-**4a**	TFE, 100 °C, 11 h[b]	80	**7-OFEt**[c]+**7-OH**[c,d]+**5a-OFEt** (21 : 33 : 46)
trans-**4b**	TFE, 100 °C, 62 h[b]	84	**5b-OFEt**+**6b-OFEt** (95 : 5)
trans-**4a**	AgClO$_4$/TFE, r.t., 2 h[e]	75	**7-OFEt**[c]+**7-OH**[c,d] (41 : 59)
trans-**4a**	AgClO$_4$/MeOH, r.t., 5 h[e]	79	**7-OMe**[c,f]+**8-OMe**[f,g] (18 : 82)
trans-**4b**	AgClO$_4$/MeOH, 70 °C, 3.5 h[e]	80	**5b-OMe**+**6b-OMe** (77 : 23)
trans-**4c**	AgClO$_4$/MeOH, r.t., 24 h[e]	68	**5c-OMe**+**6c-OMe** (63 : 37)

a) Isolated yield. b) In the presence of 1 equiv 2,6-lutidine. c) Formed almost as a single stereoisomer. d) Absent in the crude reaction mixture. e) In the presence of 2 equiv silver perchlorate and 2 equiv calcium carbonate. f) Isolated as the corresponding trisubstituted silanes **7**-**H** and **8**-**H**. g) Formed as a 1.2 : 1 stereoisomeric mixture.



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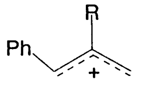
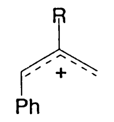
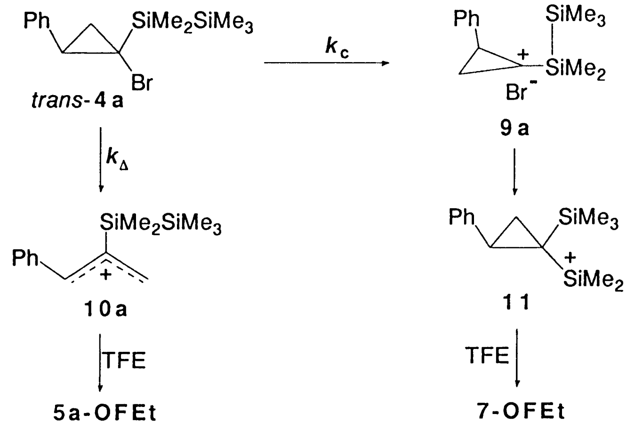


cis-**10**



trans-**10**

A *trans*-**4a**/*trans*-**4b** rate ratio of 3.48 (Table 1), which represents the α-substitution effect of $SiMe_2SiMe_3$ relative to $SiMe_3$ in the cyclopropyl system, is very small compared to the α-$SiMe_2SiMe_3$ substitution effect of $10^{4.3-5.3}$ in the benzylic system.1) It should be noted, however, that the solvolysis of *trans*-**4a** in TFE in the presence or absence of silver perchlorate gave the cyclopropane derivative **7–OFEt** (including **7–OH**) as the major product (Table 3). Obviously, the $SiMe_2SiMe_3$ group exerts a striking influence on the course of the solvolysis reaction, despite a small kinetic effect. The formation of **7–OFEt** involves a 1,2-$SiMe_3$ rearrangement from the α-silicon to the cyclopropyl carbon. Such a rearrangement is characteristic of the k_c solvolysis of α-(pentamethyldisilanyl)benzyl bromide,1) and is consistent with a σ(CC)-unassisted mechanism involving a rate-determining formation of the cyclopropyl cation **9a**, which probably gives **7–OFEt** after a rapid rearrangement to a silicenium ion **11** (Scheme 1).



Scheme 1.

There is an alternative mechanism for the solvolysis of **4a** involving ionization assisted by a Si–Si single bond ($k_{\Delta(\mathrm{SiSi})}$). It is clear, however, that the α-$SiMe_2SiMe_3$ group effects two distinct ionization processes of the cyclopropyl system, i.e., σ(CC)-assisted and -unassisted processes, whatever the real mechanism for the latter process might be (k_c or $k_{\Delta(\mathrm{SiSi})}$). Assuming that **5a–OFEt** is produced by the k_Δ mechanism and **7–OFEt** by the k_c mechanism (Scheme 1), we can calculate the k_c and k_Δ rate constants for the solvolysis of *trans*-**4a** to be 3.65×10^{-5} and 3.10×10^{-5} s^{-1}, respectively, in TFE at 100 °C. These rates constants are included in Table 1.

We could not directly measure the rate constant (k_c) for the unassisted solvolysis of *trans*-**4b**; we therefore estimated the β-silicon effect of the $SiMe_2SiMe_3$ group in the unassisted ionization of the cyclopropyl system, i.e., $k_c(SiMe_2SiMe_3)/k_c(SiMe_3)$, in the following manner by using Eqs. 1 and 2, in which k_Δ(R) and k_c(R) (R=$SiMe_2SiMe_3$, $SiMe_3$, Me, and Ph) are the σ(CC)-assisted and -unassisted rate constants for 1-R-substituted cyclopropyl compounds:

$$k_c(\mathrm{SiMe_2SiMe_3})/k_c(\mathrm{SiMe_3})=[k_c(\mathrm{SiMe_2SiMe_3})/k_\Delta(\mathrm{Me})]\times[k_c(\mathrm{Me})/k_c(\mathrm{SiMe_3})]\times[k_\Delta(\mathrm{Me})/k_c(\mathrm{Me})] \quad (1)$$

and

$$k_\Delta(\mathrm{Me})/k_c(\mathrm{Me})=[k_\Delta(\mathrm{Me})/k_\Delta(\mathrm{Ph})]\times[k_c(\mathrm{Ph})/k_c(\mathrm{Me})]\times[k_\Delta(\mathrm{Ph})/k_c(\mathrm{Ph})]. \quad (2)$$

The first rate ratio on the right-hand side of Eq. 1, $k_c(SiMe_2SiMe_3)/k_\Delta(Me)$, is given by a k_c (*trans*-**4a**)/k (*trans*-**4b**) ratio of 0.175 at 100 °C, or an extrapolated value of 0.11 at 25 °C. The second rate ratio, $k_c(Me)/k_c(SiMe_3)$, may be approximated by α-Me and α-$SiMe_3$ substitution effects in other k_c solvolysis systems. The α-silicon effect [k (α-Me)/k (α-$SiMe_3$)] was estimated to be 0.91—2.2 in 2-adamantyl system23) and (3.54—4.98)$\times10^2$ in 1-indanyl system (a rate ratio of 2,2-dimethyl-1-indanyl bromide to 2,2-dimethyl-2-silaindan-1-yl bromide);21) we therefore assume the $k_c(Me)/k_c(SiMe_3)$ ratio to be within the range 0.9—5×10^2 (25 °C). The third rate ratio in Eq. 1, $k_\Delta(Me)/k_c(Me)$, is given by Eq. 2.

The first rate ratio on the right-hand side of Eq. 2, $k_\Delta(Me)/k_\Delta(Ph)$, is given by an acetolysis rate ratio of 1-methylcyclopropyl tosylate to 1-phenyl derivative as 2.9×10^{-3} at 25 °C.2,9) Schleyer and co-workers2b) have compiled literature data concerning the solvolysis of cyclic compounds, and estimated the α-Me and α-phenyl substitution effects [$k^{\mathrm{Me}}/k^{\mathrm{H}}$ and $k^{\mathrm{Ph}}/k^{\mathrm{H}}$] in various cyclic systems. Taking advantage of their analysis, we can calculate the $k^{\mathrm{Ph}}/k^{\mathrm{Me}}$ rate ratio of 4×10^4 (25 °C) in a 7-norbornyl system which has an electronic demand similar to the cyclopropyl system; we thus take this value as being the second rate ratio of Eq. 2, $k_c(Ph)/k_c(Me)$. Brown and co-workers3) showed that the logarithmic rates ($\log k$) for the assisted (k_Δ) and unassisted (k_c) solvolyses of a series of 1-arylcyclopropyl 3,5-dinitrobenzoates in 80% aqueous acetone are well linearly correlated with σ^+, yielding ρ^+ values of -7.07 and -2.47 for the k_c and k_Δ processes, respectively. Although a phenyl group is not included in their analysis, we can calculate the k_c and k_Δ rate constants for the 1-phenyl derivative by extrapolation of the reported $\log k$–σ^+ plots to $\sigma^+=0$ as follows: $k_c=1.3\times10^{-10}$ s^{-1} and $k_\Delta=2.7\times10^{-7}$ s^{-1} (25 °C); hence, the third rate ratio of Eq. 2, $k_\Delta(Ph)/k_c(Ph)$, is calculated to be 2.1×10^2. Consequently, the $k_\Delta(Me)/k_c(Me)$ ratio is calculated to be $(2.9\times10^{-3})\times(4\times10^4)\times(2.1\times10^2)=2.4\times10^4$ (25 °C). Using this value, we can estimate the β-silicon effect of the $SiMe_2SiMe_3$ group in the k_c solvolysis of the cyclopropyl system as follows:

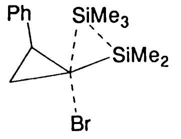
$$k_c(\mathrm{SiMe_2SiMe_3})/k_c(\mathrm{SiMe_3})=0.11\times(0.9-5.0\times10^2)\times(2.4\times10^4)=10^{3.4-6.1}\ (25\ ^\circ\mathrm{C}).$$

Although the above analysis includes several assumptions, it can be said that the α-$SiMe_2SiMe_3$ group markedly accelerates the unassisted solvolysis of the cyclopropyl compounds. The acceleration of $10^{3.4-6.1}$ by an α-$SiMe_2SiMe_3$ group is consistent with our earlier observation that α-(pentamethyldisilanyl)benzyl bromide **1** solvolyzes $10^{4.3-5.3}$ times more rapidly than does α-(trimethylsilyl)benzyl bromide at 25 °C.[1]

The trans/cis isomeric rate ratio (k^t/k^c) for **4a** (Table 2) seems to be instructive in connection with the possibility of the σ(SiSi)-assisted ionization ($k_{\Delta(\mathrm{SiSi})}$). The overall k^t/k^c ratio for **4a** is described by Eq. 3, in which the subscript "un" indicates the σ(CC)-unassisted process, i.e., k_c or $k_{\Delta(\mathrm{SiSi})}$:

$$\begin{aligned} k^t/k^c &= (k^t_\Delta+k^t_{un})/(k^c_\Delta+k^c_{un}) \\ &= [(k^t_\Delta/k^c_\Delta)+(k^t_{un}/k^c_{un})\times(k^c_{un}/k^c_\Delta)]/(1+k^c_{un}/k^c_\Delta). \end{aligned} \tag{3}$$

Equation 3 indicates that $k^t/k^c<k^t_\Delta/k^c_\Delta$ if $k^t_{un}/k^c_{un}<k^t_\Delta/k^c_\Delta$, irrespective of a value of k^c_{un}/k^c_Δ. The k^t_Δ/k^c_Δ ratio for **4a** is probably similar to 1.7, which was observed for **4b**. If the k_{un} process arises from σ-participation by the Si–Si bond, $k^t_{un}/k^c_{un}<1$ is expected, since the transition state **12** for the trans isomer must be sterically less favorable than that (**13**) for the cis isomer.



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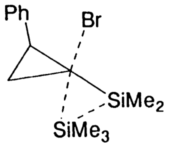

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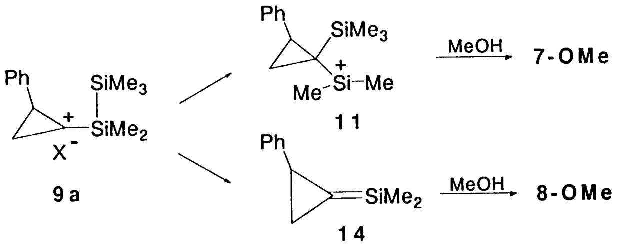
Accordingly, the $k_{\Delta(\mathrm{SiSi})}$ mechanism would show a k^t/k^c ratio of less than 1.7, which is significantly smaller than the observed value of 2.99. Although we cannot eliminate the $k_{\Delta(\mathrm{SiSi})}$ process, the result prefers the k_c mechanism in which $k^t_{un}/k^c_{un}>1$ is expected because of the anticipated relief of strain of the ground state of the trans isomer.

The rate acceleration by the $SiMe_2SiMe_3$ group is very small in the k_Δ process, compared to the k_c process: k_Δ(*trans*-**4a**)/k_Δ(*trans*-**4b**)=1.60. The reduced effect of the α-substituent on the k_Δ process is ascribed to an extensive internal charge delocalization in the transition state.[9] The small **4a**/**4b** rate ratio for the k_Δ process eliminates the idea that the formation of the allyl cation **10** is not a concerted process but, rather, is a stepwise one via the cyclopropyl cation **9**. Such a stepwise mechanism should exhibit a pronounced **4a**/**4b** rate ratio, like that observed in the k_c process.

The trans/cis rate ratio of 1.7 for **4b** is consistent with the concerted disrotatory ring opening.[9] The value, however, is somewhat smaller than that for the secondary cyclopropyl system, e.g., $k^t/k^c=4$, in the acetolysis of 2-phenylcyclopropyl halides.[20] The reduced k^t/k^c ratio for **4b** may be partly ascribed to an increase in the cis steric interaction between the phenyl and $SiMe_3$ groups in *cis*-**10b** generated from *trans*-**4b**.

Finally, it is interesting to compare the Ag(I)-induced solvolysis with simple solvolysis. The *trans*-**4a**/*trans*-**4b** rate ratio is significantly larger in the presence of $AgClO_4$ (8.2 at 80 °C) than in the absence of it (3.5 at 100 °C) (Table 2). In addition, the $AgClO_4$-induced solvolysis of *trans*-**4a** in TFE and methanol exclusively gives the cyclopropyl ring-retained compounds, **7** and **8** (Table 3). A possible explanation for these observations is to assume a return process from a cyclopropyl cation/Br^- ion pair in the solvolysis in the absence of $AgClO_4$. The $AgClO_4$-induced solvolysis probably proceeds via a cyclopropyl cation/ClO_4^- ion pair which does not undergo return. Both ion pairs may undergo a rearrangement, as well as an elimination of the β-$SiMe_3$ group at varying ratios, depending on the solvent nucleophilicity. In a weakly nucleophilic solvent, like TFE ($N_{\mathrm{OTs}}=-3.0$[24]), the cation **9a** undergoes a rearrangement exclusively, whereas a strongly nucleophilic solvent, like methanol ($N_{\mathrm{OTs}}=-0.04$[24]), tends to attack the β-silicon of the cation to promote an elimination of the $SiMe_3$ group; a resultant silene intermediate **14** would react with methanol to give a stereoisomeric mixture of **8**–**OMe**, as illustrated in Scheme 2.



Scheme 2.

Experimental

The IR spectra were recorded on a Hitachi R-215 spectrophotometer. NMR spectra were recorded on a Hitachi R-20B spectrometer in carbon tetrachloride. GLC analyses were performed with a Hitachi 163 gas chromatograph using columns packed with 10% Silicone GE SE-30 on Chamelite CS (Column A), 25% Silicone DC-550 on Chamelite CS (Column B), and 25% Apiezon Grease L on Chromosorb W (Column C).

cis-2-Phenyl-1-(trimethylsilyl)cyclopropyl bromide (*cis*-**4b**), its *trans*-isomer (*trans*-**4b**), and *trans*-1-methyl-2-phenylcyclopropyl bromide (*trans*-**4c**) were prepared by various reported methods.[16,17] Solvent 2,2,2-trifluoroethanol (TFE) was dried over Molecular Sieve 4A for one week, and then distilled over sodium carbonate.

Synthesis of *trans*-1-(Pentamethyldisilanyl)-2-phenylcyclopropyl Bromide (*trans*-4a). Into a solution of 1,1-dibromo-2-phenylcyclopropane (6.33 g, 23.0 mmol) in a mixture of THF (25 cm^3) and ether (10 cm^3) was added butyllithium (1.6 M (1

M=1 mol dm^{-3}) in hexane, 15.0 cm^3) at such a rate as to maintain the temperature below −100 °C under argon, followed by the addition of a solution of chloropentamethyldisilane (3.83 g, 23 mmol) in THF (5 cm^3). The mixture was stirred for 2.5 h at that temperature and worked up with water. Fractionation of a crude oil gave 3.45 g (57%) of *trans*-**4a**: Bp 116—117 °C (1 Torr: 1 Torr=133.3 Pa); IR (neat) 1610, 1500, 1250, 830, 800, 700 cm^{-1}; NMR δ=−0.43 (3H, s), −0.14 (3H, s), 0.07 (9H, s), 1.26—1.69 (2H, m), 2.91 (1H, dd, *J*=9.6 and 7.6 Hz), 7.20 (5H, almost s). Anal. Found: C, 51.32; H, 7.05%. Calcd for $C_{14}H_{23}BrSi_2$: C, 51.36; H, 7.09%.

Synthesis of *cis*-1-(Pentamethyldisilanyl)-2-phenylcyclopropyl Bromide (*cis*-4a).[17] A mixture of 1,1-dibromo-2-phenylcyclopropane (2.0 g, 7.3 mmol), chloropentamethyldisilane (1.21 g), and magnesium (0.18 g) in HMPA (10 cm^3) was stirred for 4 h at 50 °C. A crude oil obtained after the usual workup was subjected to bulb-to-bulb distillation (100 °C, 2 Torr) to give a mixture (2.54 g) of *trans*- and *cis*-**4a** at a ratio 1 : 1.34. *cis*-**4a**: NMR δ=0.15 (15H, s), 1.31—1.69 (2H, m), 2.06 (1H, dd, *J*=9.0 and 6.6 Hz), 7.16 (5H, almost s).

Kinetic Measurements. Solvolysis was carried out in TFE at 100 °C using the usual ampoule technique involving 18 small glass ampoules, each containing 0.50 cm^3 of a 0.003 mol dm^{-3} TFE solution of **4a**—**4c** containing diphenylmethane as a GLC internal standard. The decrease in the reactant was followed directly by a GLC analysis at appropriate intervals. The solvolysis followed good first-order kinetics (correlation coefficient r>0.999) for the three compounds.

The cis/trans isomeric rate ratios for **4a** and **4b** were determined by competition experiments using a 0.01 mol dm^{-3} TFE solution of isomeric pairs containing diphenylmethane as the internal standard. The relative rate of silver perchlorate-induced solvolysis between **4a** and **4b** was determined in TFE and in methanol by competition experiments using 0.03 mol dm^{-3} solutions for each component containing 0.5 equiv silver perchlorate and 0.5 equiv 2,6-lutidine.

Product Studies. Solvolysis in TFE. Compound *trans*-**4a** (0.693 g) was solvolyzed in TFE (10 cm^3) in the presence of 2,6-lutidine (0.227 g) as a buffer in a glass ampoule at 100 °C for 11 h. A GLC analysis of a crude oil (587 mg) obtained after the usual workup indicated the formation of three major products (Column A, 160 °C, retention time t_R; 3.0, 3.6, and 4.2 min respectively) at a ratio 11 : 5 : 8. Each component was separated by column chromatography over silica gel and by GLC and was respectively identified as 2-(pentamethyldisilanyl)-3-phenyl-3-(2,2,2-trifluoroethoxy)-1-propene (**5a–OFEt**), dimethyl[*trans*-2-phenyl-1-(trimethylsilyl)cyclopropyl](2,2,2-trifluoroethoxy)silane (**7–OFEt**), and dimethyl[*trans*-2-phenyl-1-(trimethylsilyl)cyclopropyl]silanol (**7–OH**). **5a–OFEt**: NMR δ=0.0 (9H, s), 0.05 (3H, s), 0.08 (3H, s), 3.67 (2H, q, *J*=8.4 Hz), 4.97 (1H, broad s), 5.44—5.58 (2H, m), 7.27 (5H, almost s). Anal. Found: C, 54.53; H, 7.07%. Calcd for $C_{16}H_{25}F_3OSi_2$: C, 55.46; H, 7.27%. **7-OFEt**: NMR δ=−0.30 (9H, s), 0.18 (3H, s), 0.22 (3H, s), 0.98—1.25 (2H, m), 2.36 (1H, dd, *J*=7.8 and 5.4 Hz), 3.86 (2H, q, *J*=9.0 Hz), 7.16 (5H, almost s). Found: C, 55.42; H, 7.23%. Calcd for $C_{16}H_{25}F_3OSi_2$: C, 55.46; H, 7.27%. **7-OH**: IR 3350, 1260, 1080, 940, 850, 790, 700 cm^{-1}; NMR δ=−0.30 (9H, s), 0.13 (3H, s), 0.19 (3H, s), 0.97—1.25 (2H, m), 2.37 (1H, dd, *J*=7.2 and 5.4 Hz), 7.16 (5H, almost s). Found: C, 63.83; H, 8.80%. Calcd for $C_{14}H_{23}OSi_2$: C, 63.57; H, 9.15%. Besides the above products, a trace amount of another compound, assignable to 2-(pentamethyldisilanyl)indene, was also formed [NMR δ=0.09 (9H, s), 0.26 (6H, s), 3.35 (2H, broad s), 7.0—7.45 (5H, m)].

In a similar procedure to that described above was solvolyzed *trans*-**4b** (0.690 g) in TFE (10 cm^3) in the presence of 2,6-lutidine (0.275 g) at 100 °C for 62 h. A crude oil obtained after a workup was subjected to bulb-to-bulb distillation [75—85 °C (3 Torr)] to give 451 mg of an oil, which was shown to be a mixture of two products [Column B, 170 °C, t_R; 5.6 and 8.0 min respectively] at a ratio 95 : 5. They were isolated by GLC and assigned to 3-phenyl-3-(2,2,2-trifluoroethoxy)-2-trimethylsilyl-1-propene (**5b–OFET**) and 1-phenyl-3-(2,2,2-trifluoroethoxy)-2-trimethylsilyl-1-propene (**6b–OFEt**), respectively. **5b–OFEt**: IR 1660, 1280, 1250, 1160, 1110, 840, 700 cm^{-1}; NMR δ=0.0 (9H, s), 3.66 (2H, q, *J*=8.4 Hz), 4.96 (1H, broad s), 5.54 (2H, broad s), 7.25 (5H, almost s). Found: C, 58.10; H, 6.58%. Calcd for $C_{14}H_{19}F_3OSi$: C, 58.31; H, 6.64%. **6b–OFEt**: NMR δ=0.22 (9H, s), 3.38 (2H, d, *J*=1.8 Hz), 3.67 (2H, q, *J*=8.4 Hz), 6.9—7.3 (6H, m). In addition to these two products, a trace amount of another compound, assignable to 2-(trimethylsilyl)indene, was also formed [IR 1540, 1250, 1040, 840, 760, 710 cm^{-1}; NMR δ=0.06 (9H, s), 3.45 (2H, d, *J*=1.9 Hz), 6.94—7.34 (5H, m)].

Silver Perchlorate-Induced Solvolysis. In TFE. Compound *trans*-**4a** (1.02 g) was treated with silver perchlorate (1.27 g) in TFE (10 cm^3) in the presence of 2,6-lutidine (0.65 g) at room temperature for 2 h. GLC analysis of the reaction mixture indicated the formation of **7–OFEt** as a single component. A crude oil (0.882 g) obtained after the workup was subjected to column chromatography to give 334 mg (31%) of **7–OFEt** and 361 mg (44%) of **7–OH**.

In Methanol. Compound *trans*-**4a** (0.600 g, 1.77 mmol) was solvolyzed in methanol (25 cm^3) in the presence of silver perchlorate (2.0 equiv) and calcium carbonate (2 equiv) at room temperature for 5 h. GLC and NMR analyses of a crude oil (0.472 g, 78%) obtained after the workup showed the formation of two products (Column A; 160 °C, t_R=2.4 and 3.9 min respectively) in a ratio of 4.5 : 1. The major component was identified as methoxydimethyl(2-phenylcyclopropyl)silane (**8–OMe**): NMR δ=−0.18 (3H, s), 0.0 (3H, s), 0.0—0.3 (1H, m), 1.3—1.6 (2H, m), 2.6—2.8 (1H, m), 3.12 (3H, s), 7.19 (5H, almost s). The minor one was assigned to methoxydimethyl[trans-2-phenyl-1-(trimethylsilyl)cyclopropyl]silane (**7–OMe**): NMR δ=−0.33 (9H, s), 0.08 (6H, broad s), 1.15 (2H, m), 2.34 (1H, dd, *J*=7.2 and 5.4 Hz), 3.43 (3H, s), 7.19 (5H, almost s). The oil (0.472 g) was treated with $LiAlH_4$ (75 mg) in THF under reflux for 6 h. The usual workup, followed by bulb-to-bulb distillation (100 °C, 47 Torr), gave 0.263 mg of a colorless oil which was shown to be a mixture of two components in a ratio of 4.7 : 1. Each component was isolated by GLC. The more abundant component was shown to be a 1.2 : 1 mixture of two stereoisomers of dimethyl(2-phenylcyclopropyl)silane (**8–H**): IR 2110, 1250, 890, 700 cm^{-1}; NMR (Signals for the less abundant stereoisomer were shown in *italics.*) NMR δ=*−0.21* (d, *J*=3.6 Hz, Me), *−0.18* (d, *J*=3.6 Hz, Me), and 0.11 (d, *J*=3.6 Hz, 2Me) (6H, altogether), 0.0—0.4 (1H, m), 0.6—1.3 (2H, m), 1.79 (m) and *2.31* (m) (1H, altogether), *3.60* (1H, m) and 3.83 (m) (1H, altogether), 7.03—7.07 (5H, m). Found: C, 74.63; H, 8.94%. Calcd for $C_{11}H_{16}Si$: C, 74.93; H, 9.15%. The less abundant component was assigned to (*trans*-1-dimethylsilyl-2-phenylcyclopropyl)trimethylsilane (**7–H**): IR 2110, 1250, 1170, 960, 940, 895, 825, 760, 700 cm^{-1}; NMR δ=−0.30 (9H, s), 0.06—0.22 (6H, m), 0.91—1.28 (2H, m), 2.27 (1H, dd, *J*=7.8 and 5.4 Hz), 3.80

(1H, septet, J=3.6 Hz), 7.15 (5H, almost s). Found: C, 67.61; H, 9.57%. Calcd for $C_{14}H_{24}Si_2$: C, 67.66; H, 9.73%.

Compound *trans*-**4b** (0.490 g, 1.82 mmol) was solvolyzed in methanol (25 cm^3) in the presence of 2 equiv of silver perchlorate and calcium carbonate under reflux for 3.5 h. A crude oil (0.386 g, 87%) obtained after the workup was shown to be a mixture of **5b**-**OMe** and **6b**-**OMe** in the ratio 3.3 : 1.

5b-OMe: IR 1605, 1250, 1095, 960, 940, 840, 760, 695 cm^{-1}; NMR δ=−0.04 (9H, s), 3.23 (3H, s), 4.65 (1H, broad s), 5.50 (2H, m), 7.22 (5H, almost s).

6b-OMe: IR 1610, 1600, 1250, 1115, 1095, 840, 780, 750, 695 cm^{-1}; NMR δ=−0.06 (9H, s), 3.24 (1H, collapsed with a peak at 3.28), 3.28 (3H, s), 4.00 (2H, broad s), 6.9—7.3 (6H, broad m).

Compound *trans*-**4c** (0.460 g) was solvolyzed in methanol (25 cm^3) in the presence of 2 equiv of silver perchlorate and calcium carbonate at room temperature for 24 h. GLC and NMR analyses indicated that a crude oil (284 mg, 68%) obtained after the workup was a 1.7 : 1 mixture of **5c**-**OMe** [NMR δ=1.50 (3H, s), 3.26 (3H, s), 4.48 (1H, s), 4.89 (1H, broad s), 5.05 (1H, broad s), 7.22 (5H, almost s)] and **6c**-**OMe** [NMR δ=1.83 (3H, s), 3.28 (3H, s), 3.87 (2H, broad s), 6.42 (1H, broad s), 7.20 (5H, almost s)].

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