

Silicon Effects. IV.¹⁾ Solvolysis of 1-(Pentamethyldisilanyl)-2-phenylcyclopropyl Bromide in 2,2,2-Trifluoroethanol via $\sigma(\text{CC})$ -Assisted and -Unassisted Ionization Processes

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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.

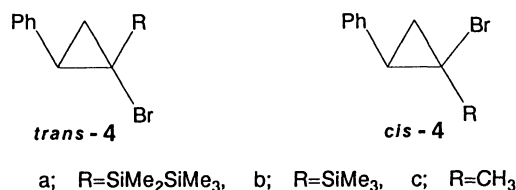
Cyclopropyl compounds may undergo solvolysis by two different ionization mechanisms: One involves a σ -assisted ionization (k_Δ) via a concerted disrotatory ring opening to form the corresponding allylic cations; the other involves a simple ionization (k_c) to cyclopropyl cations without any ring opening.^{2–9)} 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 alkylthio⁶⁾ 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 $\sigma(\text{CC})$ -participation, an enhanced k_Δ reactivity would result; however, if it works independently of $\sigma(\text{CC})$ -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.



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

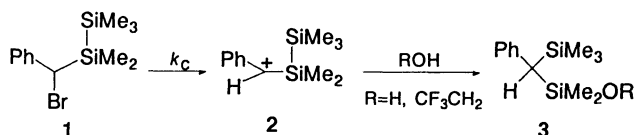


Table 1. Rates of Trifluoroethanolysis for **4a–4c**^{a)}

Substrate	10 ⁵ <i>k</i> /s ⁻¹ (<i>k</i> _{rel})		
	<i>k</i> _{obsd}	<i>k</i> _Δ	<i>k</i> _c
<i>trans</i> - 4a	6.75±0.06 (3.48)	3.10 (1.60) ^{b)}	3.65 ^{b)}
<i>trans</i> - 4b	1.94±0.03 (1.0)	1.94 (1.0)	
<i>trans</i> - 4c	20.8±0.1 (10.7)	20.8 (10.7)	
<i>cis</i> - 4a	2.26 ^{c,d)} (1.16)		
<i>cis</i> - 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.

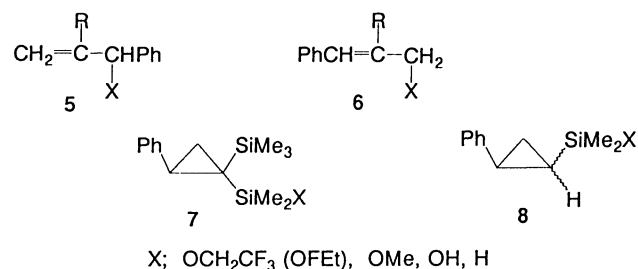
d) Calculated from a *trans*-**4a**/*cis*-**4a** rate ratio of 2.99.e) Calculated from a *trans*-**4b**/*cis*-**4b** rate ratio of 1.70.Table 2. Comparison of the Reactivities between **4a** and **4b**

Conditions	<i>k</i> (4a)/ <i>k</i> (4b)		<i>k</i> ^t / <i>k</i> ^{c a)}	
	<i>trans</i>	<i>cis</i>	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*^t/*k*^c ratios for **4a** and **4b**. c) Determined by competition experiments. d) In the presence of 1.5 equiv AgClO₄ 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=CH₂CF₃) 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.

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 LiAlH₄. 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.

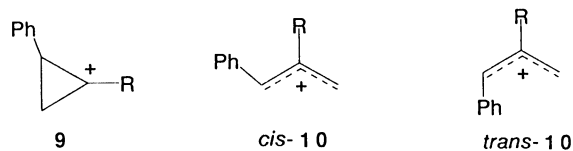
Discussion

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-SiMe₃ 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.

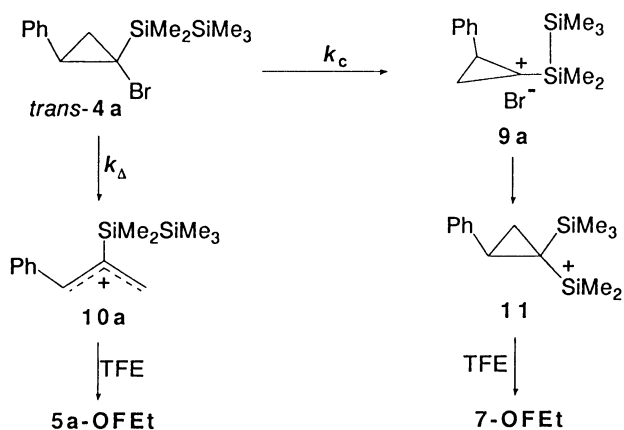
Table 3. Solvolysis Products

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



A *trans-4a*/*trans-4b* rate ratio of 3.48 (Table 1), which represents the α -substitution effect of $\text{SiMe}_2\text{SiMe}_3$ relative to SiMe_3 in the cyclopropyl system, is very small compared to the α - $\text{SiMe}_2\text{SiMe}_3$ 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 $\text{SiMe}_2\text{SiMe}_3$ 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 $\sigma(\text{CC})$ -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 $\text{Si}-\text{Si}$ single bond ($k_{\Delta(\text{SiSi})}$). It is clear, however, that the α - $\text{SiMe}_2\text{SiMe}_3$ group effects two distinct ionization processes of the cyclopropyl system, i.e., $\sigma(\text{CC})$ -assisted and -unassisted processes, whatever the real mechanism for the latter process might be (k_c or $k_{\Delta(\text{SiSi})}$). 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 $3.10 \times 10^{-5} \text{ s}^{-1}$, respectively, in TFE at 100°C . These rate 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 $\text{SiMe}_2\text{SiMe}_3$ group in the unassisted ionization of the cyclopropyl system, i.e., $k_c(\text{SiMe}_2\text{SiMe}_3)/k_c(\text{SiMe}_3)$, in the following manner by using Eqs. 1 and 2, in which $k_\Delta(\text{R})$ and $k_c(\text{R})$ ($\text{R}=\text{SiMe}_2\text{SiMe}_3$, SiMe_3 , Me , and Ph) are the $\sigma(\text{CC})$ -assisted and -unassisted rate constants for 1-R-substituted cyclopropyl compounds:

$$k_c(\text{SiMe}_2\text{SiMe}_3)/k_c(\text{SiMe}_3) = [k_c(\text{SiMe}_2\text{SiMe}_3)/k_\Delta(\text{Me})] \times [k_c(\text{Me})/k_c(\text{SiMe}_3)] \times [k_\Delta(\text{Me})/k_c(\text{Me})] \quad (1)$$

and

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

The first rate ratio on the right-hand side of Eq. 1, $k_c(\text{SiMe}_2\text{SiMe}_3)/k_\Delta(\text{Me})$, is given by a k_c (*trans-4a*)/ k_c (*trans-4b*) ratio of 0.175 at 100°C , or an extrapolated value of 0.11 at 25°C . The second rate ratio, $k_c(\text{Me})/k_c(\text{SiMe}_3)$, may be approximated by α - Me and α - SiMe_3 substitution effects in other k_c solvolysis systems. The α -silicon effect [$k(\alpha\text{-Me})/k(\alpha\text{-SiMe}_3)$] was estimated to be 0.91–2.2 in 2-adamantyl system²³⁾ and $(3.54\text{--}4.98) \times 10^2$ 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 $k_c(\text{Me})/k_c(\text{SiMe}_3)$ ratio to be within the range 0.9– 5×10^2 (25°C). The third rate ratio in Eq. 1, $k_\Delta(\text{Me})/k_c(\text{Me})$, is given by Eq. 2.

The first rate ratio on the right-hand side of Eq. 2, $k_\Delta(\text{Me})/k_\Delta(\text{Ph})$, 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-workers^{2b)} have compiled literature data concerning the solvolysis of cyclic compounds, and estimated the α - Me and α -phenyl substitution effects [$k^{\text{Me}}/k^{\text{H}}$ and $k^{\text{Ph}}/k^{\text{H}}$] in various cyclic systems. Taking advantage of their analysis, we can calculate the $k^{\text{Ph}}/k^{\text{Me}}$ 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, $k_c(\text{Ph})/k_c(\text{Me})$. 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 $\log k - \sigma^+$ plots to $\sigma^+ = 0$ as follows: $k_c = 1.3 \times 10^{-10} \text{ s}^{-1}$ and $k_\Delta = 2.7 \times 10^{-7} \text{ s}^{-1}$ (25°C); hence, the third rate ratio of Eq. 2, $k_\Delta(\text{Ph})/k_c(\text{Ph})$, is calculated to be 2.1×10^2 . Consequently, the $k_\Delta(\text{Me})/k_c(\text{Me})$ ratio is calculated to be $(2.9 \times 10^{-3}) \times (4 \times 10^4) \times (2.1 \times 10^2) = 2.4 \times 10^4$ (25°C). Using this value, we can estimate the β -silicon effect of the $\text{SiMe}_2\text{SiMe}_3$ group in the k_c solvolysis of the cyclopropyl system as follows:

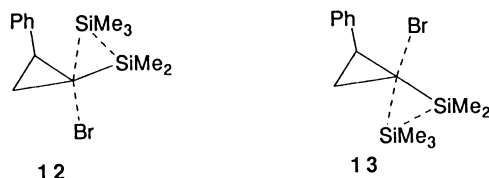
$$k_c(\text{SiMe}_2\text{SiMe}_3)/k_c(\text{SiMe}_3) = 0.11 \times (0.9 - 5.0 \times 10^2) \times (2.4 \times 10^4) = 10^{3.4-6.1} \quad (25^\circ\text{C}).$$

Although the above analysis includes several assumptions, it can be said that the α -SiMe₂SiMe₃ group markedly accelerates the unassisted solvolysis of the cyclopropyl compounds. The acceleration of $10^{3.4-6.1}$ by an α -SiMe₂SiMe₃ 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 $\sigma(\text{SiSi})$ -assisted ionization ($k_{\Delta(\text{SiSi})}$). The overall k^t/k^c ratio for **4a** is described by Eq. 3, in which the subscript "un" indicates the $\sigma(\text{CC})$ -unassisted process, i.e., k_c or $k_{\Delta(\text{SiSi})}$:

$$k^t/k^c = (k_{\Delta}^t + k_{\text{un}}^t)/(k_{\Delta}^c + k_{\text{un}}^c) \\ = [(k_{\Delta}^t/k_{\Delta}^c) + (k_{\text{un}}^t/k_{\text{un}}^c) \times (k_{\text{un}}^c/k_{\Delta}^c)] / (1 + k_{\text{un}}^c/k_{\Delta}^c). \quad (3)$$

Equation 3 indicates that $k^t/k^c < k_{\Delta}^t/k_{\Delta}^c$ if $k_{\text{un}}^t/k_{\text{un}}^c < k_{\Delta}^t/k_{\Delta}^c$, irrespective of a value of $k_{\text{un}}^t/k_{\Delta}^c$. The $k_{\Delta}^t/k_{\Delta}^c$ 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, $k_{\text{un}}^t/k_{\text{un}}^c < 1$ is expected, since the transition state **12** for the trans isomer must be sterically less favorable than that (**13**) for the cis isomer.



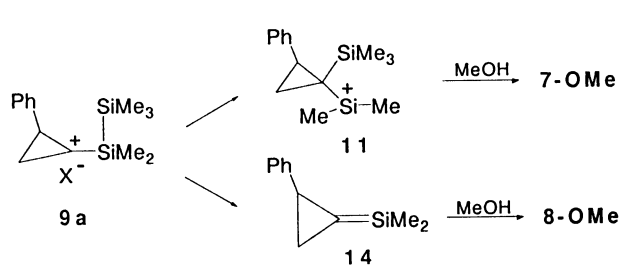
Accordingly, the $k_{\Delta(\text{SiSi})}$ mechanism would show a k^t/k^c ratio of less than 1.7, which is significantly smaller than the observed value of 2.99. Although we cannot eliminate the $k_{\Delta(\text{SiSi})}$ process, the result prefers the k_c mechanism in which $k_{\text{un}}^t/k_{\text{un}}^c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

The rate acceleration by the SiMe₂SiMe₃ group is very small in the k_{Δ} process, compared to the k_c process: $k_{\Delta}(\text{trans-4a})/k_{\Delta}(\text{trans-4b}) = 1.60$. 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 SiMe₃ 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 AgClO₄ (8.2 at 80°C) than in the absence of it (3.5 at 100°C) (Table 2). In addition, the AgClO₄-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 AgClO₄. The AgClO₄-induced solvolysis probably proceeds via a cyclopropyl cation/ClO₄⁻ ion pair which does not undergo return. Both ion pairs may undergo a rearrangement, as well as an elimination of the β -SiMe₃ group at varying ratios, depending on the solvent nucleophilicity. In a weakly nucleophilic solvent, like TFE ($N_{\text{OTs}} = -3.0^{24}$), the cation **9a** undergoes a rearrangement exclusively, whereas a strongly nucleophilic solvent, like methanol ($N_{\text{OTs}} = -0.04^{24}$), tends to attack the β -silicon of the cation to promote an elimination of the SiMe₃ 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 cm³) and ether (10 cm³) was added butyllithium (1.6 M (1

$M=1 \text{ mol dm}^{-3}$) 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 $116\text{--}117^\circ\text{C}$ (1 Torr: 1 Torr=133.3 Pa); IR (neat) 1610, 1500, 1250, 830, 800, 700 cm^{-1} ; NMR $\delta=-0.43$ (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 $\text{C}_{14}\text{H}_{23}\text{BrSi}_2$: 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 $\delta=0.15$ (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 $0.003 \text{ mol dm}^{-3}$ 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 $\delta=0.0$ (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, 7.27%. Calcd for $\text{C}_{16}\text{H}_{25}\text{F}_3\text{OSi}_2$: C, 55.46; H, 7.27%. 7-OFet: NMR $\delta=-0.30$ (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 $\text{C}_{16}\text{H}_{25}\text{F}_3\text{OSi}_2$: C, 55.46; H, 7.27%. 7-OH: IR 3350, 1260, 1080, 940, 850, 790, 700 cm^{-1} ; NMR $\delta=-0.30$ (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 $\text{C}_{14}\text{H}_{29}\text{OSi}_2$: 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

$\delta=0.09$ (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 [$75\text{--}85^\circ\text{C}$ (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 $\delta=0.0$ (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 $\text{C}_{14}\text{H}_{19}\text{F}_3\text{OSi}$: C, 58.31; H, 6.64%. 6b-OFet: NMR $\delta=0.22$ (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 $\delta=0.06$ (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 $\delta=-0.18$ (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 $\delta=-0.33$ (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 $\delta=-0.21$ (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 $\text{C}_{11}\text{H}_{16}\text{Si}$: 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 $\delta=-0.30$ (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 solvolized in methanol (25 cm³) 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 $\delta=-0.04$ (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 $\delta=-0.06$ (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 solvolized in methanol (25 cm³) 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 $\delta=1.50$ (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 $\delta=1.83$ (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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