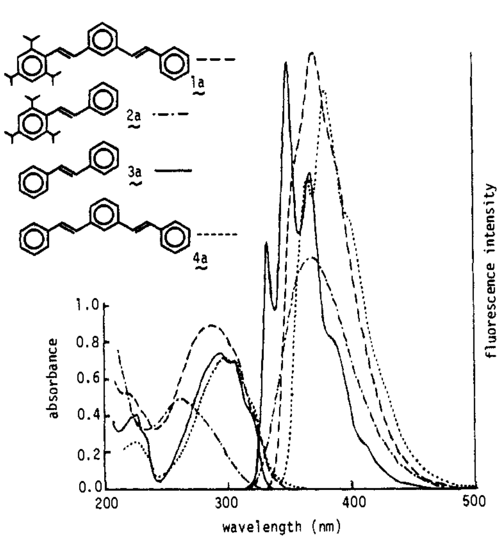

Figure 2. Absorption (at room temperature) and fluorescence spectra (at 77 K) for **1a**, **2a**, **3a**, and **4a** in methylcyclohexane: **1a**, 2.3 × 10^{-5} (---); **2a**, 2.9 × 10^{-5} M (·-·); **3a**, 2.9 × 10^{-5} M (—); **4a**, 1.5 × 10^{-5} M (···).

2,4,6-triisopropylstyryl unit.[3] The absorption spectra of the four isomers are displayed in Figure 1. The isomers **1c** and **1d**, which lack the unsubstituted *trans*-styryl unit, underwent a significant blue shift.

The quantum yield for trans–cis isomerization was measured in degassed hexane at 25 °C, by irradiation at 313 nm (K_2CrO_4, 0.6 g, and Na_2CO_3, 2.1 g, in water, 1 L).[4] The trans to cis isomerizations of *trans*-2,4,6-triisopropylstilbene (**2a**) and *trans*-stilbene (**3a**) were found to proceed in comparable efficiencies: $\Phi_{\text{trans}\rightarrow\text{cis}} = 0.35$ and 0.50, respectively. By contrast, the trans to cis isomerization of **1a** occurred in high selectivity at the hindered olefinic double bond: $\Phi_{1a\rightarrow1b} = 0.34$, $\Phi_{1a\rightarrow1c} = 0.026$ and $\Phi_{1a\rightarrow1d} = 0.00$.

The absorption spectra of **1a**, **2a**, **3a**, and **4a** are summarized in Figure 2. Comparison of the spectra of **2a** and **3a** demonstrates that 2,4,6-triisopropyl substitution produces a considerable hypsochromic and hypochromic shift (**2a**, λ_{max} 262 nm (ϵ 18 000); **3a**, λ_{max} 294 (26 000), 307 (24 000), 320 sh (14 000)). The spectrum for **1a** (λ_{max} 285 nm (ϵ 39 000), 307 sh (32 000), 323 sh (17 000)) is approximately the sum of the spectra for **2a** and **3a**, indicating that the two olefinic moieties in the **1a** molecule are relatively independent because of their cross-conjugation. Similarly the absorption maxima of *trans*-stilbene (**3a**) and *trans,trans-m*-distyrylbenzene (**4a**) are nearly at the same position because of the cross-conjugation that **4a** has. These results reveal that, although the incident light is absorbed mainly by the unhindered stilbene side of **1a**, it is the hindered stilbene moiety that photoisomerizes. It is noticeable that steric hindrance apparently functions to collect the excitation energy, as in the meta-substituted aromatic polyketones.[1]

Very interestingly, benzophenone (BP)-sensitized photolysis of **1a** in degassed hexane ([**1a**] = 0.01 M, [BP] = 0.1 M, $h\nu > 350$ nm (phenanthrene in methanol, 5 g/L)[4]) produced almost exclusively the cis,trans isomer **1c**, i.e., $\Phi_{1a\rightarrow1b} = 0.026$, $\Phi_{1a\rightarrow1c} = 0.49$, and $\Phi_{1a\rightarrow1d} = 0.00$.[6] The BP-sensitized trans–cis isomerization of **2a** and **3a** proceeded with the almost same efficiency: $\Phi_{\text{trans}\rightarrow\text{cis}} = 0.47$ and 0.50, respectively. Quenching studies of BP phosphorescence by **1a**, **2a**, and **3a** in degassed benzene at room temperature afforded $k_q\tau$ values of 17 000, 12 000, and 27 000 M^{-1}, respectively. On the basis of reported triplet lifetime of BP ($\tau = 6.5$ μs),[7] the triplet quenching rate by **1a**, **2a**, and **3a** was estimated to be 2.6 × 10^9, 1.8 × 10^9, and 4.1 × 10^9 M^{-1} s^{-1}, respectively. While this result suggests an existence of appreciable steric hindrance to the triplet energy transfer (the k_q ratio of **3a** to **2a** = 2.3), the effect is not sufficiently large to explain the high reaction selectivity ($\Phi_{1a\rightarrow1c}/\Phi_{1a\rightarrow1b} = 19$).

As a result, if the excited state of **1a** can be formulated by intramolecular energy migration (Scheme Ib), it may be concluded that $k_{et} >> k_{-et}$ for direct excitation and $k_{et} << k_{-et}$ for benzophenone sensitization. Since the transients of *trans*-stilbene photoisomerization are very short-lived ($^1t^*$, 10^{-10} s; $^1p^*$, 10^{-9} s; $^3t^*$, 10^{-7} s; $^3p^*$, 10^{-7} s),[8] the rate for the intramolecular energy migration must be very rapid. However, the origin of the observed highly regioselective photoisomerization of **1a** in both the singlet and triplet excited states is not yet clear. The fluorescence spectra of **1a**–**4a** are shown in Figure 2. The distilbenes **1a** and **4a** emit quite different fluorescence from *trans*-stilbene (**3a**), contrary to the analogous absorption spectra of these compounds (vide supra). Therefore, the two olefinic moieties of **1a** and **4a** will have a significant intramolecular interaction in the excited singlet state and hence a straightforward rationalization of the high regioselectivity of the present photoreaction appears unlikely.[9] We are continuing further effort to reach the solution.

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(4) The trans–cis photoisomerization of *trans*-stilbene (**3a**)[5] was used as a standard.

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(6) Upon continued irradiation a quasiphotostationary mixture consisting of **1a** (39%), **1b** (8%), **1c** (44%), and **1d** (9%) was obtained.

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(9) A large fluorescence Stokes shift for **2a** compared with that for *trans*-stilbene (**3a**) suggests a large change in geometry upon excitation of **2a**.[10] The positions of their fluorescence maximum (**2a**, 369 nm; **3a**, 350 nm) seem to indicate that the relaxed excited singlet state of **2a** is lower in energy than *trans*-stilbene singlet. However, the slightly structured fluorescence for **1a** is shifted to somewhat shorter wavelenths than that for **4a** (**1a**, 370 nm; **4a**, 380 nm). Thus, the highly regioselective isomerization of **1a** in the excited singlet state cannot be interpreted simply in terms of the fluorescence maxima.

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γ-Silicon Stabilization of Carbonium Ions in Solvolysis. 1. Solvolysis of *cis*- and *trans*-3-(Trimethylsilyl)cyclohexyl *p*-Bromobenzenesulfonates

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We wish to report the first conclusive evidence for the stabilization of a carbonium ion center by a γ-situated silyl group. We believe that the intramolecular mode of electronic interaction involved is of general significance but not generally recognized. The effects of the trimethylsilyl substituent (Me_3Si) on carbonium ion reactions have been examined previously by several authors.[1-4] Relative to carbon, an α-silyl group retards[1] but a β-silyl group strongly accelerates[2,3] solvolysis. Lambert[3] found *cis*-2-(trimethylsilyl)cyclohexyl trifluoroacetate to solvolyze 33 500 times

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(1) (a) Sommer, L. H.; Whitmore, F. C. *J. Am. Chem. Soc.* **1946**, *68*, 481. (b) Stang, P. J.; Ladika, M.; Apeloig, Y.; Stanger, A.; Schiavelli, M. D.; Hughey, M. R. *J. Am. Chem. Soc.* **1982**, *104*, 6852. (c) Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* **1985**, *107*, 2806.

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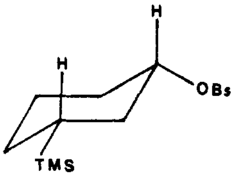
Table I. Rate Constants[a] for Solvolyses at 25 °C

	solvent[b]				
compound	80E	70E	60E	97T	70T
cis-3-(trimethylsilyl)cyclohexyl brosylate (**1**)	3.40 (0.01)	8.96 (0.09)		176.3 (0.80)	
trans-3-(trimethylsilyl)cyclohexyl brosylate (**2**)	0.89 (0.02)		3.2 (0.2)	1.99 (0.04)	4.13 (0.07)
trans-4-*tert*-butylcyclohexyl brosylate (**4**)[c]	0.22	0.50		0.39	1.00
cis-4-*tert*-butylcyclohexyl brosylate (**3**)[c]	1.26	2.75		1.66	5.01

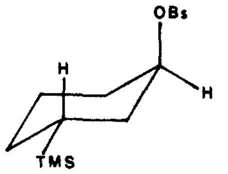
[a] k's are in units of 10^{-5} s^{-1}. All kinetic runs reported are the averages of several determinations. The errors in the rate constants are included in parentheses. [b] 80E is 80 vol % ethanol–20 vol % water, 97T is 97 wt % 2,2,2-trifluoroethanol–3 wt % water. [c] Reference 23.

faster than the unsubstituted parent but 75 times slower than the trans isomer. He suggested that electron release from the 2-Me_3Si group occurred by both inductive and hyperconjugative interactions; but later ab initio calculations[5] indicated only a very small inductive effect. Moreover, *cis*- and *trans*-4-(trimethylsilyl)-cyclohexyl tosylates solvolyze at rates comparable to the 4-*tert*-butyl analogs.[4] Fleming and Patel found that treatment of γ-Me_3Si substituted tertiary alcohols with a boron trifluoride–acetic acid complex in methylene chloride led to olefin formation via Wagner–Meerwein rearrangement and loss of the Me_3Si group.[6]

As a complement to earlier studies,[7] we decided to explore the possibility that γ-Me_3Si groups could promote neighboring alkyl or hydrogen participation in the solvolysis of secondary sulfonates. We now report results of our initial studies of the solvolysis of the title compounds, **1** and **2** (OBs is *p*-bromobenzenesulfonate or "brosylate").



(1)



(2)

3-(Trimethylsilyl)cyclohexanone was prepared[8,9] and reduced[10] to both *cis*- and *trans*-3-(trimethylsilyl)cyclohexanols by standard methods. The cis and trans β-d_4 alcohols were prepared via exchange of the ketone with deuterium oxide in the presence of sodium carbonate and reduction with diborane. The diborane-d_6 reduction of 3-(trimethylsilyl)cyclohexanone afforded a mixture of cis and trans α-*d* alcohols. The alcohols were converted to the corresponding brosylates by a modification of the Tipson procedure.[11] The alcohols were separated, and the brosylates were purified by high-pressure liquid chromatography on a silica gel column using an ethyl acetate/hexane solvent mixture. ^1H (360 MHz) and ^{13}C (75 MHz) NMR spectra were consistent with assigned structures. Kinetic measurements were done conductometrically,[12] using a bipolar pulse conductance apparatus.[13]

The rate constants for the solvolyses of the isomeric 3-(trimethylsilyl)cyclohexyl brosylates in several solvents at 25 °C are listed in Table I, along with values for the 4-*tert*-butylcyclohexyl brosylates.[14] The observed isotope effects are listed in Table II. The ratios of products from the solvolysis reactions are given in Table III.

Table II. Isotope Effects[a] for Solvolysis of Substituted Cyclohexyl Brosylates at 25 °C

			solvent[b]			
compound	equatorial[c] substituent	OBs conf.[c]	80E	70E	50E	97T
1-α-*d*	cis-3-Me_3Si	e	1.157	1.14		1.174
2-α-*d*	trans-3-Me_3Si	a	1.20			1.17
4-α-*d*	trans-4-*t*-Bu	e			1.17[d]	
3-α-*d*	cis-4-*t*-Bu	a			1.202[d]	
1-β-d_4	cis-3-Me_3Si	e	1.005	0.99		0.972
2-β-d_4	trans-3-Me_3Si	a				2.86
4-β-d_4	trans-4-*t*-Bu	e			2.425[d]	
3-β-d_4	cis-4-*t*-Bu	a			2.862[d]	

[a] The errors for the isotope effects are all between 0.005 and 0.01. [b] Solvents are as described in Table I. [c] Conformation in the most stable ground state; e = equatorial, a = axial. [d] These isotope effects were measured at 35 °C.[23]

Table III. Product Yields in Solvolysis, 25 °C

	solvent[a]				
product[b] formed by	80E	70E	70T	97T	98H
(A) *cis*-3-Me_3Si-cyclohexyl Brosylate (**1**)					
1,3 elimination (bicyclohexane)	16%	18%	7%	8%	
substitution (retained config)	84%	82%	93%	92%[c]	
ratio of ether to alcohol	0.7/1	0.4/1	0.6/1	11/1[c]	
(B) *trans*-3-Me_3Si-cyclohexyl Brosylate (**2**)					
W-M rearrangement (cyclohexene)	16%	14%	44%	51%	59%
1,2-elimination (3- and 4-Me_3Si-cyclohexene)	?	60%	42%	36%	30%
substitution (retained config)	?	18%	14%	13%	10%

[a] Solvents are as described in Table I. 98H is 98 wt % hexafluoroisopropyl alcohol–2 wt % water. [b] Relative abundance and identity of products were determined by ^2H NMR of reaction mixtures at 55 MHz. Chemical shifts, which vary slightly with solvent, are as follows in 97T: bicyclohexane (1-*d*, δ 1.44; 2,2,6,6-d_4, δ 0.42, 1.95); cyclohexene (1-*d*, δ 6.0; 3-*d*, δ 2.22; 4,4-d_2, δ 1.70); 3-Me_3Si-cyclohexene (2-*d*, δ 6.0; 6,6-d_2, δ 2.2); 4-Me_3Si-cyclohexene (1-*d*, δ 6.0; 3,3-d_2, δ 2.2); *cis*-3-Me_3Si-cyclohexanol (1-*d*, δ 3.78; 2,2,6,6-d_4, δ 1.34, 1.44, 2.32, 2.33); *trans*-3-Me_3Si-cyclohexanol (1-*d*, δ 4.32; 2,2,6,6-d_4, δ 2.0, 1.6, 1.7) *cis*-3-Me_3Si-cyclohexyl trifluoroethyl ether (1-*d*, δ 3.67; 2,2,6,6-d_4, δ 1.34, 1.44, 2.32, 2.33); *trans*-3-Me_3Si-cyclohexyl trifluoroethyl ether (1-*d*, δ 4.2; 2,2,6,6-d_4, δ 2.0, 1.6, 1.7). [c] Stereochemistry of substitution products and ether to alcohol ratio were confirmed by GC/MS. A small amount of trans ether, representing less than 4% of the total products, was also detected.

"Ethanol–trifluoroethanol" plots[15] using the data in Table I give (a), for compound **1**, a linear correlation with slope 0.90, indicating a limiting solvolysis, and (b), for compounds **2**–**4** quite different plots with ethanol correlation lines of slope about 0.6 which lie significantly above the points for the trifluoroethanol (TFE) solvents.

The isotope effects and rates for compound **2** are very similar to those for the 4-*tert*-butyl analog; however, the major product in TFE and hexafluoroisopropyl alcohol is cyclohexene formed by loss of the Me_3Si group after a Wagner–Meerwein rearrangement similar to those noted by Fleming and Patel.[6] The large β-d_4 effect and the predominance of the cyclohexene product confirm that β-H participation occurs in the rate-determining step. Since there is very little or no rate acceleration, the γ-Me_3Si group does not promote participation but merely traps the carbonium ion intermediate subsequently. The likely explanation is that in any conformation in which the trans-2 hydrogen is antiperiplanar to the leaving group, as it must be in order to participate max-

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imally, the Me_3Si group is gauche to the migrating bond, an orientation that allows for only minimal hyperconjugative stabilization of the developing vacancy at the β-C by the γ-C–Si bond.[5]

The results for the cis isomer are quite different; the rate constants are larger than those for the analogous equatorial brosylate, *trans*-4-*tert*-butylcyclohexyl brosylate, particularly in 97T (452x), and the β-*d* isotope effects are much smaller. In the ethanolic solvents, no β-d_4 isotope effect is observed, and the effect in 97T is slightly inverse. The α-*d* isotope effects are also smaller than expected. These results indicate that the reaction involves participation. The consistant formation of small yields of bicyclo[3.1.0]hexane suggest silicon-promoted carbon participation.[16]

The orientation of the two substituents in the transition state is approximately diequatorial rather than diaxial; in this conformation, all four β-C–H bonds have dihedral angles of 60° with the developing p-orbital vacancy, which allows for very little C–H hyperconjugative stabilization and gives small or inverse β-*d* isotope effects. In the alternate, higher energy, 1,3-diaxial conformation[17] two of the β-C-H bonds would be antiperiplanar to the leaving group, favoring hyperconjugation, rearrangement,[6] and large β-d_4 effects, contrary to the observations. Thus the silicon stabilizes the transition state, and presumably the carbonium ion intermediate, through a "W" conformation[18] implicating the "percaudal"[19] interaction which involves overlap of the reacting orbital on the α-carbon with the back lobe of the carbon–silicon bonding orbital. Although earlier workers have speculated on this mode of carbonium ion stabilization, evidence confirming it was not obtained.[20]

Experiments designed to characterize this interaction further are currently in progress.

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Registry No. 1, 99810-99-8; **2**, 99811-00-4; cyclohexene, 110-83-8; *cis*-3-TMS-cyclohexanol, 7452-98-4; bicyclo[3.1.0]hexane, 285-58-5.

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(16) Silicon-promoted carbon participation is chosen to indicate bridging by the γ-carbon through the back lobe of the carbon–silicon bonding orbital.

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Phenoxychlorocarbene. Spectroscopy and Photochemical Interconversion of Geometric Isomers

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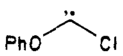
We wish to describe the first direct observation of phenoxychlorocarbene (**1**) and report evidence for the photochemical interconversion of its two geometric isomers.



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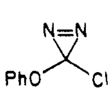
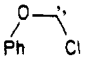


2

$PhOCHCl_2$

3



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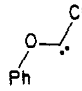

5

Irradiation ($\lambda > 360$ nm) of 3-chloro-3-phenoxydiazirine (**2**)[1,2] matrix isolated in argon or N_2 at 10 K (**2**:Ar or N_2 = ca. 1:800) led to disappearance of the IR absorptions of **2** and to growth of new bands shown in figure 1. UV spectra of the same sample in N_2 indicated the loss of **2** and growth of a broad absorption centered at 320 nm. Continued irradiation at these wavelengths destroyed the primary photoproduct bands in both the IR and UV spectra, and produced the photochemically stable products benzoyl chloride, chlorobenzene, and CO (by IR).

That the initial photoproduct absorptions are due to carbene **1** is supported by trapping. Irradiation of diazirine **2** in a N_2 matrix containing HCl (N_2:HCl:**2** = 4500:1:2) gave the above photoproduct IR bands. Warming the matrix to 33 K converted this product to dichloromethyl phenyl ether (**3**)[4] by IR.

The correspondence of the time evolution of the UV spectrum with that of the IR bands of **1** provides strong evidence for the assignment of the 320-nm UV band to **1**. Moreover, the rate of disappearance of the IR absorptions of **1** was found to be greatest when irradiation was in the region of 330–290 nm. Comparison of the UV absorbances of **1** and starting **2** (ϵ ca. 50 cm^{-1} M^{-1})[1] indicates an approximate extinction coefficient of 100 cm^{-1} M^{-1} for the carbene at 320 nm. The UV spectrum of **1** is also quite similar to that observed for methoxychlorocarbene.[3b]

No evidence for the intermediacy of a diazo compound was observed in the IR spectrum, nor were IR absorptions attributable to COCl,[5] benzoyl,[6,7] or phenyl[8] radicals observed. In a similar fashion to methoxychlorocarbene,[3] **1** exhibits strong IR absorptions at frequencies close to 1300 cm^{-1}. This absorption was assigned to a COC antisymmetric stretch in the methoxycarbene; support came from isotopic labeling.[3] The anomalously high frequency was attributed to partial C–O double-bond character, as predicted theoretically. The situation is somewhat more complicated here since the O–aryl stretching modes may also come in this region, and coupling with ring vibrations can cause splitting in the substituent deformations.[9] A reasonable model for carbene **1**, phenyl chloroformate, shows two intense C–O stretches[10] in the region 1100–1200 cm^{-1}. Corresponding vibrations of higher energy in **1** are consistent with C–O stretching modes with significant double-bond character.

Calculations on hydroxymethylene predict the existence of two geometric isomers.[11] Interestingly, irradiations of **1** at different wavelengths, with careful monitoring, indicated two distinct sets of IR absorptions for carbene **1** which exhibited different wavelength dependencies. Irradiation at 366 nm more rapidly destroyed those bands associated with the 1251-cm^{-1} band (species A, Figure 1). Conversely, absorptions associated with the bands at 1285 and 1275 cm^{-1} (species B) were more labile at 304 nm. Moreover, irradiation at 366 nm not only converted A into benzoyl chloride,

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