

Unimolecular rearrangement of α -silylcarbenium ions. An ab initio study

Soo Gyeong Cho

Agency for Defense Development, P.O. Box 35-1, Yuseong, Taejon 305-600, South Korea

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Abstract

The unimolecular rearrangements of hydrogen, methyl and phenyl groups at the Si atom in α -silylcarbenium ions have been investigated using an ab initio molecular orbital method. MP2/6-31 + G*//HF/6-31G* calculations predict that all three groups migrate from the Si to an adjacent C $_{\alpha}$ with no energy barrier. Thus, the silicenium ion is the only stable species in each potential energy surface. The conformation of the benzylsilicenium ion, (C₆H₅)CH₂-SiH₂⁺, indicates that the phenyl ring is significantly bent toward the silyl cationic center in order to interact with the vacant 3p(Si⁺) orbital. In contrast to MP2 results, Hartree-Fock calculations (both HF/3-21G* and HF/6-31G* levels) predict small energy barriers for 1,2-migrations of H and Me (1.4 kcal mol⁻¹ for H migration, and 1.5 kcal mol⁻¹ for Me migration, respectively, at the HF/6-31G* level). This difference provides convincing evidence that the incorporation of electron correlation is of particular importance in describing the potential energy surface for the rearrangement of α -silylcarbenium ions to silicenium ions. The results of the calculations have also been applied to the possible rearrangement mechanism of α -chlorosilanes to chlorosilanes, assuming that the experimental conditions are favorable toward the generation of ionic species. Various factors which may govern the migratory aptitudes of various R groups, i.e. (1) activation energies, (2) overall reaction energies and (3) the conformational preference of reactants have been investigated. The calculated activation energy obtained, namely the energy for the generation of the silicenium ion and the Cl⁻ ion from an α -chlorosilane, is consistent with the experimental migratory aptitude in the gas phase observed in mass spectrometers.

Keywords: Silicon; Ab initio; Rearrangement; Molecular mechanics; Gaussian calculations

1. Introduction

The rearrangement of α -chlorosilanes to chlorosilanes has long been investigated by silicon chemists [1–4]. The rearrangement can proceed (1) under thermal conditions [2], (2) with Lewis acid catalysts [3] and (3) in the presence of nucleophiles [4]. The rearrangement mechanism appears to be different according to the conditions employed. For instance, the rearrangement with nucleophiles is generally accepted to proceed via a pentacoordinated Si intermediate [4,5]. A dissociative ionic mechanism including 1,2-R migration of the α -silylcarbenium ion has been proposed both (1) in the gas-phase reaction and (2) in condensed-phase reactions with the aid of a Lewis acid.

Although charged species are thermodynamically unstable in the gas phase, there have been numerous reports for the presence of silicenium ions in the gas phase, especially in mass spectrometers [6,7]. Apeloig et

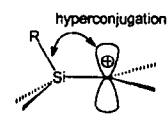
al. have investigated the rearrangement of α -silylcarbenium ions in the gas phase by using tandem mass spectrometric techniques, and also applied ab initio methods to determine the energy barriers for 1,2-H and 1,2-Me migrations [6]. Bakhtiar et al. have also employed the Fourier transform mass spectrometer and investigated the relative migratory aptitudes of H, Me and Ph groups of α -silylcarbenium ions [7].

The Lewis acid-induced rearrangement of α -chlorosilanes has been frequently employed for the syntheses of chlorosilanes [3]. However, the rearrangement mechanism under Lewis acid-catalyzed conditions is not as yet fully understood. Various mechanisms have been proposed based on experimental results (see Scheme 1). Concerted double migrations have been suggested by Eaborn and coworkers [3g]. On the other hand, a dissociative ionic mechanism has been proposed by Whitmore et al. [3a]. They assumed that the reaction proceeded in a similar fashion to the AlCl₃-induced rear-

rearrangement of neopentyl chloride. The mechanism involves an initial slow, rate-determining step of Cl abstraction by AlCl_3 yielding an α -silylcarbenium ion, followed by the 1,2-migration of an alkyl (or aryl) group generating a silicenium ion (see Scheme 1). This mechanism has been further supported by Kumada and coworkers [3c–e]. One of facts against for this mechanism was the failure to observe the key intermediate, the silicenium ion, in solution. In 1983, Lambert and Schulz claimed the generation of a silicenium ion in solution [8]. Apeloig et al. also supported Lambert by providing strong evidence for the presence of silicenium ion by both experimental observations and calculations [6]. In spite of some controversies regarding to the generation of distinctively three-coordinated silicenium ions [9], it is now generally accepted that the difficulty in observing the silicenium ion in solution comes from its ability to coordinate strongly with other species and not from its thermodynamic stability [10]. In contrast to the gas phase, the ionic dissociation of α -chlorosilanes in solution, especially in the presence of a Lewis acid, may be quite favorable. Hence, a theoretical examination of the potential energy surfaces (PESs) of α -silylcarbenium ions and silicenium ions in the gas phase could provide insight into the mechanism of the rearrangement of α -chlorosilanes both in the gas phase and under Lewis acid-catalyzed conditions.

2. Computational details

All ab initio molecular orbital calculations were carried out using the GAUSSIAN-92 [11] series of programs on a Cray Y-MP computer. Geometry optimization was undertaken at the restricted Hartree–Fock (RHF) level using the 3-21G* [12] and 6-31G* [13] basis sets. For R (R = H, Me, and Ph) migration, symmetry constraints were employed in order to maintain the eclipsed relationship between the migrating group and the vacant $2p(\text{C}^+)$ orbital in the adjacent cationic center (see



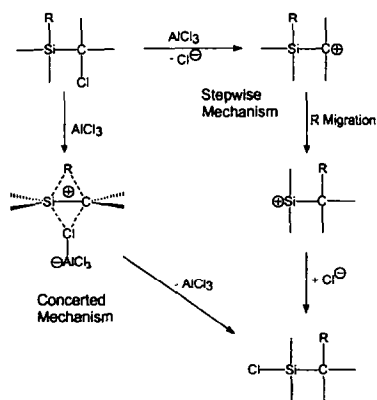
Scheme 2.

Scheme 2). Due to the symmetric restriction, some ground structures are not found to be energy minima in the PESs. However, the energy minima are easily located by rotating the orientation of the vacant p orbital. Single-point calculations using 6-31G* optimized geometries were performed by utilizing second-order Møller–Plesset perturbation theory [14] to include the effects of electron correlation. Additional single-point calculations at the MP2/6-31 + G*//HF/6-31G* level (*a//b* is Pople's notation, which represents a single-point calculation at the *a* level of theory on the geometry optimized at the *b* level of theory.) were undertaken to verify the effect of diffusion functions on the energetics, especially the steps including ionic species. The transition structure (TS) was located by using the eigenvector following algorithm, and confirmed as a true TS by having only one negative Hessian. The harmonic frequency analysis using analytic second derivatives was carried out at both HF/3-21G* and HF/6-31G* levels at all stationary points to confirm the nature, minimum or TS, and to provide zero-point vibrational energy (ZPVE) corrections. Molecular mechanics (MM) calculations were performed by using Allinger's MM3 force field [15]. Force field parameters for α -chlorosilanes were taken from recent data [30]. The values of $C_{\text{ar}}\text{-Si-C-Cl}$ torsional parameters, i.e. $V_1 = -0.116$, $V_2 = 0.116$ and $V_3 = 0.252$, were developed to reproduce HF/6-31G* calculated rotational isomerism of (chloromethyl)phenylsilane.

3. Results and discussion

3.1. Selection of model compounds

α -Silylcarbenium ions ($\text{R-SiH}_2\text{-CH}_2^+$, R = H, Me and Ph) which can provide the migrations of H, Me and Ph groups are selected for this study. We have chosen these compounds in order to compare the migratory aptitudes of H, Me and Ph groups in α -silylcarbenium ions. Bakhtiar et al. have experimentally investigated the migratory aptitudes of these groups by using Fourier transform mass spectroscopy in the gas phase [7a]. They employed $\text{Ph(Me)SiH-CH}_2\text{Cl}$ (**4**) which can generate the Ph(Me)SiH-CH_2^+ ion and subsequently provide three different migrated products in a competitive fashion. The relative migratory aptitude observed in their experiments was $\text{Ph} > \text{H} \gg \text{Me}$, which apparently disagrees with other gas-phase thermal rearrangements per-



Scheme 1.

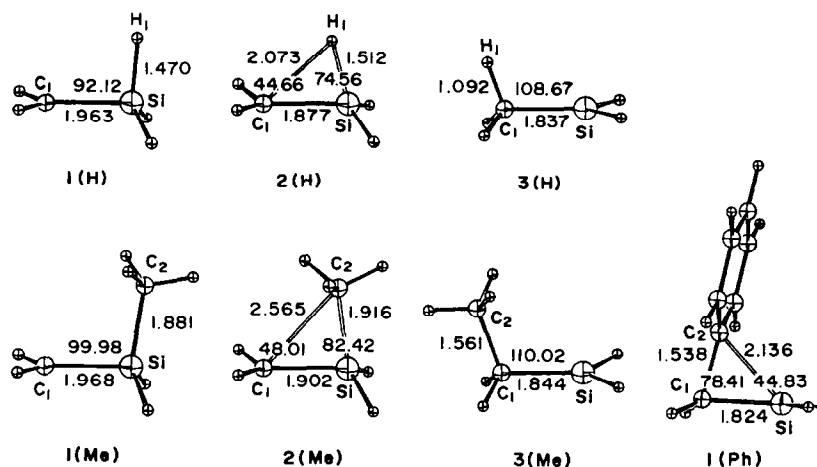


Fig. 1. ORTEP drawings and geometric parameters of HF/6-31G* calculated stationary points.

formed by Clarke et al. (H > Ph > Me) [2h]. Clarke et al. also employed **4** and found that H migration was favored over Ph migration. This difference in the relative migratory aptitudes of R groups from the same starting material may arise from the different experimental conditions employed, which probably induce the rearrangement to take place via a different reaction mechanism. The experimental conditions employed by Bakhtiar et al. were obviously favorable toward generating the ionic species. Thus, careful investigations of the relative migratory aptitudes of various R groups in the

gas phase may shed light on understanding the reaction mechanism for the migration of α -chlorosilanes to chlorosilanes under Lewis acid-catalyzed conditions, if indeed the rearrangement proceeds via a dissociative ionic mechanism.

3.2. PESs during 1,2-migrations

We have located all the stationary points on the PESs for H, Me and Ph migrations at HF/3-21G* and HF/6-31G* levels of theories. ORTEP drawings of

Table 1
Calculated energies (hartrees)

	HF/3-21G* // HF/3-21G* ^a	HF/6-31G* // HF/6-31G* ^a	MP2/6-31G* // HF/6-31G* ^a	MP2/6-31 + G* // HF/6-31G* ^a
1(H)	-327.681 1972 [31.95] ^b	-329.333 6172 [32.15]	-329.504 2493	-329.506 2868
2(H)	-327.679 6436 [31.79, -436.79i ^c]	-329.331 3983 [32.00, -466.73i ^c]	-329.510 3060	-329.512 3480
3(H)	-327.749 299 [34.79, -22.29i ^{c,d}]	-329.398 3452 [34.64, -21.37i ^{c,d}]	-329.593 1377	-329.594 9689
$E_a^{\ddagger,e}$	0.97(0.83)	1.39(1.25)	-3.80(-3.94)	-3.80(-3.94)
E_r^f	-42.73(-40.17)	-40.62(-38.38)	-55.78(-53.54)	-55.65(-53.41)
1(Me)	-366.529 2379 [51.73]	-368.389 5628 [51.81]	-368.692 5876	-368.695 7671
2(Me)	-366.528 1422 [51.86, -154.95i ^c]	-368.387 2171 [51.89, -132.12i ^c]	-368.698 2094	-368.701 7350
3(Me)	-366.568 3053 [54.54]	-368.432 5528 [54.41]	-368.758 2310	-368.761 0022
E_a^{\ddagger}	0.69(0.81)	1.47(1.54)	-3.52(-3.59)	-3.74(-3.81)
E_r	-24.52(-21.99)	-26.98(-24.64)	-41.19(-38.85)	-40.94(-38.60)
1(Ph)	-556.043 1167 [91.70]	-558.972 4546 [91.23]	-559.930 7095	-559.943 3820

^a Pople's notation. ^b The values in brackets are the zero-point vibrational energies (in kcal mol⁻¹). ^c Imaginary frequency, in cm⁻¹. ^d The imaginary frequency comes from the orientation of vacant p orbitals. However, the energy difference is less than 1 kcal mol⁻¹. ^e Activation energy barrier, in kcal mol⁻¹. The values in parentheses are corrected for ZPVE with the correction factor of 0.9. ^f Energy of the rearrangements of α -silylcarbenium ions, in kcal mol⁻¹; for the values in parentheses, vide supra.

HF/6-31G* optimized geometries are depicted in Fig. 1. Improvement of the basis set from 3-21G* to 6-31G* has little effect on the nature of the PES. For H and Me migrations, each PES has three stationary points, namely (1) the α -silylcarbenium ion [**1(H)** and **1(Me)**], (2) the silicenium ion [**3(H)** and **3(Me)**] and (3) the TS connecting the α -silylcarbenium ion and the silicenium ion [**2(H)** and **2(Me)**]. On the other hand, only one stationary point, **1(Ph)**, is found in the PES for the migration of Ph. However, incorporation of the electron correlation changes the PESs for the migrations of H and Me substantially. Thus, H and Me groups as well as the Ph group migrate from Si to C $_{\alpha}$ with no energy barriers at the MP2 levels (see Table 1). Thus, the silicenium ions [**3(H)**, **3(Me)** and **1(Ph)**] are the only stationary point in each PES.

One of the interesting geometric features in **1(Ph)** is a significant bent of the benzene ring toward the Si⁺ center in the β position. Although **1(Ph)** is indeed a silicenium ion, the Si–C₁–C₂ angle is bent to 78.4° to increase the interactions between the phenyl ring and the Si⁺ center. In **1(Ph)**, the distance between Si and C₂ is 2.136 Å, which should probably not be considered as a bond although it is only about 0.3 Å longer than the normal Si–C bond. Another interesting geometric feature is the C–Si–X angles (X = H and C) in **1(H)** and **1(Me)** optimized with HF/6-31G* method. Although they are not energy minima at the MP2 level, the SCF results are quite informative. We have found that the C–Si–X angles are noticeably shrunk by dissociation of Cl[–] from α -chlorosilanes [92.1° in **1(H)**, and 100.0° in

1(Me), respectively]. This shrinkage is probably attributed to either (1) strong electrostatic interactions between the migrating center and the adjacent carbenium center or (2) hyperconjugations of a migrating bond with the vacant 2p(C⁺) orbital in an adjacent carbenium ion. The migrating H [in **1(H)**] and Me [in **1(Me)**] are shown to be negatively charged (see Table 2). This result agrees with previous theoretical studies in which the alkyl group and hydrogen attached directly to Si atom are usually negatively charged [16]. Thus, as the migrating center gets closer to the carbenium ion, it enhances the electrostatic attraction between two oppositely charged centers. This favorable electrostatic interaction may also be a driving force for the rearrangement. Another plausible explanation for the shrinkage of the C–Si–X angles is the hyperconjugation between the migrating bond and the vacant 2p(C⁺) orbital of the adjacent carbenium ion.

As mentioned previously, conformations have been restricted to those eclipsed between the migrating group and the vacant p orbital (see Scheme 2). Thus, some of ground structures are not energy minima. For instance, **3(H)** has a small negative imaginary frequency ($-21.37i$ cm⁻¹) which vanishes when the vacant 3p(Si⁺) orbital is properly oriented. Our examinations of the true minima due to orientation of the vacant p orbital show that the energy difference is quite low (less than 1.0 kcal mol⁻¹). In both SiH₃CH₂⁺ and MeSiH₂CH₂⁺, the eclipsed conformations are favored slightly over the staggered conformations in the HF/6-31G* level (0.21 kcal mol⁻¹ in SiH₃CH₂⁺ and 0.46

Table 2
Mulliken population of molecular fragments in each stationary point for H, Me and Ph migrations calculated by 3-21G* and (6-31G*) methods

	1(X)	2(X)	3(X)
<i>X = H</i>			
H ₁	-0.037 (-0.047)	-0.061 (-0.077)	0.321 (0.283)
C ₁ (-CH ₂ -)	0.315 (0.400)	0.279 (0.360)	-0.397 (-0.281)
Si(-SiH ₂ -)	0.722 (0.647)	0.782 (0.718)	1.076 (0.998)
<i>X = Me</i>			
C ₂ (CH ₃ -)	-0.175 (-0.099)	-0.168 (-0.100)	0.160 (0.143)
C ₁ (-CH ₂ -)	0.286 (0.378)	0.263 (0.344)	-0.220 (-0.114)
Si(-SiH ₂ -)	0.889 (0.712)	0.905 (0.756)	1.060 (0.971)
<i>X = Ph</i>			
C ₂	-0.403 (-0.264)		
C ₁ (-CH ₂ -)	-0.035 (0.013)		
Si(-SiH ₂ -)	0.910 (0.758)		

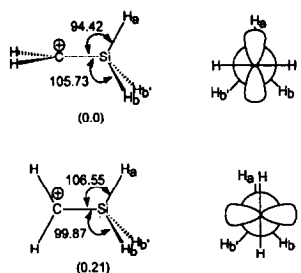


Fig. 2. Variation of C^+-Si-H angles of **1(H)** due to the orientation of the vacant $p(C^+)$ orbital (calculated by HF/6-31G* method). The values in parentheses are relative energies in kcal mol^{-1} .

kcal mol^{-1} in $\text{MeSiH}_2\text{CH}_2^+$, respectively). Despite the small energy change, the $C-Si-X$ ($X = C, H$) angles in **1(H)** and **1(Me)** optimized by SCF methods undergo a noticeable change due to alignment with the vacant p orbital. The $C-Si-H$ angle for the eclipsed hydrogen is 94.4° while the $C-Si-H$ angles for the other hydrogens are 105.7° . The large angle variation is also observed in the staggered conformation of **1(Me)** (see Fig. 2). This directionality may suggest that strong hyperconjugation is in fact present in α -silylcarbenium ions.

In addition, we have examined the energy profiles for H, Me and Ph migrations in terms of the change in the $C-Si-X$ angle ($X =$ migrating center). These results are depicted in Figs. 3–5. One of reasons for choosing the $C-Si-X$ angle as a geometric variable in our figures arises from earlier intrinsic reaction coordinate calculations using the HF/6-31G* method. We have calculated 15 points starting from the TS in both directions. For both Me and H migrations, the geometries converted smoothly to those of the α -silylcarbenium and silicenium ions. This change can be easily verified by observing the new sp^2 center whose angle gets closer to 120° . The change in the $C-Si-X$ angle is also relatively

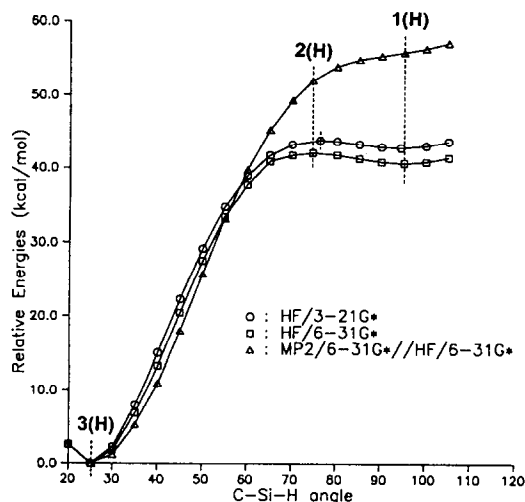


Fig. 3. Energy profiles for 1,2-H migration relative to a change in the $C-Si-H$ angle.

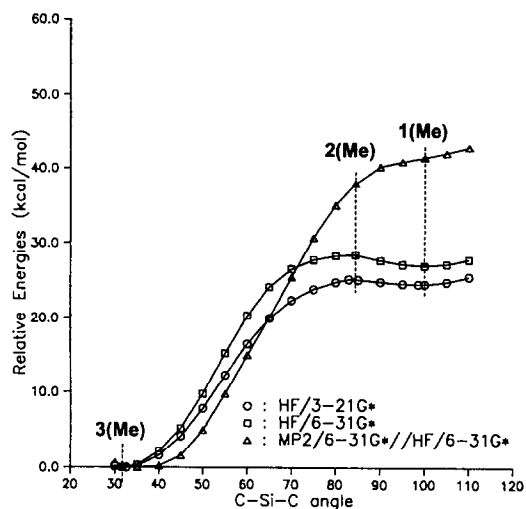


Fig. 4. Energy profiles for 1,2-Me migration relative to a change in the $C-Si-C$ angle.

large and is quite linear as the reaction proceeds. Energy profile diagrams using the $C-Si-X$ angle readily affirm the difference of the PESs arising from the SCF and MP2 methods. Migrations of the H or Me group of α -silylcarbenium ions occur spontaneously at the MP2 levels, but have small energy barriers at SCF levels.

3.3. Comparison with previous *ab initio* results

Earlier calculations using the double ζ basis set with the inclusion of the polarization functions by Hopkinson and Lien [17] showed that **3(H)** is more stable than **1(H)** by ca. 40 kcal mol^{-1} , and the energy barrier is only $0.1 \text{ kcal mol}^{-1}$. On the basis of the tendencies in their calculational results, Hopkinson and Lien suggested that **1(H)** may not be a minimum and **2(H)** may not be a

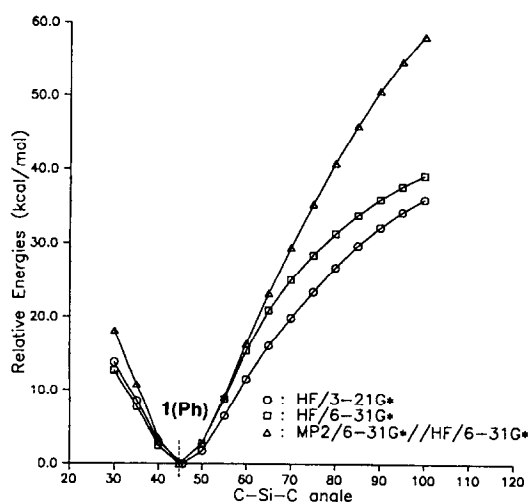


Fig. 5. Energy profiles for 1,2-Ph migration relative to a change in the $C-Si-C_{ar}$ angle.

saddle point at a considerably higher level of theory. Our MP2/6-31G*//HF/6-31G* calculations confirm Hopkinson and Lien's suggestion. Our HF/3-21G* results with the ZPVE correction, show that the energy difference between **1(H)** and **3(H)** (40.2 kcal mol⁻¹) is essentially identical to that of Hopkinson and Lien [17]. However, the inclusion of an electron correlation effect alters the energy difference to 53.5 kcal mol⁻¹, which is considerably higher than HF values (see Table 2). Very recently, Gordon and coworkers also investigated the rearrangement of **1(H)** to **3(H)** independently from us. They explored the unimolecular decomposition processes of **3(H)** at the MP2/6-31G** level [18]. Although the basis set employed by us is slightly smaller than that of Gordon and coworkers, our results are in good agreement with theirs.

Several previous studies have also been carried out to investigate the PES of 1,2-Me migration. Earlier results indicated that the energy barriers for 1,2-Me migration in α -silylcarbenium ions was only a few kcal mol⁻¹. Apeloig and Stanger estimated the rearrangement barrier of MeCH⁺-SiHMe₂ to Me₂CH-Si⁺HMe to be 2–3 kcal mol⁻¹ [6b], based on HF/6-31G* calculations and corrected for the correlation energy using the empirical 'additivity approximation'. Apeloig et al. investigated the PES between MeC⁺H-SiMe₃ and Me₂CH-Si⁺Me₂ [6a], but although they calculated the energetics of the ground states, they did not calculate the energy barrier between them. Recently, Hopkinson and coworkers have investigated the energy barrier between **1(Me)** and **3(Me)** at the MP2/6-31G** level. They have found that 1,2-Me migration proceeds without an energy barrier [19], which is consistent with the results of this study. Hopkinson and coworkers have also explored the conformations of **3(Me)** and found that the most stable conformation at the MP2/6-31G**

level is that in which the eclipsed H _{β} is bent toward Si⁺ in order to interact strongly with the vacant Si(3p⁺) orbital. In our studies, symmetry restrictions imposed to the conformation of **3(Me)** may prevent the conversion of the **3(Me)** conformation to the global minimum mentioned by Hopkinson and coworkers. To clarify this difference, we have repeated part of the calculations of Hopkinson and coworkers with the MP2/6-31G* level, and confirmed that their results are correct. The conformer in which the eclipsed H _{β} interacts with Si⁺ is 2.0 kcal mol⁻¹ more stable than **3(Me)** at both the MP2/6-31G* and MP2/6-31G** levels. Nevertheless, the energy difference is relatively small and, more importantly, makes little impact on our energy diagrams. To our knowledge, reliable ab initio calculations have not been applied, as yet, to the rearrangement of Ph.

3.4. Migratory aptitude of H, Me and Ph groups of α -chlorosilanes

When α -silylcarbenium ions are generated from α -chlorosilanes, they are converted spontaneously to silycenium ions. Thus, the relative migratory aptitudes of R groups as measured by Bakhtiar et al. [7a] may not be accounted for solely in terms of the unimolecular migration of the α -silylcarbenium ions. Since their starting materials were α -chlorosilanes, we feel that a dissociation step should be included to explain the relative migratory aptitudes of H, Me and Ph. If the rearrangement of chlorosilanes to α -chlorosilanes proceeds via a dissociative ionic mechanism, the rate-determining step is probably the dissociation of Cl⁻ from α -chlorosilanes, which is a highly endothermic process. We have attempted to estimate the activation energies for the rearrangement of α -chlorosilanes to chlorosilanes. Table

Table 3
Energetics^a of various reaction steps in the rearrangement of α -chlorosilanes to chlorosilanes

	HF/3-21G*// HF/3-21G* ^b	HF/6-31G*// HF/6-31G*	MP2/6-31G*// HF/6-31G*	MP2/6-31 + G*// HF/6-31G*
$\Delta E_1 = E(X-SiH-CH_2^+{}^c) + E(Cl^-) - E(X-SiH_2-CH_2-Cl)$				
X = H	223.55	221.06	245.23	235.62
X = Me	217.18	214.83	237.67	228.59
X = Ph	209.43	206.49	226.31	218.69
$\Delta E_2 = E[3(X)^d] + E(Cl^-) - E(X-SiH_2-CH_2-Cl)$				
X = H	154.51	152.58	163.49	154.02
X = Me	167.35	161.19	172.56	163.72
X = Ph	148.98	141.81	146.1	139.75
$\Delta E_3 = E(X-CH_2-SiH_2Cl) - E(X-SiH_2-CH_2-Cl)$				
X = H	-45.49	-41.80	-41.16	-41.08
X = Me	-30.26	-31.06	-29.99	-29.57
X = Ph	-32.86	-34.24	-34.20	- ^c

^a Energies in kcal mol⁻¹. ^b Pople's notation. ^c The conformations of α -silylcarbenium ions used are the ones of the corresponding α -chlorosilanes, except the dissociation of Cl⁻. This assumes the geometries have not been changed during the dissociation. ^d **1(X)** for X = Ph.

^e SCF convergence failed for Ph-CH₂-SiH₂Cl.

3 summarizes the thermodynamics for the dissociation step. The term ΔE_1 is the energy solely required for the ionic dissociation of the C_α -Cl bond, the conformation for the rest of the molecule being frozen. The ionic dissociation energies for the C_α -Cl bond are ca. 219–236 kcal mol⁻¹ at the MP2/6-31 + G* level, which reveals that the rearrangement of α -chlorosilanes to chlorosilanes via a dissociative ionic mechanism in the gas phase is highly unfavorable. Thus, we believe that an ionic mechanism is only possible if the conditions are specifically designed to favor the generation of ionic species such as in mass spectrometers. On comparing the relative energetics of the ionic dissociation of Cl⁻ with the relative migratory aptitudes suggested by Bakhtiar et al., the difference is evident. Thus, the ionic dissociation of Cl⁻ alone is not capable of explaining the relative migratory aptitudes of R groups in α -chlorosilanes.

Overall reaction energies for the rearrangement of α -chlorosilanes to chlorosilanes may be an important factor in governing the relative migratory aptitudes. In order to explore this possibility, we have calculated the overall reaction energies for the conversion of α -chlorosilanes to chlorosilanes (see column for ΔE_3 in Table 3). The overall reaction energy for 1,2-H migration (41.2 kcal mol⁻¹ at the MP2/6-31G* level) is marginally larger than those for 1,2-Ph and 1,2-Me migrations (34.2 kcal mol⁻¹ and 30.0 kcal mol⁻¹, respectively, at the MP2/6-31G* level). The overall energies calculated at SCF levels also show the same trend as those calculated at the MP2 level. If the overall energy is the governing factor for migration, the relative migratory aptitude should be H \gg Ph > Me, which also disagrees with Bakhtiar's experimental results [7a]. However, the relative migratory aptitude derived from the overall energies seems to be in accord with the gas-phase thermolysis data obtained by Clarke et al. [2h]. The experimental conditions employed by Clarke et al. may not favor an ionic dissociative mechanism, and suggest that the rearrangement proceeds via a concerted mechanism with a doubly bridged TS. Although careful examinations of the TSs for the concerted mechanism provide information on the relative migratory aptitudes in more detail, our results strongly suggest that overall reaction energies may be one of the possible

candidates for governing the migratory aptitudes of R groups in the gas-phase thermolysis. On the other hand, if the reaction proceeds via a dissociative ionic mechanism, the migratory aptitudes of R groups appear not to be governed by overall reaction energies.

Since α -silylcarbenium ions are not energy minima in PESs, migrations of R groups may occur concurrently with the formation of the carbenium ion center. Hence, the rate-determining step is the departure of Cl⁻ and the formation of the silicenium ion, which appears to occur as two consecutive steps but turns out to be a single process in our MP2 calculations. The quantity ΔE_2 is the energy of the rate-determining step in the rearrangement of α -chlorosilanes to chlorosilanes, provided (1) that migration proceeds through ionic dissociation and (2) 1,2-migration is concurrent with the dissociation of the Cl⁻ ion. Based on ΔE_2 , the relative migratory aptitude is Ph > H > Me. This result is consistent with recent gas-phase experiments by Bakhtiar et al. [7a]. The energy barriers calculated at the MP2/6-31 + G*//HF/6-31G* level are about 140–164 kcal mol⁻¹, which are quite high. As mentioned earlier, this process may not be readily feasible in both the gas phase and the condensed phase. Generally, a polar medium solvates the ionic species, which may noticeably reduce the activation energies. Thus, Lewis acid-catalyzed rearrangements in the condensed phase are possibly favorable toward this mechanism. We have also utilized SCRF calculations [20] to estimate the energetics in various solvents with different polarities (see Table 4). However, irrespective of the polarity, the energy barriers remain virtually constant. This result is rather surprising since it could be assumed that TSs with a distinctively localized charge are possibly stabilized by polar solvents. This surprising outcome may arise from (1) a strong charge separation in α -chlorosilanes [3o] and/or (2) strong coordination of polar solvents to the Cl⁻ ion. The Mulliken charges of the Si atoms in α -chlorosilanes are about 0.70–0.85 while those of the C_α atom are approximately 0.7 at the HF/6-31G* level. Hence, stabilization of α -chlorosilanes by solvents is also substantial. Although the Lewis acid-catalyzed rearrangement proceeds via ionic dissociation, a considerable reduction in the energy barrier is not expected simply as a result of electrostatic

Table 4
The values of ΔE_2 ^a in different media^b calculated by the SCRF/6-31G* method

	Gas phase	Solution phase		
		$\epsilon = 10$	$\epsilon = 40$	$\epsilon = 80$
X = H	152.58	152.78	152.81	152.81
X = Me	161.19	160.55	160.45	160.43
X = Ph	141.81	141.79	141.79	141.79

^a For definition, see Table 3 and main text. ^b HF/6-31G* calculated a_0 (cavity radius) values are used; 3.74 Å for SiH₃CH₂Cl, 3.31 Å for **3(H)**, 3.95 Å for MeSiH₂CH₂Cl, 3.58 Å for **3(Me)**, 4.50 Å for PhSiH₂CH₂Cl, 4.22 Å for **1(PH)** and 2.93 Å for Cl⁻.

Table 5
MM3 force field parameters ^a employed in this work

Bending			
Angle	type	K_b ^b	θ_0
Si–C–Cl ^c	all	0.15	106.00
Torsion			
Dihedral angle	V_1	V_2	V_3
C–Si–C–Cl ^c	–0.980	0.350	0.340
C _{ar} –Si–C–Cl	0.116	–0.116	0.252
H–Si–C–Cl ^c	0.0	0.0	0.420
Electronegativity correction terms to l_0			
Bond	End of bond	Atom type	δl_0
Si–C ^c	C	Cl	+0.011

^a Except when noted standard parameters distributed with the MM3 program were used. ^b Values in mdyne Å rad^{–2}. ^c See Ref. [30].

interaction with the solvent. Strong coordination of solvents to the Cl[–] ion should be considered explicitly in order to describe the energetics in polar solutions more accurately.

3.5. MM results of the conformational preference of 4

Since the unimolecular rearrangement of α -silylcarbenium ions proceeds without an energy barrier, any group resided in a position *anti* to a departing Cl[–] ion may have the best chance of migrating from Si to the α -carbon. Thus, the migratory aptitudes of R groups may also depend on the conformational preference of α -chlorosilanes. This possibility has prompted us to apply MM calculations to the rotational isomerism of 4 to provide the competitive migration of H, Me and Ph groups.

We have previously developed MM2 parameters for α -chlorosilanes [30,21]. A number of ‘electronegativity correction’ terms for bond angles as well as bond lengths have been utilized to reproduce the structures and energetics more accurately [30]. The ‘electronega-

tivity correction’ terms for bond lengths were initially proposed by Allinger et al. [22], and have been taken into consideration in subsequent MM2/MM3 programs. However, the ‘electronegativity correction’ terms for bond angles have not been applied to MM methods. During force field developments for α -chlorosilanes, we found large bond angle variations which could not be accommodated by the equilibrium values. Our new ‘electronegativity correction’ terms for bond angles enable us to reproduce the geometries of α -chlorosilanes more accurately. In this study, we have repeated part of our previous calculations with MM3 force fields without employing the ‘electronegativity correction’ terms for bond angles. This simplifies the parameters. The MM3 parameters utilized in this calculation are summarized in Table 5. Our results demonstrate that the rotational barriers and relative conformational energies of some α -chlorosilane compounds are predicted properly, although we still feel that the prediction of the geometries of α -chlorosilanes could be improved significantly by using the ‘electronegativity correction’ terms for bond angles. Our new MM3 calculations predict that the

Table 6
Conformational energies of PhSiH₂–CH₂Cl calculated by ab initio and MM methods

	HF/6-31G*//HF/6-31G*	MP2/6-31G*//HF/6-31G*	MM3
<i>gauche</i>	0.28 ^a (–1018.7240039) ^b [66.64] ^c	0.10 (–1019.8163173)	0.24 [63.6]
<i>anti</i>	0.0 (–1018.7244552) [180.0]	0.0 (–1019.8164719)	0.0 [180.0]
<i>gauche / gauche</i>	3.31 (–1018.7191739)	3.05 (–1019.8116049)	3.32
<i>gauche / anti</i>	2.18 (–1018.720975)	2.37 (–1019.8127013)	2.19

^a Relative energies (in kcal mol^{–1}). ^b The values in parentheses are total energies (in hartrees). ^c The values in brackets are the C_{ar}–Si–C–Cl torsional angles.

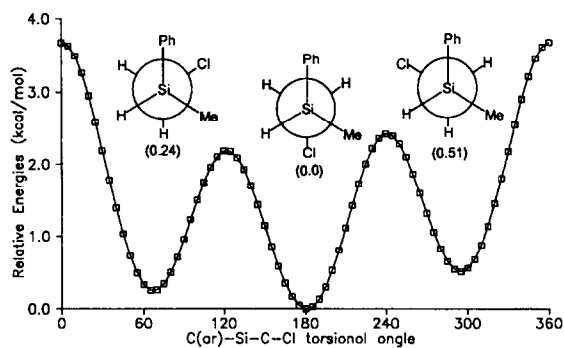


Fig. 6. The rotational isomerism of **4** as calculated by MM3 methods. The values in parentheses are relative conformational energies in kcal mol⁻¹.

rotational barrier of ClCH₂SiH₃ is 2.52 kcal mol⁻¹, while our previous MM2 results gave a value of 2.56 kcal mol⁻¹. The rotational barriers for *gauche/gauche* and *gauche/anti* conformers of ClCH₂SiH₂Me are 2.47 and 2.88 kcal mol⁻¹ by the MM2 method and are now predicted to be 2.43 and 2.78 kcal mol⁻¹ by the MM3 method without employing the ‘electronegativity correction’ term for bond angles.

In order to calculate the rotational isomerism of **4**, we need a new parameter, i.e. the C_{ar}-Si-C-Cl torsional parameter. First, we calculated the rotational isomerism of PhSiH₂-CH₂Cl at a reliable level employing ab initio methods. The results are summarized in Table 6. At the MP2/6-31G*//HF/6-31G* level, the *anti* conformation of PhSiH₂-CH₂Cl is favored over the *gauche* conformation by only 0.1 kcal mol⁻¹. Our MM3 results with the new torsional parameter predict the *gauche/anti* difference to be 0.24 kcal mol⁻¹. Next, we turn to the rotational isomerism of **4** employing the MM3 method. Our MM3 results predict that the overall minimum in the conformational energy surface of **4** is indeed one in which the Ph group is *anti* to Cl (see Fig. 6). Nevertheless, as might be expected, the conformational preference is not that large. The

conformation in which Ph is *anti* to Cl is 0.24 kcal mol⁻¹ more stable than the one in which H is *anti* to Cl, and 0.51 kcal mol⁻¹ more stable than that in which Me is *anti* to Cl, respectively. This conformational preference maintains the population *anti* to Ph/H/Me in the ratio 48:32:20 at room temperature. At higher temperatures, the preference is less. Although the conformational preference of **4** is in accord with Bakhtiar’s experimental migratory tendencies, we still feel that the conformational preference of α -chlorosilanes may not be the determining factor in explaining the relative migratory aptitudes of the R groups.

3.6. Comments on the rearrangement mechanisms of α -chlorosilanes to chlorosilanes

As discussed previously, the rearrangement mechanism of α -chlorosilanes to chlorosilanes appears to differ significantly according to the experimental conditions. Thus, our investigations on the unimolecular rearrangement of α -silylcarbenium ions may be valid only under certain reaction conditions, namely (1) rearrangements in gas-phase mass spectrometers (condition I) and (2) rearrangements in polar solvents, either under thermal or Lewis acid-catalyzed conditions (condition II). We feel confident that our results are in good agreement with rearrangements performed under condition I when compared with experimental data from Bakhtiar et al. [7a]. Our results may also provide some valuable information regarding the rearrangement mechanism under condition II. However, a Lewis acid or solvent as well as the reagent should be explicitly included in theoretical studies in order to accurately model the reaction circumstances of condition II.

Other than the conditions mentioned above, extreme care is necessary in comparing our calculational results with experimental data, for example those from gas-phase thermolyses. Rearrangements of α -chlorosilanes to chlorosilanes in the gas phase probably proceed via a

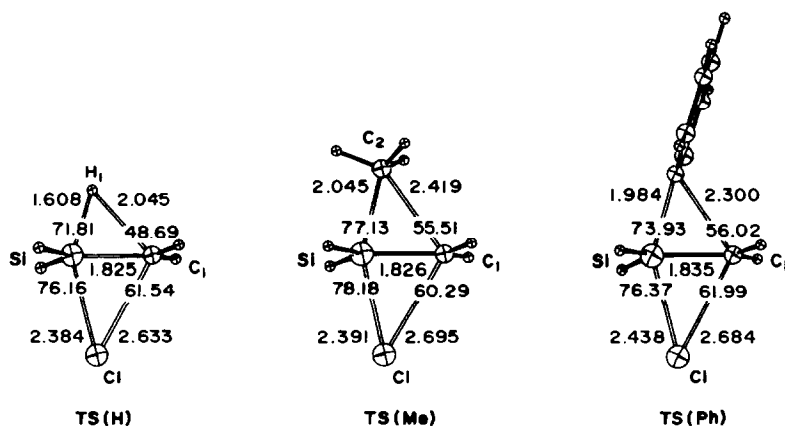


Fig. 7. ORTEP drawings and geometric parameters for dyotropic type TSs in H, Me and Ph migrations as calculated at the HF/6-31G* level.

Table 7
Calculated energetics for the dyotropic rearrangements of H, Me and Ph groups

	Symmetry	NIMAG ^a	HF/6-31G*//HF/6-31G*	MP2/6-31G*//HF/6-31G*
TS(H) ^b	C _s	1 [−816.26i] ^c	−789.0643840 ^d (64.70) ^e	−789.3924490 (71.11)
TS(Me)	C ₁	1 [−593.42i]	−828.1039391 (69.96)	−828.5662582 (74.42)
TS(Ph)	C _s	1 [−460.74i]	−1018.6261806 (61.66)	−1018.71381 (64.41)

^a The number of imaginary frequencies. ^b For definition, see Fig. 7. ^c The values in brackets are the magnitudes of the imaginary frequency (in cm^{−1}). ^d Values in hartrees. ^e The values in parentheses are the activation energies for the dyotropic rearrangements (in kcal mol^{−1}).

dyotropic mechanism, in which two groups migrate simultaneously [23]. We have optimized the TSs to allow for the dyotropic rearrangement of H, Me and Ph groups at the HF/6-31G* level (see Fig. 7). Fig. 7 clearly shows that both R and Cl groups migrate toward adjacent C_α and Si atoms whilst maintaining an antiperiplanar relationship. The calculated activation energies for such dyotropic rearrangements are summarized in Table 7. The activation energies calculated by MP2/6-31G*//HF/6-31G* methods for H, Me and Ph are 71.1, 74.7 and 64.4 kcal mol^{−1}, respectively. The activation energies for a dyotropic mechanism are noticeably smaller than the corresponding values for an ionic dissociative mechanism. Thus, in agreement with Clarke et al., a dyotropic rearrangement is indeed the most favorable mechanism in the gas-phase thermolysis [2h] unless the reaction conditions are specifically designed to generate ionic species. However, our calculated migratory aptitudes, i.e. Ph > H > Me, do not agree with the experimental values given by Clarke et al., i.e. H > Ph > Me. Clarke et al. utilized **4** as a starting material for studying the competitive migrations of H, Me and Ph groups. Since the rearrangement of each R group from **4** occurs under a different environment at the Si atom, steric and/or electronic, caution should be exercised in comparing the experimental migratory aptitudes directly with the calculated values. Our preliminary results also reveal that the activation energies in dyotropic rearrangements are substantially influenced by different substituents at the Si and/or C_α atoms [24]. From MP2/6-31G*//HF/6-31G* calculations, Ph and Me substituents at the Si atom stabilize the TSs by ca. 2 and 3 kcal mol^{−1}, respectively. Thus, the relative ease of rearrangement of H and Ph groups may be significantly different if the substituent effect is taken into account. Further studies on dyotropic rearrangements including the effect of substituents are in progress and will be published subsequently in detail [24].

4. Conclusions

We have examined the unimolecular rearrangement of α -silylcarbenium ions to silicenium ions using ab

initio MO calculations. On incorporating the electron correlation effect, the PESs connecting the α -silylcarbenium ion and silicenium ion are dramatically different from those calculated at SCF theory level. Our MP2/6-31 + G*//HF/6-31G* results predict that H, Me and Ph groups in α -silylcarbenium ions migrate spontaneously from Si to C_α with no energy barrier. We have also applied our results to the rearrangement of α -chlorosilanes to chlorosilanes. For most such rearrangements in the gaseous phase, our calculations show that they occur via a dyotropic mechanism, in which both groups migrate simultaneously. In contrast, the activation energies for the ionic dissociation of α -chlorosilanes are approximately 140–165 kcal mol^{−1}, which appears to be highly unfavorable in the gaseous phase. However, provided the experimental conditions are favorable towards the generation of ionic species, such an ionic dissociative mechanism could be feasible. The experimental migratory aptitudes as measured in a mass spectrometer by Bakhtiar et al. appear to correlate well with our activation energies for the dissociation of an α -chlorosilane to Cl[−] and a silicenium ion as obtained by MP2 calculations.

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