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The Origin of β-Silicon Effect in Electron-Transfer Reactions of Silicon-Substituted Heteroatom Compounds. Electrochemical and Theoretical Studies[1]

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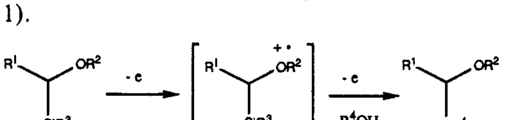
Abstract: Silyl substitution at the carbon adjacent to the oxygen causes significant decrease in the electrochemical oxidation potentials of ethers and alcohols, and this effect strongly depends upon the geometry of the molecule. Two explanations are possible: (a) the cation radical intermediate is stabilized by overlap of the filled C–Si bond with the half-vacant 2p orbital of the oxygen; (b) overlap of 2p orbital of the oxygen with the filled C–Si bond in the neutral molecule raises its HOMO level which in turn favors electron transfer. Theoretical studies using MO calculations indicate that the second effect is dominant. The geometric requirements can also be explained in terms of the HOMO level. The HOMO level varies with the torsion angle of Si–C–O–H(C), and when the C–Si bond achieves coplanar orientation with the p orbital of the oxygen, the HOMO level becomes the maximum. The plots of experimental oxidation potentials of some cyclic silyl-substituted ethers in which rotation around the C–O bond is restricted vs the torsion angle fit well to the plots of HOMO energy. Although the most stable conformation does not seem to be suitable for the electron transfer in acyclic systems, significant silicon effects are observed even for such systems in the electrochemical studies. The electron transfer seems to take place not in the most stable conformation but in the higher energy conformation, which is favorable for the oxidation. Temperature dependence of oxidation potentials has been examined in order to reveal the effect of conformation. The electrochemical oxidation of silyl-substituted ethers having an additional silyl group or oxygen atom has also been studied. The β-silicon effect for the electron-transfer reaction of sulfides, amines, and carbamates has been discussed, and the energy level of the p orbital of the heteroatom relative to that of the C–Si bond is suggested to be very important.

The ability of β-situated silyl groups to stabilize cations or to promote the formation of cations is well known as β-silicon effect and is of considerable research interest from a viewpoint of both theoretical studies and synthetic utility.[2] Although the β-silicon effect for cationic[3] and radical[4] species has been studied extensively, relatively little information has been available for the β-silicon effect for cation radical species. Since one-electron oxidation is the most common way of generating cation radical species of organic compounds, studies on electron-transfer reactions of organosilicon compounds, especially organosilicon compounds containing heteroatoms, seem to be important for the elucidation of β-silicon effect for cation radicals. Several reports on this subject have appeared in the literature so far. Pioneering work by Cooper and Owen revealed that substitution of a silyl group at the carbon adjacent to the heteroatom such as nitrogen, sulfur, and phosphorus causes a decrease in the oxidation potential, although the magnitude is not so large.[5] Since electrochemical oxidation is considered to proceed via initial formation of cation radical intermediates,[6] this observation indicates that silicon promotes the formation of the β cation radical. Kira and Sakurai generated the cation radical of silyl-substituted ethers and sulfides by γ irradiation and studied their structures with ESR.[7] Mariano studied photoelectron transfer reactions of silyl-substituted amines and ethers extensively.[8] He claimed that facility of the electron-transfer reactions would be a result of the good overlap existing between the filled C–Si σ orbital and the half-vacant heteroatom orbital of the cation radical intermediate. The electron-transfer reaction of silicon-substituted amines in flavin enzyme is also reported, suggesting the importance of this type of reaction in the study of biological systems.[9] Recently we have found that substitution of a silyl group at the carbon adjacent to the oxygen atom of ethers and alcohols resulted in dramatic decrease in the oxidation potentials.[10] The magnitude of the silicon effect is much greater than that for amines and sulfides. The electrochemical oxidation of such silyl-substituted ethers and alcohols gave rise to facile cleavage of the carbon–silicon bond (eq 1).



(1)

On the basis of geometric dependence of the oxidation potential, we proposed that the overlap between the C–Si σ bond and the lone pair of the oxygen atom plays an important role. Block also reported that substitution of a silyl group at the carbon bearing the heteroatom resulted in a decrease in the ionization potentials of ethers and sulfides in photoelectron spectroscopic studies.[11] He also observed geometric requirements and claimed the importance

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[1] Part 7: Electrochemical oxidation of organosilicon compounds. For part 6, ref 12.

[2] For example: (a) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981. (b) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: West Berlin, 1983.

[3] For example: Lambert, J. B.; Finzel, R. B. *J. Am. Chem. Soc.* **1982**, *104*, 2020–2022. See also refs 18 and 19 and references cited therein.

[4] Auner, N.; Walsh, R.; Westrup, J. *J. Chem. Soc., Chem. Commun.* **1986**, 207–208.

[5] Cooper, B. E.; Owen, W. J. *J. Organomet. Chem.* **1971**, *29*, 33–40. See also: Knyazhevskaya, V. B.; Traven, V. F.; Stepanov, B. I. *Zh. Obshch. Khim.* **1980**, *50*, 606–613; *Chem. Abstr.* **1980**, *93*, 167061c.

[6] For example: (a) Weinberg, N. L.; Weinberg, H. R. *Chem. Rev.* **1968**, *68*, 449–523. (b) Schaefer, H. J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 911–934. (c) Shono, T. *Electroorganic Chemistry as New Tool in Organic Synthesis*; Springer-Verlag: West Berlin, 1984. (d) Torii, S. *Electroorganic Synthesis: Methods and Applications*; Kodansha Verlag Chemie: 1985.

[7] Kira, M.; Nakazawa, H.; Sakurai, H. *Chem. Lett.* **1986**, 497–500.

[8] (a) Brumfield, M. A.; Quillen, S. L.; Yoon, U. C.; Mariano, P. S. *J. Am. Chem. Soc.* **1984**, *106*, 6855–6856. (b) Hasegawa, E.; Xu, W.; Mariano, P. S.; Yoon, U.-C.; Kim, J.-U. *Ibid.* **1988**, *110*, 8099–8111. (c) Xu, W.; Jeon, Y. T.; Hasegawa, E.; Yoon, U. C.; Mariano, P. S. *Ibid.* **1989**, *111*, 406–408 and references cited therein.

[9] Silverman, R. B.; Banik, G. M. *J. Am. Chem. Soc.* **1987**, *109*, 2219–2220. Oxidative cleavage of the C–Si bond adjacent to nitrogen is also reported by Chan; see: Chan, T. H.; Chem, L. M.; Wang, D. *J. Chem. Soc., Chem. Commun.* **1988**, 1280–1281.

[10] (a) Yoshida, J.; Murata, T.; Isoe, S. *J. Organomet. Chem.* **1988**, *345*, C23–C27. See also: (b) Koizumi, T.; Fuchigami, T.; Nonaka, T. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 219–225.

[11] Block, E.; Yencha, A. J.; Aslam, M.; Eswarakrishnan, V.; Luo, J.; Sano, A. *J. Am. Chem. Soc.* **1988**, *110*, 4748–4753. See also: Block, E.; Aslam, M. *Tetrahedron* **1988**, *44*, 281–324.

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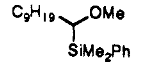
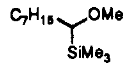
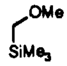
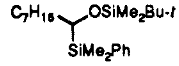
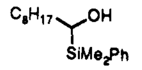
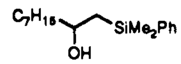
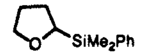
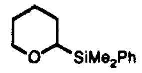
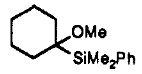
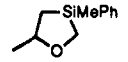
Table I. Electrochemical Oxidation Potentials of Silicon-Substituted Ethers and Related Compounds[a]

compound	cyclic voltammetry E_p (V)	rotating disk electrode $E_{1/2}$ (V)	rotating disk electrode E_d (V)
	>2.5		
	>2.5		
	2.25		1.95
 (1)	1.60	1.50	1.33
 (2)	1.72		
	1.90		
 (3)	1.95		
 (4)	1.70	1.43	1.25
 (5)	2.26		1.73
 (6)	2.15	1.84	1.98
 (7)	1.67	1.53	1.39
 (8)	2.08	(1.70)	1.54
 (9)	1.63	1.50	1.35
 (10)	1.45	1.38	1.26
 (11)	1.82		1.64

[a] Cyclic voltammetry and rotating disk electrode were carried out with a glassy carbon working electrode in 0.1 M $LiClO_4/CH_3CN$. Ag/AgCl was used for the reference electrode.

of overlap between the C–Si bond and the orbital of the heteroatom.

All studies mentioned above indicate that there exist definite β-silicon effects in electron-transfer reactions of heteroatom compounds. *Silicon promotes the generation of the β cation radical of the heteroatom.* Although this concept has currently received increasing research interest even from a synthetic point of view,[12] no detailed and quantitative study on the origin of the β-silicon effect for the electron-transfer reactions has been reported so far. Even the question of whether the β-silicon effect for carbocations can be simply extended to that for cation radicals of heteroatoms or not has been left unanswered. In order to get deeper insight into such β-silicon effect we have carried out both experimental studies on their electrochemical oxidation and theoretical studies using MO calculations.

Results and Discussion

R_3SiCH_2OR'. We first examined the silyl-substituted compounds containing oxygen as the heteroatom, because they exhibit β-silicon effect most strikingly among silyl-substituted heteroatom compounds containing oxygen, nitrogen, and sulfur. Several silicon-substituted ethers and related compounds were synthesized, and their oxidation potentials were determined with cyclic voltammetric (CV) and rotating disk electrode (RDE) techniques (Table I). The following points warrant comment.

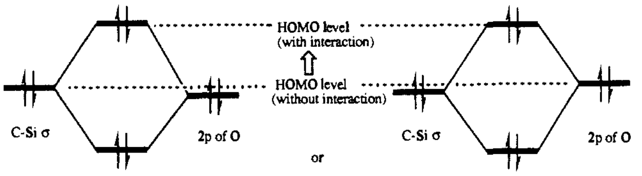


Figure 1. Energy level diagram of interaction of the C–Si σ orbital and 2p orbital of the oxygen atom.

1. It is generally difficult to oxidize aliphatic ethers.[13] For example, 1-methoxyoctane does not exhibit an oxidation wave less than 2.5 V vs Ag/AgCl in acetonitrile. 1-(Dimethylphenylsilyl)-1-methoxydecane (**1**), however, exhibited an oxidation wave at the peak potential of 1.6 V, indicating that substitution of a silyl group at the carbon adjacent to the oxygen lowers the oxidation potential at least by 0.9 V.

2. The oxidation potential of silicon-substituted ether **1** is much less than that of the corresponding compounds without the ether functionality such as octyldimethylphenylsilane.[14,15]

3. Trimethylsilyl group is also effective as a silyl group as demonstrated by compound **2**.

4. The oxidation potential of *tert*-butyldimethylsilyl ether **3** is higher than the corresponding methyl ether **1**.

5. Silyl substitution at the carbon adjacent to the oxygen of alcohols (compound **4**) also causes a decrease in their oxidation potentials.

6. Oxidation potentials of alcohols having a silyl group at two carbon distance from the oxygen such as compound **5** are very high. Therefore the effect of silicon is very small when it is separated by two carbon atoms from the oxygen.

7. In cyclic systems the effect of silicon strongly depends on the geometry of the molecule. The oxidation potential of 2-(dimethylphenylsilyl)tetrahydrofuran (**7**) is comparable to those of acyclic compounds. However, the oxidation potentials of the corresponding six-membered ring, 2-(dimethylphenylsilyl)tetrahydropyran (**8**) is much greater. The difference in oxidation potential cannot be attributed to that between the parent compounds. Although it is difficult to determine the electrochemical oxidation potentials of the parent cyclic ethers (>2.5 V), vertical ionization potential of tetrahydrofuran is reported to be greater than that of tetrahydropyran.[16] In the silylated analogue the order of the oxidation potential is reversed.

8. The oxidation potential of epoxy silane **6** is very high in comparison with other acyclic and cyclic silyl-substituted ethers. Since the ionization potential of the parent compound, ethylene oxide, is also greater than that of other cyclic ethers,[16] it is difficult to evaluate the effect of silyl-substitution in the epoxy silane with the electrochemical means. Block reported, however, that there exist significant silicon effects in the ionization potentials of epoxides.[11,17]

CV and RDE studies revealed that substitution of a silyl group at the carbon adjacent to the oxygen causes a significant decrease in the oxidation potential and that this effect is strongly affected by the geometry of the molecule. The latter fact suggests an important role played by the overlap between the carbon–silicon bond and the p orbital of the oxygen atom. Two explanations seem to be possible.

1. The cation radical intermediate, which is formed by one-electron oxidation of the neutral molecule, is stabilized by overlap of the half-vacant orbital of oxygen atom with the filled C–Si σ

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[12] For example: Yoshida, J.; Matsunaga, S.; Isoe, S. *Tetrahedron Lett.* **1989**, *30*, 219–222. See also ref 8.

[13] Shono, T. In *The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Sulphur Analogues*; Patai, S., Ed.; Wiley: New York, 1980; Chapter 8.

[14] The peak oxidation potential of tetraethylsilane is reported to be 2.56 V vs NaCl-SCE. See: Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4790–4798.

[15] Electrochemical oxidation of tetraalkylsilanes in the presence of fluoride ion is reported; see: Alyev, I. Y.; Rozhkov, I. N.; Knunyants, I. L. *Tetrahedron Lett.* **1976**, 2469–2470.

[16] Levy, G.; De Loth, P. *C. R. Hebd. Seances Acad. Sci. Ser. C* **1974**, *279*, 331–334; *Chem. Abstr.* **1975**, *82*, 30545*s*.

[17] Block also reported that the silicon effect of epoxides is greater than acyclic ethers, indicating geometric requirement of the silicon effect.[11]

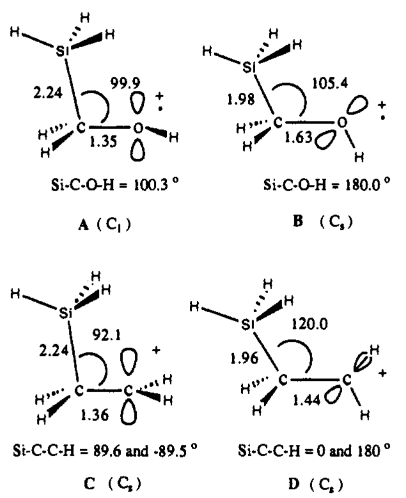

Figure 2. Geometrical parameters computed for the cation radical and cation with the 3-21G basis set. Distances are in angstroms; angles are in degrees.

bond. Silicon is known to have a definite stabilizing effect on β carbocations in cases where the C–Si bond can achieve coplanar arrangement with the vacant 2p orbital of the carbocation center. Experimental[18] and theoretical[19] studies revealed that $Me_3SiCH_2CH_2^+$ is stabilized by about 1.6–1.7 eV relative to ethyl cation. Since the cation radical is also an electron-deficient species that has a positive charge, it seems to be reasonable to expect a similar stabilizing effect of silicon. Inductive effect of silicon does not seem to account for the geometry dependence of the oxidation potential. For carbocations the inductive effect of silicon is reported to be very small.[19]

2. The overlap between the C–Si σ bond and the 2p orbital of the oxygen atom in the neutral molecule may raise the HOMO level[20] to promote the electron transfer from the molecule (Figure 1). Both experimental and theoretical studies revealed that β-silyl substitution of olefins causes significant destabilization of the HOMO by the interaction of the C–Si bond with the olefin π system.[21] As a matter of fact, the oxidation potentials of allylsilanes are about 0.5 V less than those of the corresponding alkenes.[22] So similar interaction of the C–Si bond and the nonbonding 2p orbital of the oxygen may cause destabilization of the HOMO of silyl-substituted ethers.

In order to examine the first possibility, ab initio calculations of the cation radical species were carried out using UHF/3-21G.[23] We chose SiH_3CH_2OH as a model compound. Geometry optimization gave structures A and B (Figure 2).[24] Although the structure A is established to be a minimum by frequency calculations, the structure B is found to have one imaginary frequency and is considered to be a saddle point. In A the C–Si bond and the p orbital of the cation radical center are in the same plane, so that significant interaction between them is expected, whereas in B they are in perpendicular orientation, and therefore they cannot interact with each other. Thus the cation radical A can be stabilized by the adjacent C–Si bond, whereas such stabilization is impossible in B.

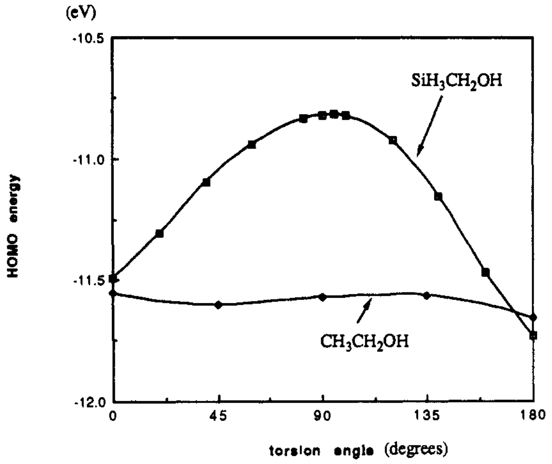

Figure 3. Plots of HOMO energy of SiH_3CH_2OH and CH_3CH_2OH calculated with 3-21G vs torsion angle of Si–C–O–H or C–C–O–H.

The C–Si bond in A (2.24 Å) is much longer than normal C–Si bonds (1.92 Å),[25] indicating that the C–Si bond is weakened in cation radical A. This is consistent with facile cleavage of the C–Si bond by electrochemical oxidation.[26-28] On the other hand, the length of the C–Si bond in B (1.98 Å) is almost the same as the normal one, whereas the C–O bond (1.63 Å) is longer than the normal one, suggesting that breaking of the C–O bond would take place. But this is not the case. Therefore A seems to be the likely intermediate of the electrochemical oxidation.[29] However, it is surprising that A is only about 0.3 eV more stable than B. This roughly means that the silicon stabilization energy of the cation radical is about 0.3 eV, if the inductive effect of silicon is negligible.[30] Similar results were obtained with calculations at STO-3G (ΔE = 0.11 eV) and STO-3G* (ΔE = 0.12 eV) levels, the latter including d orbitals of silicon. The value of 0.1–0.3 eV is very small in comparison with the significant stabilization energy reported for β carbocations.[18,19] Although high level ab initio calculations of $SiH_3CH_2CH_2^+$ have already been reported by Jorgensen et al.,[19a] we also carried out similar calculations at the same level (UHF/3-21G) as that used for the calculations of the cation radical. The geometry optimization gave structures C and D, which are very similar to those obtained by Jorgensen. By the frequency calculations C is characterized as a minimum, but D is found to be a saddle point. In C the C–Si bond is in the same plane as the p orbital of the carbocation, whereas in D they are perpendicular. The calculations showed that C is 1.1 eV more stable than D, indicating that silicon stabilizes the β carbocation by about 1.1 eV. This value is comparable with the stabilization energy reported in the literature.[18,19]

The value calculated for silicon-stabilization energy of β cation radical is comparable to that reported for β-silyl carbon radicals (about 0.12 eV).[4] Although the fully occupied C–Si σ orbital

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(18) Hajdasz, D.; Squires, R. *J. Chem. Soc., Chem. Commun.* **1988**, 1212–1214.

(19) (a) Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496–1500. (b) Ibrahim, M. R.; Jorgensen, W. L. *Ibid.* **1989**, *111*, 819–824.

(20) A linear correlation of oxidation potentials with HOMO energy levels has been reported. Miller, L. L.; Nordblam, G. D.; Mayeda, E. A. *J. Org. Chem.* **1972**, *37*, 916–918 and references cited therein.

(21) (a) Girodan, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 6544–6546. (b) Bock, H.; Kaim, W. *Ibid.* **1980**, *102*, 4429–4438.

(22) (a) Yoshida, J.; Murata, T.; Isoe, S. *Tetrahedron Lett.* **1986**, *29*, 3373–3376. (b) Koizumi, T.; Fuchigami, T.; Nonaka, T. *Chem. Express* **1986**, *1*, 355–358. See also: Schaefer, H. J.; Hermeling, D.; Lange, K.-H. *Extended Abstracts*, Spring Meeting of the Electrochemical Society, May 6–11, 1984, Cincinnati, OH, p 441.

(23) (a) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939–947. (b) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *Ibid.* **1982**, *104*, 2797–2803.

(24) Similar conformers have been reported for the cation radical $CH_3CH_2OH^{\cdot+}$. See: Bouma, W. J.; Nobes, R. H.; Radom, L. *J. Am. Chem. Soc.* **1983**, *105*, 1743–1746.

(25) The length of C–Si bond in H_3SiCH_3 was calculated to be 1.92 Å at 3-21G level.

(26) The C–Si bond is cleaved selectively without affecting the C–H bond adjacent to the oxygen. See ref 10.

(27) Oxidative cleavage of C–Si bond, see: (a) Tamao, K.; Kakui, T.; Akita, M.; Iwahara, T.; Kanatani, R.; Yoshida, J.; Kumada, M. *Tetrahedron* **1983**, *39*, 983–990. (b) Tamao, K. In *Organosilicon and Bioorganosilicon Chemistry*; Sakurai, H., Ed.; Ellis Horwood: Chichester, 1985 and references cited therein.

(28) Electrochemical cleavage of metal–carbon bonds, see: Pickett, C. J. In *The Chemistry of the Metal–Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1985.

(29) ESR study revealed that the cation radical of $CH_3SCH_2Si(CH_3)_3$ has a similar conformation in which C–Si bond and the p orbital of S are in the same plane.

(30) Jorgensen et al. reported that inductive effect of Si to β carbocation is very small. See ref 19.

interacts strongly with the vacant orbital of the carbocation, its interaction with the half-vacant orbital of the radical or the cation radical seems to be much weaker.

It is interesting to analyze the angle of Si–C–O in the cation radical and the carbocation. In A the Si–C–O angle (99.9°) is somewhat smaller than that in B (105.4°), suggesting some interaction between the C–Si bond and the p orbital of the oxygen in A. This is consistent with the fact that SOMO is delocalized to both the C–Si bond and 2p orbital of the oxygen. Kira and Sakurai also revealed in the ESR study that the SOMO of the cation radical of $(CH_3)_3SiCH_2OCH_3$ is no longer regarded as an oxygen nonbonding orbital but as one including large contribution from the C–Si bonding orbital.[7] Large difference in the angle of Si–C–C in C (92.1°) and D (120°) is noteworthy, and this reflects a much larger interaction between the C–Si bond and the vacant orbital of the carbocation.

Since stabilization of the β-cation radical does not fully account for the β-silicon effect for electron-transfer reactions, the second possibility has been examined. HOMO energies of the neutral molecule of SiH_3CH_2OH were determined by MO calculations (RHF/3-21G). As shown in Figure 3, the HOMO energy varies dramatically with the Si–C–O–H torsion angle. When the torsion angle is 0°, the HOMO energy level is relatively low. In this conformation the C–Si bond is perpendicular to the p orbital of the oxygen, and the HOMO mainly reflects the C–Si σ bond. The energy level of the nonbonding 2p orbital of the oxygen is slightly lower than that of the C–Si σ orbital. The HOMO energy increases with the torsion angle and becomes the maximum when the torsion angle is about 95°. In this conformation the C–Si bond is almost in the same plane as the p orbital of the oxygen so that they can interact with each other effectively. Indeed, the HOMO is delocalized over the oxygen p orbital and the C–Si bond. Further increase in the torsion angle resulted in decrease in the HOMO energy, and the HOMO energy becomes the minimum when the torsion angle reaches 180°. In this conformation the C–Si bond becomes perpendicular to the p orbital of the oxygen again, and they cannot overlap with each other. Difference in HOMO energies between the maximum and the minimum is about 0.9 eV, indicating that silicon destabilizes the HOMO by about 0.9 eV. This value is much greater than the calculated silicon stabilization energy for the cation radical intermediate (0.1–0.3 eV) and can explain the experimental β-silicon effect.

For comparison, the HOMO energy of CH_3CH_2OH, which has CH_3 group instead of SiH_3, was also calculated. The HOMO energy does not vary with the C–C–O–H torsion angle appreciably as shown in Figure 3. Presumably the energy level of the C–C bonding orbital is much lower than the p orbital of the oxygen, and therefore, they cannot interact with each other. On the other hand, the energy level of the C–Si orbital is comparable to that of the oxygen p orbital so that they can interact with each other effectively.

Similar results were obtained with the calculations at STO-3G level and MNDO[31] calculations. The effect of silicon d orbitals is negligibly small because the calculations including silicon d orbitals (STO-3G*) gave essentially the same results.

In order to test the reliability of the present calculations, especially the relationship between the HOMO level and the torsion angle, we plotted the experimental oxidation potentials of some silicon-substituted ethers in which the rotation around the C–O bond is restricted. As shown in Figure 4 the plots of the experimental oxidation potentials fit well to the HOMO energy–torsion angle curve obtained by the MO calculations (Figure 3). Therefore we conclude that the rise of the HOMO energy by the overlap between the C–Si bond and the p orbital of the oxygen plays the major role in promoting the electron-transfer reactions. Stabilization of the cation radical by the overlap with the C–Si bond may also play some role, but its contribution seems to be less important.

The fact that the oxidation potential varies dramatically with the torsion angle of Si–C–O–C indicates that we can control the oxidation potential by simply changing the geometry of the molecule. This idea seems to provide a useful concept for designing organic molecules having a specific oxidation potential, and various applications will hopefully appear in the future.

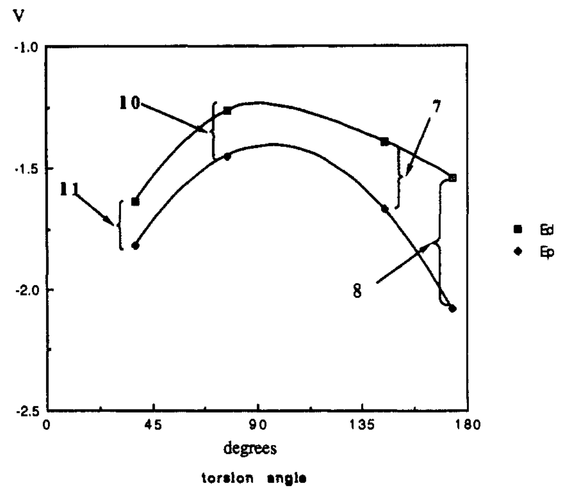

Figure 4. Plots of oxidation potentials of some silyl-substituted ethers vs the torsion angle of Si–C–O–C.

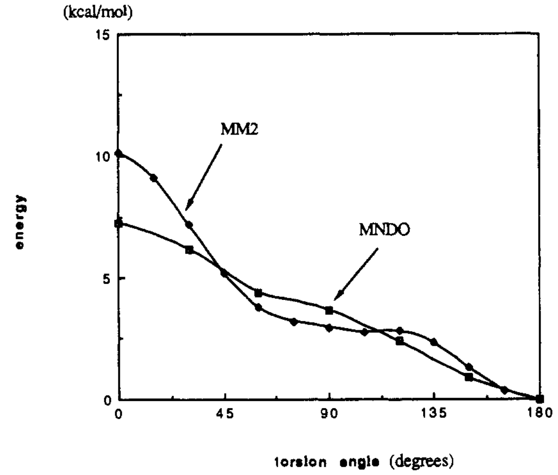

Figure 5. Potential function for rotation about Si–C–O–C of $(CH_3)_3SiCH_2OCH_3$ calculated with MM2 and MNDO.

In acyclic silyl-substituted ethers the rotation around the C–O bond is free although there exists some rotational barrier. Then the question of at which conformation the electron transfer takes place in acyclic systems becomes important. For example, in the most stable conformer of $(CH_3)_3SiCH_2OCH_3$ the C–Si bond and O–C bond should be in anti orientation. This is consistent with MNDO and MM2[32] calculations (Figure 5). In such conformation the torsion angle of Si–C–O–C is almost 180°, and therefore the HOMO level should be the minimum and is almost same as the HOMO level of the compound without a silyl group. The experimental oxidation potential of $(CH_3)_3SiCH_2OCH_3$, however, is much less than those of simple ethers (Table I). This fact implies that the electron transfer takes place at the conformation which is more favorable for the electron transfer but energetically less favorable. In the case of alkyl-substituted derivatives $(CH_3)_3SiCH(R)OCH_3$ such as **2**, the conformation where the C–R and O–C bonds are anti is also stable, and this conformation seems to be more favorable for the electron transfer because the torsion angle of Si–C–O–C is about 60°. Contribution of this conformation seems to be responsible for the lower oxidation potentials of alkyl-substituted derivatives, although inductive effect of R group may also be important.

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(31) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899–4907.

(32) Extensive work on molecular mechanics of organosilicon compounds has been reported; see: Frierson, M. R.; Imam, M. R.; Zalkow, V. B.; Allinger, N. L. *J. Org. Chem.* **1988**, *53*, 5248–5258 and references cited therein.

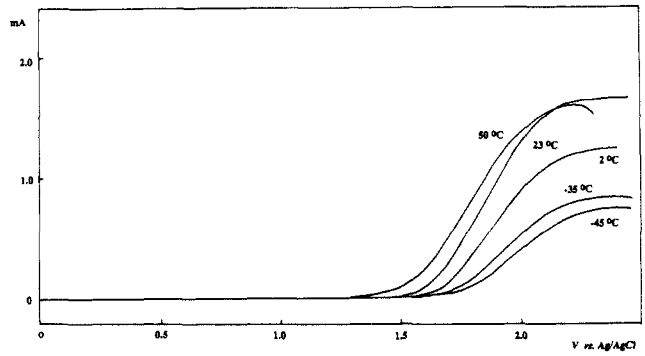


Figure 6. Voltammograms of (methoxymethyl)trimethylsilane in 0.1 M $LiClO_4/CH_3CN$ at various temperatures (RDE).

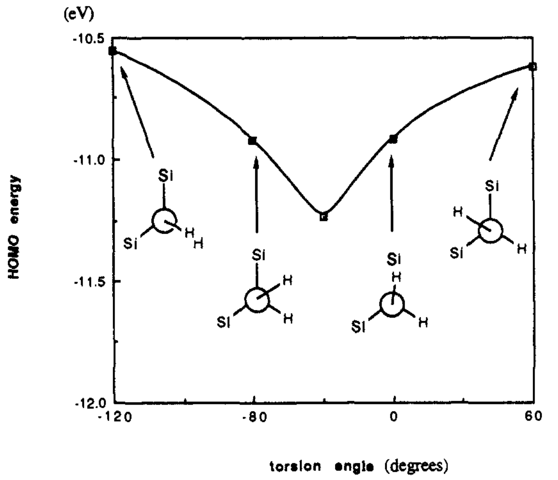


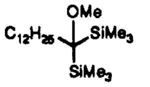
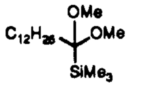
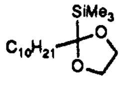
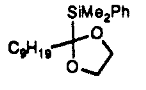
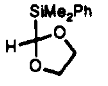
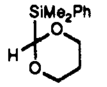
Figure 7. Plots of HOMO energy of $(SiH_3)_2CHOH$ calculated with 3-21G vs torsion angle of Si–C–O–H.

In order to get experimental information about the conformational factors, the temperature dependence of the oxidation potentials was examined (Figure 6).[33] As the temperature is lowered, the oxidation potential shifts to anodic. At the higher temperatures the conformers of low oxidation potential have significant population and the electron transfer takes place preferably at such conformers. This is consistent with the energy profile about the rotation around the C–O bond shown in Figure 5. At the lower temperatures, however, the molecule is fixed to the most stable conformation and this conformation is not suitable for the electron transfer. Therefore the oxidation potential is high. The limiting current also decreases with lowering the temperature. This is presumably attributed to decrease in the rate of the subsequent chemical reaction.

$(R_3Si)_2CHOR'$. Silicon-substituted ethers having two silyl groups were also synthesized,[12] and their oxidation potentials were determined with CV and RED. As shown in Table II the additional silyl group causes further decrease in oxidation potentials. This result is consistent with the HOMO level obtained with ab initio MO calculations (Figure 7). The additional silyl group causes rise of the maximum of the HOMO level. Increase in the population of favorable conformers for the electron transfer also seems to be important.

$R_3SiCH(OR')_2$. Oxidation potentials of silyl-substituted ethers having an additional oxygen atom at the carbon bearing silicon (silyl-substituted acetals) were also examined. The substitution of an additional oxygen atom causes a further decrease in the oxidation potential. Presumably the population of favorable conformations for the electron transfer increases as the number of oxygen atoms increases. It is also noteworthy that significant geometry dependence was observed for cyclic silyl-substituted acetals. 2-Silyl-1,3-dioxolanes (**14**–**16**) exhibited the oxidation waves at 1.4–1.5 V (CV) whereas the oxidation potential of the corresponding 2-silyl-1,3-dioxane (**17**) was much higher (about 2.0 V) at room temperature. The temperature dependence of the oxidation potentials of **16** and **17** is noteworthy (Figure 8). The oxidation potential of the six-membered **17** decreases significantly with increasing the temperature, whereas the oxidation potential of the five-membered **16** decreases slowly. The following explanation seems to be reasonable. In the most stable conformation of **17** the silyl group seems to occupy the equatorial position, and the C–Si bond and the p orbital of the oxygen atom (lone pair) are in almost perpendicular orientation. Since at low temperatures the molecule is fixed to this conformation which is unfavorable for the electron transfer, the oxidation potential is very high. As the temperature increases the molecule becomes more flexible and the electron transfer takes place presumably at the distorted conformation in which some overlap between the C–Si bond and the p orbital of the oxygen can be attained. Therefore the oxidation potential decreases dramatically. On the other hand, in **16** the most stable conformation seems to be suitable for the electron transfer because the geometry allows the effective overlap between the C–Si bond and the p orbital of the oxygen atom.

Table II. Electrochemical Oxidation Potentials of Silicon-Substituted Ethers and Related Compounds[a]

compound		cyclic voltammetry E_p (V)	rotating disk electrode $E_{1/2}$ (V)	rotating disk electrode E_d (V)
	(**12**)	1.48	-	1.29
	(**13**)	1.50	-	1.30
	(**14**)	1.45	1.36	1.20
	(**15**)	1.47	1.27	1.14
	(**16**)	1.50	1.55	1.37
	(**17**)	(2.0)	-	1.50

[a] Cyclic voltammetry and rotating disk electrode were carried out with a glassy carbon working electrode in 0.1 M $LiClO_4/CH_3CN$. Ag/AgCl was used for the reference electrode.

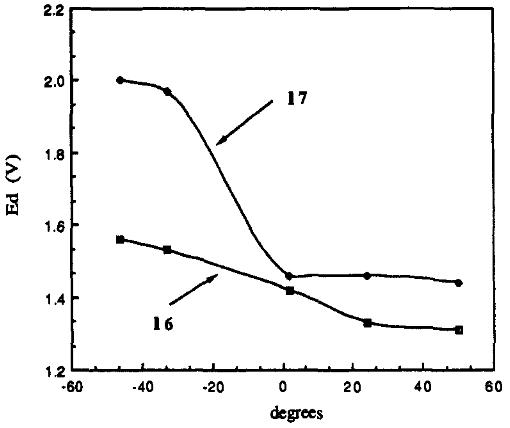


Figure 8. Temperature dependence of oxidation potentials of silyl-substituted cyclic acetals.

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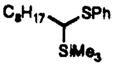
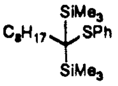
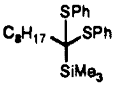
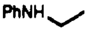
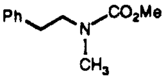
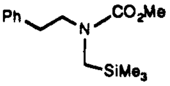
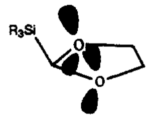
(33) (a) Klein, A. J.; Evans, D. H. *J. Am. Chem. Soc.* **1979**, *101*, 757–758. (b) Nelsen, S. F.; Clennan, E. L.; Evans, D. H. *Ibid.* **1978**, *100*, 4012–4019. (c) Nelsen, S. F.; Echegoyen, L.; Clennan, E. L.; Evans, D. H.; Corrigan, D. A. *Ibid.* **1977**, *99*, 1130–1134.

Table III. Electrochemical Oxidation Potentials of Silicon-Substituted Sulfides, Amines, and Carbamates

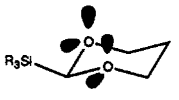
compound	E_p (V)[a]	$E_{1/2}$ (V)[b]
	1.20	
	1.10	
	1.10	
	1.20	
	1.10	1.15
		1.26
		0.59
		0.44
	1.95	
	1.45	

[a] Data from our study. Cyclic voltammetry was carried out using a glassy carbon electrode in 0.1 M $LiClO_4/CH_3CN$. Ag/AgCl was used for the reference electrode. See also refs 34 and 35. [b] Data from ref 5.

Therefore even at low temperatures **16** can be oxidized smoothly at the electrode.



16



17

$R_3SiCH_2YR'_n$ ($Y = S, N$). Oxidation potentials of silicon-substituted compounds containing heteroatom other than oxygen were also examined. Oxidation potentials of silicon substituted sulfides,[34] amines,[5] and carbamates[35] and related compounds are summarized in Table III. It is interesting to note that silyl substitution causes little decrease in oxidation potentials of sulfides in contrast to the dramatic silicon effect observed for ethers and alcohols. This is consistent with MNDO calculations of the model compound, SiH_3CH_2SH. The variation of the HOMO energy with the torsion angle is small in comparison with that for SiH_3CH_2OH. Presumably the energy level of the p orbitals of sulfur is much higher than the C–Si bond, and they do not interact with each other effectively (Figure 9). The additional silyl group does not affect the oxidation potentials of sulfides significantly. The decrease in oxidation potentials of amines caused by silyl substitution is also small. It is presumably because the energy level of 2p orbital of the nitrogen atom is also higher than the C–Si orbital and because their interaction is less effective than that of the oxygen 2p orbital and the C–Si bond. On the other hand, the oxidation potential of carbamates decreases significantly by silyl substitution. The conjugation with the carbonyl group lowers the energy level of the nitrogen p orbital and enables the effective interaction with the C–Si bond.

Conclusion

The β-silicon effect for electron-transfer reactions of heteroatom compounds is ascribed to the rise of the HOMO energy by the interaction of the C–Si σ orbital and the p orbital of the heteroatom. The magnitude of the β-silicon effect depends upon the geometry of the molecule and becomes the maximum when the C–Si bond and the p orbital of the heteroatom achieves the coplanar orientation. The stabilization of the cation radical intermediate by the C–Si bond may also have some contribution, but less important. As to the heteroatom, oxygen exhibits β-silicon effect most strikingly among oxygen, sulfur, and nitrogen. The energy level of the p orbital of oxygen is close to that of the C–Si bond, so they can interact effectively. On the other hand, the energy levels of sulfur and nitrogen p orbitals are much higher than the C–Si bond and therefore their interaction is less effective. The results obtained in this study give significant insight into the β-silicon effect for electron-transfer reactions of heteroatom compounds. The present study also provides important information for elucidation of the unified view of the β-silicon effect and for the development of new synthetic methodologies utilizing the concept of the β-silicon effect.

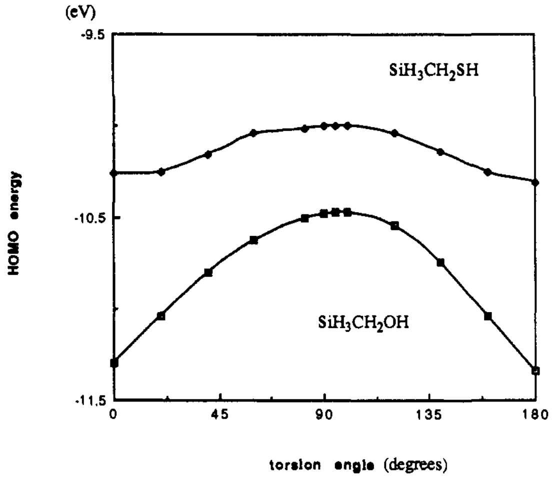


Figure 9. Plots of HOMO energy of SiH_3CH_2SH and SiH_3CH_2OH calculated with MNDO vs torsion angle of Si–C–S–H or Si–C–O–H.

Experimental Section

General Comments. Glass-support precoated (Merck silica gel 60 F_{254}, 0.25 mm) plates were employed for analytical TLC. Vapor-phase chromatography (VPC) was performed on a Shimadzu gas chromatograph equipped with 2 m × 3 mm column packed with Silicone OV-1 (2%) on Chromosorb WAW DMCS. Proton NMR spectra were determined on a Hitachi R-90H spectrometer (90 MHz) or a JEOL JNM-GX-400 spectrometer (400 MHz). Carbon NMR spectra were determined on a JEOL JNM-GX-400 spectrometer. Infrared (IR) spectra were determined on a JASCO A-102 diffraction grating spectrophotometer. Mass spectra were obtained on a JEOL JMS-D300 mass spectrometer. Ionization potential was 70 eV.

Materials. Octyl methyl ether was prepared by methylation of 1-octanol with methyl iodide using sodium hydride as base. Octyldimethylphenylsilanes were prepared by the reaction of chlorodimethylphenylsilane with octylmagnesium bromide. 1-(Dimethylphenylsilyl)ethylene oxide (**6**) was prepared by epoxidation of vinyldimethylphenylsilane with MCPBA (*m*-chloroperoxybenzoic acid).[36] Synthesis of some materials used in this study are described below. Other compounds were commercially available.

1-(Dimethylphenylsilyl)-1-octanol (4). A solution of (dimethylphenylsilyl)lithium[37] in THF (0.46 M, 8.0 mL) was added to a stirred solution of octanal (0.456 g, 3.6 mmol) in THF (3 mL) at 0 °C. After the addition was completed, the mixture was warmed to room temperature and quenched with water. The mixture was partitioned between dilute aqueous $KHSO_4$ and ether, and the ether layer was separated and dried. After removal of the solvent, the residue was purified with flash chromatography on silica gel (ethyl acetate/hexane 1:19) to obtain the title product (0.474 g, 50%): TLC R_f 0.45 (ethyl acetate/hexane 1:9); ^1H NMR (90 MHz) δ 0.33 (s, 6 H), 0.72–0.96 (m, 3 H), 1.07–1.63 (m, 14 H), 3.30–3.55 (m, 1 H), 7.23–7.62 (m, 5 H); IR (neat) 3650–3100 (br), 2940 (m), 2900 (s), 2830 (m), 1455 (w), 1425 (w), 1245 (m), 1110 (m), 830 (m), 810 (m), 770 (m), 730 (m), 695 (m) cm^{-1}; low-resolution

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(34) Yoshida, J.; Isoe, S. *Chem. Lett.* **1987**, 631–634. See also Koizumi, T.; Fuchigami, T.; Nonaka, T. *Chem. Lett.* **1987**, 1095–1096.

(35) Yoshida, J.; Isoe, S. *Tetrahedron Lett.* **1987**, *28*, 6621–6624.

(36) Eisch, J. J.; Trainor, J. T. *J. Org. Chem.* **1963**, *28*, 487–492.

(37) For example: Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988; p 53.

Table IV. Calculated HOMO Energies and Total Energies of SiH_3CH_2OH and SiH_3CH_2SH[a]

torsion angle of Si–C–Y–H (deg)[b]	HOMO energy and total energy (in parentheses) (eV)				
	SiH_3CH_2OH				SiH_3CH_2SH: MNDO
	3-21G	STO-3G	STO-3G*//STO-3G	MNDO	
0	−11.493 (−10963.796)	−9.455 (−10892.746)	−9.517 (−10894.389)	−11.297 (−631.084)	−10.267 (−546.945)
20	−11.309 (−10963.823)			−11.044 (−631.093)	−10.255 (−547.058)
40	−11.096 (−10963.882)	−8.948 (−10892.823)	−9.021 (−10894.455)	−10.804 (−631.112)	−10.161 (−546.970)
60	−10.940 (−10963.932)			−10.626 (−631.126)	−10.041 (−547.010)
67.1		−8.706 (−10892.862)	−8.782 (−10894.486)		
81.9	−10.834 (−10963.950)			−10.505 (−631.129)	−10.013 (−546.997)
90	−10.819 (−10963.948)	−8.599 (−10892.838)	−8.677 (−10894.460)	−10.482 (−631.128)	−10.000 (−546.999)
95	−10.815 (−10963.947)			−10.475 (−631.127)	−9.997 (−546.999)
100	−10.821 (−10963.945)			−10.475 (−631.127)	−9.998 (−547.000)
120	−10.924 (−10963.950)	−8.690 (−10892.808)	−8.768 (−10894.432)	−10.546 (−631.140)	−10.041 (−547.010)
140	−11.154 (−10963.979)	−8.941 (−10892.842)	−9.015 (−10894.465)	−10.743 (−631.174)	−10.142 (−547.033)
160	−11.471 (−10964.013)			−11.042 (−631.213)	−10.255 (−547.058)
180	−11.729 (−10964.028)	−9.526 (−10892.920)	−9.576 (−10894.538)	−11.340 (−631.230)	−10.308 (−547.068)

[a] All calculations were carried out with geometry optimization. [b] SiH_3CH_2OH, Y = O; SiH_3CH_2SH, Y = S.

Table V. Calculated HOMO Energies and Total Energies of CH_3CH_2OH[a]

torsion angle of C–C–O–H (degree)	HOMO energy and total energy (in parentheses) (eV)		
	3-21G	STO-3G	MNDO
0	−11.555 (−4169.078)	−9.50 (−4139.400)	−11.198 (−663.928)
30		−9.536 (−4139.446)	−11.242 (−663.949)
45	−11.605 (−4169.136)		
60			−11.310 (−663.979)
61.5		−9.566 (−4139.495)	
90	−11.574 (−4169.122)	−9.516 (−4139.451)	−11.295 (−663.976)
120		−9.478 (−4139.400)	−11.254 (−663.963)
135	−11.565 (−4169.094)		
140		−9.526 (−4139.419)	
150			−11.274 (−663.981)
180	−11.659 (−4169.143)	−9.612 (−4139.484)	−11.296 (−663.998)

[a] All calculations were carried out with geometry optimization.

MS *m/e* 249 (70), 231 (8), 209 (48), 165 (12), 152 (16), 137 (100), 135 (80), 75 (20); high-resolution MS (M − CH_3) calcd for $C_{15}H_{25}OSi$ 249.1674, found 249.1689.

1-(Dimethylphenylsilyl)-1-methoxydecane (1). 1-(Dimethylphenylsilyl)-1-decanol was prepared from decanal in a similar fashion as described above. To a solution of 1-(dimethylphenylsilyl)-1-decanol (0.566 g, 1.93 mmol) in 3.0 mL of THF were added sodium hydride (60% in oil, 0.13 g, 3.3 mmol) and iodomethane (0.2 mL, 3.2 mmol), and the mixture was refluxed for 5 h. The reaction mixture was partitioned between ether and water, and the organic layer was separated and dried. After removal of the solvent, the residue was purified with flash chromatography on silica gel to obtain the title product (0.559 g, 94%): TLC R_f 0.65 (ethyl acetate/hexane 1:19); VPC t_R 5.6 min (160–230 °C, 10 °C/min); ^1H NMR (90 MHz) δ 0.29 (s, 3 H), 0.30 (s, 3 H), 0.72–1.65 (m, 19 H), 2.96 (br, t, 1 H), 3.24 (s, 3 H), 7.18–7.55 (m, 5 H); IR (neat) 2920 (s), 2850 (sh), 1455 (w), 1425 (m), 1090 (br m), 830 (m), 810 (m), 770 (w), 700 (m) cm^{-1}; low-resolution MS *m/e* 291 (33), 216 (6), 179 (14), 165 (8), 150 (38), 134 (100), 88 (37), 74 (87); high-resolution MS (M − CH_3) calcd for $C_{18}H_{31}OSi$ 291.2142, found 291.2141.

1-[(*tert*-Butyldimethylsilyl)oxy]-1-(dimethylphenylsilyl)octane (3). A solution of imidazole (0.32 g, 4.7 mmol) and *tert*-butyldimethylchlorosilane (0.524 g, 3.48 mmol) and **4** (0.44 g, 1.68 mmol) in DMF (2 mL) was stirred at room temperature for 15 h. The reaction mixture was partitioned between saturated aqueous $NaHCO_3$ and pentane, and the pentane layer was separated and dried. After removal of the solvent, the residue was purified with flash chromatography on silica gel (hexane) to obtain the title product (0.551 g, 86%): TLC R_f 0.56 (hexane); VPC t_R 13.5 min (100–230 °C, 10 °C/min); ^1H NMR (90 MHz, $CDCl_3$) δ −0.16 (s, 3 H), 0.00 (s, 3 H), 0.27 (s, 3 H), 0.29 (s, 3 H), 0.84 (s, 9 H), 0.76–1.60 (m, 15 H), 3.52 (t, J = 6 Hz, 1 H), 7.25–7.58 (m, 5 H); IR (neat) 2920 (vs), 2860 (sh), 1460 (m), 1425 (w), 1250 (s), 1110 (m), 1050 (br s), 835 (vs), 810 (s), 770 (s), 730 (s), 700 (s) cm^{-1}; low-resolution MS *m/e* 321 (5), 243 (12), 210 (24), 209 (100), 189 (8), 147 (16), 73 (10); high-resolution MS (M − C_4H_9) calcd for $C_{18}H_{33}OSi_2$ 321.2068, found 321.2067.

1-(Trimethylsilyl)-1-methoxyoctane (2). To a stirred solution of hexamethyldisilane (1.1 mL, 5.5 mmol) in HMPA (3.5 mL) was added a solution of methyllithium in ether (1.4 M, 3.9 mL, 5.5 mmol) at 0 °C, and the mixture was stirred at this temperature for 15 min.[38] Then octanal (0.65 mL, 4.1 mmol) was added. After being stirred at 0 °C for 10 min and at room temperature for 5 min, the reaction was quenched with the addition of 1% aqueous HCl (35 mL). The mixture was extracted with ether and dried. After removal of the solvent the residue was purified with flash chromatography on silica gel (ethyl acetate/hexane 1:19) to obtain 1-(trimethylsilyl)-1-octanol (0.368 g, 44%). To a stirred solution of 1-(trimethylsilyl)-1-octanol (0.335 g, 1.7 mmol) in THF (2 mL) was added sodium hydride (60% in oil, 0.15 g, 3.8 mmol). Iodomethane (0.3 mL, 4.8 mmol) was added, and the mixture was refluxed for 1 h. The reaction mixture was partitioned between water and ether, and the ether layer was separated and dried. After removal of the solvent the residue was purified with flash chromatography on silica gel (ethyl acetate/hexane 1:19) to obtain the title product (0.371 g, quantitative yield): TLC R_f 0.45 (1:19 ethyl acetate/hexane); VPC t_R 5.0 min (100–230 °C, 10 °C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 0.06 (s, 9 H), 0.76–1.67 (m, 15 H), 2.7 (br, 1 H), 3.33 (s, 3 H); IR (neat) 2920 (vs), 1450 (w), 1245 (m), 1090 (br m), 830 (s) cm^{-1}; low-resolution MS *m/e* 201 (90), 103 (36), 89 (43), 73 (100), 69 (42); high-resolution MS (M − CH_3) calcd for $C_{11}H_{25}OSi$ 201.1672, found 201.1664.

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[38] For example: Still, W. C. *J. Org. Chem.* **1976**, *41*, 3063–3064.

2-(Dimethylphenylsilyl)tetrahydrofuran (7).[39] To a mixture of 2,3-dihydrofuran (2.6 mL, 29 mmol) and TMEDA (0.8 mL) was added a solution of butyllithium in hexane (1.6 M, 20 mL, 32 mmol) at 0 °C. After being stirred at room temperature for 30 min, the supernatant was removed by a syringe, and the solid material was washed with dry hexane (4 mL × 2). Dry ether (5 mL) and chlorodimethylphenylsilane (2.0 mL, 12 mmol) were added, and the mixture was stirred at room temperature for 30 min. The reaction mixture was partitioned between water and ether, and the ether layer was separated and dried. After removal of the solvent, the residue was purified with flash chromatography on silica gel (ethyl acetate/hexane 1:19) to obtain the 2-(dimethylphenylsilyl)-2,3-dihydrofuran (2.541 g, 12 mmol, quantitative). This product (0.373 g, 1.83 mmol) was hydrogenated (1 atm) with Pd/Al_2O_3 (3%, 20 mg) in ethanol (20 mL) (5 h). Flash chromatography (ethyl acetate/hexane 1:39) afforded the title product (0.310 g, 82%): TLC R_f 0.28 (1:19 ethyl acetate/hexane); VPC t_R 5.4 min (100–170 °C, 10 °C/min); ^1H NMR (400 MHz, $CDCl_3$) δ 0.30 (s, 3 H), 0.33 (s, 3 H), 1.57–1.67 (m, 2 H), 1.76–1.83 (m, 2 H), 1.91–1.99 (m, 1 H), 3.45 (dd, J = 6.84, 11.23 Hz, 1 H), 3.69 (quasi q, J = ca. 7 Hz, 1 H), 3.79 (quasi q, J = ca. 7 Hz, 1 H), 7.31–7.35 (m, 3 H), 7.54–7.57 (m, 2 H); IR (neat) 2950 (s), 2850 (m), 1430 (m), 1245 (s), 1110 (s), 1040 (vs), 910 (m), 830 (vs), 810 (vs), 770 (s), 730 (vs), 700 (vs) cm^{-1}; low-resolution MS m/e 191 (1), 179 (18), 178 (100), 163 (92), 135 (53), 121 (17), 104 (67); high-resolution MS (M − CH_3) calcd for $C_{11}H_{15}OSi$ 191.0890, found 191.0872.

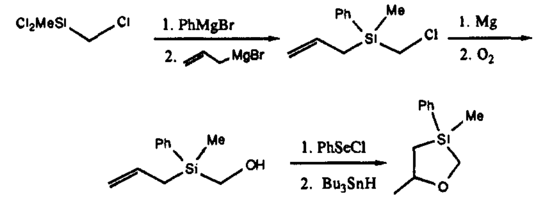
2-(Dimethylphenylsilyl)tetrahydropyran (8).[39] The title compound was synthesized from 2,3-dihydropyran by essentially the same procedure for the synthesis of **7**: TLC R_f 0.43 (1:39 ethyl acetate/hexane); VPC t_R 6.2 min (100–230 °C, 10 °C/min); ^1H NMR (400 MHz, $CDCl_3$) δ 0.29 (s, 3 H), 0.30 (s, 3 H), 1.38–1.81 (m, 6 H), 3.25 (dd, J = 2.32, 12.09 Hz, 1 H), 3.34 (d of t, J = 2.20, 11.60 Hz, 1 H), 3.95–4.02 (m, 1 H), 7.32–7.38 (m, 3 H), 7.53–7.56 (m, 2 H); IR (neat) 2930 (s), 2840 (m), 1430 (m), 1245 (m), 1195 (w), 1115 (m), 1080 (s), 1045 (m), 1025 (w), 880 (m), 835 (s), 780 (m), 730 (m), 700 (s) cm^{-1}; low-resolution MS m/e 220 (M, 1), 206 (19), 205 (96), 191 (9), 138 (14), 137 (100), 135 (36), 75 (6); high-resolution MS calcd for $C_{13}H_{20}OSi$ 220.1284, found 220.1290. Anal. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15. Found C, 70.56; H, 9.23.

1-(Dimethylphenylsilyl)-1-methoxycyclopentane (9). To a solution of cyclopentanone (0.446 g, 5.30 mmol) in THF (5 mL) was added a solution of (dimethylphenylsilyl)lithium in THF (0.5 M, 14 mL, 7 mmol) at 0 °C, and the mixture was stirred at this temperature for 1 h. After addition of water, the product was extracted with ether, dried, and purified with flash chromatography on silica gel to obtain 1-(dimethylphenylsilyl)-1-cyclopentanol (0.162 g, 14%). To a solution of this product (0.110 g, 0.499 mmol) in THF (5 mL) was added sodium hydride (60% in oil, 0.070 g, 1.8 mmol). Iodomethane (0.20 mL, 3.2 mmol) was added, and the mixture was refluxed for 8 h. The reaction mixture was partitioned between water and ether, and the ether layer was separated and dried. After removal of the solvent the residue was purified by flash chromatography on silica gel (ethyl acetate/hexane 1:19) to obtain the title product (0.089 mmol, 77%): TLC R_f 0.69 (1:9 ethyl acetate/hexane); VPC t_R 5.6 min (100–250 °C, 20 °C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 0.36 (s, 6 H), 1.28–1.95 (m, 8 H), 3.11 (s, 3 H), 7.10–7.51 (m, 5 H); IR (neat) 2950 (s), 1430 (w), 1245 (m), 1105 (m), 1070 (m), 830 (s), 805 (s), 770 (m), 730 (m), 700 (s) cm^{-1}; low-resolution MS m/e 219 (84), 141 (14), 136 (14), 135 (100), 99 (31), 98 (31), 75 (17); high-resolution MS (M − CH_3) calcd for $C_{13}H_{19}OSi$ 219.1203, found 219.1203.

1-(Dimethylphenylsilyl)-1-methoxycyclohexane (10). The title compound was synthesized from cyclohexanone by essentially the same procedure for the synthesis of **9**: VPC t_R 6.4 min (100–250 °C, 20 °C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 0.35 (s, 6 H), 1.17–2.03 (m, 10 H), 3.20 (s, 3 H), 7.23–7.60 (m, 5 H); IR (neat) 2930 (vs), 1445 (w), 1425 (w), 1245 (m), 1080 (s), 800 (s), 770 (s), 730 (m), 700 (s) cm^{-1}; low-resolution MS m/e 233 (100), 197 (5), 155 (27), 135 (74), 113 (36), 112 (24), 75 (19); high-resolution MS (M − CH_3) calcd for $C_{14}H_{21}OSi$ 233.1362, found 233.1369.

1,4-Dimethyl-1-phenyl-3-oxasilacyclopentane (11). The title compound was prepared according to eq 2.

To a solution of dichloromethyl(chloromethyl)silane (8.404 g, 51.4 mmol) in ether (10 mL) was added a solution of phenylmagnesium bromide in ether (15 mL) (prepared from bromobenzene (7.985 g, 50.8 mmol) and magnesium (2.247 g, 92.5 g-atom)) at 0 °C. After the addition was completed the mixture was stirred at room temperature for 4 h. A solution of allylmagnesium bromide in ether (15 mL) (prepared from allyl bromide (9 mL, 104 mmol) and magnesium (4.140 g, 170.4 g-atom)) was added at 0 °C. After the addition was completed, the mixture was stirred at room temperature overnight. The reaction mixture was partitioned between ether and brine. The organic layer was separated and dried over Na_2SO_4. After evaporation of the solvent, the residue was purified with bulb-to-bulb distillation (230–240 °C/30 mmHg) to obtain allyl(chloromethyl)methylphenylsilane (7.399 g, 69%).



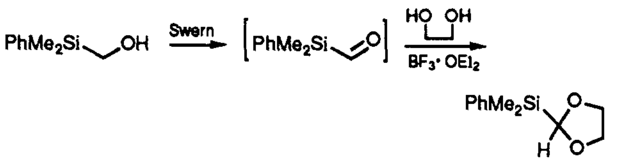
(2)

Allyl(chloromethyl)methylphenylsilane (2.127 g, 10.1 mmol) was allowed to react with magnesium (0.802 g, 33 mmol) in ether (10 mL) to yield the corresponding Grignard reagent. Oxygen gas was bubbled through the Grignard solution at 0 °C for 2 h and 45 min. Dimethyl sulfide (1 mL) was added and the mixture was stirred at room temperature overnight. The reaction mixture was partitioned between brine and ether, and the organic layer was separated and dried. After removal of the solvent the residue was purified with flash chromatography (ethyl acetate/hexane 1:4 elusion) to obtain allyl(hydroxymethyl)methylphenylsilane (1.088 g, 56%).

Selenoetherification was carried out according to the literature.[40] To a solution of triethylamine (0.2 mL, 1.43 mmol) and allyl(hydroxymethyl)methylphenylsilane (0.198 g, 1.03 mmol) in dichloromethane (5 mL) was added benzeneselenenyl chloride (0.234 g, 1.22 mmol) at −78 °C. The mixture was stirred at this temperature for 0.5 h and at room temperature overnight. The reaction mixture was partitioned between brine and ether, and the organic layer was separated and dried. After removal of the solvent the residue was purified with preparative TLC (ethyl acetate/hexane 1:9 elusion) to obtain 1-methyl-1-phenyl-4-[(phenylselenyl)methyl]-3-oxasilacyclopentane (0.142 g, 40%).

The selenide thus obtained was reduced with tributyltin hydride.[40,41] To a solution of 1-methyl-1-phenyl-4-[(phenylselenyl)methyl]-3-oxasilacyclopentane (0.142 g, 0.41 mmol) and tributyltin hydride (0.20 mL, 0.743 mmol) in benzene (5 mL) was added AIBN (azobis(isobutyronitrile)) (0.044 g) and the mixture was refluxed for 1 h. After being cooled to room temperature, the solvent was removed under reduced pressure. The residue was purified with preparative TLC (ethyl acetate/hexane 1:9 elusion) to obtain 1,4-dimethyl-1-phenyl-3-oxasilacyclopentane (0.077 g, 98%): TLC R_f 0.49 (ethyl acetate/hexane 1:9); VPC t_R 4.4 min (100–230 °C, 10 °C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 0.59 and 0.60 (2 s, total, 3 H), 0.62–1.07 (m, 2 H), 1.45 (d, J = 5.9 Hz), 1.46 (d, J = 5.9 Hz) (total 3 H), 3.25–4.11 (m, 3 H), 7.32–7.77 (m, 5 H); IR (neat) 3050 (m), 2930 (vs), 2850 (s), 2000 (w), 1450 (m), 1425 (s), 1370 (s), 1245 (s), 1140 (vs), 1105 (vs), 1050 (s), 995 (s), 880 (s), 835 (s), 720 (s), 695 (s) cm^{-1}; low-resolution MS m/e 177 (100), 149 (100), 135 (44), 120 (66), 114 (14), 105 (14), 91 (26); high-resolution MS (M − CH_3) calcd for $C_{10}H_{13}OSi$ 177.0736, found 177.0739. The product was a mixture of two stereoisomers (1:1), but the torsion angles of Si–C–O–C of two isomers calculated with MM2 were very close.

2-(Dimethylphenylsilyl)-1,3-dioxolane (16). The title compound was prepared by Swern oxidation of (hydroxymethyl)dimethylphenylsilane[42] followed by the reaction of the in situ generated formylsilane with ethylene glycol (eq 3).[43]



(3)

To a solution of dimethyl sulfoxide (1.5 mL, 21.1 mmol) in ether (15 mL) was added oxalyl chloride (1.5 mL, 17.2 mmol) at −78 °C. After being stirred at this temperature for 5 min and at −35 °C for 0.5 h, (hydroxymethyl)dimethylphenylsilane (1.03 g, 6.19 mmol) was added at −78 °C. The mixture was stirred at this temperature for 5 min and at −35 °C for 0.5 h. Triethylamine (4.0 mL, 28.7 mmol) was added at −78 °C, and the mixture was stirred at this temperature for 15 min and at

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0 °C for 2 h. Ethylene glycol (12 mL, 215 mmol) and boron trifluoride etherate (4.3 mL, 35.0 mmol) were added at 0 °C. The mixture was stirred at 0 °C for 2 h and at room temperature overnight. The reaction mixture was poured into saturated aqueous $NaHCO_3$, and organic materials were extracted with ether and dried over Na_2SO_4. After the solvent was evaporated, the residue was purified with flash chromatography (ethyl acetate/hexane 1:9 elusion) to yield the title compound (0.859 g, 67%): TLC R_f 0.57 (ethyl acetate/hexane 1:9); VPC t_R 4.54 min (100–230 °C, 10 °C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 0.38 (s, 6 H), 3.65–3.85 (m, 4 H), 4.66 (s, 1 H), 7.25–7.60 (m, 5 H); IR (neat) 3060 (m), 3040 (m), 2950 (vs), 2860 (vs), 2760 (s), 1425 (s), 1245 (s), 1110 (s), 1080 (vs), 830 (s), 810 (s), 730 (s), 695 (s) cm^{-1}; low-resolution MS *m/e* 208 (0.02), 207 (0.6), 193 (0.02), 179 (0.7), 165 (100), 137 (22), 135 (18), 103 (8), 73 (12); high-resolution MS calcd for $C_{11}H_{16}O_2Si$ 208.0919, found 208.0924. Anal. Calcd for $C_{11}H_{16}O_2Si$: C, 63.42; H, 7.74. Found C, 63.30; H, 7.43.

2-(Dimethylphenylsilyl)-1,3-dioxane (17). The preparation was essentially the same method as that for **16** using trimethylene glycol as diol (60% yield): TLC R_f 0.57 (ethyl acetate/hexane 1:9); VPC t_R 5.63 min (100–230 °C, 10 °C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 0.33 (s, 6 H), 1.24–1.43 (m, 2 H), 3.51–4.21 (m, 4 H), 4.75 (s, 1 H), 7.24–7.65 (m, 5 H); IR (neat) 2950 (s), 2840 (s), 2760 (m), 1425 (s), 1245 (s), 1105 (vs), 975 (s), 840 (s), 810 (s), 695 (s) cm^{-1}; low-resolution MS *m/e* 222 (2), 221 (9), 207 (7), 189 (1), 179 (4), 177 (2), 165 (56), 137 (26), 135 (70), 87 (100), 59 (14); high-resolution MS calcd for $C_{12}H_{18}O_2Si$ 222.1075, found 222.1055. Anal. Calcd for $C_{12}H_{18}O_2Si$: C, 64.8; H, 8.16. Found C, 63.76; H, 8.16.

2-Decyl-2-(trimethylsilyl)-1,3-dioxolane (14). A mixture of undecanoyltrimethylsilane (245 mg, 1.10 mmol),[44] ethylene glycol (10 mL, 180 mmol), boron trifluoride etherate (2 mL, 16.3 mmol), and 2.5 mL of chloroform was refluxed for 3 h. The mixture was partitioned between aqueous $NaHCO_3$ and chloroform. The organic layer was separated and dried. After removal of the solvent the residue was purified with flash chromatography on silica gel (ethyl acetate/hexane 1:9) to yield the title product (265 mg, 92%): TLC R_f 0.77 (ethyl acetate/hexane 1:9); VPC t_R 7.0 min (100–230 °C, 10 °C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 0.08 (s, 9 H), 0.73–0.93 (m, 3 H), 1.11–1.60 (m, 18 H), 3.78–3.98 (m, 4 H); IR (neat) 2910 (vs), 2850 (m), 1465 (m), 1245 (s), 1140 (m), 1105 (m), 840 (vs), 750 (m) cm^{-1}; low-resolution MS *m/e* 286 (0.2), 271 (1), 243 (1), 241 (2), 227 (0.5), 213 (100), 145 (12), 73 (16); high-resolution MS ($M - CH_3$) calcd for $C_{15}H_{31}O_2Si$ 271.2092, found 271.2122.

2-Nonyl-2-(dimethylphenylsilyl)-1,3-dioxolane (15). The title compound was prepared from decanoyldimethylphenylsilane[45] by essentially the same procedure as that of **14**: TLC R_f 0.71 (ethyl acetate/hexane 1:9); VPC t_R 9.7 min (100–230 °C, 10 °C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 0.37 (s, 6 H), 0.75–0.95 (m, 3 H), 1.10–1.38 (m, 16 H), 3.50–3.95 (m, 4 H), 7.20–7.70 (m, 5 H); IR (neat) 2910 (vs), 2840 (m), 1425 (m), 1245 (m), 1110 (m), 830 (m), 810 (m), 775 (m), 730 (m), 700 (m) cm^{-1}; low-resolution MS *m/e* 334 (0.1), 320 (0.5), 291 (3), 199 (100); high-resolution MS calcd for $C_{20}H_{34}O_2Si$ 334.2328, found 334.2355.

Cyclic Voltammetry. Cyclic voltammetry was performed on a Hokuto Potentiostat/Garvanostat HA-301 connected to a function generator HB-104 and Graphtec WX1000 X-Y plotter using undivided cell equipped with a glassy carbon anode and a platinum cathode in 0.1 M $LiClO_4/CH_3CN$. Ag/AgCl (saturated aqueous KCl) was used as the reference electrode. Sweep rate was 50 mA/s.

Rotating Disk Electrode. Rotating disk electrode was carried out with Nikko Keisoku RRDE-1 which was partially modified by ourselves. Other apparatus and conditions were the same as those for CV except for the sweep rate (10 mA/s). The rotation rate was set at 1000 rpm. Half-wave potentials were obtained from the current–potential curves. Sometimes the plateau in high potential region was not observed presumably because of adhesion on the electrode surface, and it was difficult to determine the half-wave potentials ($E_{1/2}$). Therefore we also determined the decomposition potential (E_d) at which the oxidation began to take place.

MO Calculations. Ab initio calculations were carried out by using OCU version of GAUSSIAN 80 series of programs.[46] Geometry optimizations were carried out on all neutral molecules, cation radicals, and cations at HF level with the 3-21G basis. Vibrational frequencies were calculated for the cation radicals and cations at the optimized geometries in order to characterize stationary points as minima or saddle points using GAUSSIAN 82 series of programs.[47] MNDO calculations were carried out by using the program QCMP002[48] with geometry optimization. The HOMO energies and total energies are summarized in Tables IV and V.

MM2 Calculations. MM2 calculations were carried out by using MM2(77)[49] and MM2PP programs[50] connected to molecular modeling system (SYMMETRY).[51] Since some parameters for bending and torsional energy have not yet been reported in the literature, we used the following values as tentative parameters:

2	2	1	19	–0.684	–0.979	0.850
19	1	6	1	0.400	0.520	0.467
19	1	6	20	0	0	0
1	19	1	6	0.100	0.100	0.180
19	1	1	6	0.100	0.100	0.180
19	1	6	21	0.800	0.000	0.090
6	1	19	2	0.000	0.000	0.180
2	2	2	19	–0.270	15.000	0.000
2	1	19	2	2.10	0.270	0.093
6	1	19		0.700	107.40	0

Although these parameters have not been optimized as yet, the potential function for rotation about Si–C–O–C of $(CH_3)_3SiCH_2OCH_3$ calculated using these parameters fits rather well to that obtained with MNDO calculations (Figure 5).

Acknowledgment. We thank Dr. A. Ichimura, Osaka City University, for suggestions for the measurement of RDE and valuable discussion about the electrochemical studies. We also thank Dr. K. Kitaura, Institute of Molecular Science, for valuable suggestions and discussion about the theoretical studies (especially for frequency calculations) and Mr. K. Honda, Osaka City University, for technical suggestions about the computation. We also thank Ministry of Education, Science and Culture, Japan for Grant-in-Aid for Scientific Research (No. 63540408) and Chisso for gifts of some organosilicon compounds.

Supplementary Material Available: Listing of full geometrical results for the cation radicals and cations in this study (4 pages). Ordering information is given on any current masthead page.

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[44] Undecanoyltrimethylsilane was prepared by the reaction of lithiomethoxybis(trimethylsilyl)methane[12] with decanal followed by the treatment with diluted aqueous HCl. Detailed procedure will be reported elsewhere.

[45] Dodecanoylphenyldimethylsilane was prepared by the reaction of dodecanal with (dimethylphenylsilyl)lithium followed by Swern oxidation.[42]

[46] The GAUSSIAN 80 series of programs: Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1981**, *13*, 406.

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[48] PC version of MNDO (QCMP002). The original program was written by W. Thiel and it was converted on PC by J. D. Bowen.

[49] MM2(77): The NEC PC version of QCMP004 converted by E. Osawa.

[50] MM2PP: A MM2 program including MMPI available from Toray System Center.

[51] Osaka City University System of Molecular Modeling and Calculations for Chemistry.