literature,[2] the ΔG° values in hexane solution were obtained to be +21.6 kcal/mol for AP–P, –6.1 kcal/mol for AP–CNP, +28.2 kcal/mol for DMAP–P, and +2 kcal/mol for DMAP–CNP. At the actual distance of hydrogen bonding interaction or exciplex formation, the donor and acceptor will be closer resulting in the smaller ΔG° values.

Moreover, the hydrogen bonding interaction will decrease the ionization potential of the proton donor and increase the electron affinity of the proton acceptor facilitating the CT from the proton donor to the proton acceptor. The hydrogen bonding interaction between AP and P is stronger in the excited state than in the ground state, leading to the red shift of the electronic spectra. The stronger hydrogen bonding interaction in the excited state will make the proton in the hydrogen bond shift slightly toward acceptor, which will further lower the ionization potential of the π-electron system of AP and enhance the electron affinity of the π-electron system of P, resulting in the stronger CT interaction. As a result of the stronger CT interaction, the proton of the donor will be further shifted toward the acceptor. Such a shift of the proton in the CT state, however, seems to cause a large destabilization of the ground state where the CT from the proton donor to the acceptor is negligible. If this is the case, the energy gap between the CT state and the ground state becomes very small, making the nonradiative deactivation feasible.

The above interpretation of the deactivation mechanism due to the hydrogen bonding interaction is supported also by the results of recent detailed ab initio MO CI studies upon such model systems as aniline–pyridine and phenol–pyridine, which predict a strong CT from D–H in the S_1 state to hydrogen bonded A when the D–H proton is slightly moved toward A and a large destabilization of the ground state with the proton shift.[13]

It should be noted here with respect to the proton shift in the CT state that a neutral radical formation due to the mechanism of CT followed by proton transfer may be realized in an extreme case: $(D^*{-}H\cdots A) \rightarrow (\dot{D}^+{-}H\cdots\dot{A}^-) \rightarrow (\dot{D} + H{-}\dot{A})$. In the case of the present system as well as dibenzocarbazole–P systems,[6] however, the formation of the neutral radicals is negligible, which indicates that the crossing to the ground state from the CT state is considerably faster than the neutral radical formation.

Comparison of Transient Behaviors of the AP–P Hydrogen Bonding System with Those of the DMAP–CNP Exciplex System. The lifetime of the CT state of the DMAP–CNP system in hexane (~5 ns) is much longer than that of the AP–P hydrogen bonding system in the same solvent (~260 ps). This difference is probably due to the fact that a very rapid nonradiative crossing to the ground state from the CT state is the most dominant process in the latter, which is a characteristic phenomenon observed when two conjugated π-electron systems are directly combined by hydrogen bonding, while the nonradiative process from the exciplex state of the former system is considerably slower owing to the absence of such a hydrogen bonding interaction directly combining the two conjugate π-electronic systems.

However, since the radiative transition probability k_f of the DMAP–CNP exciplex in hexane is much smaller than that of the typical pyrene–DMA exciplex, a nonparallel structure of the CT state where a weak hydrogen bonding interaction exists between the ring nitrogen of the CNP anion and the C–H hydrogen of the dimethylamino group of the DMAP cation has been assumed, as is discussed in a previous section. Notwithstanding the existence of the hydrogen bonding interaction assumed above, since it does not directly combine the two conjugate π-electron systems, it does not cause the rapid deactivation process in a few hundred picosecond region.

Acknowledgment. We are grateful to Dr. M. Irie of the Institute of Scientific and Industrial Research for his help in the measurement of the absorption spectrum of the AP cation radical by ^{60}Co γ radiolysis.

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Registry No. 1-Aminopyrene, 1606-67-3; pyridine, 110-86-1; *N,N*-dimethyl-1-aminopyrene, 5522-42-9; 4-cyanopyridine, 100-48-1.

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(12) Furue, M., private communication.

(13) Tanaka, E.; Nishimoto, K., private communication.

Electron Spin Resonance Studies of 1,4-Disilacyclohexa-2,5-diene Free Radical Reactions

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Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received December 17, 1982*

Abstract: The photolysis reaction between hexamethyl-1,4-disilacyclohexa-2,5-diene and *tert*-butyl peroxide in cyclopropane solvent has been studied by electron spin resonance. At low temperature (–105 °C) a *tert*-butoxy radical adds to one of the carbon–carbon double bonds to form an α-silyl carbon-centered radical. At higher temperatures (–30 °C) initial abstraction of a silane hydrogen apparently occurs. The resulting silyl radical is not observed but instead undergoes an unprecedented rearrangement to yield a silacycloprop-2-yl radical. A similar rearrangement reaction is seen when hexamethyl-1,4-dichloro-1,4-disilacyclohexa-2,5-diene is coirradiated with a tetrasubstituted tetraaminoethylene. Confirmation of the ESR assignments was done with the aid of deuterium-labeling experiments and computer simulation of the observed ESR spectra.

Organosilicon radicals which are substituted by aryl or olefinic groups are presently of considerable interest.[1] Electron spin resonance studies of these radicals can provide valuable information about spin delocalization onto the carbon framework,[2] resulting from π interaction between silicon and the 2p orbitals of the adjacent carbon atoms. Such π delocalization may be related to the interactions in the recently discovered multiply bonded silicon species.[3,4] Only two arylsilyl radicals have been studied to date by ESR; both show spin delocalization onto the carbon π framework, but delocalization is much less than in

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(1) (a) Sakurai, H.; Umino, H.; Sugiyama, H. *J. Am. Chem. Soc.* **1980**, *102*, 6837. (b) Gynane, M.; Lappert, M.; Riley, P.; Riviere, P.; Riviere-Baudet, M. *J. Organomet. Chem.* **1980**, *202*, 5.

(2) (a) McConnell, H. *J. Chem. Phys.* **1956**, *24*, 632. (b) Heller, C.; McConnell, H. *Ibid.* **1960**, *32*, 1535.

(3) Si=C: Brook, A. G.; Abdesaker, F.; Gutekunst, B.; Gutekunst, G.; Kallury, K. *Chem. Commun.* **1981**, 191.

(4) Si=Si: West, R.; Fink, M.; Michl, J. *Science* **1981**, *214*, 1343.

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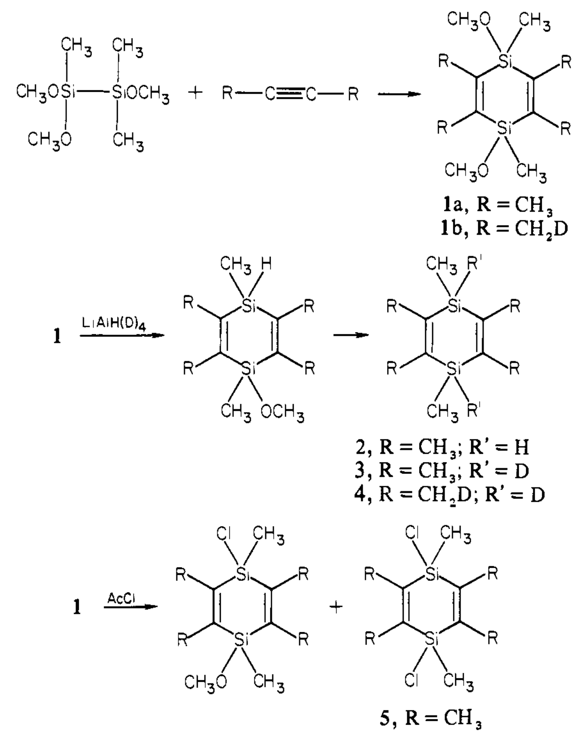
Scheme I



analogous triarylmethyl radicals.[1]

No examples of silicon radicals substituted by olefinic groups have been reported,[5] but the carbon analogues (allylic radicals) are well known. ESR studies of such species show that extensive π-delocalization of the unpaired electron takes place.[6] One example of this type is the cyclohexadienyl radical, which can be formed by the homolytic abstraction of a C–H bond of 1,4-cyclohexadiene.[7] In the present work we have investigated an analogous reaction in the silicon series, that between a 1,4-disilacyclohexa-2,5-diene and *tert*-butyl peroxide.

Results

Synthesis. The general approach to the synthesis of 1,4-disubstituted 1,4-dimethyl-1,4-disilacyclohexa-2,5-dienes is shown in Scheme I. Pyrolysis of *sym*-tetramethoxydimethyldisilane with 2-butyne gave the corresponding tetrasubstituted 1,4-dimethoxy-1,4-dimethyl-1,4-disilacyclohexa-2,5-diene (**1**) as a mixture of cis and trans isomers.[8] Reduction of the methoxy groups was easily accomplished with lithium aluminum hydride or $LiAlD_4$. Attempts to synthesize 1,4-dichlorosilacyclohexa-2,5-diene (**5**) from the direct reaction of *sym*-tetrachlorodimethyldisilane with acetylenes were not successful, so this derivative was prepared from the reaction of **1b** with refluxing acetyl chloride. A 1:1 mixture of isomers was formed independent of the isomer ratio of the starting dimethoxide.

Synthesis of 1,4-dimethyl-2,3,4,5-tetra(deuteriomethyl)-1,4-dideuterio-1,4-disilacyclohexa-2,5-diene (**4**) requires 1,4-dideuterio-2-butyne as the acetylene precursor. Reduction of 1,4-dichloro-2-butyne with lithium aluminum hydride did not give 2-butyne. Several products were obtained presumably due to competitive S_N2' reactions of the propargyl chlorides. However, the acetylene was formed when the more nucleophilic reagent, lithium triethylboron hydride (or deuteride), was used.

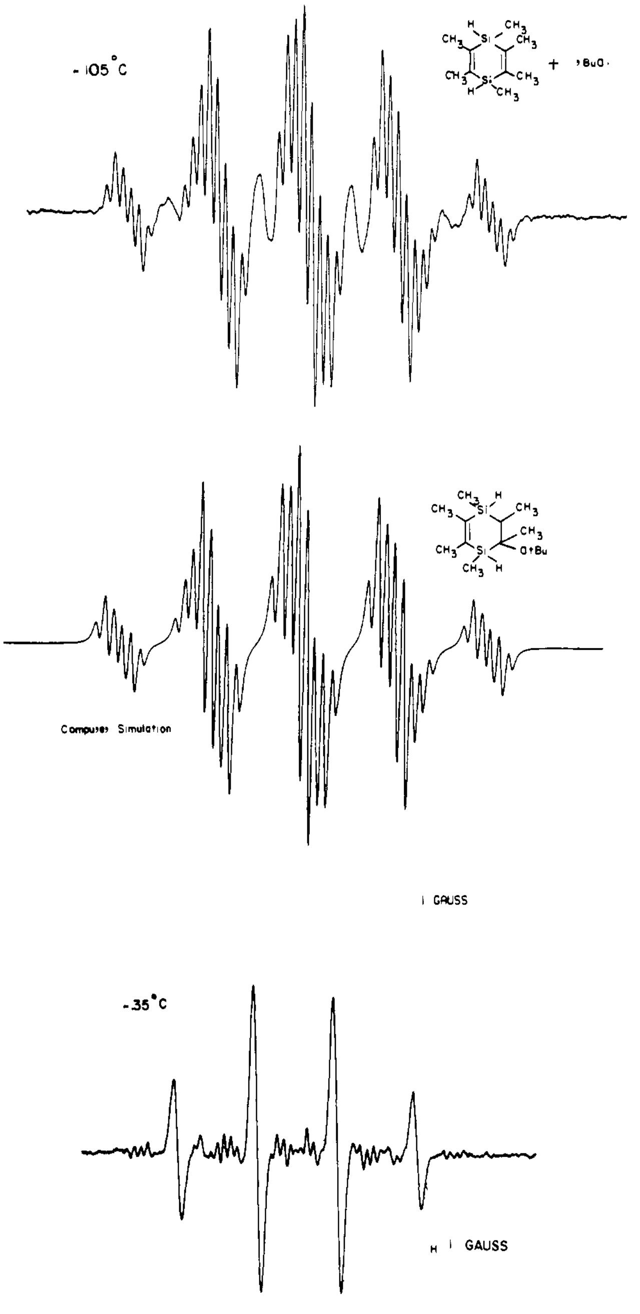


Figure 1. ESR spectrum of the radical produced from **2** and *t*-BuOOH. Above, spectrum of low-temperature radical **8a** at −105 °C; center, computer simulation of −105 °C spectrum; below, spectrum of the high-temperature radical at −35 °C.

Electron Spin Resonance Spectra. Irradiation of a mixture of *sym*-hexamethyl-1,4-disilacyclohexa-2,5-diene (**2**) and *tert*-butyl peroxide in cyclopropane solvent at −105 °C gave rise to the ESR spectrum shown in Figure 1. A major five-line pattern appears with each line split by a smaller coupling. At higher temperature, −35 °C, a different spectrum is obtained, a simple 1:3:3:1 quartet with $a_H = 20.5$ G and $g = 2.0030$. At intermediate temperatures, the two spectra both appear superimposed.

Both spectra decay within minutes when the irradiation is turned off. If the quartet spectrum is generated at −35 °C and rapidly cooled to −105 °C, the pattern is unchanged and persists indefinitely at this temperature. The fact that no reversion to the low-temperature five-line pattern was observed upon cooling shows decisively that the two spectra are due to two different radicals.

Photolysis of *sym*-hexamethyl-1,4-dideuterio-1,4-disilacyclohexa-2,5-diene (**3**) at −105 °C under the same conditions gave an ESR spectrum in which the major five-line pattern which was

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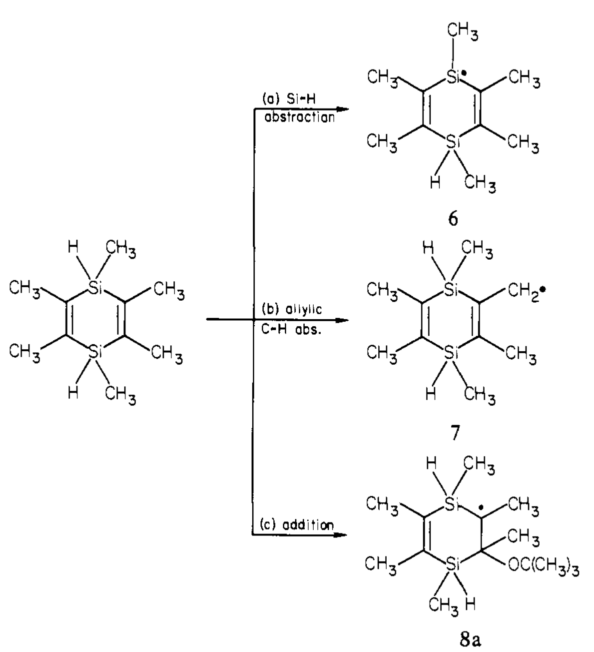
[5] For a review of silyl radicals see: Sakurai, H. In "Free Radicals"; Kochi, K., Ed.; Wiley-Interscience: New York, 1973; Vol. 2.

[6] Krusic, P.; Kochi, J. *J. Am. Chem. Soc.* **1968**, *90*, 7155, 7157.

[7] (a) Fessenden, R.; Schuler, R. *J. Chem. Phys.* **1963**, *38*, 773. (b) Fessenden, R.; Schuler, R. *Ibid.* **1963**, *38*, 2147. (c) Fischer, H. *Z. Naturforsch. A* **1962**, *17*, 693. (d) Fischer, H. *J. Chem. Phys.* **1962**, *37*, 1094. (e) Leon, J. A.; Koski, W. S. *J. Am. Chem. Soc.* **1966**, *88*, 224. (f) Tim, M.; Wood, D. *Ibid.* **1975**, *97*, 1004. (g) Kira, M.; Sakurai, H. *Ibid.* **1977**, *99*, 3892.

[8] Atwell, W.; Weyenberg, D. *J. Am. Chem. Soc.* **1968**, *90*, 3848. Compounds **2**, **3**, **4**, and **5** appear to be new.

Scheme II



observed for **2** is replaced by a major quartet. The intensities of the major four lines were exactly 1:3:3:1 indicating coupling to three equivalent protons, presumably a methyl group. Each of the major lines was split into six peaks with $a_H \sim 2$ G. At higher temperatures photolysis of **3** produced a different quartet in the ESR, identical with the high-temperature spectrum from **2** ($a_H = 20.5$ G). These results show that Si–H coupling is involved in the low-temperature ESR spectrum from **2**, but not in the high-temperature spectrum.

In order to distinguish the methyl groups on silicon from the allylic methyl groups, the hexadeuterio derivative **4** was prepared. Photolysis of **4** in the ESR cavity with *tert*-butyl peroxide as a radical initiator gave the spectrum shown in Figure 2. At low temperature a major 1:2:1 triplet was observed with each line split by a small coupling into a multiplet. At −35 °C a different 1:2:1 triplet spectrum was obtained, with splitting constant 20.5 G as for **2** and **3**. Each line of the triplet was split into three lines of equal intensity, indicating coupling to one deuterium atom ($a_D = 3.65$ G).

Discussion

Low-Temperature Radicals. As shown in Scheme II, there are at least three reactions leading to free radicals that **2** could undergo in the presence of *tert*-butoxy radical: (a) abstraction of a silicon–hydrogen bond to form the silyl radical, (b) C–H abstraction of an allylic methyl hydrogen to form an allylically stabilized, carbon-centered radical, or (c) addition of a *tert*-butoxy radical to one of the carbon–carbon double bonds to form an α-silyl, carbon-centered radical.

Neither the high- nor the low-temperature spectrum in Figure 1 is consistent with pathway b. The radical formed by such a process should show major splitting by a CH_2 group, a methyl group, and an Si–H proton, leading to a much more complicated splitting pattern than is observed. The low-temperature spectrum in Figure 1 could however be rationalized as coming from either pathway a or c.

The silicon-centered radical formed via pathway a might be expected to show major coupling to the $Si-CH_3$ group and to the Si–H proton four atoms removed.[9] If these splittings were nearly equivalent, an accidental five-line pattern would be produced. The low-temperature spectrum could also arise from the radical formed in pathway c, in which major coupling would be expected from the $C-CH_3$ group and the Si–H proton α to the radical center. Accidental equivalence of these splittings might likewise lead to a five-line pattern.

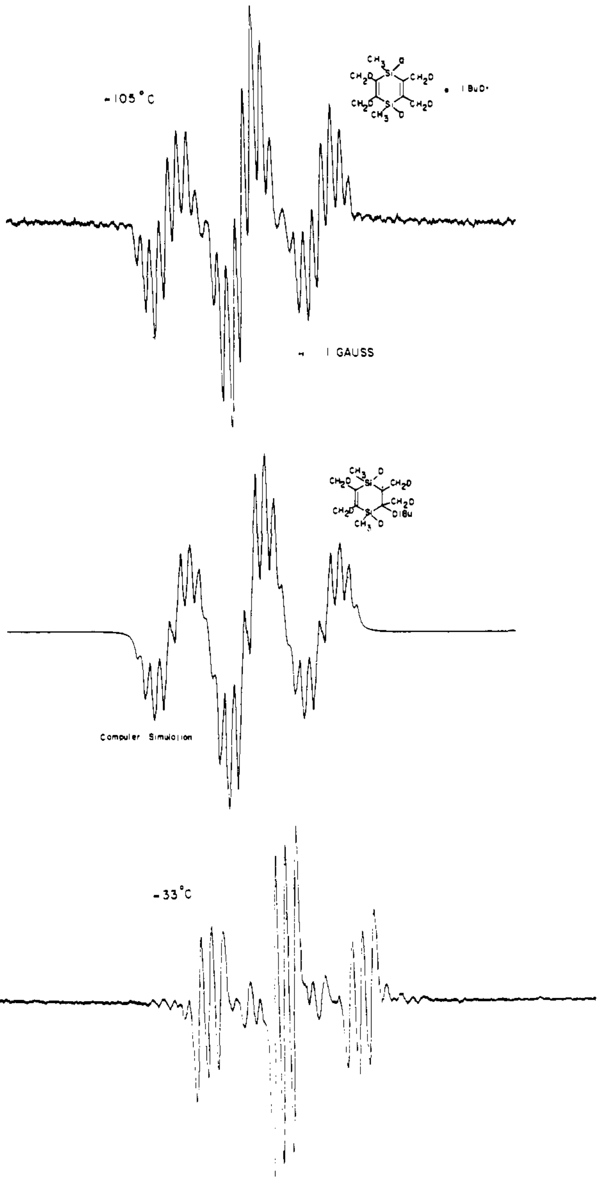


Figure 2. ESR spectrum of the radicals produced from **4** and *t*-BuOOH. Above, spectrum of low-temperature radical **8b** at −105 °C; center, computer simulation of −105 °C spectrum; below, spectrum of the high-temperature radical at −35 °C.

Substitution of deuterium for hydrogen on silicon does not differentiate between pathways a and c in the ESR experiment, since both of the possible radical products would show splitting by an Si–H proton. However, substitution of deuterium on the allylic methyl groups in compound **4** leads to unequivocal evidence as to the nature of the low-temperature radical. As shown in Figure 2, photolysis of **4** and *tert*-butyl peroxide at −105 °C gives rise to a major triplet. The triplet spectrum excludes pathway a, which would lead to a radical with a quartet ESR pattern. However, it is consistent with pathway c, in which addition of *t*-BuO· to one of the carbon–carbon double bonds takes place to give the α-silyl carbon-centered radicals **8a** or **8b**.

Careful examination of the low-temperature spectrum for **8a** (Figure 1) reveals that each of the outermost lines of the pentet

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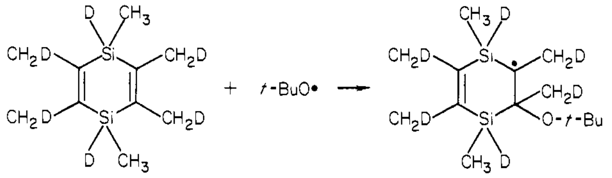
[9] 1,4-Cyclohexadiene shows an a_{H_4} splitting of 47 G.[7b] The splitting by Si–H in the 1,4-disilacyclohexadiene radical would be expected to be smaller due to the longer silicon–hydrogen bond lengths and the less effective overlap of a silicon 3p orbital and a carbon 2p orbital.

(10) Cooper, J.; Hudson, A.; Jackson, R. *Mol. Phys.* **1972**, *23*, 209.

(11) Bennett, S.; Eaborn, C.; Hudson, A.; Hussain, H.; Jackson, R. *J. Organomet. Chem.* **1969**, *16*, P36.

(12) Bennett, S.; Eaborn, C.; Hudson, A.; Jackson, R.; Root, K. *J. Chem. Soc. A* **1970**, 348.



4 8b

is split into six lines while the three center lines are split into eight-line patterns. The ratio of the intensities for the small coupling of the outer lines is approximately 1:3:4:4:3:1. Splitting by five equivalent nuclei should give intensities of 1:5:10:10:5:1, inconsistent with the results. Coupling by three protons with $a_{\mathrm{H}} = x$ (x = small splitting) and one proton with $a_{\mathrm{H}} = 2x$ would give rise to a six-line splitting pattern with the observed line intensities. The major five-line pattern can be explained as arising from coupling to three equivalent nuclei with $a_{\mathrm{H}} = y$ (y = major splitting) and one nucleus with $a_{\mathrm{H}} = y - 2x$. This would give rise to the observed six lines for the two end peaks and eight lines for each of the center peaks. A computer simulation of the low-temperature spectrum for **8a** is shown in Figure 1. Three-bond couplings are found for the remote Si–H atom (a_{H_γ} = 3.5 G) and for the α-silicon methyl group (a_{H} = 2.1 G).

Substitution of hydrogen by deuterium should decrease the magnitude of the observed splittings by the ratio of the gyromagnetic ratios for hydrogen and deuterium ($\gamma_{\mathrm{H}}/\gamma_{\mathrm{D}} = 6.514$). The spectrum of the low-temperature radical **8b** was simulated by using the same values as for **8a** but substituting the appropriate ratios for the two protons replaced by deuterium. The calculated and observed spectra are in good agreement, as seen from Figure 2. Similar substitution for only the Si–H proton gave a good simulation of the spectrum for the low-temperature radical from **3**.

High-Temperature Radicals. The ESR spectra obtained at −35 °C, shown in Figures 1 and 2, cannot be due to a silicon-centered radical. This is shown from the presence of deuterium coupling in the high-temperature ESR spectrum from the reaction of **4** with t-BuO·. The large magnitude of the $\beta_{\mathrm{C-H}}$ hyperfine splittings are also inconsistent with a silyl radical, since values of $\beta_{\mathrm{C-H}}$ for Si–CH_3 groups are generally less than 10 G.[10–12]

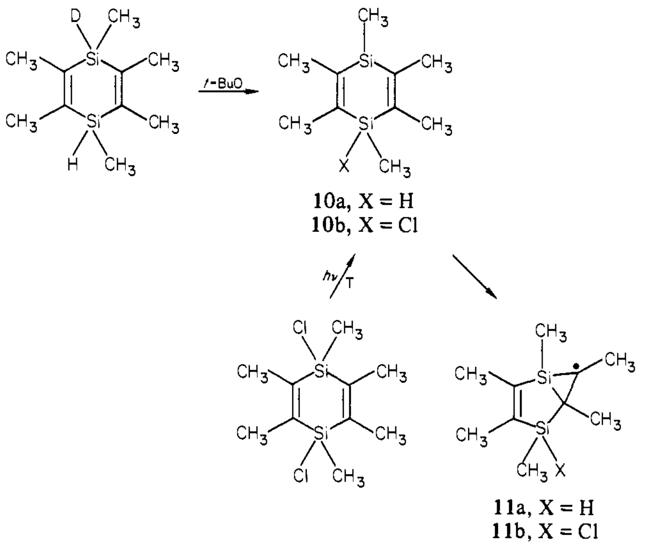
It was recently reported[1b] that silicon-centered radicals can be generated from the co-irradiation of a chlorosilane and an electron-rich tetraaminoethylene (**9**). Photolysis of **5** together with **9** in toluene produced a radical with a 1:3:3:1 quartet ESR spectrum, invariant with temperature over the range −80 to −20 °C. The hyperfine splitting constant of 20.5 G for this spectrum is identical with those for the quartet spectra from **2** and **3** at −35 °C. It appears that these spectra are due to similar radicals, differing only in the substitution of H, D, or Cl at the silicon atom remote from the radical center.

Photochemical reaction of **5** and **9** probably leads initially to the silyl radical **10b**, but for the reasons discussed above this species cannot be responsible for the observed ESR spectrum. We propose that **10b** undergoes rearrangement to the silacycloprop-2-yl radical **11b**, and that a similar radical **11a** is formed from **2** at high temperatures, perhaps through intermediate **10a** (Scheme III). Similar structures with deuterium substitution are proposed for the radicals obtained at −35 °C from **3** and **4**.

The proposed structure **11** accounts for the –CH_2D coupling observed for the high-temperature radical from **4**. Lack of observed coupling to the protons on the other methyl groups attached to the silacyclopropane ring is accounted for if the ring fusion forces these to lie on the opposite side of the three-membered ring from the (pyramidal) radical center.[13]

Rearrangement of an allyl to a cyclopropyl radical is unknown in the all-carbon case and is probably substantially disfavored. Two factors make such rearrangement more likely in the silicon system. First, the silyl radicals **10a,b** unlike allyl radicals, probably receive little stabilization by electron delocalization onto the vinyl groups. Second, the rearranged radicals **11a,b** may be substantially stabilized by having silicon atoms both α and β to the radical center.[14]

Scheme III



10a, X = H
10b, X = Cl

11a, X = H
11b, X = Cl

The temperature dependence of the ESR spectra from **2**, **3**, and **4** can be explained as arising from steric protection of the Si–H group. At low temperatures, the allylic methyl groups probably shield the silyl hydrogen from the bulky *tert*-butoxy radical, so that addition occurs preferentially. As the temperature is raised, the activation energy for abstraction is reached and the hydrogen atom is removed by t-BuO·. Electron transfer to **5** does not have any steric requirements, so that the same ESR spectrum is observed at all temperatures from −80 to −20 °C.

Further evidence for the intermediacy of a silicon-centered radical comes from the reaction of **2** with *tert*-butyl hypochlorite. This compound acts as a radical self-trapping reagent in which the chlorine atom reacts with the initially formed radical intermediate.[15] Thermolysis of a mixture of **2** and *tert*-butyl hypochlorite in the injection port of a gas chromatograph at 200 °C gave quantitative conversion to the 1,4-dichloride, **5**. In this case, trapping of the initially formed silacyclohexadienyl radical with chloride is apparently faster than rearrangement to the silacyclopropane radical.

Experimental Section

General. ESR spectra were recorded on a Varian Model E15 x-band spectrometer with 100-kHz modulation. The frequency was generated via a Varian E101 microwave bridge and monitored by a Hewlett-Packard Model 5245L frequency counter. The cavity temperature was maintained with a Varian Model 4343 variable-temperature unit.

In a typical experiment, 30 mg of the desired silane precursor and an equivalent volume of *tert*-butyl peroxide were placed in a quartz tube (4 mm o.d.). About 20 μL of cyclopropane was vacuum transferred to the tube, which was then sealed under a high vacuum (5×10^{-5} torr). The sample was placed in the cavity and irradiated with a Bausch and Lomb Model MP-200 mercury light source, focused onto the sample with a quartz lens. Anisotropic g values were measured against a strong pitch sample (g (ref) = 2.0028). Computer simulations were performed with a program designed by Professor J. Harriman, University of Wisconsin.

Synthesis of 1,4-Dimethoxy-1,2,3,4,5,6-hexamethyl-1,4-disilacyclohexa-2,5-diene (1). The procedure used was a modification of the synthesis described by Atwell and Weyenberg.[8] *sym*-Tetramethoxydi-

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(13) The silane hydrogen in **11a** is probably also directed away from the radical center; construction of models indicates that this is the least crowded of possible conformations. Three-bond coupling to Si–H might be expected if the hydrogen were on the same side of the ring as the unpaired electron.

(14) (a) Wilt, J.; Kolewe, O. *J. Am. Chem. Soc.* **1965**, *87*, 2071. (b) Wilt, J.; Kolewe, O.; Kraemer, J. *Ibid.* **1969**, *91*, 2624. (c) Krusic, P.; Kochi, J. *Ibid.* **1969**, *91*, 6161. (d) Wilt, J.; Aznavoorian, P. *J. Org. Chem.* **1978**, *43*, 1285.

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methyldisilane (6.36 g, 0.030 mol) and 2-butyne (2.9 g, 0.054 mol) were placed neat into a 25-mL thick-walled sealed tube (3-mm glass) and after several freeze–thaw degassing cycles the tube was sealed under a high vacuum (5×10^{-5} torr). The reaction vessel was placed in a Lindberg Type furance and pyrolyzed for 18 h at 250–60 °C. **CAUTION**: During two of the experiments the tube exploded violently; appropriate high-pressure safety procedures should be employed. The tube was removed and cooled to −196 °C before opening. The volatile reaction products, mostly $(MeO)_2SiMe_2$, were removed in vacuo leaving 3.5 g (90%) of crude 1,4-dimethoxy-1,2,3,4,5,6-hexamethyl-1,4-disilacyclohexa-2,5-diene as an oily solid. This material was generally used without further purification, but was recrystallized from CCl_4 if higher purity was required. NMR analysis showed it to be a mixture of cis and trans isomers but absolute assignment was not possible even with the use of $Eu(fod)_3$ shift reagent. NMR (major isomer) ($CDCl_3$) δ 3.20 (s, 6 H), 1.80 (s, 12 H), 0.0 (s, 6 H); (minor isomer) δ 3.17 (s, 6 H), 1.80 (s, 12 H), 0.02 (s, 6 H).

Synthesis of 1,2,3,4,5,6-Hexamethyl-1,4-disilacyclohexa-2,5-diene (2). To a solution of 1.4 g (3.7×10^{-2} mol) of lithium aluminum hydride in 25 mL of THF was added slowly at room temperature 1.5 g (5.8×10^{-3} mol) of a mixture of isomers of 1,4-dimethoxy-1,2,3,4,5,6-hexamethyl-1,4-disilacyclohexa-2,5-diene (**1**) over a period of 30 min. The resulting mixture was stirred at room temperature for 24 h and then poured *slowly* onto a mixture of 10% aqueous HCl and crushed ice. The product was extracted with ether, removed, and washed several times with water. The organic layer was dried over sodium sulfate and filtered and removal of the solvent gave 0.80 g (71%) of **2** as a clear liquid. Careful purification by preparative GC (6 ft × $^3/_8$ in. 20% SE30 on Chromosorb W 60/80, 170°) yielded the product as a solid with a melting point slightly above room temperature. NMR (CCl_4, $CHCl_3$) δ 4.1 (m, 2 H, Si–H), 1.8 (s, 12 H, allylic Me), 0.2 (2 d of d, 6 H, Si–CH_3). The Si–CH_3 resonance for each isomer is split into a doublet of doublets by unequal coupling to both Si–H protons. IR 2950, 2900, 2845 (s, C–H stretch), 2085 (vs, Si–H), 1565 (w, C=C), 1360–1450 (w, C–H bending), 1245 cm^{-1} (s, Si–C stretch); MS calcd $C_{10}H_{20}Si_2$ *m/e* 196.11035, obsd 196.1104, dev 0.25 ppm.

Synthesis of 1,4-Dideuterio-1,2,3,4,5,6-hexamethyl-1,4-disilacyclohexa-2,5-diene (3). The procedure was identical with that used in the synthesis of the 1,4-dihydro derivative **2** except that lithium aluminum deuteride was used as the reducing agent. Proton NMR showed collapse of the two doublets of doublets at δ 0.2 for **2** to a broad singlet. NMR (CCl_4, ref $CHCl_3$) δ 1.85 (s, 12 H, allylic methyl), δ 0.2 (bs, 6 H, D–Si–CH_3); MS calcd $C_{10}H_{18}Si_2D_2$ *m/e* 198.1229, obsd 198.1228, dev 0.5 ppm.

Synthesis of 1,4-Dideuterio-2-butyne. 1,4-Dichloro-2-butyne (6.1 g, 0.05 mol) was slowly added at room temperature to 100 mL of a 1.0 M solution of lithium triethylboron deuteride in THF. The resulting mixture was stirred at 25 °C for 10 h after which an excess of water was slowly added to react with the triethylborane formed. Fractional distillation gave 0.95 g (34%) of 1,4-dideuterio-2-butyne, bp collected 28–32 °C.

Synthesis of Hexadeuterio Derivative 4. The synthesis employed was the same as described for **1** and **2** except that 1,4-dideuterio-2-butyne was used in place of 2-butyne in the synthesis of the 1,4-dimethoxy derivative and lithium aluminum deuteride was used as a reducing agent. NMR δ 0.20 (s, 6 H), 1.75 (t, J = 2 Hz, 8 H); MS calcd 202.1476, obsd 202.1481, dev −4.6 ppm.

Synthesis of 1,4-Dichloro-1,2,3,4,5,6-hexamethyl-1,4-disilacyclohexa-5-diene (5). A solution of 8.5 g (0.033 mol) of a mixture of isomers of **1** in 30 mL of acetyl chloride was heated to reflux for 3 days. The excess acetyl chloride and the methyl acetate formed were distilled under nitrogen with the final amounts being removed under high vacuum. Sublimation (70 °C, 1 torr) from the distillation residue yielded 5.2 g (60%) of 1,4-dichloro-1,2,3,4,5,6-hexamethyl-1,4-disilacyclohexa-2,5-diene. GC analysis showed the product to be a nearly 1:1 mixture of isomers. NMR (CCl_4, $CHCl_3$ ref) (isomer **a**) δ 1.85 (s, 12 H), 0.42 (s, 6 H); (isomer **b**) δ 1.85 (s, 12 H), 0.39 (s, 6 H); MS calcd 264.0324, obsd 264.0325, dev 0.4 ppm.

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Registry No. *cis*-**1a**, 85977-35-1; *trans*-**1a**, 85977-36-2; **1b**, 85995-12-6; **2**, 85977-37-3; **3**, 85977-38-4; **4**, 85995-11-5; *cis*-**5**, 83447-54-5; *trans*-**5**, 83447-55-6; **8a**, 85977-39-5; **8b**, 85977-40-8; **9**, 4363-45-5; **11a**, 85977-41-9; **11b**, 85977-42-0; *tert*-butyl hypochlorite, 507-40-4; *tert*-butyl peroxide, 110-05-4; *sym*-tetramethoxydimethyldisilane, 18107-32-9; 2-butyne, 503-17-3; 1,4-dideuterio-2-butyne, 85977-43-1; 1,4-dichloro-2-butyne, 821-10-3.

Molecular Quadrupole Moments, Magnetic Anisotropies, and Charge Distributions of Ferrocene and Ruthenocene

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Abstract: Measurements of the infinite-dilution molar Kerr constants, field-gradient birefringence constants, and Cotton–Mouton constants of ferrocene and ruthenocene as solutes in cyclohexane at 25 °C are reported. The observations yield the effective polarizability anisotropy, the electric quadrupole moment, and the magnetic anisotropy of each molecule. Analysis of these properties shows that ferrocene and ruthenocene are more polarizable in directions parallel, rather than perpendicular, to the ligand–metal–ligand axes; it suggests that the bonding results in transfer of electronic charge from the metal atom toward the cyclopentadienyl rings; and it enables the observed magnetic anisotropies to be separated into oppositely signed diamagnetic and temperature-independent paramagnetic contributions. A useful new synthesis of ruthenocene is described.

Introduction

Although the basic qualitative features of the bonding in ferrocene and related metallocenes are considered to be well understood,[1] it is nevertheless true, as noted by Haaland,[2] that little is known with certainty concerning the charge distributions in such molecules. In the case of ferrocene, much controversy has surrounded the question of whether the bonding results in transfer of electronic charge *to* or *from* the cyclopentadienyl rings.[3] Early molecular-orbital studies[4,5] generated conflicting views, but subsequent theoretical work,[6] with a wide range of computational

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