

# JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Registered in U.S. Patent Office. © Copyright, 1978, by the American Chemical Society

VOLUME 100, NUMBER 25

DECEMBER 6, 1978

## Nuclear Magnetic Resonance and Electron Spin Resonance Observation of Hindered Rotation in *sym*-Tetra-*tert*-butyldisilane and the Corresponding Disilanyl Radical

David A. Stanislawski, A. C. Buchanan III, and Robert West\*

Contribution from the Department of Chemistry, University of Wisconsin,  
Madison, Wisconsin 53706. Received April 28, 1978

**Abstract:** The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of *sym*-tetra-*tert*-butyldisilane show that it adopts the *gauche* conformation below room temperature. These first NMR observations of hindered rotation in a disilane give a  $\Delta G^\ddagger$  of  $13.73 \pm 0.1$  kcal/mol. Two independent methods indicate that the entropy term is small ( $\Delta S^\ddagger = -5.4 \pm 3.0$  eu). The decrease in importance of the entropy term for the disilane compared to related ethanes is attributed to the decrease in steric repulsions which results from increasing the central bond length. The ESR spectrum of the disilanyl radical, generated by hydrogen abstraction, is indicative of an equilibrium conformation in which the  $\beta$ -silicon-hydrogen approaches the nodal plane of the half-filled p orbital. The usefulness of the hyperfine splitting of the  $\beta$  hydrogen,  $a(\text{SiH}_\beta)$ , as a conformational probe is discussed.

Dynamic nuclear magnetic resonance has become one of the most valuable techniques for determining the structure and stereochemistry of molecules.<sup>1</sup> The characteristics of NMR permit observation of dynamic processes with barrier heights within the range of about 5–25 kcal/mol. The barriers to rotation about carbon-carbon bonds often lie within this range and thus many NMR investigations of rotation in organic molecules have appeared.

Disilanes, compared with their carbon congeners, exhibit lower rotational barriers about the central bond as the data in Table I indicate. As might be expected, the increased bond lengths in the disilanes reduce their rotational barriers below those found for the analogous carbon compounds.<sup>2–11</sup> Until now, all experimental investigations of rotation about silicon-silicon bonds have required the use of microwave spectroscopy, vibrational spectroscopy, or electron diffraction.<sup>2,5,10</sup> Unfortunately, these three methods are generally useful only for simple molecules since the complexity of the data and its subsequent analysis increases rapidly as the number of atoms increases. Rotational barriers for more complex alkyl and aryl disilanes have only been estimated from empirical force field (EFF) calculations.<sup>3,7</sup>

Ingold and co-workers have recently reported extremely high rotational barriers determined from the NMR spectra of *sym*-tetra-*tert*-butylethane (**1**) and *sym*-tetra(trimethylsilyl)ethane (**2**).<sup>12</sup> Their interest in these compounds arose from



**1**



**2**

their studies of persistent carbon-centered radicals which resulted when bulky *tert*-butyl and trimethylsilyl groups were

substituted on ethane.<sup>13</sup> These highly substituted ethyl radicals also exhibit restricted rotation. Conformational assignments have been made for radicals using the electron spin resonance hyperfine splittings (hfs) from the  $\beta$  hydrogens,  $a(\text{H}_\beta)$ . Following this method, Sakurai and co-workers have interpreted the ESR spectrum of the *sym*-tetramethyldisilanyl radical to indicate conformational preferences at low temperatures.<sup>14</sup>

In this paper we report an investigation by NMR and ESR of the effects of *tert*-butyl substitution on the stereochemistry of disilanes. The species investigated were *sym*-tetra-*tert*-butyldisilane (**3**) and its corresponding radical, **4**.



**3**



**4**

### Experimental Section

**1,1,2,2-Tetra-*tert*-butyldisilane (3).** **3** was prepared by coupling di-*tert*-butyldichlorosilane and/or di-*tert*-butylchlorosilane under reaction conditions slightly modified from those previously reported.<sup>15</sup> The coupling was run using sodium-potassium alloy and proceeds in reasonable yield in either THF (40%) or cyclohexane (53%) solvent. The compound was purified by vacuum distillation (84–95 °C at 0.25 Torr) and confirmed by its IR and NMR spectra.

**NMR Spectra.** The variable-temperature  $^1\text{H}$  NMR spectra were obtained on Varian XL-100-15 and Bruker WH-270 spectrometers operating in the FT mode. Variable-temperature  $^{13}\text{C}$  resonance spectra were acquired on the Varian XL-100 spectrometer. All spectra were run in  $\text{CD}_2\text{Cl}_2$  solvent with  $\text{Me}_4\text{Si}$  as an internal reference. The probe temperature was monitored using a Doric DS-35 thermocouple indicator to an accuracy of  $\pm 1$  °C.

Theoretical spectra were calculated using a program based on the matrix formulations of the Bloch equations as described by Reeves

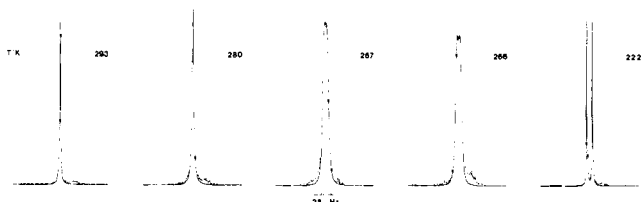


Figure 1. Experimental  $^1\text{H}$  NMR spectra (dashed lines) and theoretical spectra (solid lines) determined for the primary hydrogens of **3** in  $\text{CD}_2\text{Cl}_2$  at various temperatures. The low-intensity peaks in the experimental spectra arise from sample impurities.

Table I. Rotational Barriers for Some Disilanes and Their Carbon Congeners

compd	method <sup>a</sup>	rotational barrier, kcal/mol	ref
$\text{H}_3\text{SiSiH}_3$	V	1.22	2
	EFF	1.2	3
$\text{H}_3\text{CCH}_3$	MW	2.88	4
$\text{H}_3\text{SiSiH}_2\text{F}$	MW	1.05	5
$\text{H}_3\text{CCH}_2\text{F}$	MW	3.33	6
$\text{H}_3\text{SiSiHF}_2$	EFF	0.85	7
$\text{H}_3\text{CCHF}_2$	MW	3.18	8
$\text{H}_3\text{SiSiF}_3$	EFF	0.81	7
$\text{H}_3\text{CCF}_3$	V	3.21	9
$\text{Cl}_3\text{SiSiCl}_3$	ED	0.65	10
$\text{Cl}_3\text{CCCl}_3$	ED	10.8	11
$\text{Me}_3\text{SiSiMe}_3$	EFF	1.05	3

<sup>a</sup> V = vibrational, EFF = empirical force field, MW = microwave, ED = electron diffraction.

and Shaw.<sup>16</sup> The actual program employed makes the assumption that  $\Delta S^\ddagger = 0$ . The best fit values were determined by superpositioning of the simulated spectra on the experimental spectra.

**ESR Spectra.** Solutions of **3** with di-*tert*-butyl peroxide (1:1 v/v) or with di-*tert*-butyl peroxide and *tert*-butylbenzene (1:1:1 v/v/v) were carefully degassed and sealed in quartz tubes. The solutions were irradiated with a water-filtered Bausch and Lomb SP-200 super pressure mercury source in the ESR cavity of a Varian V-4502-12 spectrometer using 100-kHz modulation and a Varian V-4557 variable temperature accessory. The microwave frequency was measured with a Hewlett-Packard 5245L counter and 5256A frequency converter. The *g* factor and hyperfine splitting constant were measured relative to an aqueous solution of Fremy's salt ( $g = 2.0057$ ;  $a_N = 13.096$  G).

There is no observable temperature dependence in the ESR spectrum from  $-60$  to  $-20$  °C. At  $-25$  °C the disilanyl radical exhibits no apparent decay in signal intensity after 8 h. However, if the temperature is raised above  $-20$  °C, decomposition of **4** results in several unidentified ESR signals.

### NMR Results and Discussion

**NMR Spectra.** The 270-MHz  $^1\text{H}$  NMR spectrum of **3** taken at ambient temperature shows two singlets for the methyl and SiH protons at 1.15 and 3.61 ppm, respectively. The SiH resonance remains a singlet at all temperatures. The changes observed in the methyl region at various temperatures are depicted in Figure 1 along with the calculated spectra. The low-temperature limiting spectrum shows two equivalent methyl resonances with a chemical shift separation ( $\Delta\nu$ ) of 15.2 Hz. The 5.6-Hz separation observed at low temperatures at 100 MHz is consistent with this value.

The  $^{13}\text{C}$  NMR spectrum of **3** also shows two singlets at ambient temperature. The methyl carbons are found at 31.2 ppm and the quaternary carbons appear at 20.3 ppm. At low temperatures the methyl resonance splits into two equivalent signals with a separation of 23.2 Hz. No splitting of the quaternary carbons is observed.

The  $\Delta\nu$ 's for **3** observed on the various spectrometers are collected in Table II along with the corresponding coalescence temperatures and the calculated free energies of activation.

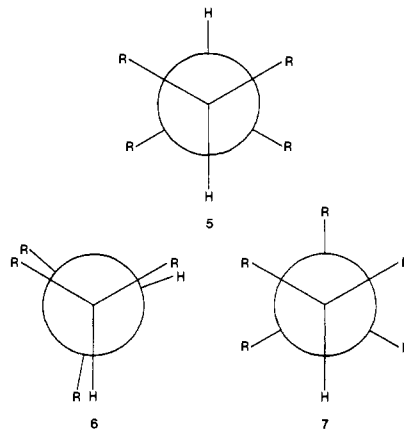
Table II. Rate Parameters for Internal Rotation of **3** Taken from the Variable Temperature NMR Data

parameter	$^{13}\text{C}$ at 25.2 MHz	$^1\text{H}$ at 270.1 MHz	$^1\text{H}$ at 100.1 MHz
$\Delta\nu$ , Hz	23.2	15.2	5.6
$T_c$ , K	273	267	257
$\Delta G^\ddagger$ , kcal/mol	13.8	13.8	13.7

Table III. Thermodynamic Activation Parameters for Disilane **3** and Related Compounds

compd	$\Delta G^\ddagger$ , kcal/mol	$\Delta H^\ddagger$ , kcal/mol	$\Delta S^\ddagger$ , eu	ref
$(t\text{-Bu})_2\text{SiHSiH}(t\text{-Bu})_2$	13.7	12.3	-5.4	this work
$(t\text{-Bu})_2\text{CHCH}(t\text{-Bu})_2$	>23			12
$(\text{Me}_3\text{Si})_2\text{CHCH}(\text{SiMe}_3)_2$	18.8	9.6	-26	12
$(t\text{-Bu})_2\text{PP}(t\text{-Bu})_2$	12.6	15.7	+14	21

**Conformation of 3.** The splitting of the methyl resonance of **3** into two signals at low temperatures (Figure 1) indicates that interconversion of conformational isomers is slow on the NMR time scale. The anti conformation, **5**, would give rise only to one signal, and therefore the two different methyl resonances



must arise from the distinct methyl pairs of the eclipsed conformation, **6**, or the gauche conformation, **7**.

Ingold has presented similar results for compounds **1** and **2** and favors the gauche conformation on steric grounds, especially because relieving these steric repulsions by angle bending leads to a lower energy conformation for the gauche rotamer.<sup>12</sup> These steric effects are, however, easily removed, for NMR coupling constants indicate that tetraphenylethane adopts the anti conformation,<sup>17</sup> and tetramethylethane exhibits no conformational preference, displaying NMR signals for both gauche and anti rotamers in a 2:1 statistical ratio.<sup>18</sup>

EFF calculations on disilanes suggest that hexamethyl-disilane has the staggered conformation<sup>3</sup> but that hexaphenyldisilane should be nearly eclipsed.<sup>19</sup> An eclipsed rotamer might also be possible for **3**, but molecular models indicate that the increased bond lengths are not sufficient to remove serious steric repulsions between geminal *tert*-butyl groups in the molecule. Therefore, we favor the gauche form for the disilane **3** in accord with Ingold's findings for the ethanes **1** and **2**.<sup>20</sup>

**Entropy Effects on the Free Energy of Activation of 3.** Thermodynamic activation parameters for rotation in the disilane **3** and related compounds are listed in Table III.<sup>12,21</sup>

Although the free energy of activation for the ethanes **1** and **2** is high, the enthalpy term for **2** was determined to be within the typical 6–14 kcal/mol range found for hindered rotation about carbon-carbon bonds.<sup>12</sup> The rest of the activation energy for **2** was accounted for by the large entropy term,  $-26 \pm 2$  eu.

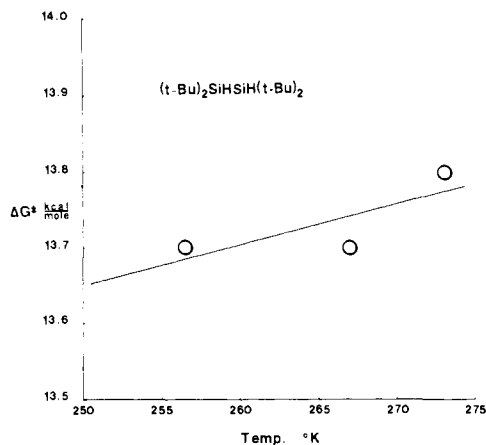


Figure 2. Least-squares plot of the free energy of activation vs. the coalescence temperature obtained at various magnetic field strengths.

Table IV. ESR Parameters for Disilanyl Radicals<sup>a</sup>

radical	$a(\text{CH}_\beta)$	$a(\text{SiH}_\beta)$	$a(\text{H}_\gamma)$	$a(^{29}\text{Si}_\alpha)$	$g$	ref
$(t\text{-Bu})_2\text{HSiSi}(t\text{-Bu})_2$		$<3.4^b$	$c$	116	2.0038	this work
$(\text{CH}_3)_2\text{HSiSi}(\text{CH}_3)_2$	7.79	6.63–9.14 <sup>d</sup>	0.25	142 <sup>e</sup>	2.00375	14
$(\text{CH}_3)_3\text{SiSiH}(\text{CH}_3)^f$	8.15		0.30	142 <sup>e</sup>	2.0037	25
$(\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_2$	8.21		0.47	137	2.0037	25

<sup>a</sup> Hyperfine splitting constants in gauss. <sup>b</sup> Value quoted is  $\Delta H_{p-p}$  of central line. <sup>c</sup> Not resolved. <sup>d</sup> Temperature dependent: 6.63 at 20 °C, 9.14 at –120 °C. <sup>e</sup> Reference 30. <sup>f</sup>  $a(\text{H}_\alpha) = 16.30$  G.

Ingold and co-workers therefore suggested that when the free energy of activation is higher than expected, as in the case of compounds with extremely bulky substituents, significant entropy effects can account for the additional energy.<sup>22</sup>

The enthalpy and entropy of activation for rotation of the disilane **3** were determined employing the dependence of the coalescence temperature upon the NMR resonance frequency.<sup>23</sup> A least-squares analysis of the resultant rate parameters for chemical exchange between two equally populated sites (Figure 2) gave a  $\Delta H^\ddagger$  of  $12.3 \pm 0.8$  kcal/mol and a  $\Delta S^\ddagger$  of  $-5.4 \pm 3.0$  eu. Although the value of  $\Delta S^\ddagger$  is based on only three experimental points, the  $\Delta S^\ddagger$  for **3** appears to be quite small (near zero as suggested by the line-shape analysis) and negative. This result is reasonable for a simple intramolecular rate process and receives additional support from the excellent agreement between the two independent determinations of  $\Delta G^\ddagger$  ( $13.76 \pm 0.1$  kcal/mol from line-shape analysis vs.  $13.73 \pm 0.1$  kcal/mol by the above method).

That the entropy term makes a substantially smaller contribution to  $\Delta G^\ddagger$  for the disilane **3** than for hindered ethanes can be rationalized by referring to models, which show that **1** is a remarkably hindered species. Rotation about the central C–C bond must be accompanied by a concerted rotation of the methyl groups in order for them to get by each other. A similar situation occurs for **2** since the increased C–SiMe<sub>3</sub> bond length is compensated for by the similarly lengthened Si–CH<sub>3</sub> bond. The smaller  $\Delta G^\ddagger$  is attributed to the greater flexibility of these longer bonds. Compound **3**, however, shows a considerably lengthened central bond as well as an increased Si–CMe<sub>3</sub> bond length. This combined lengthening moves the methyl groups considerable further apart and substantially reduces the contact between methyl groups, thus leading to less hindered rotation.

### ESR Results and Discussion

**ESR Spectrum.** Photolysis of a solution of di-*tert*-butyl peroxide and **3** at –25 °C rapidly produced a steady-state concentration of the disilanyl radical, **4**, from hydrogen abstraction by the photochemically generated *tert*-butoxy radi-

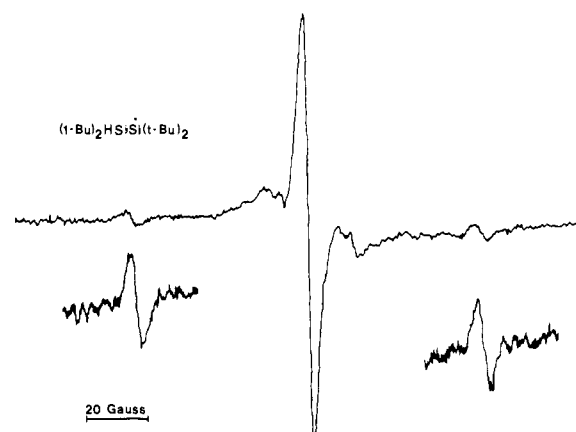
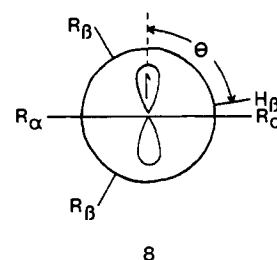


Figure 3. ESR spectrum of **4** at –25 °C. Inserts are for the <sup>29</sup>Si satellites obtained at higher spectrometer gain.

cals. The ESR spectrum shown in Figure 3 consists of a broad single line flanked by silicon-29 ( $I = 1/2$ , 4.7% abundance) satellites.<sup>24</sup> The  $g$  value and silicon hfs are given in Table IV and are consistent with those for other tabulated disilanyl radicals.<sup>14,25</sup> The peak to peak line width ( $\Delta H_{p-p}$ ) of 4.2 G decreased to 3.4 G when the photolysis was carried out in *tert*-butylbenzene as solvent. The hfs due to the  $\beta$  hydrogen,  $a(\text{H}_\beta)$ , was not resolved but must be less than the  $\Delta H_{p-p}$  of 3.4 G.

**Hfs and Conformational Assignment for 4.** The ESR measurement of  $a(\text{H}_\beta)$  has allowed the determination of equilibrium conformations for substituted ethyl radicals. This splitting arises primarily from hyperconjugation and is dependent on the angle,  $\theta$ , between the principal axis of the  $p$  orbital containing the unpaired electron and the C–H bond on the  $\beta$ -carbon atom as shown in **8**. This hfs can be represented by the



empirical relationship  $a(\text{H}_\beta) = B_0 + B \cos^2 \theta$  where  $B_0$  and  $B$  are constants ( $B_0 \approx 3 \pm 2$ ,  $B = 48 \pm 5$  G).<sup>26</sup>

Although most silyl radicals exhibit pyramidal geometry, disilanyl radicals are believed to be planar or quasi-planar from ESR<sup>25,27</sup> and chemical evidence.<sup>28,29</sup> It therefore appears that hyperconjugation provides an important mechanism in determining the magnitude of  $\beta$ -SiH as well as  $\beta$ -CH splittings in disilanyl radicals.<sup>14</sup> However, because only one another  $\beta$ -SiH splitting for a disilanyl radical has been reported, an empirical relationship for assigning the angle,  $\theta$ , based on values of  $a(\text{SiH}_\beta)$  cannot yet be developed.

The ESR parameters for **4** and for other known disilanyl radicals are shown in Table IV. The smaller value of  $a(^{29}\text{Si}_\alpha)$

Table V.  $a(H_\beta)$  for Some Substituted Ethyl Radicals

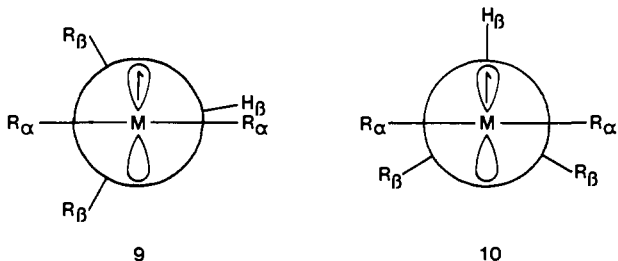
radical	$T, ^\circ\text{C}$	$a(H_\beta), \text{G}$	ref
$(t\text{-Bu})_2\text{HCC}(t\text{-Bu})_2$	25	$<3.5^a$	31
$\{(\text{CH}_3)_3\text{Si}\}_2\text{HCC}\{\text{Si}(\text{CH}_3)_3\}_2$	25	$<0.27^a$	31
$(\text{CH}_3)_2\text{HCC}(\text{CH}_3)_2$	20	$11.9^b$	31
	-120	9.8	
$(\text{CH}_3)_2\text{HCCH}_2$	-98	32.2	32
	-145	35.1	

<sup>a</sup> Value quoted is  $\Delta H_{p-p}$  of central line. <sup>b</sup> Hfs for unique hydrogen;  $a(H_\beta) = 22.9 \text{ G}$  for the methyl hydrogens.

in **4** compared to the other disilanyl radicals indicates reduced s character in the orbital containing the unpaired electron and thus a more nearly planar radical center.

The value of  $a(\text{Si-H}_\beta)$  is remarkably low, within the line width of the single-line ESR spectrum. This fact along with the temperature independence of the ESR spectrum over the range studied indicates that **4** is locked in conformation **9**. As discussed earlier, it is not possible to calculate the angle  $\theta$ , but a comparison of  $a(\text{SiH}_\beta)$  with that in  $\text{Me}_2\text{HSi-SiMe}_2$  suggests that the  $\beta$ -SiH bond is approaching the nodal plane of the half-filled p orbital (i.e.,  $\theta$  is approaching  $90^\circ$ ). This conformation must result from steric repulsions between the *tert*-butyl groups, consistent with the high activation barrier for rotation about the Si-Si bond determined for the parent disilane **3**.

These findings are in direct contrast to the results on *sym*-tetramethyldisilanyl radical,  $\text{Me}_2\text{HSiSiMe}_2$ .<sup>14</sup> For this species  $a(\text{SiH}_\beta)$  increases markedly with the lower temperatures implying that **10** is the equilibrium conformation for this



radical. This conformation, with  $\theta = 0^\circ$ , must be favored by hyperconjugation between the  $\beta$ -SiH bond and the p orbital on silicon. Greatly reduced steric hindrance in this radical compared to **4** allows this conformation to be sustained.

It is interesting to compare these results with those for the substituted ethyl radicals shown in Table V.<sup>31,32</sup> The extraordinarily low value observed for  $a(H_\beta)$  in  $(t\text{-Bu})_2\text{HCC}(t\text{-Bu})_2$  and  $(\text{Me}_3\text{Si})_2\text{HCC}(\text{SiMe}_3)_2$ <sup>31</sup> shows that these hindered radicals, like **4**, are locked in conformation **9**. The less hindered  $\text{Me}_2\text{HC-CMe}_2$ ,<sup>31</sup> however, does not adopt conformation **10** as does its silicon analogue but shows a weak preference for **9** (more pronounced at lower temperatures). This connotes greater steric strain than in the corresponding disilanyl radical, resulting from the shorter C-C bond. Conformation **10** can, however, be observed in some substituted ethyl radicals. For example, the temperature dependence of  $a(H_\beta)$  for the isobutyl radicals,  $\text{Me}_2\text{HCCH}_2$ ,<sup>32</sup> suggests that **10** is the equilibrium conformation.

The hyperfine coupling constant,  $a(H_\beta)$ , has been extremely important in the assignment of conformations for substituted ethyl radicals. Similarly, it appears that the ESR measurement of  $a(\text{SiH}_\beta)$  will be a valuable probe in the conformational analysis of disilanyl radicals.

**Acknowledgments.** This work was supported by the U.S. Air Force Office of Scientific Research, Grant AF-AFOSR-74-2644. We thank Mr. William Erhardt for providing the line-shape program.

## References and Notes

- G. Binsch, *Top. Stereochem.*, **3**, 97 (1968).
- M. Pfeiffer and H. J. Sprangenberg, *Z. Phys. Chem. (Leipzig)*, **232**, 47 (1966).
- J. P. Hummel, J. Stackhouse and K. Mislow, *Tetrahedron*, **33**, 1925 (1977).
- D. R. Lide, Jr., *J. Chem. Phys.*, **29**, 1426 (1958).
- A. P. Cox and R. Varma, *J. Chem. Phys.*, **44**, 2619 (1966).
- P. H. Verdier and E. B. Willson, Jr., *J. Chem. Phys.*, **29**, 340 (1958).
- J. P. Lowe and R. G. Parr, *J. Chem. Phys.*, **44**, 3001 (1966).
- D. R. Herschbach, *J. Chem. Phys.*, **25**, 358 (1956).
- H. S. Gutowsky and H. B. Levine, *J. Chem. Phys.*, **18**, 1297 (1950).
- L. O. Brockway and N. R. Davidson, *J. Am. Chem. Soc.*, **63**, 3287 (1941).
- Y. Morino and E. Hirota, *J. Chem. Phys.*, **28**, 185 (1958).
- S. Brownstein, J. Dunogues, D. Lindsay, and K. U. Ingold, *J. Am. Chem. Soc.*, **99**, 2073 (1977).
- D. Griller and K. U. Ingold, *Acc. Chem. Res.*, **9**, 13 (1976).
- H. Sakurai, M. Kira, and M. Sato, *Chem. Lett.*, 1323 (1974).
- K. Triplett and M. D. Curtis, *J. Organomet. Chem.*, **107**, 23 (1976).
- L. W. Reeves and K. N. Shaw, *Can. J. Chem.*, **48**, 3641 (1970).
- D. A. Dougherty, K. Mislow, J. F. Blount, J. B. Wosten, and J. Jacobus, *J. Am. Chem. Soc.*, **99**, 6149 (1977).
- L. Lunazzi, D. Macciantelli, F. Bernardi, and K. U. Ingold, *J. Am. Chem. Soc.*, **99**, 4573 (1977).
- W. D. Hounshell, D. A. Dougherty, J. P. Hummel, and K. Mislow, *J. Am. Chem. Soc.*, **99**, 1916 (1977).
- After this paper was submitted we learned of the nearly simultaneous work by S. G. Baxter, D. A. Dougherty, J. F. Blount, and K. Mislow, *J. Am. Chem. Soc.*, in press. The EFF study in this paper confirms that the gauche form for **3** is the stable conformer, and the  $\Delta G^\ddagger$  value determined from <sup>1</sup>H NMR studies of **3** is in excellent agreement with our value.
- J. A. Brunelle, C. H. Bushweller, and A. D. English, *J. Phys. Chem.*, **80**, 2598 (1976).
- Because the P-P and Si-Si bonds as well as the P-C and Si-C bonds have similar lengths, tetra-*tert*-butyldiphosphine might be expected to exhibit similar activation energy parameters. In contrast Brunelle and co-workers have reported an unusually large positive  $\Delta S^\ddagger$  value, +14 eu, for what they note appears to be a simple intramolecular rate process.<sup>21</sup> They propose three possible sources for this large entropy term: (1) a systematic error in the line-shape analysis; (2) differential solvation effects; and (3) increased freedom of alkyl rotation in the P-P rotational transition state. Our data indicate that extra rotational freedom is not sufficient to account for this dramatic entropy increase. Special solvation effects involving phosphorus lone pairs might be responsible for a positive entropy, but it is also quite possible that a large error is introduced in the line-shape analysis. The simplified model used by Brunelle and co-workers may be insufficient to give accurate values of enthalpy and entropy of activation.
- H. S. Gutowsky and H. N. Cheng, *J. Chem. Phys.*, **63**, 2439 (1975).
- The assignment of the two sets of small peaks flanking the main spectrum is not absolutely certain. We believe that the inner pair, 22 G separation, are carbon-13 ( $I = 1/2$ , 1.1% abundance) satellites arising from the methyl carbons of the *tert*-butyl groups bonded to the silicon radical center. The outer pair, separated by 30 G, vary in intensity in different runs and are positioned where strong signals are observed during the decomposition of **4** at higher temperatures. These lines are probably due to initial concentrations of the decomposition product.
- S. W. Bennett, C. Eaborn, A. Hudson, R. A. Jackson, and K. D. Root, *J. Chem. Soc. A*, 348 (1970).
- (a) P. B. Ayscough, "Electron Spin Resonance in Chemistry", Methuen, London, 1967, p 73; (b) H. Fischer in "Free Radicals", Vol. II, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, Chapter 19.
- J. Cooper, A. Hudson, and R. A. Jackson, *Mol. Phys.*, **23**, 209 (1972).
- H. Sakurai and M. Murakami, *Chem. Lett.*, 7 (1972).
- L. H. Sommer and L. A. Ulland, *J. Org. Chem.*, **37**, 3878 (1972).
- S. W. Bennett and R. West, unpublished results.
- D. Griller and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 6203 (1974).
- R. W. Fessenden, *J. Chim. Phys. Phys.-Chim. Biol.*, **61**, 1570 (1964).