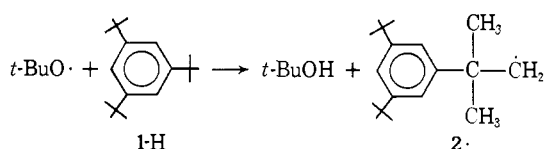
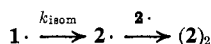


Figure 2. Epr spectrum of tri-*tert*-butylphenyl and di-*tert*-butylneophyl at -40° . Microwave power and modulation set to optimize the signal from di-*tert*-butylneophyl.

obtained by photolysis of 1-H indi-*tert*-butyl peroxide under identical conditions.⁸



Under steady illumination, the concentration ratio $[2\cdot]/[1\cdot]$ decreases with decreasing temperature. Furthermore, at any one temperature below 0° the concentration of $1\cdot$ is proportional to the first power of the light intensity, while the concentration of $2\cdot$ is proportional to the square root of the intensity. This implies that $1\cdot$ decays by a first-order process and $2\cdot$ by a second-order process. We presume that $1\cdot$ isomerizes to $2\cdot$,⁹ which then dimerizes at these temperatures.¹¹



The rate constant for this isomerization was measured by the kinetic epr technique.¹² Over the temperature range -30 to -90° , k_{isom} was independent of the concentrations of 1-Br, ditin, and cyclopropane and could be represented by

$$\log(k_{\text{isom}}/\text{sec}^{-1}) = 5.3 - 4.5/\theta$$

where $\theta = 2.3RT$ kcal/mol. The preexponential factor for this isomerization is lower than is found for most intramolecular hydrogen abstractions,¹³ possibly because this reaction involves a five- rather than the more usual six-membered transition state.

Photolysis in cyclopropane of the ditin and 1-Br fully deuterated in the *tert*-butyl groups yielded a much more

(8) No signal was produced from the peroxide in the absence of 1-H.
(9) Photolysis of 1-Br in cyclohexane at room temperature yields 1-H in over 65% yield.¹⁰

(10) I. T. McMaster, unpublished work.

(11) At higher temperatures $2\cdot$ would isomerize to the 2-methyl-2-(3',5'-di-*tert*-butylbenzyl)ethyl radical, see e.g., E. J. Hamilton, Jr., and H. Fischer, *Helv. Chim. Acta*, **56**, 795 (1973).

(12) See K. Adamic, D. F. Bowman, T. Gillan, and K. U. Ingold, *J. Amer. Chem. Soc.*, **93**, 902 (1971), and subsequent papers in this series.

(13) See, e.g., L. Endrenyi and D. J. LeRoy, *J. Phys. Chem.*, **70**, 4081 (1966); K. W. Watkins and L. A. Ostreko, *ibid.*, **73**, 2080 (1969); K. W. Watkins, *J. Amer. Chem. Soc.*, **93**, 6355 (1971); *Can. J. Chem.*, **50**, 3738 (1972); *J. Phys. Chem.*, **77**, 2938 (1973); K. J. Mintz and D. J. LeRoy, *Can. J. Chem.*, **51**, 3534 (1973).

stable phenyl radical having the expected epr signal (i.e., a triplet due to meta protons, with $a^D(o\text{-}tert\text{-butyl}) = 0.047$ G). The ^{13}C coupling to the six methyl groups of the ortho-*tert*-butyls was also resolved. There was only sufficient material for kinetic measurements at -30° . Decay was first order with $(k_{\text{isom}})_D = 0.38 \text{ sec}^{-1}$, giving an isotope effect (primary plus secondary) for isomerization, $(k_H/k_D)^{-30^\circ} \approx 50$.

A few unsuccessful experiments may also be worth reporting. Ditin and trimethylsilane reacted directly with 1-Cl in the absence of light to yield epr signals that did not appear to be $1\cdot$. These reactions were soon over and so the epr signals did not persist for long enough to be analyzed in detail. 2,4,6-Triphenylbromobenzene treated in the same way as 1-Br gave no epr signal, possibly because of its low solubility in cyclopropane.

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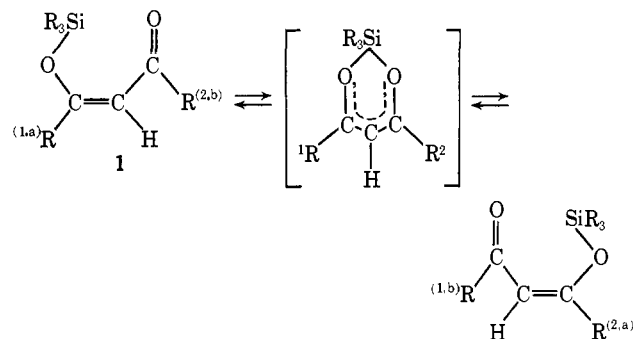
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Rearrangements of 1-Acetylacetonato-1-methyl-1-silacyclobutane via Internal Nucleophilic Displacement¹

Sir:

Several acyclic silyl enol ethers²⁻⁵ and related compounds^{6,7} have been reported wherein the *seqcis* or *Z* isomers (1) undergo a facile 1,5-silyl group migration



between two oxygen centers exclusively with retention of configuration at silicon.³⁻⁵ In accord with our originally proposed mechanism,¹ more recent results⁵ indicate that these degenerate migrations are better viewed as internal nucleophilic displacement processes rather than as sigmatropic shifts. We now wish to

(1) This research was sponsored in part by the National Science Foundation Grant GP-29435.

(2) (a) J. J. Howe and T. J. Pinnavaia, *J. Amer. Chem. Soc.*, **91**, 5378 (1969); (b) T. J. Pinnavaia, W. T. Collins, and J. J. Howe, *ibid.*, **92**, 4544 (1970).

(3) I. K. Kusnezowa, K. Ruhlmann, and E. Grundemann, *J. Organometal. Chem.*, **47**, 53 (1973).

(4) J. A. Lindemulder, A. Schwartz, and T. J. Pinnavaia, Abstracts, 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973, INOR 20.

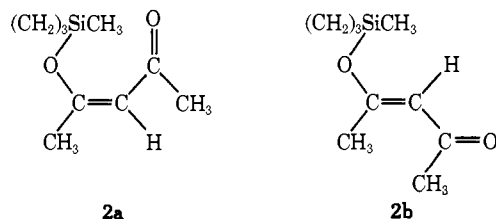
(5) H. J. Reich and D. A. Murcia, *J. Amer. Chem. Soc.*, **95**, 3418 (1973).

(6) Y. N. Kuo, F. Chen, and C. Ainsworth, *Chem. Commun.*, 137 (1971).

(7) (a) H. Shanan-Atidi and Y. Shvo, *Tetrahedron Lett.*, **7**, 603 (1971). (b) For a description of nomenclature see J. E. Blackwood, C. L. Gladys, K. L. Loening, A. E. Petrarca, and J. E. Rush, *J. Amer. Chem. Soc.*, **90**, 509 (1968).

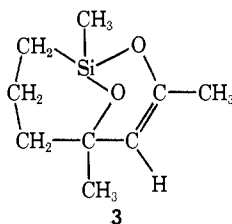
report for a silacyclobutane enol ether the dramatic effect of angle strain at silicon on the rate of 1,5 migration and the discovery of a new intramolecular rearrangement in which the silacyclobutane ring is opened *via* a related internal nucleophilic displacement mechanism.

The reaction of 1-chloro-1-methyl-1-silacyclobutane and acetylacetone in the presence of pyridine afforded a 2:1 mixture of *seqcis* (**2a**) and *seqtrans* (**2b**) diastereoisomers



of 1-acetylacetonato-1-methyl-1-silacyclobutane: bp 54–55° (0.5 Torr); ir (CCl₄) 1677, 1662, 1622, 1589, and 1044 cm⁻¹; nmr (CCl₄) **2a** τ 9.63 (s, 3 H) 8.08 (s, 6 H) 4.82 (s, 1 H), **2b** τ 9.58 (s, 3 H) 7.99 (d, 3 H, $J < 0.5$ Hz) 7.75 (d, 3 H, $J < 0.5$ Hz) 4.70 (m, 1 H). The *seqtrans* configuration is stereochemically rigid as evidenced by the presence of equally intense COCH₃ and =CCH₃ lines in the nmr spectrum. However, the rapid degenerate rearrangement of the *seqcis* form causes the magnetically nonequivalent methyl groups (equivalent to environments a and b of groups R¹ and R² in **1**) to be time-averaged. The rearrangement is sufficiently rapid in CHF₂Cl to give a single methyl line even at -142°. The value of k_{-142} is conservatively estimated to be >20 sec⁻¹ ($\Delta G^\ddagger < 6.7$ kcal/mol) based on the assumption that the frequency separation in absence of exchange is at least 10 Hz. In comparison, the rate of 1,5-silyl group migration at -142° for the analogous acyclic Si(CH₃)₃ derivative is 1.0 × 10⁻¹⁰ sec⁻¹ ($\Delta G^\ddagger = 13.4$ kcal/mol).^{2b} The marked increase in rate due to angle strain at silicon is in accord with the angle strain effects recently reported by Sommer⁸ for front-side SN2 Si displacements at bridgehead silicon and further supports the view that the 1,5 migrations involve internal nucleophilic displacement.

In CCl₄ solution at slightly elevated temperatures, **2a** undergoes a facile irreversible rearrangement *via* opening of the silacyclobutane ring to give exclusively the unique bicyclic compound 1,3,5-trimethyl-2,9-dioxo-1-silabicyclo[3.3.1]non-3-ene (**3**): bp 36–37° (0.5

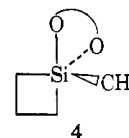


Torr); ir (CCl₄) 1657, 1586, 1050 cm⁻¹; nmr (CCl₄) τ 9.78 (s, 3 H) 8.79 (d, 3 H, $J = 0.95$ Hz) 8.23 (s, 3 H) 4.80 (q, 1 H, $J = 0.95$ Hz). At 100° the half-life for rearrangement is ~3 min. In marked contrast to this result, thermal ring opening reactions of silacyclobutanes normally require 1–3 hr reaction times at temperatures $\geq 150^\circ$ and afford polymers of the type

(8) G. D. Homer and L. Sommer, *J. Amer. Chem. Soc.*, **95**, 7700 (1973).

$[-(\text{CH}_2)_3\text{-SiR}_2-]_n$.⁹ If the usual ionic mechanism for ring opening⁹ operated for **2a**, then the *seqtrans* configuration **2b** should also react at a comparable rate to provide **3** or polymeric products. However, **2b** reacts much more slowly ($t_{1/2} \approx 1$ hr) than **2a**, presumably *via* its isomerization¹⁰ to **2a** and subsequent rearrangement to **3**. As in the 1,5-silyl migration, therefore, the silacyclobutane ring opening must be facilitated by internal nucleophilic attack by the initially uncoordinated carbonyl oxygen atom.

The degenerate silyl group migration and ring opening processes may be viewed as concerted reactions in which either the Si–O or Si–CH₂ bond is opened as the new Si–O bond is being formed. Alternatively, both processes may proceed through a common trigonal bipyramidal^{11,12} intermediate in which the carbon and diketone rings span axial-equatorial positions (**4**).



This structure would lead to release of angle strain at silicon (the CSiC angle in silacyclobutanes is $80 \pm 2^\circ$ ¹³) and lower ΔG^\ddagger for silyl group migration relative to the unstrained acyclic Si(CH₃)₃ derivative. Also, rupture of the Si–CH₂ bond in the rearrangement **2a** → **3** would be facilitated by the CH₂ group leaving from an axial position. If an intermediate is formed in the silyl group migration, it is likely that the leaving oxygen departs from the same position assumed by the entering oxygen atom (axial) *via* pseudorotation about the equatorial CH₃ group.

(9) N. S. Nametkin and V. M. Vdovin, *J. Polym. Sci., Part A-2*, 1043 (1964).

(10) The half-life for rotation about the C—C bond in the trimethylsilyl derivative of triacetyl methane is estimated to be 2.6 min at 100°. An analogous process for **2b** → **2a** should be appreciably slower because of the higher C—C bond order.

(11) Although only a few pentacoordinated silicon structures are known,¹² the coordination geometry in each case is trigonal bipyramidal.

(12) H. Burger, *Angew. Chem., Int. Ed. Engl.*, **12**, 474 (1973).

(13) L. V. Vilkov, V. S. Mastryukov, Y. V. Baurova, V. M. Vdovin, and P. L. Grinberg, *Dokl. Chem.*, **177**, 1146 (1967).

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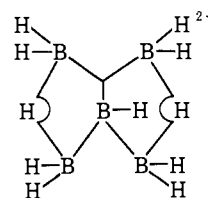
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Static Structure of the Fluxional Molecule

$\text{B}_5\text{H}_9[\text{P}(\text{CH}_3)_3]_2$, an Isoelectronic Analog of $\text{B}_5\text{H}_{11}^{2-}$

Sir:

Bis ligand adducts of pentaborane(9), $\text{B}_5\text{H}_9\text{L}_2$, are analogs of the hypothetical anion $\text{B}_5\text{H}_{11}^{2-}$, the predicted pyramidal valence structure¹ of which can be represented by the resonance form



(1) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963, p 221.