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) diastereo-

2a   2b
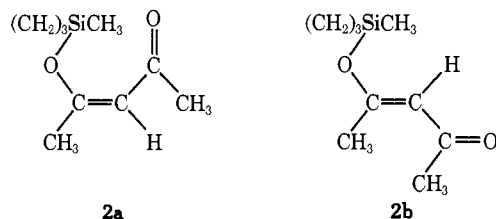
mers of 1-acetylacetonato-1-methyl-1-silacyclobutane: bp 54–55° (0.5 Torr); ir (CCl₄) 1677, 1662, 1622, 1589, and 1044 cm⁻¹; nmr (CCl₄) 2a τ 9.63 (s, 3 H) 8.08 (s, 6 H) 4.82 (s, 1 H), 2b τ 9.58 (s, 3 H) 7.99 (d, 3 H, $J < 0.5$ Hz) 7.75 (d, 3 H, $J < 0.5$ Hz) 4.70 (m, 1 H). The seqtrans configuration 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 Sommer[8] 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-dioxa-1-silabicyclo[3.3.1]non-3-ene (3): bp 36–37° (0.5


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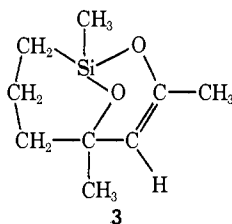
Torr); ir (CCl₄) 1657, 1586, 1050 cm⁻¹; nmr (CCl₄) τ 9.78 (s, 3 H) 8.79 (d, 3 H, $J = 0.95$ Hz) 8.23 (s, 3 H) 4.80 (q, 1 H, $J = 0.95$ Hz). At 100° the half-life for rearrangement is ∼3 min. In marked contrast to this result, thermal ring opening reactions of silacyclobutanes normally require 1–3 hr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

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

[−(CH₂)₃–SiR₂–]ₙ.[9] If the usual ionic mechanism for ring opening[9] 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 ($t_{1/2} \simeq 1$ hr) than 2a, presumably via its isomerization[10] 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 diketonate rings span axial–equatorial positions (4).

4
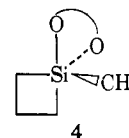
This structure would lead to release of angle strain at silicon (the CSiC angle in silacyclobutanes is 80 ± 2°[13]) and lower $\Delta G^\ddagger$ for silyl group migration relative to the unstrained acyclic Si(CH₃)₃ derivative. Also, rupture of the Si–CH₂ bond in the rearrangement 2a → 3 would be facilitated 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 triacetylmethane is estimated to be 2.6 min at 100°.[7a] 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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Static Structure of the Fluxional Molecule B₅H₉[P(CH₃)₃]₂, an Isoelectronic Analog of B₅H₁₁²⁻

Sir:

Bis ligand adducts of pentaborane(9), B₅H₉L₂, are analogs of the hypothetical anion B₅H₁₁²⁻, the predicted pyramidal valence structure[1] of which can be represented by the resonance form
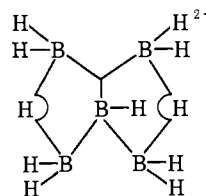
(1) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963, p 221.
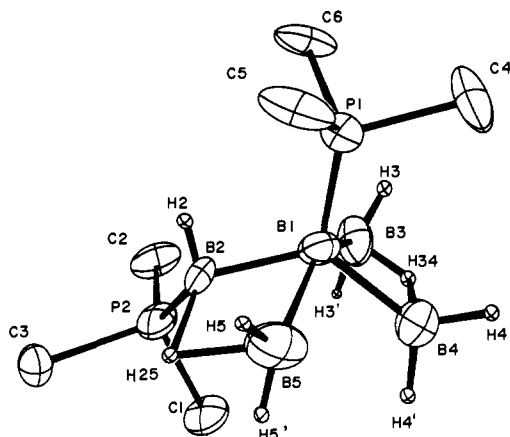
Figure 1. Structure of $B_5H_9[P(CH_3)_3]_2$ showing thermal motion ellipsoids.

Figure 2. Boron-11 nmr spectrum of $B_5H_9[P(CH_3)_3]_2$ at 70.6 MHz in CH_2Cl_2 (δ $BF_3O(C_2H_5)_2$ = 0).

A recent study[2] of $B_5H_9[N(CH_3)_3]_2$ and $B_5H_9[P(CH_3)_3]_2$ proposed pyramidal structures with ligands added cis or trans to each other on basal boron atoms.

Boron-11 and proton nmr from this laboratory support the suggested[2] arrangement of ligands proposed for $B_5H_9[N(CH_3)_3]_2$ and are therefore not discussed here.

On the other hand the X-ray structure determination of $B_5H_9[P(CH_3)_3]_2$, Figure 1, is unambiguous with respect to showing $P(CH_3)_3$ coordination at the apex and a basal site. The structure is a shallow pyramid (C_1 point symmetry) with basal borons distorted from a square arrangement. This structure is a member of a class of boron hydride derivatives which do not belong to any of the presently recognized categories: closo, nido, and arachno.[3-7]

Disorder in the crystal is manifested in the form of a pseudomirror plane which contains P(1), P(2), B(1), B(4), and C(1). Reflection through this mirror plane forms the enantiomer of the structure in Figure 1. We interpret this disorder to arise from the crystallization of $B_5H_9[P(CH_3)_3]_2$ as a racemic mixture with enantiomers cocrystallizing in the same crystals.

Temperature dependent pmr spectra in CH_2Cl_2 indicate that $B_5H_9[P(CH_3)_3]_2$ is fluxional in solution.[8] At ambient temperature the ^{11}B decoupled spectrum consists of two methyl resonances [each split into a doublet by spin coupling with ^{31}P (τ 8.74 ppm, J_{P-H} = 12 Hz, 8.89, J_{P-H} = 10 Hz, τ_{TMS} 10.00 ppm)] and a single resonance at τ 9.49 ppm.[8] With decreasing temperature the single resonance separates into two peaks. One peak, assigned to the terminal hydrogens,[9] moves to a

position under the methyl resonances while the other peak, assigned to the bridge hydrogens,[9] moves to a position of τ 12.54 ppm at $-79°$.

The ^{11}B nmr spectrum at 70.6 MHz and 16° (Figure 2) consists of three single basal resonances (1:2:1) with no apparent $^1H-^{11}B$ or $^{31}P-^{11}B$ spin coupling. This is the expected averaged spectrum which could arise from a fluxional system which allows ready interconversion of enantiomorphs, perhaps through twisting of BH_2 groups to put a terminal H in a bridging position while a bridging H moves to a terminal position.
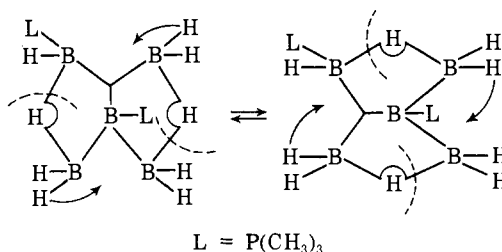
L = $P(CH_3)_3$

Crystals of $B_5H_9[P(CH_3)_3]_2$ are orthorhombic: a = 12.824 (11), b = 10.804 (8), c = 11.075 (8) Å. Systematic absences define the space group as P_{nma} or P_{na2_1}. Assuming Z = 4, D_{calcd} = 0.932 g/cm^3 in agreement with values for other B_5H_9 derivatives.[10,11] Diffraction intensities (1210 independent reflections) favored P_{nma}, but solution of the structure was unsuccessful in this space group. The structure was solved in P_{na2_1} using a combination of heavy-atom and tangent formula recycling methods. In the final refined structure the pseudomirror plane containing P(1), P(2), B(1), B(4), and C(1) is canted some 3° with respect to the ab plane. This accounts for the unsuccessful solution of the structure in P_{nma}. Atoms on the pseudomirror plane were assigned unit weight occupancies while disordered nonhydrogen atoms refined as half-weight occupancies in full-matrix least-squares refinements. Hydrogen atoms were located from a difference Fourier. Final least-squares refinements with anisotropic temperature factors for heavy atoms and isotropic temperature factors for hydrogen atoms gave an unweighted R of 0.066. Distances P(1)–B(1) and P(2)–B(2) are 1.90 (1) and 1.98 (1) Å compared to

(2) C. G. Savory and M. G. H. Wallbridge, J. Chem., Soc. A, 179 (1973).

(3) Employing the electron counting scheme of Wade[4] and Rudolph[5] which is based upon earlier considerations of Williams[6] and Lipscomb,[7] $B_5H_9[P(CH_3)_3]_2$ is the first structure determined for a boron hydride derivative which contains $2n$ + 8 "framework electrons." According to Wade[4] and Rudolph[5] closo (B_nH_{n+2}), nido (B_nH_{n+4}), and arachno (B_nH_{n+6}) boranes contain $2n$ + 2, $2n$ + 4, and $2n$ + 6 "framework electrons" when the external B–H electrons are included in the count. Thus the "framework electron" count for each class of boranes is contained in its general formula.

(4) K. Wade, J. Chem. Soc. D, 792 (1971).

(5) R. W. Rudolph and W. R. Pretzer, Inorg. Chem., 11, 1974 (1972).

(6) R. E. Williams, Inorg. Chem., 10, 210 (1971).

(7) Reference 1, Chapter 2.

(8) Although there is no apparent $^{11}B-^1H$ spin coupling in the pmr spectrum, irradiation (white noise) in the ^{11}B resonance frequency range sharpens proton resonances.

(9) G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969, p 406.
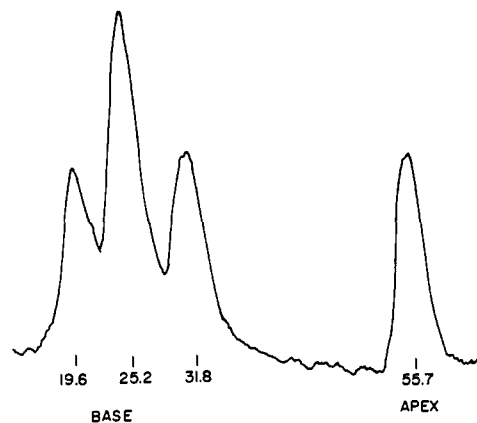
(10) L. B. Friedman and W. N. Lipscomb, Inorg. Chem., 5, 1752 (1966).

(11) J. C. Calabrese and L. F. Dahl, J. Amer. Chem. Soc., 93, 6042 (1971).

1.901 (7) and 1.906 (6) Å in $(CH_3)_3PBH_3$[12] and (CH_3)-PH_2BH_3.[12] For the B_5H_9 moiety, distances generally compare well with boron hydrides.[1] The largest non-bonded distance of adjacent borons B(2)–B(3) averages 2.95 Å compared to 2.97 Å in B_5H_{11}.[12]

(12) P. S. Bryan and R. L. Kuczkowski, *Inorg. Chem.*, 11, 553 (1972).
(13) L. R. Lavine and W. N. Lipscomb, *J. Chem. Phys.*, 22, 614 (1954).

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The Octant Rule. III.[1] An Experimental Proof for Front Octants[2]

Sir:

Although the octant rule[3,4] associated with the n–π* transition of saturated alkyl ketones was formulated over 15 years ago,[5] only the back octants have been verified experimentally. For this reason, among others, the octant rule has been challenged, and arguments supporting a "quadrant rule" have been offered.[6,7] In a "quadrant rule," as in the octant rule, all space is divided into quadrants determined by the orthogonal symmetry planes (local symmetry) of the carbonyl chromophore. In the octant rule, however, all space is further divided into octants by a third nonsymmetry derived surface approximated by a plane which is orthogonal to the two quadrant forming planes and bisects the carbon–oxygen double bond.[8] In the octant rule, the signed contribution to the Cotton effect (CE) of each dissymmetric perturber of carbonyl chromophore is determined by the octant in which it is located.[3,4] The octants reverse sign with each reflection across the octant-producing surfaces.[9] Therefore, if the octant rule is obeyed, perturbers located in front octants would give signed contributions *opposite* to those expected if a "quadrant rule" obtains.

Although there is good theoretical evidence supporting the octant rule[10,11] the experimental evidence on which it rests is drawn from numerous examples wherein the inherently symmetric[4] carbonyl chromophore is perturbed in a nonsymmetric way by atoms located *behind* the carbon of the carbonyl group (*back octants*), e.g., 3(e)-methylcyclohexanone.[12] There are extremely few examples in which dissymmetric perturbers are located in front of the carbonyl carbon or oxygen, and even these examples also have back octant perturbers. Such cases where front octant perturbers were recognized include 1-oxo, 7-oxo and 11-oxo steroids as well as 1-decalones.[13,14] Even more recent examples of front octant compounds[14-16] have back as well as front octant perturbers, although in one case[16] an effort was made to subtract the contribution of the back octant perturbers. In the present work we offer conclusive evidence for front octants from an analysis of the CD behavior of syn-(1'S)-spiro[cyclobutan-2-one-1,4'-(2'(a)-methyladamantane)] (1) in the region of its long wavelength n–π* transition. The lone dissymmetric perturber in 1 is a methyl group located in a front octant.

The synthesis of 1 was accomplished from optically active (1S)-2(a)-methyladamantan-4-one of known absolute configuration[17] using the Trost spiro-annelation procedures.[18] Steric control by its axial methyl group, coupled with two different spiro-annelation sequences, allowed us to prepare either 1 or its *anti* isomer, 2. Thus, the stereospecific reaction of (1S)-2(a)-methyl-adamantan-4-one with diphenylcyclopropylsulfonium fluoroborate and potassium hydroxide in dimethyl sulfoxide followed by workup with fluoroboric acid gave 99% pure 1 in 29% yield and recovery of 55% of starting ketone. The isomeric spiro ketone 2 was isolated from a mixture of 1 and mainly 2 produced by reaction of the cyclopropylidene derivative of (1S)-2(a)-methyladamantan-4-one with m-chloroperbenzoic acid. The configurations (syn or anti) of 1 and 2 were determined by the selection of the synthetic procedure and could be distinguished further by nmr spectroscopy in which the deshielded axial methyl group of 1 (d, centered at δ 1.11 ppm) is found farther downfield than that of 2 (d, centered at δ 1.07 ppm) and exhibits a greater downfield shift with added $Eu(dpm)_3$.

An octant projection diagram of 1 places the lone dissymmetric perturber (CH_3) in a lower right or upper left $(-)$ *front* octant, and, indeed, 1 exhibits a strong $(-)$ CE. Even the slight distortion from planarity in

(1) For Part II, see D. A. Lightner and D. E. Jackman, *J. Amer. Chem. Soc.*, 96, 1938 (1974).
(2) We gratefully acknowledge financial assistance from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant No. GP-35696A).
(3) W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *J. Amer. Chem. Soc.*, 83 4013 (1961).
(4) For leading references, see C. W. Deutsche, D. A. Lightner, R. W. Woody, and A. Moscowitz, *Annu. Rev. Phys. Chem.*, 20, 407 (1966).
(5) W. Moffitt and A. Moscowitz, Abstracts of Papers, 133rd Meeting of the American Chemical Society, April 1958.
(6) J. A. Schellman and P. Oriel, *J. Chem. Phys.*, 37, 2114 (1962); J. A. Schellman, *ibid.*, 44, 55 (1966). See also J. A. Schellman, *Accounts Chem. Res.*, 1, 144 (1968).
(7) G. Wagnière, *J. Amer. Chem. Soc.*, 88, 3937 (1966).
(8) The shape of this third surface is not well understood (ref 3). Its precise contour and location should be defined for each different type of perturber.
(9) The (+) back octants or quadrants are upper left and lower right; the (−) are upper right and lower left. The sign convention is reversed for front octants, all viewed from oxygen toward carbon.

(10) A. Moscowitz, *Advan. Chem. Phys.*, 4, 67 (1962).
(11) T. D. Bouman and A. Moscowitz, *J. Chem. Phys.*, 48, 3115 (1968).
(12) K. M. Wellman, E. Bunnenberg, and C. Djerassi, *J. Amer. Chem. Soc.*, 85, 1870 (1963).
(13) C. Djerassi and W. Klyne, *J. Chem. Soc.*, 2390 (1963).
(14) W. Klyne and D. N. Kirk in "Fundamental Aspects and Recent Developments in Optical Rotatory Dispersion and Circular Dichroism," P. Salvadori and F. Ciardelli, Ed., Heyden & Son, New York, N. Y., 1973, Chapter 3, pp 101–102.
(15) D. A. Lightner and G. D. Christiansen, *Tetrahedron Lett.*, 883 (1972).
(16) D. N. Kirk, W. Klyne, and W. P. Mose, *Tetrahedron Lett.*, 1315 (1972).
(17) G. Snatzke and G. Eckhardt, *Tetrahedron*, 25, 2601 (1969).
(18) B. M. Trost and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, 95, 5321 (1973).