to include $K_a^{RNH_3^+}$, which is exalted upon micellization.[5,14] Moreover, $[NO_2^-]$ will be abnormally high near the micelles. Both effects enhance k_{obsd}, which approaches 0.7 (chloride) and 0.6 min^{-1} (perchlorate) as F_m approaches 1.0. Because the catalysis is electrostatic in origin and depends on the cationic character of the micelles, only a minor dependence on counterion identity is observed.

The stereochemistry of 2-octanol formation depends on partition of 2-Oct—N=N—OH between nitrogen loss with (a) return of OH (retention), (b) displacement by water (inversion), and (c) escape to hydrated 2-octyl cations (racemization).[15] In water, or in highly aqueous Stern layers of alkylammonium micelles which are relatively *weakly* associated[16] with their counterions (*e.g.*, bromide, chloride, and nitrite, which have high hydration energies[17]), the partition's resultant is ~24% net inversion. But counterions which are poorly hydrated[17] and therefore *strongly* bound to the micelles[16,18] (perchlorate, fluoroborate, and *p*-tosylate) engender larger, more effectively charge-neutralized, and (probably) denser, less hydrated micelles.[16] In such "less aqueous" environments, partition process a is enhanced relative to b and c; the resultant moves toward retention.[19]

The new stereochemical salt effects differ intriguingly from the more commonly observed competitive inhibition by foreign ions of micelle-catalyzed reactions, which typically involves the exclusion, by counterion A, of reactant counterion B from the micelle which solubilizes the substrate.[20] In the present work, it seems very likely that the micelles themselves have been altered through strong binding of certain counterions, which, though not incorporated into product, modify product formation occurring within the Stern layers of which they are a part. Similar mechanisms may underlie recently observed phenomena in the micelle-catalyzed decarboxylation of the 6-nitrobenzisoxazole-3-carboxylate ion.[21]

We are continuing our studies of these and related reactions, searching for new and more stereospecific examples of micellar control of reaction stereochemistry.

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[14] M. T. Behme and E. H. Cordes, *J. Amer. Chem. Soc.*, **87**, 260 (1965), report an analogous effect.

[15] For analyses of this partition under basic conditions, see ref 8, and R. A. Moss, A. W. Fritz, and E. M. Emery, *J. Org. Chem.*, **36**, 3881 (1971).

[16] E. W. Anacker and H. M. Ghose, *J. Phys. Chem.*, **67**, 1713 (1963); R. D. Geer, E. H. Eylar, and E. W. Anacker, *ibid.*, **75**, 369 (1971); E. W. Anacker and R. D. Geer, *J. Colloid Interface Sci.*, **35**, 441 (1971), and references cited therein.

[17] H. F. Halliwell and S. C. Nyburg, *Trans. Faraday Soc.*, **59**, 1126 (1963); *J. Chem. Soc.*, 4603 (1960); S. Subramanian and H. F. Fisher, *J. Phys. Chem.*, **76**, 84 (1972).

[18] K. J. Mysels, "Study of the Properties of Micelles," Final Report to the Office of Naval Research, Project NR 356-254, Nov 1961, pp 13–14.

[19] Discussions of medium effects on deamination stereochemistry appear in E. H. White and D. J. Woodcock in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, New York, N. Y., 1968, p 440ff, and R. A. Moss, *Chem. Eng. News*, **49** (48), 28 (November 22, 1971).

[20] Examples include: R. B. Dunlap and E. H. Cordes, *J. Amer. Chem. Soc.*, **90**, 4395 (1968); L. R. Romstead and E. H. Cordes, *ibid.*, **90**, 4404 (1968); C. A. Bunton and L. Robinson, *J. Org. Chem.*, **34**, 773, 780 (1969). Other examples are cited in ref 1.

[21] C. A. Bunton, M. Minch, and L. Sepulveda, *J. Phys. Chem.*, **75**, 2708 (1971).

[22] Alfred P. Sloan Foundation Fellow; National Institutes of Health Special Postdoctoral Fellow.

[23] Johnson and Johnson Fellow.

Synthesis and Rearrangement of μ,μ'-$SiH_2(C_2B_4H_7)_2$, a Bis(carboranyl)silane Linked by a Silicon Atom Common to Two Three-Center Boron–Silicon–Boron Bonds

Sir:

The preparation and chemistry of heteroatom-bridged small carboranes of the type μ-$MR_3C_2B_4H_7$, in which M is silicon,[1] germanium,[1] tin,[2] or lead,[2] and R is hydrogen or an alkyl group, have been of recent interest in our laboratory. In each case the M atom occupies a bridging position on the edge of a pentagonal pyramidal $C_2B_4H_7$ cage, formally replacing one of the two bridge hydrogens in parent $C_2B_4H_8$.[3] The bridging heteroatom is considered to utilize approximately sp^3 tetrahedral orbitals, three of which are involved in bonding to the R ligands while the remaining orbital combines with orbitals from the adjacent borons to form a three-center two-electron B–M–B bond.[4]

Extension of this structural principle to a bis(μ-carboranyl)silane, in which two of the sp^3 orbitals on silicon participate in separate three-center bridge bonds, seemed possible in theory, although no such borane or carborane species has been described. We now report the synthesis of μ,μ'-silylenebis(2,3-dicarba-*nido*-hexaboranyl) (I) from the reaction of dichlorosilane with sodium dicarbahexaborate(1−) in tetrahydrofuran at 0°.

$$SiH_2Cl_2 + 2Na^+C_2B_4H_7^- \longrightarrow \mu,\mu'\text{-}SiH_2(C_2B_4H_7)_2 + 2NaCl$$

Compound I is obtained in 70% yield as a viscous, colorless liquid of low volatility. The mass spectrum exhibits a cutoff at *m/e* 181 corresponding to the $^{29}Si^{12}C_4{}^{11}B_8{}^1H_{16}^+$ parent ion, and the profile in the parent region is consistent with the indicated composition. The significant infrared bands are at 3020 (w) (C–H), 2590 (s) and 2530 (s) (B–H), and 2150 cm^{-1} (s) (Si–H). The 32.1-MHz ^{11}B nmr spectrum (Figure 1a) contains four doublets of equal area corresponding to four pairs of magnetically equivalent B–H groups, thus establishing that no B–Si terminal bonds are present. The doublet assigned to B(6,6′)–H is further split due to the adjacent bridge proton; in contrast, B(5,5′) is more directly affected by silicon than is B(6,6′) and fails to

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[1] M. L. Thompson and R. N. Grimes, *Inorg. Chem.*, in press; also presented in part at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, Abstract INOR-6.

[2] A. Tabereaux and R. N. Grimes, manuscript in preparation.

[3] Closely related derivatives of C,C′-$(CH_3)_2C_2B_4H_6$ containing bridging trimethylsilyl and trimethylgermyl groups have also been reported: C. H. Savory and M. G. H. Wallbridge, *Chem. Commun.*, 622 (1971).

[4] Direct crystallographic evidence for the existence of three-center B–Si–B bonds in the related species μ-$(CH_3)_3SiB_5H_8$ has been obtained in an X-ray diffraction study of the 1-bromo derivative: J. C. Calabrese and L. F. Dahl, *J. Amer. Chem. Soc.*, **93**, 6042 (1971).

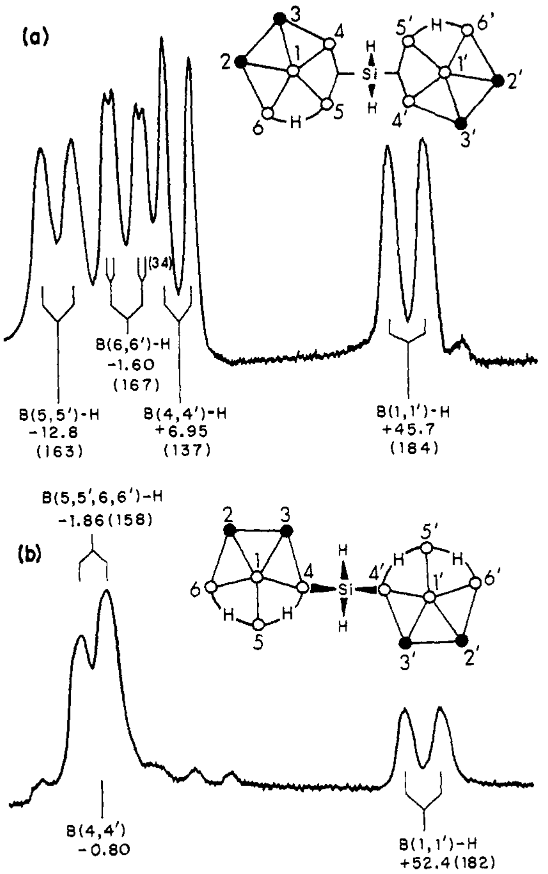

Figure 1. (a) 32.1-MHz ^{11}B nmr spectrum of μ,μ'-$SiH_2(C_2B_4H_7)_2$ in CS_2 solution. Chemical shifts are relative to $BF_3 \cdot O(C_2H_5)_2$ and coupling constants are given in parentheses. The small peak to high field of the B(1,1')-H doublet is due to traces of 4,4'-$H_2Si(C_2B_4H_7)_2$ in the sample. (b) 32.1-MHz ^{11}B nmr spectrum of 4,4'-$SiH_2(C_2B_4H_7)_2$ in CS_2 solution.

exhibit B-H bridge coupling. The unusual sharpness of the remaining low-field doublet, assigned to B(4,4'), is attributed to the "isolation" of this boron between silicon and carbon, with consequent reduction in boron-boron quadrupolar broadening.

The ^{11}B nmr spectrum is consistent with either of the two possible isomeric structures (Figure 2), since in both A and B each boron atom in one cage is magnetically equivalent to its counterpart in the other.[5] However, the silylene protons are equivalent only in isomer A, suggesting that the proton nmr spectrum of A should contain a single SiH_2 peak while that of B should exhibit two such resonances.[7] The actual spectrum (Figure 3) is clearly more consistent with structure A, although a small peak and shoulder near the large Si-H singlet suggests the presence of B as a minor component. The interesting stereochemical implications of the preferential formation of one isomer are currently under study.

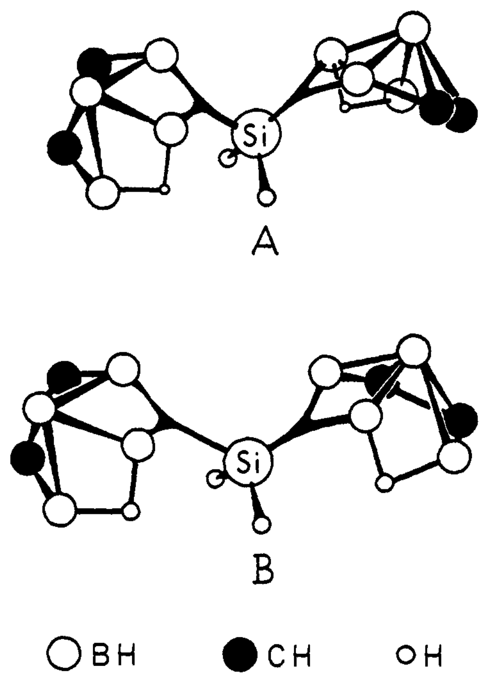

Figure 2. Proposed structures of the two possible geometric isomers of μ,μ'-$SiH_2(C_2B_4H_7)_2$. Rotation of the carboranyl groups about silicon is probable; the conformations shown are those considered to have minimal cage-to-cage steric interaction.

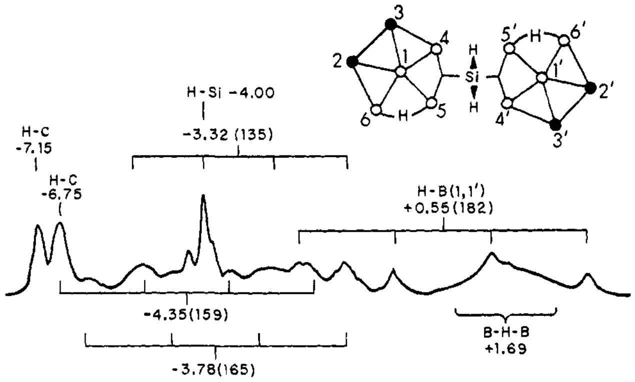

Figure 3. 100-MHz ^{1}H nmr spectrum of μ,μ'-$SiH_2(C_2B_4H_7)_2$ in CS_2 solution. Chemical shifts are relative to $(CH_3)_4Si$ and coupling constants are in parentheses.

The bridged species I undergoes quantitative isomerization at 100° in CS_2 solution to the terminally B-substituted compound 4,4'-$SiH_2(C_2B_4H_7)_2$ (II). Compound II exhibits a mass spectrum nearly identical, in the parent region, with that of I. The ^{11}B nmr spectrum (Figure 1b) is consistent with the proposed structure,[8] as is the 100-MHz proton nmr spectrum, which contains B-H quartets centered at -3.65 ppm relative to $(CH_3)_4Si$ (J = 157 Hz) and $+0.90$ (180); a broad B-H-B signal at $+2.10$; and singlet Si-H and C-H resonances at -3.60 and -6.72, respectively. As in the case of the bridged compound I, two isomers are possible for II. The structure of C_2 symmetry, depicted in Figure 1b, appears dominant on the basis of the strong Si-H singlet in the proton nmr spectrum. There are, however, indications of a small amount of the alternative C_s isomer

(5) Rotation about the B-Si-B three-center bonds is probable at room temperature in both isomers; future nmr experiments may disclose a discernible barrier to rotation at low temperatures, as has been reported for the bridging dimethylboryl group in μ-$(CH_3)_2B$-B_5H_8.[6]

(6) D. F. Gaines and T. V. Iorns, *J. Amer. Chem. Soc.*, **92**, 4571 (1970).

(7) It should be noted that if the carborane cages are effectively insulated from each other by the silicon atom, the boron and proton nmr spectra of A and B will be virtually identical except for the Si-H resonance.

(8) The spectrum is very similar to that of 4-$SiH_3C_2B_4H_7$,[1] thus further supporting the identification of II as the 4,4'-substituted isomer. However, the alternative 5,5'-substituted structure cannot be completely ruled out at this time.

which contains magnetically nonequivalent silylene protons (the structure of C_2 symmetry is logically to be expected from rearrangement of the bridged isomer A). At 150°, II undergoes further reaction yielding *closo*-$C_3B_3H_7$,[9] 4-$SiH_3C_2B_4H_7$, $C_2B_4H_8$, and solids.

Attempts to prepare the dimethylsilylene analog of I, μ,μ'-$Si(CH_3)_2(C_2B_4H_7)_2$, by reaction of $Si(CH_3)_2Cl_2$ with $NaC_2B_4H_7$ have been unsuccessful, suggesting possible inhibition by close steric interaction of the methyl groups with the carborane cages.

Acknowledgments. We are grateful to Mr. Richard Torian and Dr. Vernon Miller for assistance in obtaining the mass spectra and nmr spectra, respectively. This work was supported by the Office of Naval Research.

(9) M. L. Thompson and R. N. Grimes, *J. Amer. Chem. Soc.*, **93** 6677 (1971).

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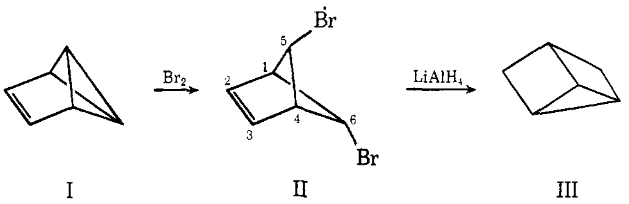
Uses of Benzvalene in Synthesis. A Synthesis of Tricyclo[2.2.0.0^{2,6}]hexane

Sir:

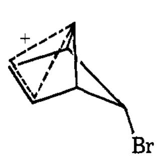
Since the valence tautomer of benzene, benzvalene (I), has become readily available,[1] we have been studying its chemistry, and we are reporting here its uses in the synthesis of other ring systems. Particularly interesting is a conversion of benzvalene in two steps, as shown in Scheme I, to tricyclo[2.2.0.0^{2,6}]hexane (III),[2]

Scheme I

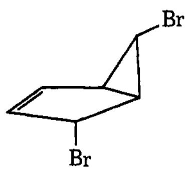


the parent of a ring system that is very simple, yet extremely rare.[2,3]

If one considers the large number of interesting products that might result after electrophilic attack on benzvalene, the observed result of bromine addition, that only a single product forms, seems remarkable,[4] especially as the isomer formed is not the thermodynamically favored one and the double bond, a usual site of electrophilic attack, is unaffected.[5] The solitary product has structure II. It is formed when 5% bromine in CCl_4 is added to solutions of benzvalene in ether at −10 to 0° until the bromine color no longer discharges.[7] The yield, determined using proton nmr spectroscopy after solvents are removed at 0° and reduced pressure, is quantitative.[8] The structure of the product is proven by its reduction[9] giving bicyclo-[2.1.1]hexane,[11] and by its proton nmr spectrum showing expectedly simple resonances[12] including two of characteristic multiplicity[13] for the protons adjacent to bromine atoms. The reason bromine adds to benzvalene as it does is possibly that initial electrophilic attack occurs from behind the central bond, where electron density is concentrated,[14,14e] to give carbonium ion IV, which like analogous species is stabilized by delocalization and reacts stereospecifically with nucleophiles.[15]



IV



V

The dibromide II is thermally unstable, carbon tetrachloride solutions rearranging to *exo,anti*-4,6-dibromobicyclo[3.1.0]hexene (V)[16] in 98% yield with a half-life of 2 hr at 37°.[17,17a] The structure of the rearrangement product is proven by its reduction[18] giving bicyclo-[3.1.0]hexene[20] and by its proton nmr spectrum showing

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(1) T. J. Katz, E. J. Wang, and N. Acton, *J. Amer. Chem. Soc.*, **93**, 3782 (1971). Yields now average 45%.

(2) D. M. Lemal and K. S. Shim, *ibid.*, **86**, 1550 (1964).

(3) (a) J. Meinwald and J. K. Crandall, *ibid.*, **88**, 1292 (1966); (b) S. Masamune and K. Fukumoto, *Tetrahedron Lett.*, 4647 (1965).

(4) The dihydro derivative, tricyclo[3.1.0.0^{4,6}]hexane [D. M. Lemal and K. S. Shim, *Tetrahedron Lett.*, 3231 (1964)], with Br_2 in CCl_4 gives complex material.

(5) Aqueous acid gives bicyclo[3.1.0]hexen-4-ol.[1,6]

(6) J. A. Berson and N. M. Hasty, Jr., *J. Amer. Chem. Soc.*, **93**, 1549 (1971).

(7) The halogens must inductively protect the olefin [*cf.* J. R. Shelton and L. Lee, *J. Org. Chem.*, **25**, 428 (1960)].

(8) The measured yield was 100.3% with nitrobenzene as internal standard.

(9) Hydrogenation (PtO_2, ethyl acetate); then $(C_6H_5)_3SnH$ to remove bromine.[10]

(10) H. G. Kuivila and L. W. Menapace, *J. Org. Chem.*, **28**, 2165 (1963).

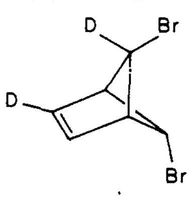
(11) The nmr spectrum is distinctive: R. Srinivasan, *J. Amer. Chem. Soc.*, **83**, 4923 (1961).

(12) In CCl_4: τ 3.22 (H_2, J = 2.0 Hz, triplet), 6.85 (H_1, $J \approx$ 2.0 Hz, quartet), 4.14 (H_6, J = 2.0 Hz, triplet), 5.37 (H_5, singlet).

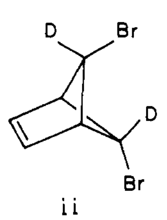
(13) J. R. Scheffer and R. A. Wostradowski, *Chem. Commun.*, 144 (1971), and references therein.

(14) (a) M. Pomerantz and E. W. Abrahamson, *J. Amer. Chem. Soc.*, **88**, 3970 (1966); (b) M. Pomerantz, G. W. Gruber, and R. M. Wilke, *ibid.*, **90**, 5040 (1968); (c) J. M. Schulman and G. J. Fisanick, *ibid.*, **92**, 6653 (1970); (d) M. D. Newton and J. M. Schulman, *ibid.*, **94**, 767 (1972).

(14e) NOTE ADDED IN PROOF. Deuterium labeling experiments show that this is only in part correct. The major pathway from I to II is initiated by attack on the double bond followed by a Wagner–Meerwein rearrangement. Benzvalene deuterated at C_5 and C_6 (*n*-BuLi–ether, D_2O, twice, 94% deuterated) gives i and ii in the ratio 87:13 [integration of the proton nmr: τ 3.22 ($H_{2,3}$, m, 1.24 H), 4.14 (H_6, t, 0.92 H), 5.37 (H_5, s, 0.065 H), 6.85 ($H_{1,4}$, t, 1.90 H)].



i



ii

(15) (a) S. Masamune, S. Takada, N. Nakatsuka, R. Vukov, and E. N. Cain, *ibid.*, **91**, 4322 (1969); (b) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, 77, 4183 (1955).

(16) Analyses for C, H, and Br were satisfactory.

(17) At least three mechanisms can be imagined. One has been suggested for analogs [ref 15a and W. R. Roth and A. Friedrich, *Tetrahedron Lett.*, 2607 (1969)].

(17a) NOTE ADDED IN PROOF. Deuterium labeling experiments show that this mechanism, in which the C_5 bridge migrates with inversion of configuration, is correct here.

(18) $LiAlH_4$ (72% yield) and then[19] Na, *tert*-butyl alcohol, and THF (68% yield).

(19) P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964).

(20) (a) J. Meinwald and P. H. Mazzocchi, *J. Amer. Chem. Soc.*, **88**, 2850 (1966); (b) G. Wittig and F. Wingler, *Chem. Ber.*, **97**, 2146 (1964).