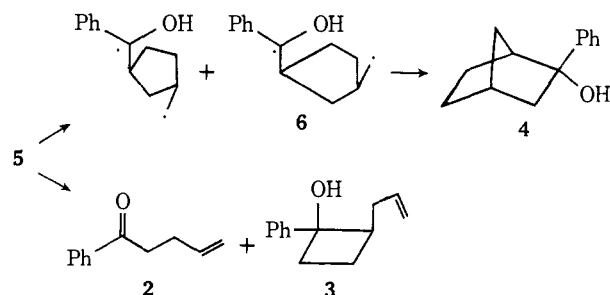


tion at 313 nm, benzene solutions of **1** yield six products as determined by gas chromatography (vpc). Five of these products were formed in comparable yields, the sixth in less than 1% yield. Three products which comprise together 78% of the products were identified as arising from the expected<sup>6</sup> intramolecular oxetane formation. Two other products were formed in sufficiently high yields to be isolated and proved to be  $\alpha$ -allylacetophenone (**2**) and 2-allyl-1-phenylcyclobutanol (**3**), the products expected<sup>2</sup> from type II photoelimination and cyclization. The sixth product was identified by its mass spectrum and vpc retention times on different columns, which all proved to be identical with those of the readily available 2-phenyl-2-norbornanol (**4**).<sup>7</sup> The relative yields of **2**:**3**:**4** were 1.4:1.0:0.1. The comparable yields of **2** and **3** are expected for  $\alpha$ -alkylated ketones.<sup>8</sup>

The competition between oxetane formation and  $\gamma$ -hydrogen abstraction will be discussed in a separate paper. We wish to focus here on the significance of the formation of **4**. The only obvious mechanism to explain its formation incorporates the hoped for internal radical cyclization, followed by coupling of the new diradical. The cyclization would be expected to proceed about equally in the *cis* and *trans* modes; only the former could couple to a stable product.

Since roughly only half of the 5-hexenyl to cyclopentylmethyl radical cyclizations in diradical **5** could yield **4**, the observed ratio of **4**/(**2** + **3**), 0.04, indicates that the 1,4-diradical cleaves or cyclizes some 12 times more rapidly than it rearranges. Any unnoticed reactions of the cyclic diradical **6** would lower the rate ratio.



Although *cis*-3-methyl-1-benzoylcyclopentane might have been produced by disproportionation of **6**, none was observed. The accepted rate for cyclization of the 5-hexenyl radical is  $10^5 \text{ sec}^{-1}$ <sup>9</sup> and is little affected by alkyl substituents.<sup>9,10</sup> On the critical assumption that each radical site in 1,4-diradicals can react independently of and unaffected by the other, we conclude that cyclization and cleavage of **5** each occur with rate constants on the order of  $6 \times 10^5 \text{ sec}^{-1}$ . Since some 60% of the diradicals formed from  $\alpha$ -methylbutyrophenone undergo disproportionation back to ground state ketone,<sup>8</sup> we estimate the rate of the analogous process in diradical **5** to be  $\sim 3 \times 10^6 \text{ sec}^{-1}$ . These rate constants for 1,4-diradical reactions are similar to

(6) N. C. Yang, M. Nussim, and D. R. Coulson, *Tetrahedron Lett.*, 1525 (1965); S. R. Kurowsky and H. Morrison, *J. Amer. Chem. Soc.*, **94**, 507 (1972).

(7) We thank Professor D. G. Farnum of MSU for an authentic sample.

(8) F. D. Lewis and T. A. Hilliard, *J. Amer. Chem. Soc.*, **92**, 6672 (1970).

(9) D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, **90**, 7047 (1968); C. Walling and A. Cioffari, *ibid.*, **94**, 6059 (1972).

(10) A. L. J. Beckwith, I. Blair, and G. Phillipou, *J. Amer. Chem. Soc.*, **96**, 1613 (1974).

those we first suggested<sup>1</sup> but are now based on much firmer grounds. O'Neal has just estimated an even longer lifetime of  $10^{-5}$  sec for the 1,4-diradical formed from 2-pentanone.<sup>11</sup>

It is important to point out that these diradicals are all triplet-derived, such that their lifetimes could be dominated by rates of spin inversion.<sup>12</sup> Whether or not this particular caveat is necessary awaits successful trapping of singlet diradicals. Meanwhile, we can conclude that spin inversion is surprisingly slow if it is rate determining in the reactions of triplet-derived 1,4-diradicals.

**Acknowledgment.** We thank the National Science Foundation for support of this work.

(11) H. E. O'Neal, R. G. Miller, and E. Gunderson, *J. Amer. Chem. Soc.*, **96**, 3351 (1974).

(12) P. D. Bartlett and N. A. Porter, *J. Amer. Chem. Soc.*, **90**, 5317 (1968).

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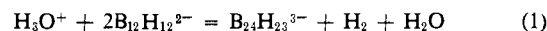
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### Coupled Products from Low-Temperature Decomposition of Hydronium Dodecahydrododecaborate(2-), $(\text{H}_3\text{O})_2\text{B}_{12}\text{H}_{12}$

Sir:

We wish to report the isolation of some rather unexpected products from two old reactions. The unusual hydrolytic stability of the  $\text{B}_{12}\text{H}_{12}^{2-}$  ion is well known, so it was not surprising that when  $(\text{H}_3\text{O})_2\text{B}_{12}\text{H}_{12}(\text{aq})$  was heated in a sealed tube, even at  $200^\circ$ , only a small amount of  $\text{B}_{12}\text{H}_{11}\text{OH}^{2-}$  was reportedly formed.<sup>1</sup> The same product is formed in somewhat higher yields when a concentrated solution of  $(\text{H}_3\text{O})_2\text{B}_{12}\text{H}_{12}$  is treated with oxalic acid.<sup>2</sup> We have found that if the same two reactions are carried out under conditions favoring dehydration, even at moderate temperatures,  $(\text{H}_3\text{O})_2\text{B}_{12}\text{H}_{12}(\text{aq})$  undergoes decomposition of the type shown below.



In addition to the two dimeric species, we have also isolated a tetramer,  $\text{B}_{48}\text{H}_{45}^{5-}$ , and, of course, the anticipated  $\text{B}_{12}\text{H}_{11}\text{OH}^{2-}$  and  $\text{B}_{12}\text{H}_{10}(\text{OH})_2^{2-}$ . The oxidative coupling is somewhat surprising in the absence of any strong oxidizing agents, considering that 1.45 V were required in the electrochemical oxidation.<sup>3</sup> This suggests that the oxidative stability of  $\text{B}_{12}\text{H}_{12}^{2-}$  may owe more to kinetic than thermodynamic factors.

The synthesis and separation of the coupled products are relatively easy due to considerable differences in the solubilities of the respective tetramethylammonium salts. A 10-g sample of  $\text{Na}_2\text{B}_{12}\text{H}_{12} \cdot 2\text{H}_2\text{O}$  was passed through an acid ion exchange column (Dowex 50W-X8), and the effluent was concentrated by rotary evaporation until a white precipitate appeared. Addition of 8 g of oxalic acid resulted in a very vigorous reaction with

(1) E. L. Muetterties, J. H. Balthis, Y. T. Chia, W. H. Knoth, and H. C. Miller, *Inorg. Chem.*, **3**, 444 (1964).

(2) W. H. Knoth, J. C. Sauer, D. C. England, W. R. Hertler, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **86**, 3973 (1964).

(3) R. J. Wiersema and R. L. Middaugh, *Inorg. Chem.*, **8**, 2074 (1969).

frothing, and after 10 min over a steam bath the slurry was treated with 10 ml of water and filtered. The precipitate which was free of boranes was discarded while the filtrate was slowly neutralized with 10% aqueous  $\text{Me}_4\text{NOH}$ . After each small aliquot of base was added, the resulting precipitate was collected and another aliquot of base added to the new filtrate. The number of solid fractions depends on the amount of  $\text{Me}_4\text{NOH}$  per aliquot. The tlc of each fraction was recorded, and those in which the same spot predominated were combined. The solubility and the  $R_f$  values both increased in the order  $[\text{Me}_4\text{N}]_3\text{B}_{48}\text{H}_{45}$  (I) <  $[\text{Me}_4\text{N}]_3\text{B}_{24}\text{H}_{23}$  (II) <  $[\text{Me}_4\text{N}]_3\text{B}_{24}\text{H}_{22}\text{OH}$  (III) <  $[\text{Me}_4\text{N}]_2\text{B}_{12}\text{H}_{12}$  (IV) <  $[\text{Me}_4\text{N}]_2\text{B}_{12}\text{H}_{11}\text{OH}$  (V) <  $[\text{Me}_4\text{N}]_2\text{B}_{12}\text{H}_{10}(\text{OH})_2$  (VI). The new products are described in the order that they come out of solution. They can all be recrystallized from boiling water. The yield of V was 27%, and only small amounts of IV and VI were seen; these will not be discussed as they are familiar products.<sup>2</sup>

The yield of crude I was 6.8 g (59%). Though  $R_f = 0$  on PEI-F, the salt moved on silica gel when eluted with  $\text{CH}_3\text{CN}-\text{NH}_4\text{OH}-\text{H}_2\text{O}$  (12:5:3). The  $^{11}\text{B}$  nmr of compound I consisted of a doublet at  $\delta$  31.7 ppm ( $J = 130$  Hz). The uv spectrum in  $\text{CH}_3\text{CN}$  consisted of an intense band at 2170 Å and a weak one at 2550 Å. The ir spectrum included absorptions at 3610(m), 3020(m), 2940(w), 2480(vs, B-H), 2200(s, BHB), 1600(w,  $\text{H}_2$ ), 1745(s), 1275(w), 1030(m), 1025(m), 940(s), 750(s), and 715(s). *Anal.* Calcd for  $[(\text{CH}_3)_4\text{N}]_3\text{B}_{48}\text{H}_{45} \cdot 5\text{H}_2\text{O}$ : C, 23.4; H, 11.3; N, 6.83; B, 50.6; neut equiv, 205. Found: C, 23.8; H, 11.3; N, 6.70; B, 50.2; neut equiv, 202. The neutralization curve exhibited only one sharp vertical rise indicating that the bridge protons were not titrated below pH 11.5. The Onsager plot of the conductance data for the  $\text{K}^+$  and  $\text{Cs}^+$  salts exhibited considerable curvature even at low concentrations so an exact value of the limiting equivalent conductance could not be obtained. However, even the lowest extrapolation yielded a molar conductance well in excess of the value expected for a 4:1 electrolyte.<sup>3,4</sup> The low tlc  $R_f$  value and the curvature of the conductance curve are also consistent with a very high charge on the anion. A tetrameric unit of  $-5$  charge is the smallest that fits the analytical and conductance data.

Recrystallization of II until only one tlc spot of  $R_f = 0.12$  was seen yielded 0.50 g (4.1%) of material, the ir spectrum and the tlc characteristics of which matched perfectly those of an authentic sample of the same compound kindly provided us by Dr. R. L. Middaugh.<sup>3</sup> The  $^{11}\text{B}$  nmr consisted of a doublet,  $\delta$  33.7 ppm ( $J = 135$  Hz). *Anal.* Calcd for  $[(\text{CH}_3)_4\text{N}]_3\text{B}_{24}\text{H}_{23} \cdot 2\text{H}_2\text{O}$ : C, 26.4; H, 11.7; N, 7.77; B, 47.9. Found: C, 26.4; H, 11.5; N, 7.73; B, 47.8.

After recrystallization from water the yield of III,  $R_f = 0.17$ , was 0.20 g (1.6%). The  $^{11}\text{B}$  nmr consisted of a singlet at  $\delta$  13.97 (area 1) and an unsymmetrical doublet at  $\delta$  33.76 (area 23,  $J = 130$  Hz) with a shoulder at 44.17 ppm. The position of the singlet and the area ratio indicate that it represents the unique oxygen substituted boron.<sup>2</sup> The ir spectrum contained bands at 3620 (m), 3020 (m), 2480 (vs, BH), 2250 (m, BHB), 1600 (w,  $\text{H}_2\text{O}$ ), 1480 (s), 1170 (m, BO), 1080 (m), 1040 (s), 1015 (s), 940 (s), 740 (sh), 715 (m), and 705 (m).

(4) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold, New York, N. Y., 1958, p 236.

*Anal.* Calcd for  $[(\text{CH}_3)_4\text{N}]_3\text{B}_{24}\text{H}_{22}\text{OH} \cdot \text{H}_2\text{O}$ : C, 26.7; H, 11.4; N, 7.80; B, 48.1. Found: C, 27.1; H, 11.4; N, 7.56; B, 45.3.

Oxalic acid is helpful, but not essential in this reaction. Thus when a solution of  $(\text{H}_3\text{O})_2\text{B}_{12}\text{H}_{12}$  is subjected to rotary evaporation over a steam bath until a precipitate forms, the slurry converted to a clear solution with water, and then treated with  $\text{Me}_4\text{NOH}$ , the same products are obtained but in lower yields, since a greater fraction of  $\text{B}_{12}\text{H}_{12}^{2-}$  remains undecomposed.

Unless indicated otherwise the eluent used in our tlc work consisted of saturated  $\text{NH}_4\text{PF}_6$ ,  $\text{CH}_3\text{OH}$ , and  $\text{H}_2\text{O}$  (17:2:1). The  $^{11}\text{B}$  nmr were recorded in  $\text{CH}_3\text{CN}-\text{D}_2\text{O}$  solutions with a Varian XL-100-15 spectrometer, and the peaks are given in  $\delta$  parts per million relative to trimethyl borate.

Work is currently in progress on the effects of reaction conditions on the relative yields of the reported products. We have some evidence that the "tetramer" can be decomposed to other species, but the precise nature of the decomposition products is still uncertain. We are interested in finding out whether the tetramer disproportionates to form smaller and larger units, since the "polymerization" of  $\text{B}_{12}\text{H}_{12}^{2-}$  has been reported in the patent literature.<sup>5</sup> No individual components of these "polymeric" mixtures were identified, and the nature of bonding between the polyhedral units was not specified except that "boron-boron bonds" are involved; also the formulas shown do not exclude the possibility of B-O-B bridges either.

(5) U. S. Patent No. 3,350,324 (*Chem. Abstr.*, 68, 3484 (1968)); U. S. Patent No. 3,368,878 (*Chem. Abstr.*, 68, 105747 (1968)).

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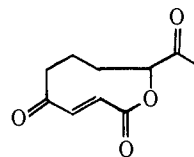
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### A Revised Structure of Vermiculine. A Novel Macrolide Dilactone Antibiotic from *Penicillium vermiculatum*

Sir:

Vermiculine is a highly crystalline antibiotic substance isolated from *Penicillium vermiculatum* Dangeard.<sup>1</sup> The unusual medium ring lactone structure (1) was



assigned on the basis of uv, ir, nmr, and mass spectral data.<sup>2</sup>

We had occasion to examine the chemistry of vermiculine as a prelude to an attempt at total synthesis.<sup>3</sup> Treatment of vermiculine with hot pyridine (80°) for 3-4 hr produced no reaction. However, treatment with aqueous methanolic sodium carbonate produced ester

(1) J. Fuska, P. Nemeč, and I. Kuhr, *J. Antibiot.*, Ser. A, 25, 208 (1972).

(2) P. Sedmera, J. Vokoun, M. Podojil, Z. Vanek, J. Fuska, P. Nemeč, and I. Kuhr, *Tetrahedron Lett.*, 1347 (1973).

(3) We are indebted to Dr. Jan Fuska and his associates for a most generous gift of vermiculine.