

IV, R = COOC₂H₅, was not stereospecific. The all-*trans* isomer of the diol IV, R = CH₂OH, was obtained in pure condition (as a colorless oil) *via* the crystalline 3,5-dinitrobenzoate derivative, m.p. 136–137°. The pure diol IV, R = CH₂OH, and the 4:1 mixture of stereoisomeric diols were transformed into 1,12-dibromo-3,10-dimethyldodeca-2,6,10-triene (IV, R = CH₂Br) by reaction with phosphorus tribromide and pyridine in ethereal solution at –15°; the two products had essentially identical infrared and n.m.r. spectra. Slow addition of the dibromide IV, R = CH₂Br, to a stirred solution of nickel carbonyl (excess) in 1,2-dimethoxyethane at 78° followed by continued heating for 12 hr., removal of solvent under reduced pressure, partitioning between ether and water, and distillation of the product from the organic layer at 100° bath temperature (6 mm.) gave 63–68% yield of II as a colorless oil, appearing homogeneous in vapor phase chromatography using fluorosilicone, tris(β-cyanoethoxy)propane, and diethylene glycol succinate columns. The product showed a parent peak in the mass spectrum at *m/e* = 190 and absorbed 3.16 molar equivalents of hydrogen based on molecular weight 190 using prerduced platinum oxide catalyst in acetic acid. Ozonolysis⁷ of the triene followed by reduction of the total mixture with sodium borohydride and acetylation gave a liquid product which was shown by v.p.c. and spectral analysis to be a 16:7.5 mixture of pentane-1,4-diol diacetate and butane-1,4-diol diacetate (91% of the theoretical yield). These facts clearly establish that the product from the reaction of dibromide IV, R = CH₂Br, with nickel carbonyl must be 1,6-dimethylcyclododeca-1,5,9-triene.

Analysis of the triene so produced by thin layer chromatography (on silica gel–silver nitrate) and n.m.r. analysis indicated that the material was, in fact, a mixture of two isomers in a ratio of *ca.* 2:1. The same mixture was obtained starting from the pure all-*trans* diol IV, R = CH₂OH, or the 4:1 mixture described above. Although it is clear that one or both of the last two steps in the synthesis of the cyclic triene may be nonstereospecific, we are inclined to believe that most of the isomerization occurs at the last stage. Further work is in progress on this point. The major isomer, which can be separated from the mixture by column chromatography using 10% silver nitrate on silica gel, is probably the all-*trans* structure II; the n.m.r. spectrum shows two sharp methyl peaks (6H) at 1.39 and 1.42 δ,⁸ a peak at 1.9 δ (12H), and broad olefinic proton absorption at 4.3–4.9 δ (4H). The minor isomer, presumably the *cis*, *trans*, *trans* form of II, shows methyl absorption at 1.58 p.p.m., closer to a normal value for C=C–CH₃.

Further work on the reactions of nickel carbonyl with dihalides and related substances is in progress with the object of investigating the scope and mechanism of this process and applying the ring closure to the synthesis of natural products.⁹

(7) Procedure of A. J. Hubert, *J. Chem. Soc.*, 4055 (1963).

(8) See ref. 6 and also E. J. Corey and A. G. Hortmann, *J. Am. Chem. Soc.*, 85, 4033 (1963), for analogous cases.

(9) This work was partially supported by the National Science Foundation (Grant GP-1955).

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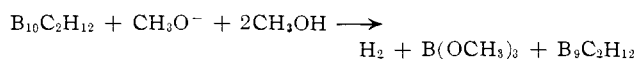
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RECEIVED FEBRUARY 4, 1964

Dicarbaundecaborane(13) and Derivatives

Sir:

Carborane [1,2-dicarbaundecaborane(12)] and its derivatives, prepared from the reaction of B₁₀H₁₂-(ligand)₂ compounds and acetylenes,^{1,2} have been selectively degraded by methanolic potassium hydroxide at 40°. The degradation reaction is described by the equation



One mole each of hydrogen and boric ester were produced and 1 equiv. of base was consumed per mole of carborane employed. The B₉C₂H₁₂ anion was precipitated as its tetramethylammonium salt I (98% yield) upon the addition of aqueous tetramethylammonium chloride. *Anal.* Calcd. for B₉C₂H₂₄N: B, 46.90; C, 34.70; H, 11.65; N, 6.74. Found: B, 46.90; C, 35.61; H, 12.30; N, 6.60. The corresponding salts were prepared from C-methyl- and C-phenylcarboranes. The infrared spectra of the B₉C₂H₁₂ anion exhibited a sharp C–H stretching band at 3.35 μ and B–H stretching centered at 4.0 μ. No absorptions which could be attributed to B–H–B bridge stretching were observed.

Acidification of a diethyl ether slurry of I with anhydrous hydrogen chloride followed by sublimation (40°) of the product retained in the ethereal solvent produced dicarbaundecaborane(13) (II) in 89% yield. Elemental analysis of B₉C₂H₁₃ was thwarted by its low stability and hydroscopic nature, m.p. 110° dec. However, II was titrated as a monoprotic acid (equiv. wt. 137; theory 134) with an apparent pK_A of 2.95 in 33% (volume) methanol–water. A cryoscopic molecular weight of 147 was observed in benzene solution. The infrared spectrum of II displayed a C–H stretching band at 3.30 μ and a B–H stretching band at 3.85 μ. A weak absorption at 5.10 μ could be reasonably attributed to a B–H–B bridge absorption although the H¹ n.m.r. spectrum of II did not reveal clean evidence for such an interaction.

The degradation reaction was examined kinetically with hydroxide ion in 50% volume aqueous ethanol at 75° and with C-phenylcarborane as the substrate. Hydrogen evolution was employed to monitor the reaction. The reaction was first order in both hydroxide ion and C-phenylcarborane with a second-order rate constant of 1.48 ± 0.03 × 10⁻⁴ l. mole⁻¹ sec.⁻¹. The similar reaction of C-phenylcarborane labeled in the 8, 9, 10, and 12 positions² with deuterium produced an identical rate constant and 97% pure hydrogen was evolved. These results clearly indicate that the 8, 9, 10,

(1) C. C. Clark, U. S. Patent 3,062,756 (Nov. 6, 1962); T. L. Heying, J. W. Ager, Jr., S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *Inorg. Chem.*, 2, 1089 (1963); H. Schroeder, T. L. Heying, and J. R. Reiner, *ibid.*, 2, 1092 (1963); T. L. Heying, J. W. Ager, Jr., S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *ibid.*, 2, 1097 (1963); S. Papetti and T. L. Heying, *ibid.*, 2, 1105 (1963); R. P. Alexander and H. Schroeder, *ibid.*, 2, 1107 (1963); M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, *ibid.*, 2, 1111 (1963); M. M. Fein, D. Grafstein, J. E. Paustian, J. Bobinski, B. M. Lichstein, N. Mayes, N. N. Schwartz, and M. S. Cohen, *ibid.*, 2, 1115 (1963); D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. S. Cohen, and M. M. Fein, *ibid.*, 2, 1120 (1963); D. Grafstein, J. Bobinski, J. Dvorak, J. E. Paustian, H. F. Smith, S. Karlan, C. Vogel, and M. M. Fein, *ibid.*, 2, 1125 (1963); D. Grafstein and J. Dvorak, *ibid.*, 2, 1128 (1963).

(2) Carborane(12) is reasonably assumed to have an icosahedral structure with two near-neighbor carbon atoms placed at positions 1 and 2. The numbering system employed was adopted by the Nomenclature Committee of the Inorganic Division of the American Chemical Society. See R. Adams, *Inorg. Chem.*, 2, 1087 (1963).

and 12 positions of the carborane icosahedron are not involved in the degradation reaction.

The evidence outlined above suggests that $B_9C_2H_{12}^-$ and $B_9C_2H_{13}$ are icosahedral fragments isoelectronic with the hypothetical $B_{11}H_{12}^{-3}$ and the known³ $B_{11}H_{13}^{-2}$ ions. The removal of a boron atom from the 4, 5, 7, or 11 positions² or from the 3 or 6 positions² is indicated by the kinetic results and hydrogen analysis data. The fact that position isomers are not observed with C-monosubstituted carboranes suggests that the boron atom in position 3 or 6 is removed. This would place the two carbon atoms as near neighbors in the pentagonal face of the assumed icosahedral fragment.

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(3) V. D. Aftandilian, H. C. Miller, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, **1**, 734 (1962).

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The Preparation of 1-[1,2-Dicarbaclovododecaboranyl(12)]- 1,2-dicarbaclovododecaborane(12)

Sir:

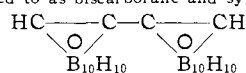
The recent reports of the preparation of icosahedral 1,2-dicarbaclovododecaborane(12) and its derivatives^{1,2} prompt us to report the preparation of 1-[1,2-dicarbaclovododecaboranyl(12)]-1,2-dicarbaclovododecaborane(12)³ and its precursor, 1-ethynyl-1,2-dicarbaclovododecaborane(12).

Treatment of an acetonitrile solution of $B_{10}H_{12}(CH_3CN)_2$ with diacetylene⁴ at the reflux temperature for a period of 5 hr. produced C-ethynylcarborane, 35%, m.p. 75–78° (*Anal.* Calcd. for $B_{10}C_4H_{12}$: B, 64.27; C, 28.54; H, 7.20. Found: B, 62.22; C, 28.70; H, 7.70), and biscarborane(12), 4%, m.p. 309–310° (*Anal.* Calcd. for $B_{20}C_4H_{22}$: B, 74.45; C, 16.53; H, 9.02. Found: B, 75.30; C, 17.50; H, 8.20). Improved yields (ca. 60%) of biscarborane were obtained from C-ethynylcarborane and $B_{10}H_{12}(CH_3CN)_2$

(1) C. C. Clark, U. S. Patent 3,062,756 (Nov. 6, 1962); T. L. Heying, J. W. Ager, Jr., S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *Inorg. Chem.*, **2**, 1089 (1963); H. Schroeder, T. L. Heying, and J. R. Reiner, *ibid.*, **2**, 1092 (1963); T. L. Heying, J. W. Ager, Jr., S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *ibid.*, **2**, 1097 (1963); S. Papetti and T. L. Heying, *ibid.*, **2**, 1105 (1963); R. P. Alexander and H. Schroeder, *ibid.*, **2**, 1107 (1963); M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, *ibid.*, **2**, 1111 (1963); M. M. Fein, D. Grafstein, J. E. Paustian, J. Bobinski, B. M. Lichstein, N. Mayes, N. N. Schwartz, and M. S. Cohen, *ibid.*, **2**, 1115 (1963); D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. S. Cohen, and M. M. Fein, *ibid.*, **2**, 1120 (1963); D. Grafstein, J. Bobinski, J. Dvorak, J. E. Paustian, H. F. Smith, S. Karlan, C. Vogel, and M. M. Fein, *ibid.*, **2**, 1125 (1963); D. Grafstein and J. Dvorak, *ibid.*, **2**, 1128 (1963).

(2) The nomenclature employed here was recently adopted by the Nomenclature Committee of the Inorganic Division of the American Chemical Society. See R. Adams, *Inorg. Chem.*, **2**, 1087 (1963).

(3) Hereafter referred to as biscarborane and symbolically described by



(4) J. B. Armitage, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 44 (1951).

in acetonitrile at the reflux temperature for 16 hr.

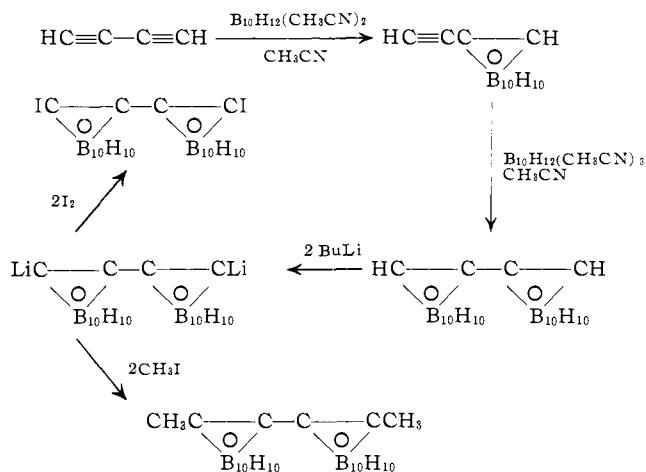
The infrared spectrum of C-ethynylcarborane contained sharp C–H stretching bands at 3.08 and 3.32 μ and a carbon–carbon triple bond stretching band at 4.70 μ . The 3.08 μ C–H band is attributed to the acetylenic C–H.

Treatment of biscarborane with 2 equiv. of butyllithium in diethyl ether solution followed by 2 equiv. of methyl iodide afforded C,C'-dimethylbiscarborane, 90%, m.p. 193–194°. *Anal.* Calcd. for $B_{20}C_6H_{26}$: B, 68.77; C, 22.90; H, 8.33. Found: B, 67.45; C, 22.81; H, 8.83. This alkylation reaction undoubtedly involves the dianion of biscarborane since similar treatment of carborane produces a nucleophilic dianion.¹

When the biscarborane dianion was treated with 2 molecular equivalents of iodine, C,C'-diiodobiscarborane was obtained in low yield, m.p. 183–184°. *Anal.* Calcd. for $B_{20}C_4H_{20}I_2$: B, 40.19; C, 8.92; H, 3.74; I, 47.14. Found: B, 39.70; C, 9.13; H, 3.96; I, 46.36.

These results constitute the first report of a species which is composed of two singly linked icosahedra. The $B_{24}H_{22}^{-2}$ ion, isoelectronic with biscarborane but linked through boron atoms, has not been reported although a $B_{20}H_{15}^{-4}$ probably composed of two singly linked B_{10} polyhedra has been described.⁵

The preparation and reactions of biscarborane(12) are summarized below.



Acknowledgment.—The authors are indebted to Mr. R. Donald Strahm for the analytical data. This research was supported by Contract No. DA-01-021 ORD-5135 with the U. S. Army Ordnance Corps.

(5) M. F. Hawthorne, R. L. Pilling, P. F. Stokely, and P. M. Garrett, *J. Am. Chem. Soc.*, **85**, 3704 (1963).

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Continuity of Bond Force Constants between Normal Molecules and Lennard-Jones Pairs

Sir:

There are a number of striking empirical correlations between bond lengths, force constants, and bond dissociation energies. One of the earliest and most widely