Organic and Biological Chemistry

Benzocarborane. High Stability but Little Aromatic Character

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Abstract: Benzocarborane consists formally of a benzene ring and an *o*-carborane cage which share an edge in common. It was synthesized starting from dilithiocarborane and *cis*-1,4-dichloro-2-butene, which gave dihydrobenzocarborane. Allylic bromination with *N*-bromosuccinimide followed by dehydrobromination in refluxing dimethylformamide yielded benzocarborane. The formally benzenoid ring appears to retain a small amount of aromatic character, shown by the proton nmr chemical shift (δ 6.37), in spite of the long carbon–carbon bond along the shared edge (~1.65 Å) and the weakness of π bonding between the carborane cage and external groups. Benzocarborane survives a few minutes exposure to concentrated sulfuric acid at 150°. The 1,4-addition of bromine to the dienoid group proceeds slowly and is reversible on heating.

Benzocarborane[2] (**1**) consists formally of two different delocalized-bond systems, a benzene ring, and an icosahedral *o*-carborane cage, fused along a common edge (Figure 1). The orbitals of the icosahedron may be factored in such a way that the two cage carbon atoms have p orbitals oriented properly to complete the π system of the benzenoid ring.[3,4] However, the multicenter bonding in the icosahedron places the highest density electron inside the cage,[3] and interaction of the surface p orbitals with organic substituents has proved very small in previous investigations.[5,6] The $B_{10}H_{10}^{2-}$ system with its more exposed apical boron atoms does exhibit π conjugation of 1,10-substituents through the borane cage.[7] The question which most interested us was whether the stability of the benzenoid π-bond system would be sufficient to overcome the resistance of the *o*-carborane toward external conjugation and result in measurable aromatic character in the carbocyclic ring.

In a preliminary communication we suggested that the nmr and ultraviolet spectra and the high stability of benzocarborane are consistent with considerable aromatic character.[8] More complete investigation has indicated that the degree of aromatic character is slight, though probably real, and the properties of benzocarborane are to a first approximation those expected of a diene made unusually inert by the electron-withdrawing character, large bulk, and extreme rigidity of the adjacent carborane cage.

Synthesis. The wrong approach, which we naturally tried first, is to imitate the customary carborane cage synthesis[9] and generate benzyne in the presence of the decaborane–acetonitrile complex, $B_{10}H_{12}(CH_3CN)_2$. A fundamental difficulty is the probable need to generate simultaneously two highly reactive intermediates, $B_{10}H_{12}(CH_3CN)$[10] as well as benzyne, and to achieve their mutual second-order reaction in competition with side reactions with more abundant species. Another problem is that benzyne precursors, including the relatively mild diazotized anthranilic acid,[11] appear to attack the decaborane in preference to generating benzyne.

The successful synthesis starts from 1,2-dilithio-*o*-carborane[12] and 1,4-dichloro-*cis*-2-butene,[13] which yield 1,4-dihydrobenzocarborane (**2**). Allylic bromination of **2** with *N*-bromosuccinimide yields 2-bromo-1,2-dihydrobenzocarborane (**3**) together with a lesser amount of 1-bromo-1,4-dihydrobenzocarborane (**4**). The nmr data supporting these structures are discussed in the next paragraph. Dehydrobromination of **3** and **4** to benzocarborane (**1**) is best accomplished by brief refluxing in dimethylformamide.

The major allylic bromination product (**3**) could be crystallized from the mixture. The CH_2CHBr group showed a typical ABX splitting pattern with $J_{AX} = 9$ and $J_{BX} = 7$ Hz, with the doublet of one of the CH_2 protons centered near δ 3.03, the other at 3.14, and the CHBr multiplet, a triplet with fine structure, at δ 4.68. Coupling of the CHBr proton to the adjacent CH=CH protons is only 1–2 Hz. The lesser isomer (**4**) could not be isolated but was detected in the product mixture by nmr. As in 1,4-dihydrobenzocarborane (**2**), the coupling between the CH=CH and CH_2 or CHBr groups is small.

In our preliminary report,[8] we had failed to detect the allylic bromides **3** and **4** and had incorrectly supposed

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[1] (a) Supported by U. S. Public Health Service Research Grant No. CA-05513 from the National Cancer Institute; (b) Alfred P. Sloan Foundation Research Fellow, 1966–1968.

[2] Systematic name: 1,2-benzo-1,2-dicarba-*closo*-dodecaborane.

[3] H. C. Longuet-Higgins and M. de V. Roberts, *Proc. Roy. Soc., Ser. Chem.*, 230, 110 (1955).

[4] R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, 36, 2179 (1962).

[5] M. F. Hawthorne, T. E. Berry, and P. A. Wegner, *J. Amer. Chem. Soc.*, 87, 4746 (1965).

[6] K. M. Harmon, A. B. Harmon, and B. C. Thompson, *ibid.*, **89**, 5309 (1967).

[7] W. H. Knoth, *ibid.*, **88**, 935 (1966).

[8] N. K. Hota and D. S. Matteson, *ibid.*, **90**, 3570 (1968).

[9] M. F. Hawthorne, T. D. Andrews, P. M. Garrett, F. P. Olsen, M. Reintjes, F. N. Tebbe, L. F. Warren, P. A. Wegner, and D. C. Young, *Inorg. Syn.*, 10, 91 (1967).

[10] M. F. Hawthorne, R. L. Pilling, and R. N. Grimes, *J. Amer. Chem. Soc.*, **89**, 1067 (1967).

[11] M. Stiles, R. G. Miller, and U. Burckhardt, *ibid.*, 85, 1792 (1963).

[12] T. L. Heying, J. W. Ager, Jr., S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *Inorg. Chem.*, **2**, 1097 (1963).

[13] R. Huisgen and E. Laschturka, *Chem. Ber.*, **93**, 65 (1960).

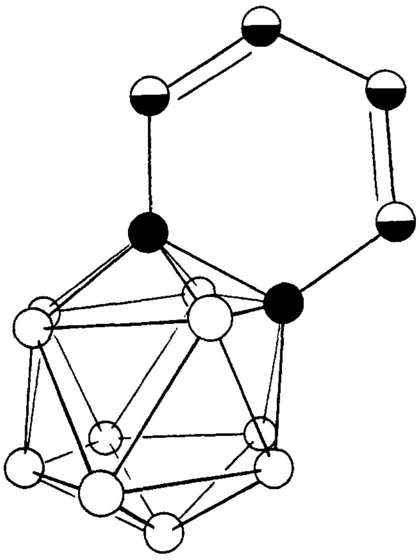
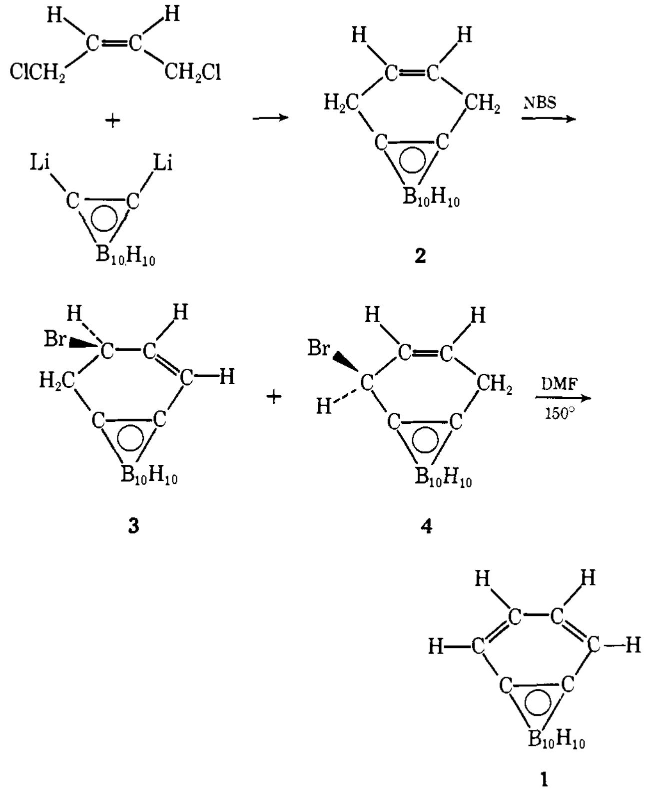


Figure 1. Benzocarborane (**1**): ○, BH; ⊖, CH; ●, C.

that the dehydrobromination to benzocarborane might be spontaneous. However, subsequent to our initial success the yields of benzocarborane became erratic and generally low. The crude products of bromination of **2** generally do contain small amounts of benzocarborane, detectable by nmr. The erratic results suggest possible catalysis or suppression of dehydrobromination by trace impurities, perhaps involving water or hydrogen bromide. It also seemed possible that the chromatography on alumina might have caused dehydrobromination, but attempted chromatography of samples of the crude allylic bromides **3** and **4** of known composition resulted in firm retention of the material on the alumina, apparently with decomposition. The bromides likewise decomposed on silica gel without yielding benzocarborane.



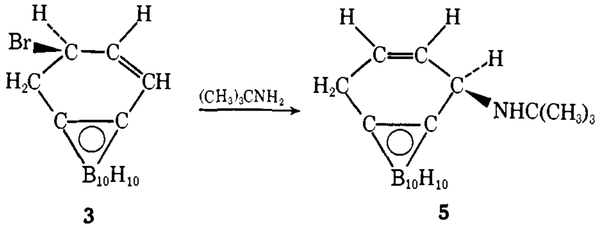
2

3

4

1

Abstraction of hydrogen bromide from **3** with base proved unexpectedly difficult. *tert*-Butylamine was chosen as a convenient sterically hindered base which could not possibly displace bromide by an S_N2 mechanism. The S_N2' process is evidently much less subject to steric hindrance, and pure **3** was converted efficiently by *tert*-butylamine to 1-(*tert*-butylamino)-1,4-dihydrobenzocarborane (**5**). The nmr spectrum of **5** showed the small splittings characteristic of 1,4-dihydrobenzocarboranes.



3

5

Sodium hydride in tetrahydrofuran converted the crude mixture of **3** and **4** to a mixture of benzocarborane and dihydrobenzocarborane. The latter might have arisen from an S_N2' displacement of bromide by hydride.

Acid proved to be a better dehydrobromination catalyst. Heating crude **3** and **4** with concentrated sulfuric acid at $\sim$150° for 5–30 min yielded 20–40% benzocarborane.

Refluxing dimethylformamide dehydrobrominated pure **3** in 86% yield or the crude mixture of **3** and **4** in about 70% yield. However, benzocarborane derived from the crude **3** and **4** contained about 5% dihydrobenzocarborane which had resisted separation from the bromo compounds by distillation and could not be removed from the benzocarborane even by chromatography. Although recrystallization of **3** would remove the impurity from this precursor, half the material was lost in this process and a more efficient route to pure benzocarborane was sought.

The addition and subsequent elimination of bromine provided the desired purification and also illustrated the behavior of benzocarborane toward electrophilic reagents. It takes more than 1 hr for benzocarborane to decolorize bromine in carbon tetrachloride under the usual test conditions, and we were misled at first into believing that no reaction occurs.[7] However, the bromine color fades in a few minutes in methylene chloride. This solvent effect implies a polar mechanism. Dihydrobenzocarborane, even though it is a simple olefin, does not react at all with bromine under these conditions. Recrystallization of the benzocarborane–bromine adduct removes any dihydrobenzocarborane impurity.

Benzocarborane dibromide consists of the two diastereoisomers **6** and **7** of 1,4-dibromo-1,4-dihydrobenzocarborane, formed in approximately equal amounts. The less soluble isomer, which can be separated only inefficiently by crystallization, shows two single peaks in the nmr at δ 4.80 and 6.01. The other isomer shows two doublets at δ 5.16 and 5.93, J = 2.7 Hz. The symmetry and simplicity of these spectra require that both isomers be 1,4-dibromides, but in the absence of detailed knowledge of the conformation of the six-mem-

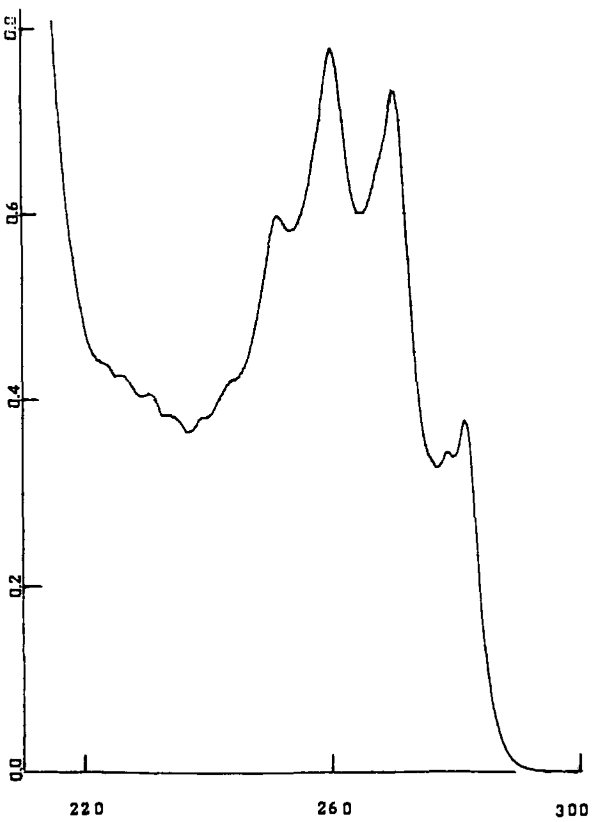
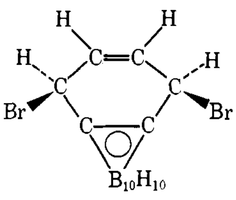


Figure 2. The ultraviolet spectrum of benzocarborane, 2.62 × 10^{-4} *M* in 2,2,4-trimethylpentane, recorded on a Cary Model 15.

bered ring there is no unequivocal basis for deciding which isomer is which.



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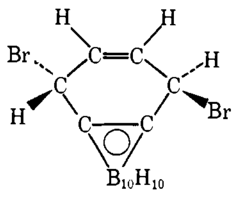

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The bromine addition is reversible. If the mixture of **6** and **7** is heated above its melting point, bromine is evolved and benzocarborane is formed, but considerable amounts of both **6** and **7** persist in the mixture. Complete debromination can be achieved with sodium iodide in acetone. In this case the isomer having the two singlets in the nmr at δ 4.8 and 6.0 reacts at once, but the other isomer requires several hours for complete reaction.

The Question of Aromaticity. Several properties of benzocarborane give a superficial and misleading appearance of aromaticity. Any compound which can survive several minutes of contact with concentrated sulfuric acid at 150° is no ordinary diene. The very slow reactions with bromine in carbon tetrachloride and with potassium permanganate in acetone are orders of magnitude remote from typical olefinic behavior. However, vinylcarboranes and allylcarboranes (including dihydrobenzocarborane) are similarly inert toward sulfuric acid or bromine.[14]

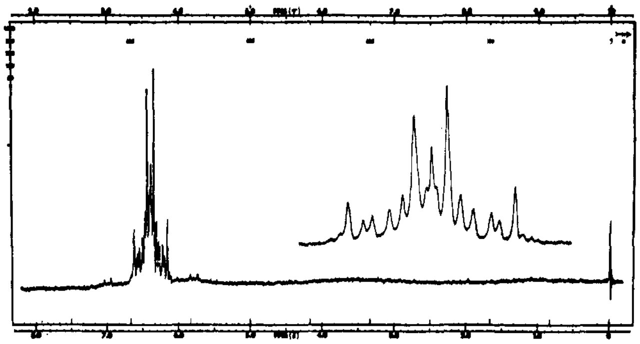

Figure 3. The 60-MHz nmr spectrum of benzocarborane in carbon tetrachloride, sweep widths 500 and 100 Hz.

The ultraviolet spectrum of benzocarborane (Figure 2) shows the vibrational fine structure typical of benzenoid hydrocarbons. The strongest peak, λ_{max} 260 nm (ϵ_{max} 2950), shows a slight bathochromic shift and a considerably higher intensity in comparison with benzene, λ_{max} 255 (ϵ_{max} 230).[15] Nothing could look more aromatic than that, until comparison is made with cyclohexadiene, λ_{max} ~258 (ϵ_{max} ~7000).[16] Cyclohexadiene has enough conformational flexibility to obscure the vibrational fine structure, but sterically rigid dienes show fine structure patterns similar to that of benzocarborane.[16]

The lack of reactivity of benzocarborane, though consistent with aromaticity, is probably mainly the result of the large steric bulk, extreme rigidity, and strong electron-withdrawing influence of the carborane group. The addition of bromine is not typical of aromatic systems, but addition–elimination sequences have been observed in bromination of hindered substituted benzenes in acetic acid.[17] The reversibility of the addition of bromine to benzocarborane implies low electron density on the carbon atoms and perhaps steric advantage in the planar free diene. Bromine was eliminated in preference to hydrogen bromide even when benzocarborane dibromide (**6** and **7**) was heated in dimethylformamide. The bromobenzocarborane obtained in earlier experiments[8] as a by-product in the synthesis of benzocarborane probably arose from a different allylic dibromide isomer formed in the free radical bromination of dihydrobenzocarborane.

Several attempts were made to nitrate benzocarborane in methylene chloride with a separate phase of nitric and sulfuric acids, either fuming or merely concentrated in various combinations more than sufficient to nitrate phenylcarborane.[5] In general, most of the benzocarborane was recovered and the nmr spectrum clearly indicated the absence of any nitration product, and much but not all of the dihydrobenzocarborane present as an impurity was destroyed. Prolonged exposure to fuming sulfuric acid at 25° degraded benzocarborane to unknown water-soluble material.

Good evidence that benzocarborane does have a little aromatic character is provided by the proton nmr spectrum (Figure 3). The chemical shift discrepancy attributed to ring current is only δ 0.2–0.3. The center

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(14) M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, *Inorg. Chem.*, **2**, 1111 (1963); D. Grafstein, J. Bobinsky, J. Dvorak, H. Smith, N. Schwartz, M. S. Cohen, and M. M. Fein, *ibid.*, **2**, 1120 (1963).

(15) A. E. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy," Edward Arnold Publishers, Ltd., London, 1954, p 120.

(16) E. Merkel, *Z. Elektrochem.*, **63**, 373 (1959). We thank Dr. J. N. Francis for pointing out this reference.

(17) P. C. Myhre, G. S. Owen, and L. L. James, *J. Amer. Chem. Soc.*, **90**, 2115 (1968).

of the multiplet in benzocarborane, δ 6.37, may be compared with that of cyclopentenocarborane, δ 6.10,[18] or 2-bromo-1,2-dihydrobenzocarborane (3), δ 6.05.

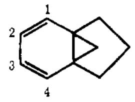
Quadrupole broadening by boron is apparent in the 1,4-proton signal, the downfield half of the A_2B_2 multiplet. The BH protons appear as an extremely broad quartet, δ ~2.2, $J_{BH} \cong 112$ Hz, partially visible as a waviness in the base line in Figure 3. The line width conceals their nonequivalence.

Cooper and Manatt have analyzed the 100-MHz spectrum of benzocarborane.[19] Their results are summarized in Table I, together with data on other dienes and aromatic compounds for comparison.[20,21] Cooper has pointed out the similarity of the coupling constant patterns of benzocarborane and the homoaromatic tricyclo[4.3.1.0]decadiene **8**.

Table I. Chemical Shifts and Coupling Constants

Compound[a]	δ_1	δ_2	J_{12}	J_{13}	J_{14}	J_{23}
Benzocarborane (**1**)	6.48	6.27	9.96	0.78	1.35	6.32
Tricyclodecadiene **8**	6.07	5.71	9.25	0.58	1.31	5.94
Cyclohexadiene	5.68	5.83	9.64	1.02	1.12	5.04
Biphenylene	6.66	6.55	6.89	0.82	1.00	8.23
Benzene	7.37		7.56	1.38	0.68	7.56

[a] Diene protons numbered as illustrated for structure **8**.



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The larger value for J_{12} than for J_{23} in benzocarborane indicates that the 1,2-bond is decidedly shorter than the 2,3-bond.[20] The difference between J_{12} and J_{23} in benzocarborane (3.64 Hz) is smaller than in cyclohexadiene (4.60), about the same as in the tricyclodecadiene **8** (3.31), and larger than in the distorted aromatic biphenylene (1.34). The larger average of these two coupling constants in benzocarborane (8.14) than in benzene (7.56) or cyclohexadiene (7.34) implies that the hydrogen atoms are forced closer together by the steric environment.[22] This is expected, since the carbon–carbon bond in carborane cage is unusually long, 1.65 ± 0.02 Å,[23] and consequently forces the hydrogen atoms closer together around the opposite side of the carbocyclic ring.

We have recently synthesized naphthocarborane, but it disappointingly failed to yield any conclusive evidence for or against some degree of aromatic character in the benzenoid ring fused to the carborane cage.[24]

Theoretical treatments of the icosahedral system[3,4] are qualitatively consistent with the experimentally observed low degree of aromatic character in the benzenoid ring of benzocarborane. Some π bonding between the cage and the ring is inevitable, since the cage atomic orbitals can be factored so that one set of p orbitals lies along the surface of the cage parallel to the π orbitals of the ring, but several factors limit ring–cage π bonding. The electron population of a cage boron p orbital is only about two-thirds. The figure for carborane carbon is higher but significantly below unity.[25] Thus, the benzenoid π orbitals of benzocarborane contain more than 5.3 electrons but less than the magic number 6. The energy levels of the cage molecular orbitals are probably much lower than those of the ring (as indicated by uv spectra) and the cage carbon atoms have a relatively high effective electronegativity. Both factors work against cage to ring electron donation, or even electron exchange. The extreme length of the carbon–carbon bond in the cage reduces the π exchange integral of that bond, thus raising the energy of those ring π orbitals which are bonding in that region and between atoms 2 and 3, but lowering the energy of the orbital which has an antibonding node across the 2,3-bond and the cage bond. Thus, the observed small ring current and grossly unequal 1,2- and 2,3-bond lengths are actually consistent with a reasonably large ring–cage π orbital overlap, which because of orbital symmetries and energies leads to only slight aromatic properties.

Experimental Section

Dihydrobenzocarborane (2). A solution of 14.4 g (0.1 mol) of *o*-carborane in 35 ml of ether was added dropwise under nitrogen to 0.2 mol of phenyllithium or butyllithium (commercial hexane solution) in 100 ml of ether, then stirred 2 hr at 25° and heated to reflux. The reflux was maintained spontaneously during the addition of 13.1 g of 1,4-dichloro-*cis*-2-butene[26] over a period of 1 hr. The solution was treated with a few milliliters of methanol to destroy unreacted lithium or alkyllithium, then washed with 100 ml of water and concentrated under vacuum. The residue was distilled at 80–110° (0.1 mm), yielding 13.0 g of distillate and 5.9 g of residue. The distillate was chromatographed on 100 g of alumina with cyclohexane. Dihydrobenzocarborane (2) eluted first, followed by immediately by *o*-carborane and other impurities. Recrystallization from methanol yielded 8.0 g (42%) of dihydrobenzocarborane, mp 100–110°. The analytical sample was sublimed and recrystallized from methylcyclohexane: mp 113–114°; nmr (CCl_4) δ 3.0 (broadened single peak, 4, CH_2), 5.65 (t, 2, J = 1.5 Hz, $CH{=}CH$); mass spectrum *m*/*e* up to 198, base peak 195 (theory 196), discrepancy probably due to H loss.

Anal. Calcd for $C_6H_{16}B_{10}$: C, 36.72; H, 8.17; B, 55.10. Found: C, 36.77; H, 8.18; B, 55.18.

Bromodihydrobenzocarborane (3 and 4). A solution of 12.7 g of crude dihydrobenzocarborane (2) (which had been chromatographed but still contained ~25% *o*-carborane) in 80 ml of carbon tetrachloride was stirred and refluxed with 12.7 g of *N*-bromosuccinimide, 0.20-g portions of benzoyl peroxide were added at 0 and 2.5 hr, and refluxing was continued a total of 13 hr. The succinimide was filtered and the filtrate was concentrated and distilled rapidly up to 150° (0.1 mm), yield 16.3 g. After a second simple distillation to remove the remainder of the high-boiling, darkening impurities, the material was fractionated slowly in a short spiral-wire column, allowing the *o*-carborane and part of the dihydrobenzocarborane to solidify in the distillation head and keeping the bromo compound refluxing gently at 100° (0.1 mm) in the pot. Simple distillation yielded 9.2 g of bromodihydrobenzocarborane, bp 90–110° (0.1 mm), which according to the nmr spectrum was about a 4:1 mixture of 2-bromo-1,2-dihydrobenzocarborane (3) and its 4-bromo-1,4-dihydro isomer (4), contaminated by small amounts of dihydrobenzocarborane and dibromo derivatives. This mixture was suitable for preparation of benzocarborane (95%

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(18) M. F. Hawthorne, personal communication, 1969.

(19) M. A. Cooper and S. L. Manatt, personal communication, 1969.

(20) M. A. Cooper and S. L. Manatt, *J. Amer. Chem. Soc.*, **91**, 6325 (1969); **92**, 1605 (1970).

(21) H. Günther, *Tetrahedron Lett.*, 2967 (1967); H. Günther and H.-H. Hinrichs, *Justus Liebigs Ann. Chem.*, 706, 1 (1967).

(22) M. A. Cooper and S. L. Manatt, *J. Amer. Chem. Soc.*, **92**, 4646 (1970).

(23) J. A. Potenza and W. N. Lipscomb, *Inorg. Chem.*, **3**, 1673 (1964); **5**, 1471, 1478, 1483 (1966); D. Voet and W. N. Lipscomb, *ibid.*, **3**, 1679 (1964).

(24) D. S. Matteson and R. A. Davis, *Chem. Commun.*, 699 (1970).

(25) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 3489 (1962).

(26) From the commercially available *cis*-2-butene-1,4-diol by the procedure of ref 13. Commercial "1,4-dichloro-2-butene" is trans.

grade). The predominant isomer **3** crystallized slowly after seeding by chilling to −75° and was recrystallized from cold pentane with 50% recovery. The analytical sample of **3** was further recrystallized and sublimed: mp 66–69°; nmr (CCl_4) δ 3.03 (d, 1, *J* = 9 Hz, 0.5C*H*$_2$), 3.14 (d, 1, *J* = 7, 0.5C*H*$_2$), with satellites 14 and 22 Hz each side of the center of gravity of the foregoing two doublets, δ 4.68 (subdivided t, 1, *J* = 7, 9, and ~1.4 Hz, C*H*Br), 6.04–6.06 (2 d partially resolved, 2, *J* = 1–2 Hz, weak satellites 12 Hz to each side, C*H*=C*H*); mass spectrum *m/e* 273 up to 278 (mol wt (calcd) 275 av, 278 max), base peak 195 ($C_6H_{15}{}^{11}B_8{}^{10}B_2$).

Anal. Calcd for $C_6H_{15}B_{10}Br$: C, 26.19; H, 5.49; B, 39.28; Br, 29.04. Found: C, 26.34; H, 5.96; B, 39.53; Br, 29.15.

The minor isomer **4** could not be isolated, but nmr peaks assigned include δ 3.43 (t or 2 d, *J* ≅ 2, C*H*$_2$) and 5.15 (about five, peaks ~2 Hz spacing, C*H*Br), with other peaks obscured by other components of the mixture.

1-(*tert*-Butylamino)-1,4-dihydrobenzocarborane (5). *tert*-Butylamine (1 ml) was added to a solution of 1.07 g of crystalline 2-bromo-1,2-dihydrobenzocarborane (**3**) in 5 ml of ether at 25°. Crystals of *tert*-butylamine hydrobromide separated within 30 sec and were filtered after a few minutes. The filtrate was diluted with ether and pentane and washed with dilute aqueous sodium dihydrogen phosphate, then water. The ether–pentane solution was concentrated and the residue was chromatographed on alumina with cyclohexane, then sublimed twice: yield 0.57 g; mp 60–63°; nmr (CCl_4) δ 0.90 (broadened d, 1, *J* = 8 Hz, N*H*), 1.03 (s, 9, C(C*H*$_3$)$_3$), 2.90 (m, 2, *J* ≅ 2, C*H*$_2$), 3.83 (d, 1, *J* ≅ 7, width at half-height 16 Hz, N–C*H*), 5.60 (m, 2, *J* ≅ 2, satellites 12 and 15 Hz each side, C*H*=C*H*); mass spectrum *m/e* 267 ($C_{10}H_{25}B_{10}N$), 252 (base peak, $C_9H_{22}{}^{11}B_8{}^{10}B_2N$ or $C_9H_{23}{}^{11}B_7{}^{10}B_3N$), 194 (benzocarborane), 125 (+2 charge from isotope pattern).

Anal. Calcd for $C_{10}H_{25}B_{10}N$: C, 44.91; H, 9.42; B, 40.43; N, 5.24. Found: C, 44.95; H, 9.37; B, 40.25; N, 5.16.

Benzocarborane (1) (95%, with 5% 2). A solution of 9.2 g of distilled bromodihydrobenzocarborane (mixture of **3** and **4**) in 100 ml of dimethylformamide was heated rapidly and refluxed 10 min, then cooled promptly. The solution was diluted with a few hundred milliliters of water and the benzocarborane was extracted with four 50-ml portions of pentane. The pentane solution was washed with water and concentrated to yield 5.5 g of residue, which was recrystallized from 45 ml of methanol and 6 ml of water, then sublimed: mp 111–118°; 3.96 g (61%) plus 0.5 g from mother liquor; mass spectrum *m/e* 194 ($C_6H_{14}{}^{11}B_8{}^{10}B_2$) with isotopic satellites; dihydrobenzocarborane (**2**) content 5% by nmr.

Benzocarborane Dibromide (6 and 7). A solution of 2.2 g of 95% benzocarborane and 1.85 g of bromine in 20 ml of methylene chloride was allowed to stand at 25° for 2.5 hr. (After 1 hr, nmr analysis showed no benzocarborane. Similar concentrations in carbon tetrachloride showed 50 mol % benzocarborane remaining after 1.2 hr.) Concentration under vacuum followed by crystallization from 4 ml of cyclohexane and 12 ml of pentane at −15° gave 1.6 g of benzocarborane dibromide (**6** and **7**, ~50:50 mixture, see Synthesis section for nmr data), second crop 0.9 g, 64%. The noncrystalline residue showed benzocarborane peaks in the nmr, as if some reversal of bromination had occurred. The analytical sample of the 50:50 mixture of **6** and **7** was recrystallized and survived slow vacuum sublimation at 40–50°, mp 75–90° dec (Br_2 evolution). The less soluble isomer (nmr singlets δ 4.8 and 6.0) was separated by slow crystallization from pentane, mp 125–128°.

Anal. Calcd for $C_6H_{14}B_{10}Br_2$: C, 20.35; H, 3.99; B, 30.53; Br, 45.13. Found (isomer mixture): C, 20.39; H, 4.01; B, 30.62; Br, 45.25; (less soluble isomer) C, 20.53; H, 4.21; B, 30.26; Br, 44.34.

Benzocarborane (1) from 6 and 7. A 1.2-g portion of recrystallized benzocarborane dibromide (**6** and **7**) was added to a solution of 4 g of sodium iodide in 10 ml of acetone. Immediate exothermic reaction and darkening occurred, but nmr analysis after 5 min indicated much remaining benzocarborane dibromide isomer characterized by doublets at δ 5.2 and 5.9, even though the other isomer had entirely disappeared. After 24 hr at 25°, a few milliliters of water was added and the benzocarborane was extracted into pentane and freed of iodine by repeated washing with concentrated aqueous sodium iodide. Crystallization from methanol–water followed by sublimation yielded 0.66 g of pure benzocarborane (**1**): mp 121–123° (capillary), 121.0, 121.3° (Mettler FP-1); see Figures 2 and 3 for uv and nmr spectra.

Anal. Calcd for $C_6H_{14}B_{10}$: C, 37.10; H, 7.26; B, 55.64. Found: C, 36.82; H, 7.41; B, 55.77.

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The Cyanohydridoborate Anion as a Selective Reducing Agent

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Abstract: Sodium cyanohydridoborate ($NaBH_3CN$) reduces a wide variety of organic functional groups with remarkable selectivity. The reduction of aldehydes and ketones is pH dependent, the reaction proceeding readily at pH 3–4. Oximes are smoothly reduced to alkylhydroxylamines and enamines are reduced to amines under acid catalysis. Reaction of an aldehyde or ketone with ammonia, primary amine, or secondary amine at pH ~7 in the presence of BH_3CN^- leads to primary, secondary, or tertiary amines, respectively, *via* reductive amination of the carbonyl group. Reaction of substituted pyruvic acids with ammonia and BH_3CN^- affords an excellent method for the synthesis of amino acids; ^{15}N labeling can be accomplished by using $^{15}NH_3$. The hydrogens of BH_3CN^- can be readily exchanged for either deuterium or tritium, thus permitting the synthesis of deuterium- or tritium-labeled alcohols, amines, and amino acids.

Considerable attention has been devoted to the study of modified boron hydrides as selective reducing agents for organic functional groups.[2,3] The earlier discovery of the reducing power[4] and the acid stability[5] of lithium cyanohydridoborate encour-

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