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IMPROVED SYNTHETIC ROUTES TO SMALL CARBORANES. BENCH-SCALE PREP--ETC(U)
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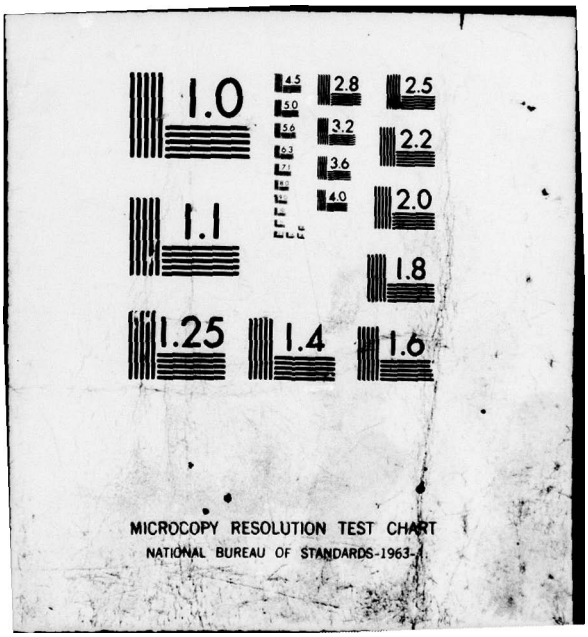
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(12) LEVEL II

OFFICE OF NAVAL RESEARCH

(15) CONTRACT NO. N00014-75-C-0305

(9) Interim TECHNICAL REPORT, NO. 31

(6) Improved Synthetic Routes to Small Carboranes. Bench-Scale Preparation of Nido-2,3-$C_2B_4H_8$ Derivatives from B_5H_9 and from $B_3H_8^-$ Salts.

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Prepared for Publication

in

Inorganic Chemistry (12) 24p.

(11) August, 1979 (14) TR-31

Approved for public release; distribution unlimited

401 147 LB

Contribution from the Department of Chemistry
University of Virginia. Charlottesville, VA
22901.

Improved Synthetic Routes to Small Carboranes. Bench-Scale Preparation of Nido-2,3-$C_2B_4H_8$ Derivatives from B_5H_9 and from $B_3H_8^-$ Salts

Narayan S. Hosmane and Russell N. Grimes*

Abstract. A method has been developed for producing the C,C'-dimethyl and C-phenyl derivatives of 2,3-$C_2B_4H_8$ in gram quantities and in yields of >50% without the use of heat, solvent, or large-volume gas bulb reactions. This approach involves formation of a $B_5H_9 \cdot L_2$ adduct (L = triethylamine or dimethylsulfide) which reacts with 2-butyne or phenylacetylene in situ, at or below room temperature, to give the corresponding $RR'C_2B_4H_6$ carborane. The carborane product is easily isolated in high purity by vacuum fractionation. The most satisfactory results are obtained with triethylamine, with B_5H_9 maintained in excess, and with simultaneous incremental addition of the amine and alkyne to the borane. The use of dimethylsulfide in place of triethylamine gives slightly higher carborane yields but results in a much slower reaction. The triethylamine method has been combined with a previously reported synthesis of B_5H_9 from $B_3H_8^-$ salts, to generate $C_2B_4H_8$ derivatives from $B_3H_8^-$ in a "one-pot" synthesis, thereby eliminating the isolation or handling of B_5H_9 and other volatile boranes. Since $B_3H_8^-$ salts are readily prepared from $NaBH_4$, this method offers a safe and relatively inexpensive route to lower carboranes.

Studies of the smaller carboranes and their metal-containing derivatives have been hampered by the absence of efficient, convenient and safe preparative routes to the lower carborane starting materials. The commonly used preparative methods for these compounds utilize reactions of alkynes with volatile boranes, usually at elevated temperatures in the gas phase;[1,2] in most cases the products are obtained as complex mixtures of carboranes and organoboranes which require gas chromatographic separation, together with solid waste materials. Since these reactions are conducted in the gas phase, considerations of safety and practicality normally restrict such preparations to a scale of a few millimoles or less. Obviously, bench-scale methods that operate under mild conditions and generate easily separable carborane products would be desirable. Especially useful would be a means of producing carboranes directly from the inexpensive bulk chemical sodium borohydride ($NaBH_4$) or from salts of $B_3H_8^-$, which are easily prepared from that compound.[3]

A small carborane of particular importance in synthetic work is nido-2,3-$C_2B_4H_8$ [dicarbahexaborane(8)]. This compound (Figure 1) and its C-substituted derivatives not only can function as versatile ligands (η^1, η^2, and η^5-coordinate) in transition metal complexes, but also serve as precursors to closo-carboranes, to tetracarbon carboranes, and to tetracarbon metallocarboranes.[1,2,4] The best available route to $C_2B_4H_8$ and its derivatives has been the method of Onak, Drake, and Dunks,[5a] in which alkyne-B_5H_9 mixtures are pyrolyzed in the gas phase. This procedure affords $R_2C_2B_4H_6$ species in varying yields (8 to 54% depending upon the alkyne employed) but owing to limitations

imposed by the gas-phase conditions, the absolute quantity of product obtained is small; typically, 1 to 3 mmol is produced in a 1-L reaction bulb. Moreover, the carborane products must be separated, usually via gas chromatography, from the complex mixtures obtained.

An alternative approach employs the alkyne-B_5H_9 reaction in the presence of weak Lewis bases, in a manner analogous to the synthesis[1,2] of 1,2-$C_2B_{10}H_{12}$ (o-carborane) from $B_{10}H_{14}$. Thus, C-substituted derivatives of $C_2B_4H_8$ have been obtained from reactions of B_5H_9, alkynes, and 2,6-dimethylpyridine,[5,6] but we have found this procedure experimentally inconvenient[7] and gas chromatographic separation of products is required, again limiting the scale of the synthesis. Accordingly, we have been exploring other reaction conditions including (1) the utilization of strong bases in the presence of B_5H_9 and alkynes, and (2) the "one-pot" synthesis of carboranes from $B_3H_8^-$ salts. We report here two routes to C-substituted $C_2B_4H_8$ derivatives which afford multigram quantities of carboranes safely and cleanly with minimal problems of separation, the second of which avoids altogether the isolation or handling of volatile boranes.

Results and Discussion

Synthesis of C-Substituted $C_2B_4H_8$ Derivatives from B_5H_9, Alkynes, and Lewis Bases. The object of this work was to develop an efficient bench-scale route to nido-$R_2C_2B_4H_6$ carboranes by utilizing the net reaction

$$B_5H_9 + RC{\equiv}CR' + L \longrightarrow RR'C_2B_4H_6 + L{\cdot}BH_3$$

where R is CH_3 or C_6H_5, R' is CH_3 or H, and L is $(C_2H_5)_3N$, $(CH_3)_2S$, or other suitable base. The process presumably involves a $B_5H_9 \cdot L_2$ adduct intermediate,[9] but these compounds were not isolated in this investigation. A variety of reaction conditions was examined, but all experiments were conducted without solvent (to facilitate the separation of products) and attemperatures no higher than 25°C. The volatile products were easily isolated by vacuum-line fractionation, and usually consisted primarily of the desired carborane, the $L \cdot BH_3$ adduct, and unreacted B_5H_9 and alkyne. In reactions involving triethylamine, it was found important to maintain an excess of alkyne and B_5H_9 over amine so that the B_5H_9– base adduct, once formed, can react immediately with alkyne; otherwise, the yield of carborane is reduced by reaction with base to generate polymer. All reactions examined generated solid polymer, and in some cases hydroboration of the alkyne occurred to a slight extent to give 2-(sec-C_4H_9)-B_5H_8. Carborane yields were improved by addition of the amine and alkyne in increments over a period of time (see Experimental Section).

In the following sections we present the conditions under which optimum production of each carborane was achieved; additional experiments are described in the Experimental Section.

2,3-$(CH_3)_2C_2B_4H_6$. The most satisfactory preparation of the dimethyl carborane involved the reaction of 50 mmol of B_5H_9 with 2-butyne and triethylamine at 0°C, with slow addition of the latter two reagents over a period of several days; this afforded 2.12 g of the carborane (20.4 mmol, 52% based on amine employed) with consumption

of 45 mmol of B_5H_9. Larger quantities of carborane (but lower percentage yields) were obtained by more rapid addition of the amine and alkyne; when all reagents were added simultaneously, 14.0 mmol (28%) of $2,3\text{-}(CH_3)_2C_2B_4H_6$ was isolated in a single run.

When dimethylsulfide was employed in place of triethylamine, the yield of carborane rose to 61%, but the reaction was extremely slow and generated only 3.7 mmol of carborane in 8 days at room temperature; two-thirds of the original pentaborane was recovered under these conditions.

$2\text{-}C_6H_5\text{-}C_2B_4H_7$. Slow incremental addition of triethylamine to a mixture of phenylacetylene and pentaborane produced 14.1 mmol (47% based on amine) of the phenylcarborane, while 31 mmol of B_5H_9 was consumed. The optimum conditions appear to be very similar to those found for the production of the dimethyl carborane, described above. It is notable that this compound is not formed in appreciable yield in the gas-phase reaction of B_5H_9 with $C_6H_5C_2H$.

$2\text{-}CH_3\text{-}C_2B_4H_7$ and $C_2B_4H_8$. Attempts to prepare the C-monomethyl derivative and the parent carborane by the foregoing procedure were complicated by the rapid polymerization of propyne-B_5H_9 and acetylene-B_5H_9 mixtures in the presence of Lewis base. Yields of the monomethyl carborane were low under all conditions examined, amounting at best to 8% (1.2 mmol) with triethylamine and 14% (1.8 mmol) with dimethylsulfide. Acetylene-B_5H_9 reactions conducted in the presence of either base gave no detectable $C_2B_4H_8$ (or other carborane) at all. Since the parent and monomethyl compounds are of lesser interest than are the C,C'-

dimethyl and C-phenyl carboranes as precursors to metallocarboranes (owing to their lower stability), we did not further pursue their preparation by this method. For these compounds, the previously described[5a] gas phase alkyne-pentaborane reaction continues to be the best available route.

Synthesis of 2,3-$(CH_3)_2C_2B_4H_6$ from $(C_2H_5)_4N^+B_3H_8^-$. Although several polyborane anions of the $B_nH_n^{2-}$ series (n = 6-12) can be prepared directly from salts of BH_4^-,[10] there are no reported syntheses of carboranes from BH_4^- or other small borane anions. In considering possible strategies for obtaining lower carboranes from BH_4^- salts, we noted that there are now efficient procedures for the conversion[3] of BH_4^- to $B_3H_8^-$ and $B_3H_8^-$ to B_5H_9.[11] It appeared feasible, therefore, to generate B_5H_9 *in situ* from $B_3H_8^-$ ion and then to combine the B_5H_9 with alkyne *in situ* in the presence of Lewis bases (vide supra) to produce $C_2B_4H_8$ derivatives. Accordingly, the following sequence has been utilized to generate carborane:

(1) $(C_2H_5)_4N^+B_3H_8^- + HCl \longrightarrow (C_2H_5)_4N^+B_3H_7Cl^- + H_2$

(2) $2(C_2H_5)_4N^+B_3H_7Cl^- \longrightarrow B_5H_9 + 2(C_2H_5)_4N^+Cl^- + 1/2B_2H_6 + H_2$

(3) $B_5H_9 + (C_2H_5)_3N + (CH_3)_2C_2 \longrightarrow (CH_3)_2C_2B_4H_6 + (C_2H_5)_3NBH_3$

Steps (1) and (2) are adapted from procedures reported previously,[11] while (3) is described above; all three reactions are conducted in the same vessel. The procedure was carried out several times on a progressively larger scale. In the largest synthesis, 25 g of

$(C_2H_5)_4N^+B_3H_8^-$ was employed to produce 1.41 g (13.6 mmol) of pure $2,3\text{-}(CH_3)_2C_2B_4H_6$, which corresponds to 20% of the theoretical yield based on triethylamine employed, or about 19% on the basis of $(C_2H_5)_4N^+B_3H_8^-$ utilized.

Experimental Section

Materials. Pentaborane(9) was taken from laboratory stock and was checked for purity (ir spectrum and vapor pressure) before each use. 2-Butyne (Chemicals Procurement Laboratories, Inc, College Point, N.Y.) was passed through traps at -23° and -78° before use. Phenylacetylene (Aldrich) was passed through a 0° trap prior to use, and propyne and acetylene (Matheson) were used as received. Triethylamine (Matheson, Coleman, and Bell) was dried over molecular sieve, distilled onto barium oxide, redistilled, and finally passed through a -23° trap in vacuo. Sodium borohydride (98%) was obtained from Metal Hydrides, Inc., and used as received.

Procedures. Except where otherwise indicated, all operations were conducted in vacuo.

$2,3\text{-}(CH_3)_2C_2B_4H_6$ from B_5H_9, $C_2(CH_3)_2$, and $(C_2H_5)_3N$. Carborane yields in this synthesis are highly dependent on reaction conditions, particularly the ratio of reactants, order of addition, rate of addition, and temperature control. The formation of carboranes is favored by (1) maintenance of an excess of B_5H_9 over amine (to minimize attack of amine on the carborane product), and (2) addition of amine and alkyne

simultaneously, so as to promote immediate reaction of the B_5H_9-amine adduct with alkyne and thereby reduce hydroboration. The hydroboration of 2-butyne to give 2-sec-butyl-pentaborane (9)[12] under these conditions occurs to only a very slight extent (<1%). The highest yield of carborane was obtained as follows. Pentaborane (50.0 mmol) was condensed into a 500 mL greasless Pyrex reactor containing a magnetic stirring bar. Freshly distilled triethylamine (5.0 mmol) and 2-butyne (15.0 mmol) were added at -196°C and the flask was warmed to 0°C and stirred at that temperature for 24 hr. After cooling to -196°, accumulated non-condensible gas (0.08 mmol) was pumped out. Additional portions of $(C_2H_5)_3N$ (5.0 mmol each) and $C_2(CH_3)_2$ (15.0 mmol each) were added to the reactor at 24-hr intervals and the above procedure was repeated each time, until a total of 40.0 mmol of $(C_2H_5)_3N$ and 120.0 mmol of $C_2(CH_3)_2$ had been added over an 8 day period. Following this the volatiles were fractionated through traps at -30, -64, -95, and -196°C, and the brownish-red nonvolatile polymer was discarded. The trap at -30° contained mainly $(C_2H_5)_3NBH_3$ and a trace of 2-sec-C_4H_9-B_5H_8, identified from their ^1H NMR, ir, and mass spectra.[12] The -64° trap contained pure 2,3-$(CH_3)_2C_2B_4H_6$ (2.12 g, 20.4 mmol, 52% yield based on $(C_2H_5)_3N$ employed), identified from its ir and mass spectra.[6,12b,13] The -95° and -196° traps contained, respectively, unreacted pentaborane (5.20 mmol) and 2-butyne (12.5 mmol).

In a somewhat different procedure, a mixture of 2-butyne (150.0 mmol) and pentaborane (60.0 mmol) was placed in vacuo into a 500 mL reactor and 10-mmol increments of triethylamine were introduced at -196°C at 2 hr intervals, with stirring of the mixture at 0°C after

each addition. Noncondensible gas was discarded each time. After a total of 50 mmol of triethylamine had been added, the mixture was stirred at 0°C for 6 hr and finally at room temperature for 2 days. Fractionation of the volatiles gave 2-sec-C_4H_9-B_5H_8 (1.20 mmol) and $(C_2H_5)_3NBH_3$ (2.40 g, 20.0 mmol) which condensed in a -30°C trap but were separated by fractionation at -23°, which allowed only the C_4H_9-B_5H_8 to pass; 2,3-$(CH_3)_2C_2B_4H_6$ (1.75 g, 16.8 mmol, 34% yield based on $(C_2H_5)_3N$ consumed); and unreacted B_5H_9 (7.30 mmol) and 2-butyne (15.0 mmol). In comparison to the first synthesis described above, this procedure gave a lower yield of carborane, but in less time (~3 days vs. 8 days). Hydroboration of the alkyne to produce C_4H_9-B_5H_8 occurred to a significant extent in the second experiment.

In still another procedure, all of the reactants (60.0 mmol B_5H_9, 150 mmol $C_2(CH_3)_2$, and 50.0 mmol $(C_2H_5)_3N$) were condensed together and stirred for 6 hr at 0°C followed by 2 days at room temperature. This gave 1.46 g (14.0 mmol) of 2,3-$(CH_3)_2C_2B_4H_6$ (28% yield based on amine consumed), with recovery of 4.0 mmol B_5H_9 and 12.0 mmol of $C_2(CH_3)_2$. Finally, when a large <u>excess</u> of triethylamine was employed the separation of carborane product from unreacted amine was difficult and the yield of carborane fell to below 20%, evidently due to reaction of the amine with carborane. We note also that a mixture of B_5H_9, $C_2(CH_3)_2$, and $(C_2H_5)_3N$ did not react noticeably at -23°C.

<u>2,3-$(CH_3)_2C_2B_4H_6$ from B_5H_9, $C_2(CH_3)_2$, and $(CH_3)_2S$.</u> A mixture of 20.0 mmol B_5H_9, 63.0 mmol $C_2(CH_3)_2$, and 40.0 mmol $(CH_3)_2S$ was stirred for 8 days at room temperature in a 500 ml greaseless flask. The

mixture became yellow after 4 hr and remained that color for the remainder of the 8-day period. No hydrogen was evolved. Fractionation of the volatiles through -23, -64, -78, -95, and -196°C traps gave $(CH_3)_2SBH_3$ (identified from its ir and mass spectra) which was collected at -23°C; $(CH_3)_2S$ (16.6 mmol), condensed at -95° ; $C_2(CH_3)_2$ (20.0 mmol, condensed at -196°); B_5H_9 (13.90 mmol, condensed at -78°); and 2,3-$(CH_3)_2C_2B_4H_6$ (0.38 g, 3.70 mmol, 61% yield based on B_5H_9 consumed, condensed at -64°). The yellow polymer was not investigated. This method gave the highest carborane yield but the rate of reaction was inconveniently slow.

2-C_6H_5-$C_2B_4H_7$ from B_5H_9, $C_6H_5C_2H$, and $(C_2H_5)_3N$. Triethylamine (30.0 mmol total) was added in 5.0-mmol portions to a mixture of phenylacetylene (7.20 g, 60.0 mmol) and pentaborane (35.1 mmol) at -196°, with stirring for 2 hr at 0° and for 2 hr at room temperature after each addition. On completion of the triethylamine addition, the mixture was stirred at room temperature for 2 days, after which the volatiles were fractionated through traps at 0°, -23°, and -196°C. The reddish-brown polymer was discarded. The contents of the 0° trap were redistilled through 0° traps several times in order to remove the last traces of triethylamineborane, $(C_2H_5)_3NBH_3$; the final 0° fraction contained pure 2-C_6H_5-2,3-$C_2B_4H_7$ (2.15 g, 14.14 mmol, 47% yield based on amine consumed), identified from its, ir, ^1H NMR, and mass spectra.[5a] The -23° trap contained unreacted $C_6H_5C_2H$ (0.90 g, 8.82 mmol and $(C_2H_5)_3NBH_3$ (not measured), which were separated by rapid passage through a 0° trap which retained the latter compound. Unreacted B_5H_9 (3.92 mmol) was collected in the -196° trap.

2-CH_3-$C_2B_4H_7$ from B_5H_9, CH_3C_2H, and $(C_2H_5)_3N$. Triethylamine (15.0 mmol total) was added in 3.0-mmol increments at -196° to a mixture of propyne (60.0 mmol) and pentaborane (20.0 mmol). After each addition, the reaction mixture was stirred for 4 hr at 0° and for 2 hr at room temperature. Following completion of the amine addition the reaction mixture was stirred at room temperature for 2 days. The red-brown polymer was discarded and the volatiles were fractionated through traps at -30°, -64°, -95°, and -196°C. The -30° condensate was $(C_2H_5)_3NBH_3$, not measured. 2-CH_3-2,3-$C_2B_4H_7$ (0.11 g, 1.2 mmol, 8% yield based on $(C_2H_5)_3N$ consumed) collected at -64°, unreacted B_5H_9 (4.50 mmol) was retained at -95°, and unreacted propyne (20.4 mmol) collected in the -196° trap.

2-CH_3-$C_2B_4H_7$ from B_5H_9, CH_3C_2H, and $(CH_3)_2S$. A mixture of pentaborane (20.0 mmol), dimethylsulfide (39.0 mmol) and propyne (60.0 mmol) was stirred for 7 days at room temperature. Fractionation as described in the foregoing experiments gave 2-CH_3-2,3-$C_2B_4H_7$ (0.16 g, 1.80 mmol, 14% yield based on pentaborane consumed), with recovery of B_5H_9 (7.0 mmol), $(CH_3)_3S$ (10.0 mmol), and propyne (10.5 mmol).

Attempted Preparation of 2,3-$C_2B_4H_8$. A mixture of pentaborane (20.0 mmol), acetylene (60.0 mmol), and triethylamine (20.0 mmol), was stirred at 0° for 6 hr and at room temperature for 2 days. At the end of this period, 50 mmol of acetylene and an unmeasured quantity of $(C_2H_5)_3NBH_3$ were recovered but no $C_2B_4H_8$, $(C_2H_5)_3N$, or B_5H_9 were found.

A mixture of pentaborane (20 mmol, acetylene (60 mmol) and dimethylsulfide (20 mmol) was stirred for 7 days at room temperature yielding only unreacted acetylene (48 mmol), dimethylsulfide (13 mmol) and pentaborane (15 mmol); no carborane was obtained. Even after the above mixture was stirred at 100°C for 14 days, no $C_2B_4H_8$ could be detected.

2,3-$(CH_3)_2C_2B_4H_6$ from $(C_2H_5)_4N^+B_3H_8^-$. Tetraethylammonium octahydrotriborate, $(C_2H_5)_4N^+B_3H_8^-$ (25.01 g, 146.3 mmol, prepared by the method of Nainan and Ryschkewitsch[3]), was placed in a 1-L greasless Pyrex flask and evacuated overnight. 100 mL of dry CH_2Cl_2 followed by 20 mmol of anhydrous HCl were condensed into the reactor at -196°C, and the mixture was stirred at room temperature. Evolution of H_2 began just below room temperature and continued for 30 min, after which the mixture was again frozen in liquid nitrogen and the H_2 (20.0 mmol) was pumped out. Additional 20-mmol portions of HCl were added, with the same procedure followed each time, until a total of 150 mmol had been added. The total of H_2 evolved was 152 mmol. The volatiles were distilled out of the flask, leaving behind a pale yellow residue which was heated in vacuo to 90-100° in an oil bath, during which the evolution of H_2 was continuously monitored via a manometer on the vacuum line. A total of 78 mmol of H_2 was accumulated, and this was pumped out through a series of traps at -196°. The condensible material in the -196° traps was recondensed in the reactor, and 2-butyne (180 mmoles) and triethylamine (67 mmoles) were added in 15-mmol and 5-mmol increments, respectively, over a 6-day period with intervals of ~12 hr between successive additions,

during which the mixture was stirred at 0°C. After all reagents had been introduced, the mixture was maintained at 0°C for 1 day, after which the volatiles were fractionated as in the B_5H_9-$(C_2H_5)_3N$-$C_2(CH_3)_2$ reaction described above, to give 1.41 g (13.6 mmol, 20.3% yield based on amine employed) of 2,3-$(CH_3)_2$-2,3-$C_2B_4H_6$. This material had exceptionally high purity as shown by gas phase ir analysis, and was easily separated from all other materials by fractionation through traps at -30° (which retained $(C_2H_5)_3NBH_3$ and a trace of 3,4-dimethyl-2-hexene, C_8H_{16}); -63° (which retained the carborane); and -196°, in which unreacted 2-butyne was collected.

As in several of the carborane syntheses described above, the time required for this procedure can be reduced significantly, at the cost of some reduction in yield. Thus, addition of the amine and alkyne in a single step (rather than incremental) followed by stirring for 3 days at room temperature, gave a 16.2% yield of the carborane.

Acknowledgment. This work was supported by the Office of Naval Research.

References and Notes

(1) Onak, T., Chapter 10 in "Boron Hydride Chemistry", Muetterties, E. L., ed., Academic Press, New York, N.Y., 1975.

(2) Grimes, R. N., "Carboranes", Academic Press, New York, N.Y., 1970.

(3) Nainan, K. C.; Ryschkewitsch, G. E., Inorg. Nucl. Chem. Lett., 1970, 6, 765.

(4) Grimes, R. N., Acc. Chem. Res., 1978, 11, 420.

(5) (a) Onak, T.; Drake, R.P.; Dunks, G.B., Inorg. Chem.,1964, 3, 1686; (b) Onak,T; Williams, R. E.; Weiss, H. G., J. Am. Chem. Soc., 1962, 84, 2830.

(6) Onak, T.; Gerhart, F. J.; Williams, R. E., J. Am. Chem. Soc., 1963, 85, 3378.

(7) The main problems are the necessity of pre-purifying the 2,6-dimethylpyridine by a rather tedious procedure,[8] and the difficulty of achieving complete separation of that reagent from the carborane product even on gas chromatography.

(8) Brown, H.C.; Johns, S.; Podall, H., J. Am. Chem. Soc., 1954, 76, 5556.

(9) (a) Zhigach, A. F.; Kazakova, E. B.; and Antonov, I. S., J. Gen. Chem. USSR, 1957, 27, 1725; (b) Burg, A. B., J. Am. Chem. Soc., 1957, 79, 2129.

(10) Middaugh, R. L., Chapter 8 in "Boron Hydride Chemistry", Muetterties, E. L., ed., Academic Press, New York, N.Y., 1975.

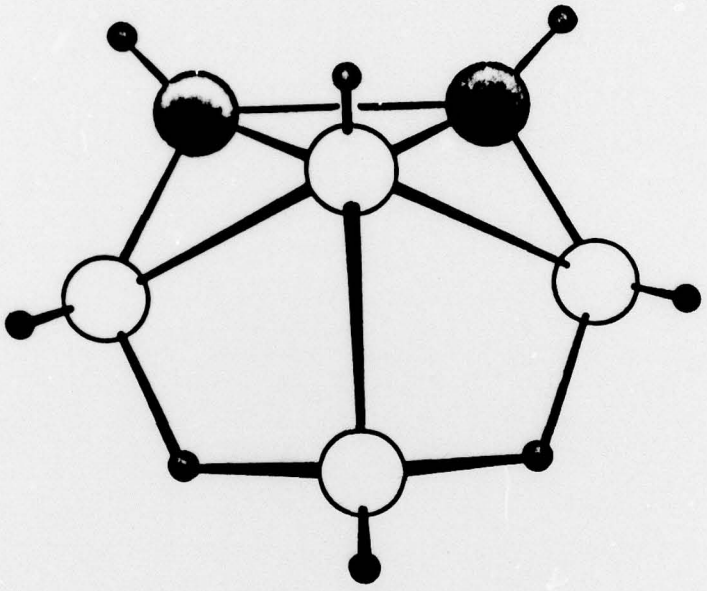
(11) Ryschkewitsch, G. E.; Miller, V. R., J. Am. Chem. Soc., 1975, 97, 6258.

(12) (a) Ryschkewitsch, G. E.; Mezey, E. J.; Altwicker, E. R.; Sisler, H. H.; Garrett, A. B., Inorg. Chem., 1963, 2, 893; (b) Grimes, R. N.; Bramlett, C. L.; Vance, R. L., Inorg. Chem., 1968, 7, 1066.

(13) Onak, T. P.; Dunks, G. B., Inorg. Chem., 1966, 5, 439.

Figure Caption

Figure 1. Structure of 2,3-$C_2B_4H_8$.



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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 31	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Improved Synthetic Routes to Small Carboranes. Bench-Scale Preparation of Nido-2,3-$C_2B_4H_8$ Derivatives from B_5H_9 and from $B_3H_8^-$ Salts		5. TYPE OF REPORT & PERIOD COVERED Interim 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Narayan S. Hosmane and Russell N. Grimes		8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-0305
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Virginia Department of Chemistry Charlottesville, Virginia 22901		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 053-569
11. CONTROLLING OFFICE NAME AND ADDRESS Chemistry Branch, Office of Naval Research Arlington, Virginia 22217		12. REPORT DATE August, 1979 13. NUMBER OF PAGES 16
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Carboranes 2,3-Dicarbahexaborane(8) Derivatives Pentaborane(9) Octahydrotriborate(1-) Salts		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) See page 1		

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
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