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Direct Synthesis of *closo*-Carboranes

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Pentaborane-9 and acetylene can react in a continuous-flow system to produce directly the smaller *closo*-carboranes 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, and 2,4-$C_2B_5H_7$ in combined yields approaching 65–70%. Reactions of decaborane-14 with acetylene under the same conditions, excepting a somewhat higher temperature, give predominantly 1,7-$C_2B_{10}H_{12}$ in yields also on the order of 70%. Optimal conditions for both systems include short residence times (~0.5 sec), high temperatures (500–600°, depending on the system), a diluent gas, and a steel wool plug or diffuser. The reactions are highly exothermic, and drastic reduction of yields can occur if the heat is not dissipated, as was evident in a scaled-up unit where very careful diluent control had to be exercised to prevent sudden surges to very high temperatures.

Introduction

In a previous publication[2] we reported a high-yield synthesis of the small *closo*-carboranes 1,5-$C_2B_3H_5$, 1,6-(and 1,2-) $C_2B_4H_6$, and 2,4-$C_2B_5H_7$, with the respective systematic names of *closo*-1,5-dicarbapentaborane-5, *closo*-1,6-dicarbahexaborane-6, and *closo*-2,4-dicarbaheptaborane-7, from the *nido*-carborane, 4,5-$C_2H_4H_8$. High yields were realized under appropriate short-term, high-temperature, continuous-flow conditions, and yields were nearly quantitative when temperature–time conditions were sufficiently mild to convert only a fraction (25–30%) of the *nido*-carborane reactant to products at one time and provided further that a low pressure, on the order of 10 mm absolute, was maintained. Even at higher temperatures, where no *nido*-carborane survived the treatment, the yield of *closo*-carboranes was still around 60%. Even with these limitations and the further limitation of a maximum yield of 40% in the synthesis of the *nido*-carborane reactant,[3,4] this method of preparing the small *closo*-carboranes represented a significant advance in the state of the art. Previously, except for $C_2B_5H_7$,[3] only trace amounts of these compounds had ever been generated, and these generally *via* silent electric discharge of flashing reactions between boranes and acetylene.[5-10]

In contrast, the icosahedral *closo*-dicarbadodecaborane 1,2-$C_2B_{10}H_{12}$ has been available in fairly high yields since its discovery.[11] Its synthesis, based on Lewis base solution chemistry, involves multistep procedures,[12] while its rearrangement to the 1,7 compound involves further handling in the form of high-temperature gas-phase pyrolysis.[13,14] Preparation of 1,12-$C_2B_{10}H_{12}$ involves similar gas-phase pyrolysis of the 1,7 compound.[15]

In our previous paper,[2] preparation of the small *closo*-carboranes required as a first step the synthesis and purification of the *nido*-carborane 4,5-$C_2B_4H_8$ by long-term reaction between pentaborane-9 and acetylene (48 hr at 215–225°) and as a second step subjection of the *nido*-carborane to short-term, high-temperature conditions to get the *closo*-carboranes. It seemed reasonable, therefore, to try to combine the two steps into one by subjecting the initial reactants, pentaborane-9 and acetylene, to the appropriate short-term, high-temperature conditions and thereby obtain the *closo*-carboranes directly in one step. As will be evident later, this new direct synthesis is not simply an extension of the earlier reaction because, first of all, the *nido*-carborane $C_2B_4H_8$ is not an intermediate here, and secondly the product distribution is significantly different. In addition to the pentaborane-9–

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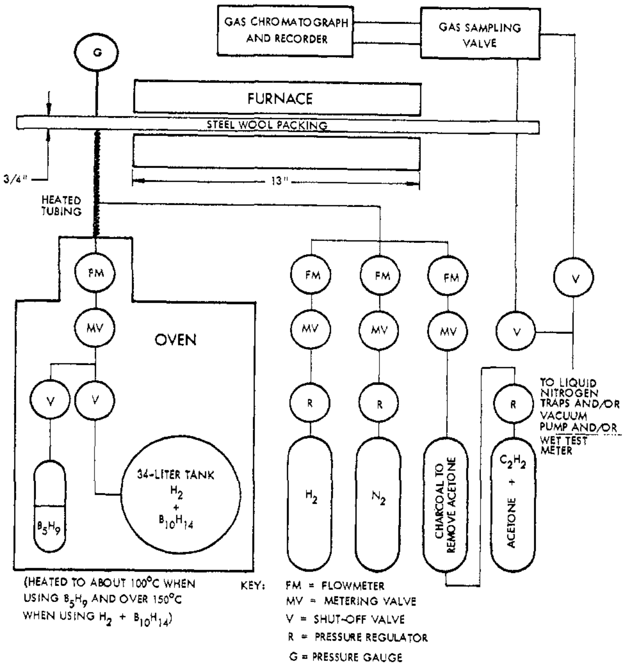

Figure 1.—Schematic diagram of apparatus for synthesizing *closo*-carboranes by direct reaction of boranes and acetylene.

acetylene experiments we studied the direct reaction between decaborane-14 and acetylene and observed the formation of the three $C_2B_{10}H_{12}$ isomers.

Experimental Section

Reagents.—The pentaborane-9 and decaborane-14 were obtained from unpurified U. S. Government stock known to be essentially free of contaminants. The acetylene was Matheson commercial grade, which was freed of acetone and water prior to use by flowing the gas through Barneby-Cheney KE charcoal previously dried by heating to about 200° in a stream of dry nitrogen. *Caution!* Pure acetylene is self-detonating and must be handled with care.[16,17] Pressures above 2 atm absolute should be avoided, and it should not be allowed to come into contact with unalloyed silver or copper (Bourdon tubes, for example).

Experimental Apparatus.—The apparatus, shown schematically in Figure 1, was constructed primarily of stainless steel (including reactor, tubing, fittings, and valves). The reactor was a 0.75-in. o.d. tube heated over a 13-in. length, regulated thermally by an "on-off" controller coupled to a thermocouple located in the annular space between the reactor and furnace. Temperatures inside the reactor were not measured, but due to the highly exothermic nature of the reaction the inside temperatures undoubtedly were substantially higher.

To permit operation at pressures in excess of the normal vapor pressure of pentaborane-9 (180 mm at room temperature), the pentaborane was pressurized to several atmospheres in a cylinder by maintaining it at 100°. To prevent condensation of the boranes in the inlet tubing and in the flowmeter, these were also maintained at 100°. Flowmeters were precalibrated under flow conditions for each gas or vapor. To deliver decaborane-14 into a 1-atm reactor, 24 g of the compound was added to a 34-l. stainless steel tank which was then evacuated and filled with hydrogen to a pressure of 64 psig. Upon heating to over 150° all of the decaborane-14 became vaporized, and well over 90% of the decaborane-14 could be utilized before the tank pressure would drop below 1 atm. In the decaborane–acetylene experiments the flowmeter and tubing were heated at 150° to prevent decaborane condensation. A valve downstream of the reactor permitted removal of aliquots of product gases for analysis by an in-line gas chromatograph. The sampling valve and tubing leading to the chromatography column were also maintained at about 100° (150° for the decaborane experiments).

The pressure in the system was monitored manually during all experiments by means of a needle valve downstream of the reactor and upstream from a metal U trap. Pressure readings were available on three 6-in. diameter gauges: 0–50 mm for low pressures, 0–800 mm for moderate pressures, and 0–3 atm for higher pressure experiments.

Analyses.—The gas chromatograph, which analyzed 10-cm^3 gaseous aliquots of the products from the flowing gas stream, consisted of a 0.25-in. o.d. × 20 ft long chromatography column containing Apiezon N on Chromosorb P. Initial identifications of eluted compounds were made either by infrared or by mass spectral analysis, and relative amounts of carboranes were determined by planimeter measurements. Elution times (column at 90°) for the principal components in the pentaborane–acetylene experiments, relative to $C_2B_5H_7$, were as follows: C_2H_2, 0.16; 1,5-$C_2B_3H_5$, 0.32; 1,6-$C_2B_4H_6$, 0.47; 1,2-$C_2B_4H_6$, 0.62; B_5H_9, 0.95; 2,4-$C_2B_5H_7$, 1.00. Similarly, in the decaborane–acetylene experiments relative elution times (column at 200°) were as follows: 1,12-$C_2B_{10}H_{12}$ (*para*), 0.54; 1,7-$C_2B_{10}H_{12}$ (*meta*), 0.61; 1,2-$C_2B_{10}H_{12}$ (*ortho*), 1.00. Sequential analyses gave quick semiquantitative or at least qualitative indications of the progress of the experiments and substantially reduced the time required to optimize the many variables, such as temperature, pressure, residence time, amount and type of diluent, borane:acetylene ratio, and reaction surface. For more quantitative data, however, in addition to the glpc analysis of an aliquot to determine relative concentrations, a collection of products was made over a period of time in a liquid nitrogen trap. The condensed products were then measured volumetrically after they had been vacuum fractionated at about −120 to −130° to eliminate most of the undesirable volatile components (mainly unreacted acetylene).

For quantitative determinations of the decaborane–acetylene reactions, in addition to glpc analysis of an aliquot, the reaction products were trapped at −195°, then sublimed through a glass U trap at 0°, which condensed out the desired products. The products were then weighed and again analyzed by glpc.

Discussion of Experimental Results

Pentaborane–Acetylene Reactions.—As part of a previous investigation a number of borane–acetylene–diluent gas mixtures had been subjected to explosion (or flashing) reactions in a steel tank to ascertain approximate explosion limits. The mixtures were found to be most susceptible to explosion when the mixture ratio approached that boron:carbon ratio stoichiometrically required for the quantitative production of boron carbide (B_4C). The addition of excess acetylene was found to lessen the possibility of an explosion, while addition of 20 parts of diluent gas (hydrogen or nitrogen) prevented explosion, irrespective of the borane:acetylene ratio. As an additional margin the amount of diluent was doubled for the initial continuous-flow experiments with a reactant ratio of 1:4:40 for pentaborane–acetylene–hydrogen.

With no packing in the reaction tube, cumulative yields of 25–30% of the three small *closo*-carboranes were observed for reaction temperatures around 500° and nominal residence times on the order of 0.5 sec. Heavy deposits of gummy-to-ceramic by-products formed around the periphery of the reactor. Substantial improvements in yields occurred when steel wool (Rhodes No 3 grade) was inserted in the reactor

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TABLE I

EXPERIMENTAL DATA ON THE PENTABORANE–ACETYLENE REACTION

Expt no.	Press., mm	Temp, °C	Packing material	Flow rate (STP), cm^3/min			Approx reactant ratio	Nominal res time, sec	B_5H_9 consumed (STP), cm^3	Mol of product per mol of B_5H_9		
				B_5H_9	C_2H_2	H_2				$C_2B_3H_5$	$C_2B_4H_6$	$C_2B_5H_7$
1	50	460	None	0.95	2.72	38.0	1:3:40	2.3	56.5	0.037	0.124	0.122
2	50	460	None	3.56	10.4	142.4	1:3:40	0.61	68.1	0.026	0.128	0.128
3[a]	50	475	None	5.13	32.6	18.7	1:6:4	1.7	50.5	Nil	0.166	0.095
4	125	525	None	19.2	73.2	382	1:4:20	0.49	93.8	0.026	0.084	0.085
5	125	525	None	19.2	73.2	420	1:4:22	0.43	96.0	0.015	0.097	0.094
6	140	525	None	8.4	135	203	1:16:24	0.71	32.0	0.007	0.044	0.044
7[b]	140	485	None	21.5	86	450	1:4:21	0.46	83.2	0.014	0.064	0.101
8[c]	140	495	None	21.5	86	450	1:4:21	0.44	103	0.016	0.131	0.183
9[a]	140	495	St wool	50.6	400	0	1:8:0	0.57	304	0.015	0.067	0.066
10	380	490	St wool	28.9	231	1137	1:8:39	0.50	272	0.047	0.264	0.305
11	380	495	St wool	28.9	231	1137	1:8:39	0.50	283	0.064	0.318	0.338
12[d]	380	485	St wool	28.9	231	1225	1:8:42	0.47	865	0.036	0.334	0.280
13	380	500	St wool	25.3	213	1250	1:8:49	0.46	759	0.064	0.290	0.336
14	760	490	St wool	59	475	2340	1:8:40	0.49	279	0.085	0.317	0.211
15	760	490	Gl wool	59	475	2340	1:8:40	0.49	325	0.074	0.278	0.176
16[a]	760	490	None	59	475	2340	1:8:40	0.49	288	0.077	0.067	0.112
17	760	490	St wool	59	238	2340	1:8:40	0.53	295	0.098	0.311	0.096

[a] Sporadic explosions noted during run. [b] BF_3 additive. [c] HCl additive. [d] Nitrogen diluent instead of hydrogen.

in amounts equivalent to about 5% of the reactor volume, and operation for as long as 25–30 min was possible before total plugging of the reactor tube occurred. The yields essentially doubled, and concomitantly the by-product deposition within the reactor was correspondingly reduced. In all, over 100 experiments were run, generally of a qualitative nature to optimize parameters, and of these 100 or so, 17 involved quantitative measurements. These 17 are listed in Table I.

Experiments 1–8 as well as no. 16 in Table I were run without any packing in the reactor, and the total yields generally were in the 20–30% range. The remaining experiments, excepting no. 15, utilized steel wool packing, and the yields improved to the 60–70% range. Experiment no. 9, although it had a steel wool insert, had a low yield because of the absence of diluent gas—with consequent sporadic explosions and formation of boron carbide and carbon rather than carboranes. As indicated in the table, three of the experiments behaved explosively, detected by perturbations, sometimes violent, in the flowmeters and pressure gauges. The tendency toward explosive reaction was observed to increase as the diluent concentration was reduced (no. 3 and 9) or as the pressure was increased (no. 16). At the higher pressure, when packing was present in the reactor and when there was sufficient diluent, the system ran smoothly. This suggests that the packing serves to inhibit propagation of flashing or explosive reactions, either as a physical barrier or diffuser or as a local heat sink. The diluent serves a similar function, but there are practical limits to the amount of diluent because the higher the diluent concentration the lower the total input of pentaborane-9 and acetylene per unit time.

The glass packing (expt 15) was better than no packing at all but not as good as steel wool, while substitution of nitrogen diluent for hydrogen (no. 12) produced no major differences in total yield. Hydrogen is preferred in these reactions because of its better heat-transfer properties and because hydrogen is a product of the reactions, which is important in larger scale operations where the diluent can be conserved by recycling it through the reactor.

In expt 7 and 8 the addition of BF_3 appeared to have an adverse effect (18% yield), while HCl was possibly helpful (33%). Trimethylamine produced no major effect one way or the other. The additive in each of these experiments was present in only a few per cent concentration.

Although there were variations, sometimes substantial, the product distribution of $C_2B_3H_5$–$C_2B_4H_6$–$C_2B_5H_7$ was generally around 1:5:5, compared with 2:1:2 for the *closo*-carboranes produced by pyrolysis of the *nido*-carborane $C_2B_4H_8$.[2] Obviously the mechanism of formation is different for the two systems. In the present direct-synthesis method $C_2B_4H_8$ has never been observed in anything more than trace quantities, even at relatively low temperatures, so almost certainly it is not an intermediate in this reaction.

The effect of varying the acetylene concentration is not obvious from the data in Table I, but from all the 100 or so experiments a molar ratio of 4 parts of acetylene to 1 part of pentaborane was about minimal for good yields, while an 8:1 ratio was generally better.

A few experiments were tried with diborane substituted for pentaborane-9, but the yields were small. When ethylene was substituted for acetylene, the same *closo*-carboranes were produced as before, but the total yields were substantially reduced to only 5–6%.

Products detected other than the small *closo*-carboranes included benzene (a few per cent), small quantities of $C_2B_6H_8$, and trace quantities of $C_2B_8H_{10}$ plus traces of mono- and dimethyl derivatives of practically all the *closo*-carboranes. Also, the 1,2 isomer of $C_2B_4H_6$ was present as 2–3% of the 1,6-$C_2B_4H_6$ yield.

Decaborane–Acetylene Reactions.—Initially we had anticipated that in the decaborane–acetylene experi-

TABLE II

EXPERIMENTAL DATA ON THE DECABORANE–ACETYLENE REACTION

Expt no.	Press., mm	Temp, °C	Flow rate (STP), cm³/min			Approx reactant ratio	Nominal res time, sec	Mol of $C_2B_{10}H_{12}$ per mol of $B_{10}H_{14}$			Product distribution			
			$B_{10}H_{14}$	C_2H_2	H_2			*ortho*	*meta*	*para*	*ortho*	*meta*	*para*	Other compd
1	380	650	19.3	216	710	1:11:37	0.61	0.021	0.518	0.005	0.036	0.892	0.007	0.065
2	380	700	19.3	216	710	1:11:37	0.58	0.038	0.450	0.010	0.007	0.815	0.019	0.096
3	760	650	42.2	606	1800	1:14:43	0.47	0.066	0.663	0.019	0.081	0.816	0.022	0.081
4	760	850	42.2	725	1800	1:17:43	0.37	0.005	0.027	0.027	0.085	0.441	0.441	0.034
5	380	580	29.0	216	1070	1:7:37	0.47				0.683	0.317		
6	380	600	42.2	216	1560	1:5:37	0.34				0.725	0.275		
7	380	600	42.2	265	1560	1:6:37	0.33				0.636	0.364		
8	380	600	13.0	216	480	1:17:37	0.86				0.539	0.461		
9	380	620	13.0	180	480	1:14:37	0.89				0.298	0.702		
10	380	640	19.3	216	710	1:11:37	0.62				0.523	0.459		
11	380	700	19.3	216	710	1:11:37	0.58				0.069	0.875	0.004	0.052
12	380	800	19.3	216	710	1:11:37	0.52				0.085	0.739	0.095	0.081

ments there would be a cascade effect in the product formation similar to the pentaborane–acetylene experiments; *i.e.*, analogous to $C_2B_3H_5$, $C_2B_4H_6$, and $C_2B_5H_7$, we expected to find $C_2B_8H_{10}$, $C_2B_9H_{11}$, and $C_2B_{10}H_{12}$. Instead we observed only the three isomers of $C_2B_{10}H_{12}$, as shown in Table II. The first four experiments listed were quantitative, and two at 650° (expt 1 and 3) produced fairly high yields of $C_2B_{10}H_{12}$, primarily as the *meta* isomer. As the temperature was raised (expt 2 and 4) the distribution shifted toward the *para* isomer, but the total yields suffered accordingly. Experiments 5–12, all semiquantitative in nature, show the general trend (with some anomaly in no. 9 and 10) from predominantly *ortho* at 580–600° to *meta* in the middle range, and finally toward *para* in the high-temperature region. Observance of this trend indicates direct assimilation of the acetylene molecule by the decaborane to form first the *o*-carborane, followed by rearrangement to the *meta* compound, and finally the low-yield, high-temperature rearrangement to the *para* compound, in line with previous studies.[13–15]

The "other" compounds in the last column of Table II were identified as hydrocarbons and trace quantities of alkylated $C_2B_{10}H_{12}$.

Scaled-Up Equipment.—Since the laboratory-scale direct synthesis of *closo*-carboranes proved to be a workable system and since we needed larger quantities for subsequent experiments, a 100-fold scaled-up device was designed and built. The information obtained from the larger equipment is pertinent here because it emphasizes problems inherent in this highly exothermic reaction system. Schematically, the scaled-up unit is the same as the drawing in Figure 1, with a few modifications. First of all, the pentaborane is introduced as a liquid just upstream of the reactor and is carried into the reactor by the acetylene and hydrogen. Another difference is a steel wool feed system whereby the wool can be drawn through the reactor tube by means of take-up and supply reels, eliminating otherwise frequent interruptions to repack the reactor. There also are filters downstream of the reactor tube to keep solids out of the trapping system. A final modification, not yet in operation but planned for the very near future, is a pump to recycle the hydrogen.

The reactor tube in this larger version has a volume of 6.5 l. and is 5 ft long × 2.5-in. outside diameter. With a reactant ratio of 1:8:40 (pentaborane-9–acetylene–hydrogen) that had been found optimal in the earlier unit, a problem occurred because of the exothermic nature of the system and the larger mass of reactants. The heat was not dissipated quickly enough, and the synergistic effect caused the temperature in a 6-in. segment of the tube to glow red (850–900°) within about 30 sec from the start of the reaction. (The furnace, hinged at the rear, can be opened for observation.) Not only does the high temperature decrease the yields due to decomposition of products but, if uncontrolled, it might continue to climb and dangerously weaken the reactor tube. In addition to the energy released by the pentaborane–acetylene reaction, energy is generated by hydrogenation, polymerization, and decomposition of the excess acetylene, which has a positive heat of formation.

To cope with this temperamental behavior the reactant ratio was cut back from 1:8:40 to about 1:2:30, and the hydrogen flow had to be monitored assiduously in accordance with the temperature profile along the reactor, increasing its flow whenever the reactor began to overheat. An obvious solution is automatic monitoring; the ultimate answer, however, may be a fluidized-bed operation.[18]

Despite the present operational handicaps the small *closo*-carboranes are produced in this system at the rate of about 1 lb/hr, and we can operate several hours before stopping to replace the steel wool reels and to clean the filters. The carboranes made in this manner are purified by a relatively large-scale vapor-phase chromatograph, capable of handling 20–30 ml of liquid per injection, which supplies sufficient amounts of purified compounds for subsequent conversion into temperature-resistant, carborane-based silastic polymers.

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