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CARBORANE CHEMISTRY: SYNTHESIS AND POLYMERIZATION

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El Monte, California

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FINAL REPORT

Carborane Chemistry: Synthesis and Polymerization

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ABSTRACT

The program has had two primary objectives: (1) to discover methods of synthesizing the smaller closo-carboranes in reasonable quantities and (2) to develop from the smaller closo-carboranes temperature-resistant silicone-carborane co-polymers analogous to Olin Mathieson's Sib polymers, which are based on $C_2B_{10}H_{12}$. With respect to the first goal, a high-yield, continuous flow synthesis of $C_2B_3H_5$, $C_2B_4H_6$ and $C_2B_5H_7$ involving direct reaction between pentaborane-9 and acetylene was discovered, and a pilot plant capable of turning out a pound-per-hour of product was built and operated. The second goal, development of polymers, has also met with considerable success, though this work is still in its early developmental stages. $C_2B_5H_7$ analogs of Olin Mathieson's Sib-1, Sib-2 and Sib-3 polymers have been synthesized, and, as might have been expected because of the smaller carborane moiety, they are somewhat less crystalline and more elastic than their $C_2B_{10}H_{12}$ counterparts. Also, improvements in elastic properties were achieved by incorporating small percentages of larger molecules, such as vinyl-$C_2B_{10}H_{12}$, in the polymer chains.

In addition to the primary objectives a large number of technical reports covering peripheral work as well as accomplishments of academic interest have been issued, and these are also discussed briefly in this report.

Section I.

INTRODUCTION

In 1964, at the inception of this program at Space-General (now Aerojet-General) Corporation, only two stable bifunctional boranes or carboranes which could conceivably be converted into polymers were available in quantity. These were the Lewis base compound, $B_{10}H_{12}(LB)_2$, and the carborane, $C_2B_{10}H_{12}$. Not only had Olin Mathieson Chemical Corporation successfully produced the so-called POP- and PNP- polymers, based upon the $B_{10}H_{12}(LB)_2$ system, but had begun to develop the industrially important SIb polymers (now called Dexsil), based upon co-polymers of $C_2B_{10}H_{12}$ and silicones. Although there were several other carboranes which appeared to possess the desired thermal stability, they were either non-functional or simply unavailable in quantity.

These, then, were the conditions under which we initiated this program, and our charter from ONR was to discover ways to produce the smaller _closo_-carboranes in quantity and to make suitable polymers from them.

Section II.

INITIAL RESEARCH PROGRAM

A. $C_2B_6H_8$ *CLOSO*-CARBORANE FROM B_6H_{10} (Ref. 1)

Our first experimental effort to obtain smaller carboranes consisted of attempts at quantity production of $C_2B_6H_8$ via the precursor molecule, B_6H_{10}, which in itself was a rare chemical and had to be prepared from the also rather scarce compound, B_5H_{11}. Our rationale was quite straightforward, viz., reactions of other boranes of the B_nH_{n+4} family, namely $B_{10}H_{14}$ and B_5H_9, with acetylene had produced the *closo*-carboranes, $C_2B_{10}H_{12}$ and $C_2B_5H_7$, respectively, so logically B_6H_{10} could also be induced to produce its *closo*-carboranes counterpart, $C_2B_6H_8$. Our approach was to produce B_6H_{10} by any means available and then try to determine whether the six-boron *closo*-carborane could be synthesized from the B_6H_{10} in high yield. Although this investigation became a chemical *cul-de-sac* insofar as quantity production of the carborane is concerned, we did discover a number of new compounds, including the coveted $C_2B_6H_8$ *closo*-carborane.

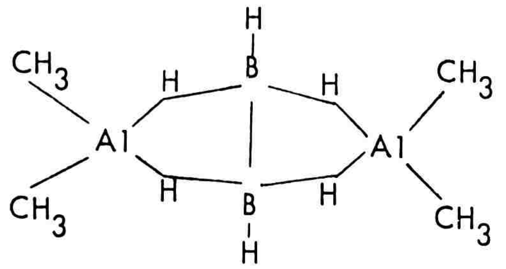
Work performed by Callery Chemical Company (Ref. 2) and by Burg, et al (Ref. 3, 4) had indicated that B_6H_{10} could best be prepared from B_5H_{11} in the presence of selected ethers, so our first task was to prepare B_5H_{11} and then subject it to aging at different temperatures in various ethers to produce B_6H_{10}. To produce B_5H_{11} we elected simply to scale up a hundredfold the method disclosed in 1933 by Burg and Schlessinger (Ref. 5), viz., pyrolysis of diborane at about 110°C. Accordingly, several pounds of diborane were ordered, and a 16-liter reactor and all associated pipe, valves, and fittings were assembled. The scaled-up equipment did indeed produce B_5H_{11} at a rate of about one liquid cc per minute in fairly high yields (Ref. 6). Even though the percent conversion per pass was low the bench scale unit could process about a quarter pound of diborane in 10 minutes, and it produced more than enough material for the experimental work necessary for studying its conversion into B_6H_{10}. To our knowledge, this is still the best system for producing B_5H_{11} today. From the B_5H_{11} made in this manner we succeeded in synthesizing B_6H_{10} in 20–40% yields, and from this in turn we made the <u>closo</u>-carborane, $C_2B_6H_8$, but not in sufficient yield to merit further attention. However, as discussed later, we now have better ways of obtaining $C_2B_6H_8$ anyway, while, moreover, Professor Sheldon Shore has developed a much superior method of producing B_6H_{10} from the readily available B_5H_9 (Ref. 7).

B. OCTABORANE-12 AND NONABORANE-15 (Ref. 8)

Both B_8H_{12} and B_9H_{15} were produced by controlled decomposition of B_5H_{11}, and both compounds produced carboranes when reacted with acetylene, but only in very low yields. Photolytic reactions between 2-butyne and B_9H_{15} generated the dimethyl-derivative of $C_2B_8H_{10}$, but in low yields. This approach to making <u>closo</u>-carboranes was abandoned because of the doubtful potential of ever achieving high yield productivity.

C. $(B_2H_4)_n$ DIBORANE-4-POLYMER (Ref. 9)

Since tetraborane, B_4H_{10}, was co-produced with B_5H_{11}, a series of experiments aimed at producing six-boron compounds from B_4H_{10} was initiated. Discovery of the diborane-4 polymer was unexpected since the plan was to react B_4H_{10} with BR_3 to produce either hydrogen-alkyl exchanged B_4H_{10} or to synthesize B_6H_{14} derivatives by removal of one BH_3 from B_4H_{10} and then dimerize the leftover B_3H_7 fragments. Actually, however, we succeeded in removing two BH_3 groups rather than just the anticipated single BH_3 group, which we had naively presumed could lead to a six-boron species by the dimerization. *No* alkyl-hydrogen exchange was observed. The material which we choose to call diborane-4, $(B_2H_4)_n$, is produced quantitatively and is a fascinating polymer in its own right; in fact, it might speciously be considered the boron analog of polyethylene. More importantly, we found a narrow temperature window (3-10°C) for B_4H_{10} reactions which is evidently warm enough for simple reactions to take place but cool enough to preclude simple decomposition of B_4H_{10}. Reactions of B_4H_{10} with $(CH_3)_3Al$, for example, produced what we believe to be



Clean reactions also take place between B_4H_{10} and both *cis*- and *trans*-butadiene in the 3-10°C window; the B_4H_{10} disappears and colorless products are produced. None of the products were characterized, however. This area could be of interest to someone not especially concerned about quantity production (B_4H_{10} is not easily available) nor about the thermal stability of the various products, for $(B_2H_4)_n$ decomposes above 120°C while the $((CH_3)_2)_4Al_2\ B_2H_2$ decomposes at room temperature over a period of several weeks.

D. ISOMERS OF METHYL DERIVATIVES OF THE NIDO-CARBORANE, CB_5H_9

Since 1962 we had collaborated with Professor Onak on an ONR-sponsored research program, and one of Dr. Onak's successes was a vastly improved method of preparing $C_2B_4H_8$ (see TR No. 15). Upon scaling up this synthesis by well over a hundredfold and pursuing an extensive program of GLC separation of the products, we noticed a number of compounds that eluted from the GLC column between benzene and toluene, which in themselves eluted after unreacted B_5H_9 and after the desired product $C_2B_4H_8$. Professor Onak had also noticed GLC "impurities" in this range. In collaboration with Dr. Onak's associate, Dr. Spielman, we separated the several peaks between benzene and toluene into pure or semi-pure fractions, and the ^{11}B nmr spectra of these fractions immediately showed that we had discovered the various methyl derivatives of the nido-carborane, CB_5H_9 (Ref. 10). It is interesting to note that the methyl derivatives of CB_5H_9 have the empirical formula, $C_2B_5H_{11}$, which is simply the addition of a C_2H_2 molecule and a B_5H_9 molecule without loss of hydrogen. Actually, Köster in Germany had discovered a more highly alkylated derivative of CB_5H_9 before we did but had assigned it the wrong structure. Actually, Köster did not have a chance of picking the correct structure since the presence of alkyl groups on the borons in his compounds precluded observation of the locations of the analogous hydrogen atoms in the ^{11}B nmr spectra.

Section III.

DEVELOPMENT OF HIGH YIELD SYNTHESES OF THE CARBORANES

During the years 1965 and 1966 most of our research was directed toward producing rare, or at least scarce, boranes, such as B_5H_{11}, B_6H_{10}, B_8H_{12} and B_9H_{15}, in the hope that we could find a good synthesis route and then convert them into *closo*-carboranes. Along with these attempts, however, we also scaled-up the known synthesis of the *nido*-carborane, $C_2B_4H_8$, which turned out to be our first successful pre-cursor of *closo*-carboranes.

A. $C_2B_4H_8$ PRODUCTION (Ref. 11)

H. G. Weiss first produced $C_2B_4H_8$ on the ZIP program by the simple co-pyrolysis of B_5H_9 and acetylene in a static system, while Onak later produced the same compound from the same reagents but in the presence of a Lewis base and obtained somewhat higher yields (Ref. 12). Later Onak reinvestigated the original Weiss synthesis and finally improved it to the extent that yields on the order of 40% could be obtained routinely (Ref. 12, 14). These reactions were generally carried out in sealed one- or two- liter glass vessels which occasionally exploded, but, barring such mishaps, Onak developed what remains to date the best method of synthesis of $C_2B_4H_8$. We then elected to scale up this reaction on the order of a hundredfold by using four 34-liter stainless steel tanks as reactors, which were heated at about 235°C over a period of 24-48 hours. During this period make-up acetylene was injected two or three different times, whenever the pressure drop indicated the need. In this manner the partial pressure of acetylene was maintained at an appropriate level, and the probability of an acetylene explosion was substantially reduced. Barring explosive reactions, which produced almost no $C_2B_4H_8$, yields of $C_2B_4H_8$ up to 40% became routine in this apparatus.

Interestingly, the most serious obstacle to obtaining high yields and a contributor to explosive reactions was the presence of solid residues (powdered as well as caked) from previous runs in the reactors, and therefore the reactors had to be cleaned assiduously between experiments. We had one tank lined with teflon and another lined with glass, but neither modification improved the yield. Later we constructed a "psuedo-ball mill" upon which we could place the used tanks, fill them with sand and water, and then rotate them for 8 hours or overnight between experiments, but this was time-consuming and a nuisance. Finally, we resorted to steam cleaning, which proved to be the best method, albeit sill time consuming.

The $C_2B_4H_8$ synthesized in this equipment was subsequently heated to about 350°C to produce $C_2B_5H_7$ in 40% yield. This was the first closo-carborane we successfully prepared in modest quantity and also the source of the first copolymer with silicone, which will be discussed in a following section. This method of producing $C_2B_4H_8$ is still the best one available, and our unit undoubtedly has a production capability at least two orders of magnitude larger than any similar equipment in existence elsewhere.

B. HIGH YIELD SYNTHESIS OF CLOSO-CARBORANES FROM THE NIDO-CARBORANE, $C_2B_4H_8$ (Ref. 15)

The fact that pyrolysis of the four-boron nido-carborane, $C_2B_4H_8$, produced a five-boron closo-carborane, $C_2B_5H_7$, strongly suggested that the reaction involved a disproportionation of two $C_2B_4H_8$ molecules into a molecule of $C_2B_5H_7$ and one of $C_2B_3H_5$ and that the $C_2B_3H_5$ was never observed as a product simply because it decomposed.

$C_2B_3H_5$ is unstable at 340-350° (Ref. 14), whereas $C_2B_5H_7$ readily survives. The regime of low temperature and long residence times had been rather thoroughly investigated, and we felt that perhaps higher yields of these same closo-carboranes could be obtained if a diametrically opposite regime of high temperature and short residence time were employed.

Consequently, apparatus was set up to allow studies of the short term, high temperature pyrolysis of $C_2B_4H_8$ under continuous flow conditions, and we subsequently determined in this equipment that $C_2B_4H_8$ could be converted almost quantitatively to a mixture of the coveted closo-carboranes, $C_2B_5H_7$ (40%), $C_2B_3H_5$ (40%), and $C_2B_4H_6$ (20%) at temperatures above 460°C with residence times of a few seconds. At last we had discovered a method whereby the smaller closo-carboranes could be produced in quantity provided that $C_2B_4H_8$ could be made available.

C. DIRECT SYNTHESIS OF THE CLOSO-CARBORANES (Ref. 16)

In 1966 we had carried out a lot of borane-acetylene explosions in vessels up to 300 liters in volume to try to produce carboranes. These experiments were conducted with quantities of diborane on the order of several pounds, but they did not, as had been hoped, produce carboranes in significant yields. We did, however, determine from these reactions that the presence of substantial amounts of hydrogen could dampen the explosive nature of the system and that the presence of even greater quantities of hydrogen precluded any possibility of ignition by either a spark or a hot wire.

Since hydrogen dilution was capable of rendering acetylene-borane mixtures incapable of explosion and in view of the fact that the high temperature, short residence time treatment of $C_2B_4H_8$ had been found to produce nearly quantitative yields of the closo-carboranes we were encouraged to reinvestigate the direct reactions between

B_5H_9 and C_2H_2. Indeed, in the presence of a great excess of hydrogen at temperatures around 500° and residence times on the order of a half-second, we were able to produce closo-carboranes under continuous flow conditions in yields up to 70%. When these results became known we suspended plans to produce closo-carboranes via $C_2B_4H_8$ intermediate, and we concentrated our efforts on the direct synthesis method. Since we are primarily interested in bifunctional closo-carboranes, we have not produced any $C_2B_4H_8$ in the last two years; the equipment is on standby, and inasmuch as we have furnished the crude product to several investigators we would be able to produce $C_2B_4H_8$ again if the demand should arise.

D. PILOT PLANT FOR DIRECT SYNTHESES

When the laboratory scale synthesis proved to be a good method for making closo-carboranes, a hundredfold pilot scale unit was designed and constructed. To heat the requisite stainless steel tube reactor (five feet long by approximately thee inches in diameter) we purchased a three-segment furnace capable of temperatures up to 1000°C. Only one temperature controller was ordered initially in the expectation that the scaled-up equipment would not require more rigorous temperature control than did the laboratory model (0.75 in diameter by thirteen inches long). A number of surplus rocket fuel tanks were purchased, assembled, and filled with various grades of steel wool so serve as filters for the product gas stream, and the filters were immersed in a water tank for rapid lowering of the temperature of the product gas stream. Two additional in-line filters were attached downstream incorporating paper filter elements to assure complete absence of particulate matter entering the liquid nitrogen cooled trapping system.

Our first two or three experiments rapidly dispelled any possibility that the scaled-up equipment without feedback controls could possibly be handled with the ease of the bench scale unit. Because of the exothermic nature of the reaction and because of the large mass of reactants, the temperature in the five-foot reactor rapidly rose to a dangerous level (glowing red tube), and we were pleased that we had purchased a segmented furnace so that we could control the temperature in each segment. It took several extra months to evaluate the effects of concentration changes and to determine exactly how to run the pilot plant manually without extensive feedback controls. Our present pilot plant, assembled almost entirely of surplus parts, is in all respects only a prototype of what should be built. However, it has successfully demonstrated that even without feedback controls the smaller carboranes can be made easily in multi-pound quantities, and it has provided ample quantities for our experimental needs. If and when a second generation pilot plant is required, we feel confident that a smoothly operating, very high yield, continuously operating pilot plant can be constructed. Production even now is no longer a problem, and our bottleneck now is the prep-scale VPC equipment that is used to separate the smaller closo-carboranes. We do however, have the capability to separate sufficient quantities for our own polymer program and for our other experimental programs.

Section IV.

POLYMER DEVELOPMENT PROGRAM

Once we had achieved the goal of being able to produce the small closo-carboranes in reasonable quantities we were able to concentrate on the preparation of the carborane-silicone co-polymers. Since $C_2B_5H_7$ was the first of these compounds to become available, made via preparation and subsequent thermal decomposition of $C_2B_4H_8$, initial efforts have been devoted to incorporating $C_2B_5H_7$ into the polymer chain.

A. POLY(CARBORANE-SILOXANES)

The thermal stability of the carboranes is one of the basic reasons for trying to incorporate them into a polymeric framework for high temperature service, and, among many possible paths to this end, the poly(carborane-siloxanes) have received a great amount of attention. These materials enhance the already good thermal stability of the unmodified siloxanes while at the same time retaining the latter's elastomeric properties. However, the poly(carborane-siloxanes) are, by virtue of their silicone nature, not the ideal polymers for applications wherein: (1) high temperature resistance should be combined with a high glass transition temperature; or (2) those in which solubility in organic solvents for ease of fabrication into films or coatings is desired.

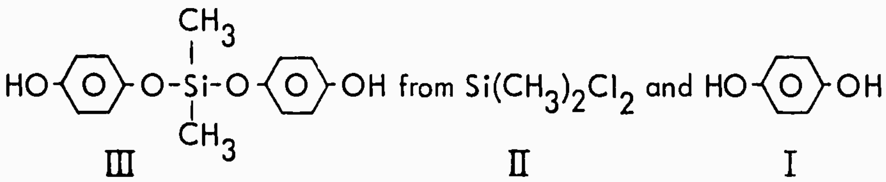
The incorporation of the carborane-silanes into a diphenol prior to the formation of poly(carborane-siloxane-carbonates) would be expected to accomplish both these ends. Furthermore, such bisphenols would halve the amount of carborane-siloxane monomer, thereby greatly reducing the cost of the resultant polymer. Consequently, some effort was expended in trying to develop copolymers of the carborane-silicone-bisphenol-A polycarbonate type.

Work by General Electric showed that the preparation of co-polymers containing unmodified methyl-silicone and bisphenol-A polycarbonates is feasible. The co-polymers, known under the developmental title of XD polymers, possess the solubility of the polycarbonates and the gas permeability of the silicones. Their mechanical properties have not been published.

Before employing carborane-containing silanes in combination with bisphenol-A, it was decided to establish polymerization conditions with ordinary silanes as models for the carborane-containing varieties. It was expected that these conditions would not differ appreciably between the models and the compounds of interest. The following reactions were therefore carried out:

1. Dimethoxy Carborane Monomer - Bisphenol-A. - Stoichiometric (1:1) amounts of the $C_2B_5H_5(Si(CH_3)_2OCH_3)_2$ monomer and bisphenol-A (recrystallized 2X from aq. EtOH) were heated together in vacuo (temperature slowly increased to 100°C over 2 hours), and a water-white polymer (MW 2400) was produced in less than quantitative yield. Infrared spectra indicated the presence of both p-substituted aromatic and silicone moieties.

2. Hydroquinone - Silane Reactions. - Attempts were made to produce the following bisphenol:

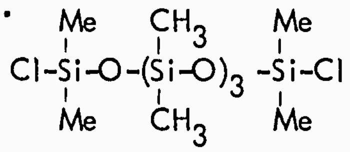


III II I

It was hoped that III would be more stable to hydrolysis than II. Had it been possible to produce III, it was planned to react it with phosgene to produce a polycarbonate-siloxane. Reactions were run in anhydrous ether at 0° and 23°C with and without $FeCl_3$ catalyst. Hydroquinone and $(CH_3)_2SiCl_2$ were also brought into contact in the neat condition. None of these reactions resulted in the desired product.

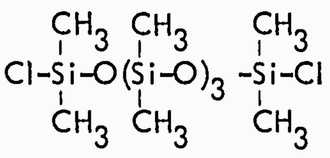
3. Disodium Salt of Bisphenol-A + Dimethyl Dichloro Silane. - Because the reaction of the silane and hydroquinone was unsuccessful it was decided to produce the disodium salt of a bisphenol to force the reaction. Bisphenol-A was chosen as a slightly more acidic bisphenol than hydroquinone. The addition of metallic sodium to a solution of bisphenol-A monoglyme yielded the disodium salt. To a monoglyme solution contining 0.2 mole of the disodium salt of bisphenol-A was added 0.1 mole of $(CH_3)_2SiCl_2$ in monoglyme. Although reaction to yield the desired product occurred, it hydrolyzed readily upon exposure to the air.

4. Disodium Salt of Bisphenol-A +



$$Cl-\overset{Me}{\underset{Me}{Si}}-O-(\overset{CH_3}{\underset{CH_3}{Si}}-O)_3-\overset{Me}{\underset{Me}{Si}}-Cl$$

Because of the hydrolytic instability of the product formed from the reaction of two moles of the disodium salt of bisphenol-A with one mole of $(CH_3)_2SiCl_2$, it was decided to react the former with

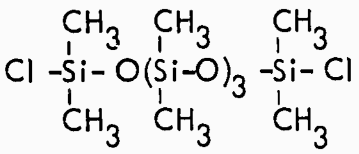


$$Cl-\overset{CH_3}{\underset{CH_3}{Si}}-O(\overset{CH_3}{\underset{CH_3}{Si}}-O)_3-\overset{CH_3}{\underset{CH_3}{Si}}-Cl$$

in order to form a more stable intermediate. However, the reaction product which resulted also hydrolyzed upon exposure to the atmosphere.

5. Direct Reaction of Phosgene, Bisphenol-A, and a Dichlorosilane to Form a Co(polycarbonate-Siloxane). - Because all attempts to produce stable siloxane-containing bisphenol intermediates proved abortive, the direct reaction of a bisphenol, a

dichloro-silane, and phosgene to produce the desired co-polymer was attempted. Fifty grams of



$$Cl-\overset{CH_3}{\underset{CH_3}{Si}}-O(\overset{CH_3}{\underset{CH_3}{Si}}-O)_3-\overset{CH_3}{\underset{CH_3}{Si}}-Cl$$

and bisphenol-A (1:4 by wt.) were dissolved in 350 ml of anhydrous pyridine in a jacketed flask at 20°C. Phosgene was introduced with rapid stirring until the completion of the reaction (sudden increase in viscosity and refluxing of phosgene). The polymer was precipitated and washed with isopropanol, dissolved in dioxane and reprecipitated with isopropanol. Dioxane cast films were clear and exhibited the combination of properties expected of such a co-polymer. The infrared showed the presence of bisphenol-A polycarbonates plus the presence of Si-O, Si-C and $Si-CH_3$.

6. Polycarbonates from Me_2SiCl_2-H_20 Prepolymer and Bisphenol-A. - In an attempt to increase the silicone character of the siloxane-polycarbonates, the length of the silicone blocks was increased by forming a pre-polymer by the hydrolysis of Me_2SiCl_2 before the addition of bisphenol-A and $COCl_2$. However, apparently due to the heterogeneous nature of the prepolymer, the resultant copolymer was of poor quality, exhibiting no strength or film-forming capability.

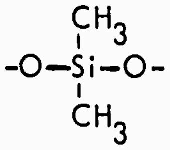
7. Diphenylsilanediol + Phosgene. - To determine whether the silane diols would form polycarboantes as readily as the bisphenols, phosgene was added to 50 grams of $O_2Si(OH)_2$ in 350 ml pyridine. A reaction to a low molecular weight product (possibly the dimer-deduced from the shrinkage of the OH band in the IR) occurred. This reaction may be significant in that it indicates a low reactivity of the Si-OH with $COCl_2$. If this supposition is correct then the siloxane-bisphenol-A polycarbonates may not have many blocks of each moiety in the copolymer.

In summary, it appears that the siloxane-bisphenol-A polycarbonates are best prepared by the direct reaction of the dichlorosilane, bisphenol-A and phosgene in solution, inasmuch as the preparation of hydrolytically stable siloxane-containing bisphenols appears less feasible. After the reaction conditions have been optimized for the model systems hitherto employed, future work will involve incorporation of the $C_2B_5H_7$ and other carborane containing monomers into the chain.

B. $C_2B_5H_7$ ANALOGS OF OLIN MATHIESON'S Sib-POLYMERS

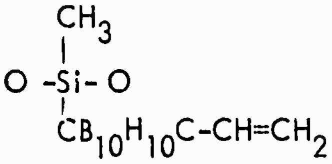
The polymers are prepared by first reacting the GLC-purified carborane with lithium butyl to make the dilithio salt, then reacting the latter with dichlorodimethylsilane to make the chloro-monomer, $Cl\ Si(CH_3)_2CB_5H_5CSi(CH_3)_2Cl$.

Polymers that have been prepared in our laboratory include those wherein the closo-carborane units $-CB_5H_5C-$ are connected by $-Si(CH_3)_2OSi(CH_3)_2-$ group (5-Sib-1 analogues), by $-Si(CH_3)_2O-Si(CH_3)_2O-Si(CH_3)_2-$ groups (5 Sib-2 analogues), and $-Si(CH_3)_2O-Si(CH_3)_2O-Si(CH_3)_2O\ Si(CH_3)_2-$ groups (5-Sib-3 analogues). The latter (5-Sib-3) polymer may be considered more of a carborane-modified silicone, while the former (5-Sib-1) is not a true silicone because it does not have the



$$-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O-$$

unit that is characteristic of all silicones. In the 5-Sib-1 analogue, unfortunately, the shorter "silicone" connective link leads to a more crystalline (less elastomeric) final material, as one would expect. However, we have found that the introduction of a few "big" carborane units of the type



$$\begin{array}{l} \quad\ \mathrm{CH_3} \\ \quad\ \ | \\ \mathrm{O-Si-O} \\ \quad\ \ | \\ \quad\ \mathrm{CB_{10}H_{10}C-CH{=}CH_2} \end{array}$$

substantially reduces the crystallizing tendency of the 5-Sib-1 so that the final product is an elastomeric carborane polymer without the classical silicone linkages. This development is significant because the inductive strengthening of the Si–O bond by the electron deficient carborane moiety causes the 5-Sib-1 polymers to exhibit greater thermal stability than either the 5-Sib-2 or 5-Sib-3 types. We have filled (utilizing numerous formulations) and cured (utilizing both peroxide catalysts and high energy irradiation) selected polymers to produce elastomeric materials which show considerable promise, but we have not yet achieved the optimal conditions for the final process since small changes in filling and curing have substantial effects upon end use properties.

Section V.

DISCUSSION OF TECHNICAL REPORTS

Technical Report No. 1. "Correlation of Chemical Shift and Spin Coupling Values in the ^{11}B nmr Spectra of Boron Compounds," by Robert E. Williams, Kenneth M. Harmon and John R. Spielman, 1 July 1964.

One of the first tasks that we undertook upon receiving ONR support in 1964 was to gather up all the loose ends of assorted ^{11}B nmr spectra that (a) had accumulated in the literature, (b) that we had published, (c) that had been collected in the period 1955-1958, and (d) to collate all of these bits and pieces of data into a report which we issued as Technical Report No. 1.

In essence, although we offer no explanation for the chemical shift values of the boron in various compounds, trends were noted which could be empirically extrapolated and which have since demonstrated their usefulness. A second useful relationship illustrated in TR No. 1 was that the ^{11}B spin-coupling to hydrogen is in most cases related directly to the s-character of that particular bond as determined by the chemical character of the other substituents attached to the boron. This was primarily an extension of Henry Bent's treatment of ^{13}C.

Technical Report No. 2. "64.16 ^{11}B nmr Spectra: Chlorodecaboranes Identified as $1\text{-}ClB_{10}H_{13}$ and $2\text{-}ClB_{10}H_{13}$," by Robert E. Williams and Eugene Pier, 1 January 1965.

About 1957 Drs. Mangold and Herman furnished to one of us (REW) for nmr analysis two samples of what they believed to be chlorodecarboranes. At that time, however, we were unable to deduce the structures of these compounds with our 1957 state-of-the-art equipment, so the samples were put aside. In 1964, when a 32 m/c ^{11}B nmr spectrometer became available, the chloroisomers were exhumed and reanalyzed. One of the compounds was pure 1-$ClB_{10}H_{13}$ while the other was identified as a mixture of 1-$ClB_{10}H_{13}$ and 2-$ClB_{10}H_{13}$. This data has been published in the open literature (Ref. 17), and Mangold and Hillman were able to publish their seven-year old synthetic work.

<u>Technical Report No. 3.</u> "Assignment of 64.16 mc ^{11}B nmr Spectrum of B_5H_{11}," by Robert E. Williams, F. James Gerhart and Eugene Pier, 2 January 1965.

This report dealt with the ambiguities that existed with respect to the structure of B_5H_{11}. Lipscomb, who has resolved the major number of correct structures for the boranes, felt the unique extra hydrogen on B_5H_{11} was a bridge hydrogen, while at another time he felt it was a terminal atom. The ^{11}B nmr spectrum at 12.8 mc had been interpreted as a reinforcement of the unique bridge hydrogen structure, while more refined x-ray data reinforced the unique terminal hydrogen structure. New ^{11}B nmr data obtained at 32 mc supported our unique bridge hydrogen structure and certainly confirmed that our interpretation of the more primitive 12.8 mc data was correct (Ref. 18). We were then left in the position of assuming that perhaps one structure was correct at low temperatures in the crystal lattice, while the other was correct at higher temperatures or in the liquid phase. In more recent years, as more compounds closely related to B_5H_{11} have been discovered and studied, it is becoming apparent that the so-called unique hydrogen in pentaborane-11 is also present in other related molecules and that to interpret selected ^{11}B nmr spectra (TR No. 17) one must assume that selected hydrogens are constantly changing from bridge status to terminal status and vice versa. It would seem then that one must consider a continuum of "kinds of hydrogen" between completely bridge and completely terminal. It is most facinating to learn that Professor Lipscomb's most recent and most sophisticated calculations suggest that the unique hydrogen in B_5H_{11} is indeed "kind of" a bridge hydrogen and "kind of" a terminal hydrogen or almost exactly half way in between the two alternative extremes. We feel quite content with Lipscomb's latest theoretical conclusions and believe that the acceptance of the various kinds of hydrogen in the boranes as having both bridge and terminal character will be eventually accepted by all borane chemists and will end future polemics by ourselves and others on this subject. Fortunately (see TR No. 17) these so-called unique hydrogens are not found in carboranes having two or more carbon atoms, and hence structural determinations for new compounds in this category will be greatly simplified and less subject to question.

Technical Report No. 4. "Hydrogen Exchange in the H_2O-$B_{10}H_{14}$-Cineole System: Suggested Structure for μ-(EtO)$B_{10}H_{13}$," by Robert E. Williams, 1 February 1965.

Prior to the demise of the OMCC Pasadena laboratory (1959) we had observed a very strange $B_{10}H_{14}$ ^{11}B nmr spectrum when $B_{10}H_{14}$ was dissolved in cineole. Unable to explain these results in 1957, the experiment was repeated in 1964. We found that it wasn't the cineole itself that caused the inexplicable spectrum, but it was the presence of moisture that permitted rapid hydrogen exchange to take place between the H_2O and the $B_{10}H_{14}$. Cineole, a ditertiary ether which is uniquely stearically hindered, forms stable oxonium salts with acids such as HCl, HBr, etc. (eq. $R_2OH^+ + Cl^-$); thus it would catalyze extensive hydrogen exchange with little hydrolytic decomposition. We feel confident that a general method of promoting borane-hydrogen exchange with little or no decomposition will be at hand in cineole solutions when the hydrogen or deuterium donor is HCl or DCl instead of water.

Technical Report No. 5. "32 mc ^{11}B nmr Spectra of $R_2C_2B_4H_6$ and 1-Iodo $B_{10}H_{13}$," by Robert E. Williams and Thomas P. Onak, 30 April 1964.

32 mc ^{11}B nmr spectra were obtained (Ref. 17) for $C_2B_4H_8$ and for $B_{10}H_{13}I$ (synthesized in 1957). The new data confirmed the earlier 12.8 megacycle spectrum of the former and added credence to our contention that the iodine was located in the one position of decaborane, an observation that was not obvious in the 12.8 megacycle spectrum.

Technical Report No. 6. "B_9H_{15} and B_8H_{12}: Synthesis, Equibria and Decomposition Kinetics," by Robert E. Williams, John R. Spielman and J. F. Ditter, 15 March 1965.

The idea here was to prepare B_9H_{15} and/or B_8H_{12} and then react them with acetylene to generate closo-carboranes, preferably $C_2B_8H_{10}$. B_9H_{15} was prepared in small quantities (low yields) by reaction between liquid B_5H_{11} and B_2H_6 at about 25 atmospheres at room temperature. In the inlet system of a mass spectrometer at about 50 microns pressure, the nonaborane-15 decomposed to octaborane-12 and the octaborane-12 in turn decayed to undetermined products, although one product almost certainly was hexaborane-10. Both decompositions occurred by first-order mechanisms. Mass spectra of these compounds were determined. Evidence also was obtained which indicated that reports of the existence of heptaboranes, at least five of which had been "observed" mass spectrally, are open to serious doubt. Certain alkylboranes, alkoxyboranes, and carboranes, which are readily generated by reactions between boranes and the common impurity, ethyl ether, have mass spectral characteristics similar to the anticipated heptaboranes, while reactions of boranes with ethane, an impurity frequently found with diborane, also could generate compounds in this spectral region.

Technical Report No. 7. "A Six-Boron Carborane, $(CH_3)_2C_2B_6H_6$, and B_6H_{10}: $P(C_6H_5)_3$ from Hexaborane-10," by Robert E. Williams and F. James Gerhart, 1 June 1965.

As mentioned in section I we were able to produce B_6H_{10} in sufficient quantities to carry out several exploratory experiments with acetylene in order to determine what closo-carboranes would be produced in these reactions. We found that dimethylacetylene did react with B_6H_{10} to produce the dimethyl derivative of the first 6-boron closo-carborane, but the yield was trivial. However, we did deduce the correct structure for this system based more upon our preconceived prejudices rather than on the ^{11}B nmr spectrum, which was uninformative. Unfortunately, at this time we did not know that short residence times at high temperatures would be considerably more likely to produce closo-carboranes in substantial yield than the long residence times at low temperatures which we employed.

Since this technical report was written and published, Professor Sheldon Shore of Ohio State has come up with a much better synthesis of B_6H_{10}. Dr. Ditter collaborated with Dr. Shore in running some B_6H_{10} — C_2H_2 reactions under high temperature, short residence time conditions, but the results were not too encouraging. Nevertheless, a technical report of this investigation will be issued during 1970.

Technical Report No. 8. "Diborane-4 Polymer," by Robert E. Williams and F. James Gerhart, 6 June 1965.

The subject matter of this report is covered under the previous section.

Technical Report No. 9. "On the Mechanism of 2,4-Dimethylene-tetraborane Formation and a Suggested Classification for Carboranes and Alkyl-boron Hydrides," by Robert E. Williams and F. James Gerhart, 1 September 1966.

When carboranes are produced from boranes and hydrocarbons, hydrogen atoms are generally lost. Presumably, the hydrogens that are lost are boron-attached hydrogens, and in the case of acetylene-borane reactions the use of deuteroacetylene had demonstrated this to be the case. We wished to confirm that this supposition also applied to the production of ethylene-tetraborane, $(CH_2)_2B_4H_8$, from B_4H_{10} and ethylene. Deuteroethylene was utilized in this synthesis, and the retention of all four deuterium atoms in 100% of the product, $(CD_2)_2B_4H_8$, confirmed that both of the hydrogens were lost from the B_4H_{10}.

Technical Report No. 10. "Analysis of Boranes and Carboranes by Mass Spectrometry," by J. F. Ditter, F. James Gerhart, and Robert E. Williams, 12 October 1966.

The most useful tool for the identification of new boranes and carboranes, in our opinion, is mass spectroscopy, and yet many investigators utilize only about half of the structural information or clues available from this source of information. From the compilation of a large number of mass spectra, some dating as far back as 1952, we demonstrated some of the trends and some of the additional structural information that can be obtained from good data. This technical report has appeared as a chapter in ACS monograph series No. 72.

Technical Report No. 11. "A Boron-Permethyl Closo-Carborane, $H_2C_2B_5(CH_3)_5$," by H. V. Seklemian and Robert E. Williams, 17 January 1967.

By a comparison of data accumulated by R. Koster on the boron peralkyl-derivatives of $C_2B_3H_5$ and similar data accumulated by Onak on the parent $C_2B_3H_5$, it was obvious that the alkyl derivatives were considerably more stable at high temperatures than the former. Moreover, Koster's derivatives for the most part had ethyl groups on the boron atoms in the carboranes, which are known to be capable of ejecting ethylene and leaving the less stable B-H moiety. We elected to undertake the preparation of similar closo-carboranes but with methyl groups on the boron atoms of the respective closo-carboranes instead of ethyl groups. In this fashion we felt that we could avoid the potential hydrocarbon elimination reaction while retaining the superior thermal characteristics of the boron-peralkyl closo-carboranes; probably the methyl derivatives would be even more stable than their ethyl analogues. As a first attempt in this direction, we chose to carry out the pyrolysis of $C_2B_4H_8$, which normally produces $C_2B_5H_7$, in the presence of a great excess of trimethylboron under which conditions we hoped that boron-alkyl derivatives of $C_2B_5H_7$ would be produced.

The evidence revealed that all of the seventeen possible boron-methyl isomers of $C_2B_5H_7$ were produced. The boron permethyl derivative of $C_2B_5H_7$, i.e., $H_2C_2B_5(CH_3)_5$, produced in abundance, and thus we had produced a closo-carborane which retained two C-H groups for future polymerization reactions while protecting the borons with methyl groups. As an example of the increased thermal stability of such species, the mass spectral fragmentation pattern of the permethyl derivative revealed that although the molecule had 17 hydrogens (compared to seven in the parent $C_2B_5H_7$) they were much more resistant to cleavage than hydrogens on the parent compound. We are just now re-entering this arena with high hopes of finding high yield synthesis of the permethyl derivatives of the smaller closo-carboranes.

Technical Report No. 12. "B_6H_{10} Preparation," by F. James Gerhart and Robert E. Williams, 1 June 1967.

Unpublished data revealed at a long past ACS meeting suggested that we could produce B_6H_{10} if we followed the original recipe assiduously, so we contacted the inventors and were graciously furnished experimental details. Eventually we realized 40% yields of B_6H_{10}, based upon B_5H_{11} as the starting material. However, since Dr. Sheldon Shore has developed a superior synthesis of B_6H_{10} based upon the readily available B_5H_9, our work as far as being a practical synthesis of B_6H_{10} is obsolete.

Technical Report No. 13. "High Yield Synthesis of the Smaller Closo-Carboranes, $C_2B_3H_5$, $C_2B_4H_6$ and $C_2B_5H_7$," by J. F. Ditter, 15 August 1967.

This reaction, although we did not know it at the time, really marked the turning point in our entire carborane synthesis investigation. The reaction, as indicated in the title, is quantitative under selected conditions and marked our first entry into the high temperature, short residence time reaction regime and is treated in detail in section II.

Technical Report No. 14. "The Preparation of Pentaborane-11 in Bench Scale Quantities," by J. F. Ditter, I. W. Searcy, and R. E. Williams, 15 October 1967.

As mentioned previously, we have on standby the largest synthesis unit for the preparation of B_5H_{11} in existence. This apparatus is a hundredfold scale up of the Burg-Schlesinger glass equipment devised over 35 years ago. This report will be submitted for publication in Industrial and Engineering Chemistry.

Technical Report No. 15. "Bench Scale Production of $C_2B_4H_8$ (nido-4,5-dicarbahexaborane-8)," by Robert E. Williams, J. F. Ditter, J. D. Oakes, and F. James Gerhart, 26 October 1967.

As mentioned in section II we scaled up the synthesis of $C_2B_4H_8$ a hundredfold by using four 34-liter stainless steel tanks, connected through a manifold instead of the previous lab scale one- or two-liter glass bulbs. We were on the point of scaling this unit up again by tenfold (going to 300 liter stainless steel tanks) when we discovered the direct synthesis method (see below), and this made any further preparation of $C_2B_4H_8$ completely unnecessary, at least on a large scale. We have on standby the largest capacity for the production of $C_2B_4H_8$ in existence, and the data obtained from this unit will be submitted to Industrial and Engineering Chemistry for Publication.

Technical Report No. 16. - "General Method for the Direct Synthesis of the Closo-Carboranes: $C_2B_5H_7$, $C_2B_4H_6$, $C_2B_3H_5$, and $C_2B_{10}H_{12}$," by J. F. Ditter, E. B. Klusmann, and Robert E. Williams, 12 June 1968.

Technical Report No. 13 (see above) which involved synthesis of closo-carboranes from $C_2B_4H_8$, marked a turning point in our program, but subsequently we recognized that the direct synthesis of the closo-carboranes from pentaborane and acetylene (TR No. 16) utilizing the high temperature, short residence time regime was a more important accomplishment. Via this method boranes which had rarely been studied in reactions above 200°C yielded copious quantities of closo-carboranes when processed at 500°C and above. This included the three $C_2B_{10}H_{12}$ isomers, prepared by direct reaction between $B_{10}H_{14}$ and acetylene. This material was first published in a brief article in Chemical and Engineering News in July of 1968, and it will appear again in the 1970 Yearbook of Science and Technology and in more detail in Inorganic Chemistry, scheduled for publication in March, 1970. Data have also been accumulated in scaling up the reaction from laboratory apparatus to a pounds-per-day unit which we now use to supply carboranes as needed for our program. The details are covered in the preceeding section, and the bottleneck has essentially been broken insofar as the subsequent production of polymers based upon the smaller closo-carboranes is concerned.

Technical Report No. 17. - "Arachno-Carboranes, Arachno-Boranes, and the Carbonium Ions, $C_3H_7^+$ and $C_4H_7^+$; Nuclear Magnetic Resonance Anomalies," by Robert E. Williams, 12 April 1969.

The contents of Technical Report No. 17 are in essence an attempt at correlation of the ^{11}B nmr spectra and the structures and tautomeric behavior of boranes and carboranes. The most important feature was the prediction that carboranes containing two or more carbon atoms will not engage in rapid tautomeric behavior and hence will have ^{11}B nmr spectra which can be interpreted in a first order fashion to reveal their structures. Of secondary importance, if one accepts the premise that the endo-hydrogens and the bridge hydrogens of the various arachno-boranes are in constant rapid exchange, the heretofore ambiguous ^{11}B nmr spectra may be easily interpreted in terms of the most probable arachno-borane structure. Thirdly, it was pointed out that certain carbonium ions, considered to be outcasts insofar as most carbonium ions are concerned, might best be considered as arachno-boranes. The classical versus nonclassical controversy might well have had the terms reversed had the arachno-boranes and arachno-carboranes been discovered before hydrocarbons.

Technical Report No. 18. - "Nonspecific Carborane Producing Reactions," by Robert E. Williams, F. James Gerhart, G. I. Hickey, and J. F. Ditter, 4 August 1969.

Over the years several types of reactions have been carried out which produce literally hundreds of different products in low yields. Two of these reactions are discussed in Technical Report No. 18, the first being diborane-acetylene explosion reactions, from which practically all of the various closo-carboranes and a host of methyl and polymethyl derivatives are produced. The second type reaction, that of the co-pyrolysis of the nido-carborane, $C_2B_4H_8$, and diborane also produces innumerable compounds, including all of the *closo*-carboranes and surprisingly many thermodynamically less favored isomers of several of the *closo*-carboranes, viz., new isomers of $C_2B_5H_7$, $C_2B_7H_9$ and $C_2B_8H_{10}$. Very few methyl derivatives of the various *closo*-carboranes were observed. However, a large number of bi-*closo*-carboranes were formed, and in fact almost all possibilities of *closo*-carboranes joined through boron-boron bonds to second *closo*-carboranes were observed. In one case, the mass spectral evidence suggests that three $C_2B_5H_7$ *closo*-carboranes have been joined, producing $C_2B_5H_6$-$C_2B_5H_5$-$C_2B_5H_6$. This report may be considered as preliminary because of the limitations of our GLC-MS equipment; more sophisticated equipment at a local NASA installation is now becoming available to us, and much more definitive analyses of these compounds will then become possible.

LIST OF REFERENCES

(For References to Technical Reports, see Section V)

1) Technical Reports No. 7 and No. 12; Robert E. Williams, and F. James Gerhart, *J. Am. Chem. Soc.*, *87*, 3513 (1965).

2) M. W. Forsyth, M. V. Hough, M. D. Ford, G. T. Hefferan, and J. L. Edwards, Abstracts, 135th National Meeting of the American Chemical Society, Bostan, Mass., April, 1959, p. 40 M.

3) J. L. Boone and A. B. Burg, *J. Am. Chem. Soc.*, *81*, 1766 (1959).

4) A. B. Burg and Reinhold Kratzer, *Inorg. Chem.* *1*, 725 (1962).

5) A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, *55*, 4015 (1933).

6) Technical Report No. 14.

7) R. A. Geanangel and S. G. Shore, *J. Am. Chem. Soc.*, *89*, 6771 (1967).

8) Technical Report No. 6; J. F. Ditter, John R. Spielman and Robert E. Williams, *Inorg. Chem.*, *5*, 118 (1966).

9) Technical Report No. 8; Robert E. Williams and F. James Gerhart, U.S. Pat. No. 3,457,039 (1969).

10) Thomas P. Onak, Gary B. Dunks, John R. Spielman, F. James Gerhart, and Robert E. Williams, *J. Am. Chem. Soc.*, *88*, 2061 (1966).

11) Technical Report No. 15.

12) T. P. Onak, R. E. Williams, and H. G. Weiss, *J. Am. Chem. Soc.*, *84*, 2830 (1962).

13) T. P. Onak, F. J. Gerhart, and R. E. Williams, *J. Am. Chem. Soc.*, *85*, 3378 (1963).

14) T. P. Onak, *Advan. Organometal. Chem.*, *3*, 263, (1965).

15) Technical Report No. 13; J. F. Ditter, *Inorg. Chem.*, *7*, 1748 (1968).

16) Technical Report No. 16; *Chem. and Eng. News*, 46, No. 29, 8 July 1968, p. 34; J. F. Ditter, E. B. Klusmann, J. D. Oakes and Robert E. Williams, *Inorg. Chem.*, Accepted for publication (March, 1970).

17) M. Hillman and D. J. Mangold, *Inorg. Chem.*, *4*, 1356 (1965).

18) R. E. Williams, F. James Gerhart, and Eugene Pier, *Inorg. Chem.*, *4*, 1239 (1965).

19) Robert E. Williams and Thomas P. Onak, *J. Am. Chem. Soc.*, *86*, 3159 (1964).

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13 ABSTRACT

The program has had two primary objectives: (1) to discover methods of synthesizing the smaller closo-carboranes in reasonable quantities and (2) to develop from the smaller closo-carboranes temperature-resistant silicone-carborane co-polymers analogous to Olin Mathieson's Sib polymers, which are based on $C_2B_{10}H_{12}$. With respect to the first goal, a high-yield, continuous flow synthesis of $C_2B_3H_5$, $C_2B_4H_6$ and $C_2B_5H_7$ involving direct reaction between pentaborane-9 and acetylene was discovered, and a pilot plant capable of turning out a pound-per-hour of product was built and operated. The second goal, development of polymers, has also met with considerable success, though this work is still in its early developmental stages. $C_2B_5H_7$ analogs of Olin Mathieson's Sib-1, Sib-2 and Sib-3 polymers have been synthesized, and, as might have been expected because of the smaller carborane moiety, they are somewhat less crystalline and more elastic than their $C_2B_{10}H_{12}$ counterparts. Also, improvements in elastic properties were achieved by incorporating small percentages of larger molecules, such as vinyl-$C_2B_{10}H_{12}$, in the polymer chains.

In addition to the primary objectives a large number of technical reports covering peripheral work as well as accomplishments of academic interest have been issued, and these are also discussed briefly in this report.

14 KEY WORDS	LINK A		LINK B		LINK C	
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