HIGH TEMPERATURE STABLE CARBORANE ADHESIVES

Contract No. NASA 9-5527

First Quarterly Progress Report

by

Dr. Robert Barnes

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2101 Webster-Seabrook Road,
Houston, Texas.

Approved: *Daniel Grafstein*

Daniel Grafstein
Principal Staff Scientist
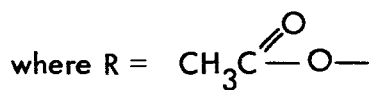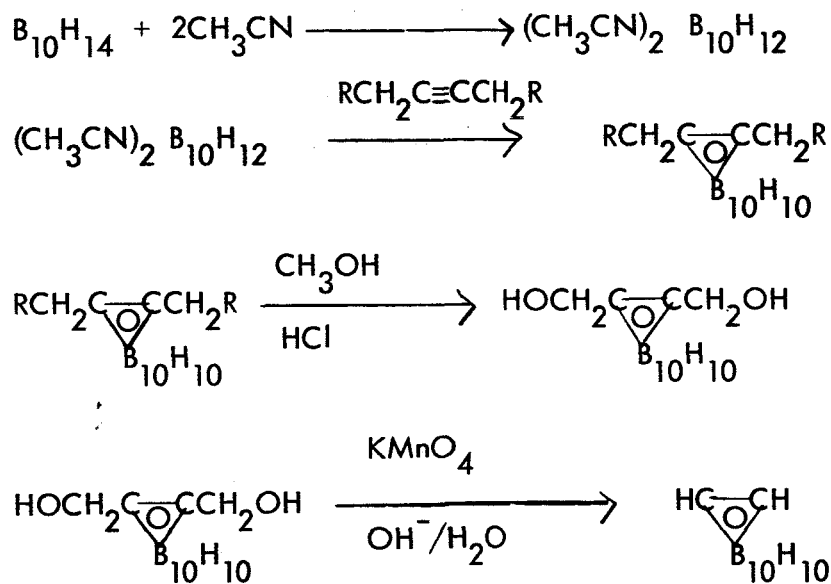Manager Chemistry Department.

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RESEARCH CENTER
AEROSPACE GROUP
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ABSTRACT

Contract NASA 9-5527

This is the first quarterly report on the synthesis and evaluation of carborane-epoxy adhesives for high temperature aerospace applications. This report covers technical progress for the period from December 21, 1965 to March 20, 1966.
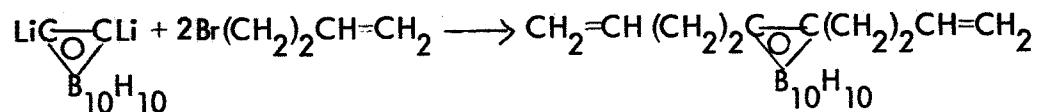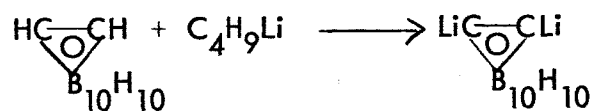
During the first quarter, efforts were concentrated on the synthesis and accumulation of significant quantities of intermediates for the preparation of several epoxyalkylcarboranes and diepoxyalkylcarboranes. In particular, the effort was concentrated on the conversion of decaborane in a stepwise fashion to carborane:

$$B_{10}H_{14} + 2CH_3CN \longrightarrow (CH_3CN)_2 \ B_{10}H_{12}$$

$$(CH_3CN)_2 \ B_{10}H_{12} \xrightarrow{\text{RCH}_2\text{C}\equiv\text{CCH}_2\text{R}} RCH_2C\underset{B_{10}H_{10}}{\overbrace{}}CCH_2R$$

$$RCH_2C\underset{B_{10}H_{10}}{\overbrace{}}CCH_2R \xrightarrow[\text{HCl}]{\text{CH}_3\text{OH}} HOCH_2C\underset{B_{10}H_{10}}{\overbrace{}}CCH_2OH$$

$$HOCH_2C\underset{B_{10}H_{10}}{\overbrace{}}CCH_2OH \xrightarrow[\text{OH}^-/\text{H}_2\text{O}]{\text{KMnO}_4} HC\underset{B_{10}H_{10}}{\overbrace{}}CH$$

where R = $CH_3C\overset{\displaystyle O}{\diagup\!\!\!\!\diagdown}O-$

The following materials were synthesized during this period by the routes indicated above.

Material	Amount, pounds
6,9-bis(acetonitrilo)decaborane	5.75 lbs.
1,2-bis(acetoxymethyl)carborane	1.0
1,2-bis(hydroxymethyl)carborane	0.5 (crude)

	Amount, grams
Carborane	15 g.

A sample of carborane was converted to the dialkenyl derivative, 1,2-bis(3-butenyl)-carborane by the following route:

$$HC\!\!-\!\!CH + C_4H_9Li \longrightarrow LiC\!\!-\!\!CLi$$
$$B_{10}H_{10} \qquad\qquad\qquad B_{10}H_{10}$$

$$LiC\!\!-\!\!CLi + 2Br(CH_2)_2CH\!\!=\!\!CH_2 \longrightarrow CH_2\!\!=\!\!CH(CH_2)_2C\!\!-\!\!C(CH_2)_2CH\!\!=\!\!CH_2$$
$$B_{10}H_{10} \qquad\qquad\qquad\qquad\qquad\qquad B_{10}H_{10}$$

A 50 gm sample of 1-(3-butenyl)carborane was purified, and its infrared spectrum was recorded and used for characterization of the above dibutenylcarborane.

ADMINISTRATIVE INFORMATION

This 12-month program is being sponsored by NASA-Manned Spacecraft Center, Houston, Texas under Contract NASA 9-5527, Control No. P.R. No. 5320022. This quarterly report covers the period December 21, 1965 through March 20, 1966. The NASA Technical Representative is Mr. Ivan K. Spiker/ES4. The Project Supervisor at the General Precision Aerospace Research Center, 1225 McBride Avenue, Little Falls, New Jersey, is Dr. Daniel Grafstein. The Principal Investigator is Dr. Robert Barnes. Infrared spectra were obtained with the assistance of Mr. Lawrence Flint.

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1. INTRODUCTION

Extreme conditions in aerospace environments have generated a need for novel high-temperature stable adhesives for bonding spacecraft heat shields to the vehicle. The adhesives must retain their strengths from 600°F to 1000°F, both during and after exposure to this environment.

Many properties peculiar to adhesives cannot be obtained by other fastening methods. Stress can be distributed uniformly over the widest possible surface area, thus promoting high strength and resistance to fatigue. The inherent flexibility of most adhesives tends to damp vibration and absorb shock. Smooth outside contours become feasible, an important requirement for high speed vehicles. The main advantages of adhesives lie in their ability to join unlike materials in a continuous bond without the stress concentration or weight penalty exacted by rivets, bolts, and welding.

Although the nature of adhesive bonds provided by polymeric systems is not well understood, the critical parameters can be established empirically. In actual practice, optimium adhesion is often obtained with mixed polymers. It has been suggested that an adhesive bond is dependent on the polar groups in the resin chain. The better adhesion obtained with higher molecular weight polymers is partially attributable to the intertwining of chain molecules.

Several materials have been investigated for use as high-temperature-stable adhesives. Ceramics have excellent thermal stability, but they demonstrate brittleness and low peel strength, and generally involve difficult processing and high temperature cures. Combinations of brazing alloys and ceramics have been investigated, but the processing is again difficult and the cure temperatures are very high. Polyaromatic systems such as the polybenzimidazoles and polyimide polymers possess good high-temperature properties, but their curing requires high temperatures and special fixtures and involves the release of volatile by-products during cure.

Epoxies are the most widely used adhesives, primarily because they display outstanding adhesion to many materials. Unlike phenolics and some other resinous adhesives, the epoxies cure without releasing water or other condensation by-products. The epoxies cure with only a fraction of the shrinkage of vinyl-type adhesives such as polyesters and acrylics and, therefore, give a stronger bond. Several other advantages of cured epoxies are their resistance to moisture and high resistance to heat transfer and electric breakdown.

Thermal stability is probably the one attribute which limits the more general applicability of epoxy adhesives. Even the best epoxy systems, such as those derived from bis-phenol A, are not serviceable above 350°F. Combined epoxy-phenolics are very versatile adhesives and are serviceable to 350°F continuously. They retain satisfactory strength for short exposures up to 500°F. Aside from the problem of thermal stability, epoxies offer an unlimited scope of modification and application possibilities. One solution to this dilema is to incorporate a group into the system to increase thermal stability without detracting from the favorable properties of the epoxy. Since the carborane polyhedron appears to impart excellent thermal and physical properties to polymer structures, it seems natural to construct a polymer system which combines a carborane moiety with an epoxy function.

2. DISCUSSION

The objective of this program is to synthesize adhesives that are stable above 600°F, and as high as 1000°F for aerospace applications. To achieve this objective, we are preparing epoxy adhesives containing carborane units in the monomer structure.

A. Chemistry of the Carboranes

The carboranes (ortho-, meta-, and para-) are low-density, non-polar, organic-like substances with camphoraceous odors. Derivatives vary from liquids such as isopropyl-carborane to high-melting, easily sublimable solids. They are extremely soluble in all the common organic solvents. Because of this high solubility, good crystallizing solvents are difficult to find. The carboranes are usually purified by sublimation, distillation or chromatographic processes. Their basic structures are inert to most oxidizing, reducing, or hydrolytic environments.

A wide range of organofunctional carboranes have been prepared, including acid chlorides, acid anhydrides, esters, lactones, phosphates, ethers, halides, Grignard reagents, silanes and epoxy compounds. Olefinic carboranes like 1-vinylcarborane, 1-isopropenylcarborane and 1-butenylcarborane are very stable and do not readily undergo radical, ionic or Ziegler-type polymerizations. Thus, they behave more like fluorinated alkenes than vinylbenzenes. Ionic addition reactions are very sluggish when the olefinic bond is not separated from the carborane nucleus by several methylene groups. On the other hand, hydrogenation and free-radical reactions, such as the light catalyzed addition of chlorine proceed normally.

Several research groups have concentrated recently on the opportunities for the synthesis of high-temperature-stable polymers by the incorporation of carborane and neocarborane units into polymer structures with other stable groups.[1]* Heavy emphasis has been placed on the silicones because they offer a minimum of synthetic difficulties. At least four distinct silicone-neocarborane and silicone-carborane copolymers have been described.
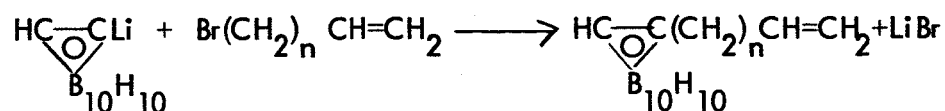
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* References are given at the end of this report.

Each has been examined and found to possess excellent thermal stabilities near 450°F. Even polysiloxanes having pendant carborane units removed by four methylene groups still display thermal stabilities about 250°C higher than the best commercial silicone. This increased thermal stability of polymers is due in part to the electron deficiency of the carborane group and its influence on the thermal stability of adjacent chemical bonds. The bulky, three-dimensional ring system also induces a degree of internal plasticization in the polymer, presumably because it prevents close-packing of the polymer chains.
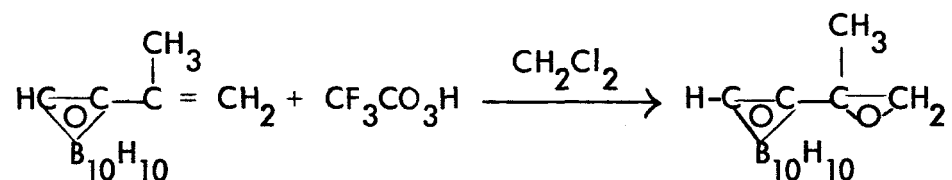
B. Technical Approach

The current program is designed to synthesize and evaluate hybrid carborane-epoxy adhesives in four phases. Phase I and II deal with the synthesis of alkenyl-carborane intermediates and their conversion to carborane-epoxy monomers. Phases III and IV deal with curing and polymerization studies on the epoxy mono-mers and an evaluation of the bond properties of the resulting adhesives.

Alkenylcarboranes have previously been prepared by the reaction of the Grignard derivative of bromomethylcarborane with bromoalkenes[2]. However, a by-product is formed due to a rearrangement of the Grignard. Therefore, we are preparing alkenylcarboranes by use of a lithiocarborane as follows:

$$HC \text{---} CLi + Br(CH_2)_n CH=CH_2 \longrightarrow HC \text{---} C(CH_2)_n CH=CH_2 + LiBr$$
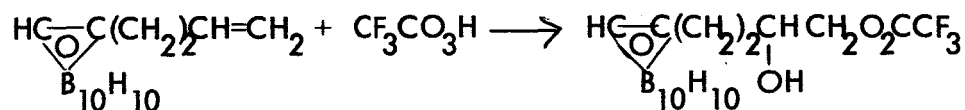$$B_{10}H_{10} \qquad\qquad\qquad\qquad B_{10}H_{10}$$

Similarly, the disubstituted carboranes are being prepared. We are using alkenes where n is 2, 3, or 4 and we expect, for reasons given below, that the best epoxies will be obtained where n is 4. However, the initial work reported here deals with carboranes where n=2 and was done to provide basic information on the chemistry of alkenylcarboranes.

Alkenylcarboranes can be converted to epoxides by trifluoroperacetic acid.

$$
HC \underset{\underset{B_{10}H_{10}}{\overset{O}{\bigtriangleup}}}{} C - \overset{\overset{CH_3}{|}}{C} = CH_2 + CF_3CO_3H \xrightarrow{CH_2Cl_2} H - C \underset{\underset{B_{10}H_{10}}{\overset{O}{\bigtriangleup}}}{} C - \overset{\overset{CH_3}{|}}{C} \overset{O}{\bigtriangleup} CH_2
$$

However, with unbuffered trifluoroperacetic acid, butenylcarborane forms a glycol trifluoroacetate, presumably through the epoxide intermediate.

$$
HC \underset{\underset{B_{10}H_{10}}{\overset{O}{\bigtriangleup}}}{} C(CH_2)_2CH=CH_2 + CF_3CO_3H \longrightarrow HC \underset{\underset{B_{10}H_{10}}{\overset{O}{\bigtriangleup}}}{} C(CH_2)_2 \overset{}{\underset{OH}{\overset{|}{C}H}} CH_2O_2CCF_3
$$

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The intermediate epoxide is isolated only when the reaction is carried out under alkaline conditions

$$HC\underset{O}{-}C(CH_2)_2CH=CH_2 + CF_3CO_3H \xrightarrow[Na_2CO_3]{} HC\underset{O}{-}C(CH_2)_2CH\underset{O}{-}CH_2$$
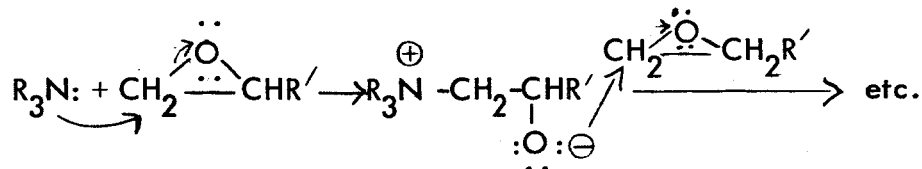$$B_{10}H_{10} \qquad\qquad B_{10}H_{10}$$
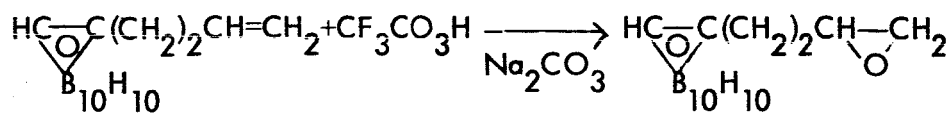
Little is known of the chemistry of this monomer. The difference between the isopropenyl and butenyl derivative in the ease-of-ring opening has been attributed to a decrease in the effect of the electron-withdrawing influence of the polyhedron on the epoxy ring. Therefore, the further the ring is from the polyhedron, the more the carborane epoxy will behave like an ordinary organic epoxy with respect to ring opening (i.e. polymerization) reactions.
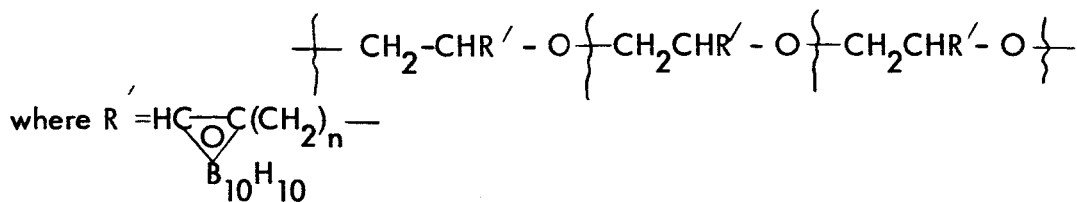
Epoxy resins can be polymerized (or cured) by 3 different reactions:

1. direct linkage between epoxy groups;

2. linkage of epoxy groups with aromatic and aliphatic radicals;

3. crosslinking with the curing agent through various radicals.

Reactions 2 and 3 introduce additional organic functions and therefore would limit the effectiveness of the carborane moiety in increasing the thermal stability of the epoxy. The following reactions illustrate the composition that would be formed from the base-catalyzed ring opening of a monoepoxyalkylcarborane.

$$R_3N: + CH_2\overset{O}{-}CHR' \longrightarrow R_3N^{\oplus}-CH_2-\underset{:O:^{\ominus}}{\overset{|}{C}HR'}\xrightarrow{CH_2\overset{O}{-}CH_2R'} etc.$$

to give

$$-\!\!\left[CH_2-CHR'-O\right.\!\left[CH_2CHR'-O\right.\!\left[CH_2CHR'-O\right]\!-$$

where $R' = HC\underset{O}{-}C(CH_2)_n-$
$$B_{10}H_{10}$$

In a similar fashion, both chain-formation and cross-linking can occur when the difunctional carborane derivative is employed.

Later in the program, and as materials become available, an evaluation will be made of the adhesive properties of the polymerized epoxycarboranes. (Phase III and IV). This will include bond strength measurements, temperature tests, density, thermal conductivity and nondestructive methods of testing. This evaluation will be accomplished in cooperation with Mr. I. K. Spiker, Technical Representative.

C. Technical Progress

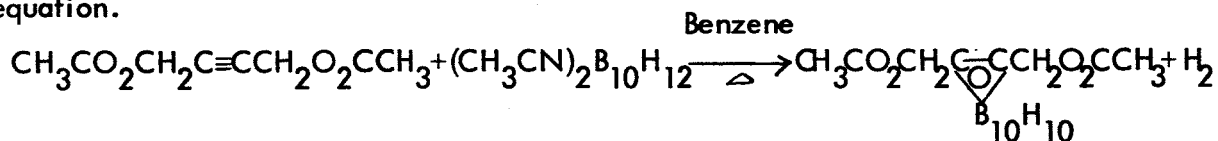1. Preparation of 6,9-bis(acetonitrilo)decaborane (BAND)

    A total of 2600 gm of BAND was prepare easily and routinely from 2100 gm of decaborane in six batches.

    $$B_{10}H_{14} + 2CH_3CN \longrightarrow (CH_3CN)_2B_{10}H_{12} + H_2$$
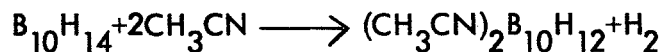
    The overall conversion of decaborane to BAND was 77%. The reaction proceeds smoothly but must be done in a laboratory hood to prevent the accumulation of large amounts of hydrogen which represents a significant safety hazard.

2. Preparation of 1,2-bis(acetoxymethyl)carborane (BAMC)

    The preparation of this material was carried out according to the following equation.

    $$CH_3CO_2CH_2C\equiv CCH_2O_2CCH_3 + (CH_3CN)_2B_{10}H_{12} \xrightarrow[\triangle]{Benzene} CH_3CO_2CH_2C = CCH_2O_2CCH_3 + H_2$$
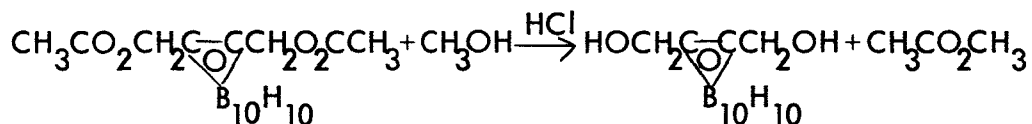 $$B_{10}H_{10}$$

    Four 175 gm batches of BAND were converted to BAMC. A total of 450 gm of BAMC was obtained for an overall conversion of BAND to product of 45%. While we would like to have accelerated matters by running this reaction in one large batch, safety precautions mitigated against any further increase in batch size. An exotherm always develops at the boiling point of the benzene solvent liberating large amounts

of hydrogen and solvent. Although the reaction is run in a laboratory hood, the accumulation of any substantial quantity of flammable or potentially explosive gases represents a significant safety hazard. Secondly, considerable quantities of BAND are converted to a by-product called "B-solids." Above $85°C$, a violent fume-off may develop due to the decomposition of this material. Batch sizes are kept low in order to avoid accumulation of "B-solids" and in order to minimize any side reactions of this little characterized by-product.

The crude BAMC must be recrystallized several times from pentane to remove impurities which lower the melting point from the reported value of $42-44°C$ [2] to near room temperature. However, unreacted butyne will not be removed by this process since its solubility in pentane parallels that of BAMC. The presence of this impurity may cause the difficulty observed in the purification of 1,2-bis(hydroxymethyl)carborane obtained in the next step.

3. Preparation of 1,2-bis(hydroxymethyl)carborane (BHMC)

   The material was prepared by the acid-catalyzed transesterification of BAMC.

   $$CH_3CO_2CH_2C{-}CCH_2O_2CCH_3 + CH_3OH \xrightarrow{HCl} HOCH_2C{-}CCH_2OH + CH_3CO_2CH_3$$
   $$B_{10}H_{10} \qquad\qquad\qquad B_{10}H_{10}$$

   A total of 250 gm of BAMC was treated in the above manner and gave 214 gm (theoretical -177 gm) of brown product. The color and excess weight might be due to products of a transesterification of impurities in the BAMC. Recrystallization of a small amount from cyclohexane gave a white product. The bulk of the crude product is to be purified in a Soxhlet extractor with cyclohexane.

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4. Preparation of Carborane

Carborane was prepared by the oxidation of 1,2-bis(hydroxymethyl)carborane with alkaline potassium permanganate.

$$3HOCH_2C\underset{B_{10}H_{12}}{-}CCH_2OH + 4KOH + 8KMnO_4 \longrightarrow 3C_2B_{10}H_{12} + 8MnO_2 + 6K_2CO_3 + 8H_2O$$
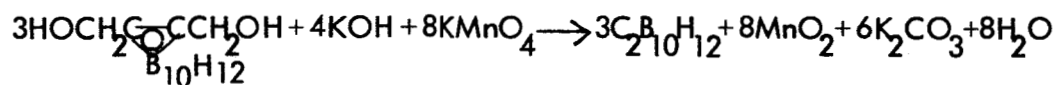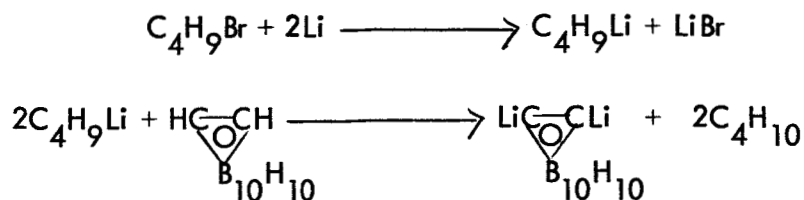
The finely powdered potassium permanganate was added at such a rate that there was no appreciable quantity of unreacted reagent present at any time. Two small batches of BHMC were treated in this manner, giving a total of 15 gm. of carborane.
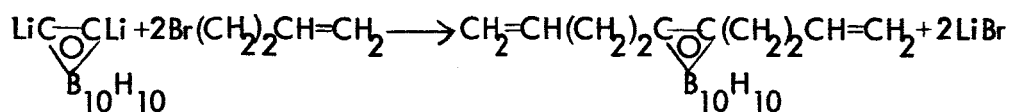
5. Purification of 1-(3-butenyl)carborane

The infrared spectrum (KBr pellet) of the product obtained on crystallization from methanol-water is shown in Figure 1. The prominent portions of the spectrum are peaks at 3085 cm^{-1} (shoulder), C-H stretch of the methylene of the -CH=CH$_2$ group; 3070 cm^{-1}, carborane C-H stretch; $2585cm^{-1}$, terminal B-H stretch; 910 cm^{-1}, CH$_2$ out of-place deformation of the -CH=CH$_2$ group and 715 cm^{-1}, carborane cage structure. [3-4] (The broad peaks at 3600 to 3200 cm^{-1} and the peaks at $1650 - 1700$ cm^{-1} and $1550-1600$ cm^{-1} are due to water and impurities in the potassium bromide.) The assignment of the peaks at 3080 cm^{-1} and 3065 cm^{-1} is made on the basis of reversal of relative intensities in the spectrum of the product obtained in the preparation of the bis(butenyl)carborane.

6. Preparation of 1,2-bis(3-butenyl)carborane

The bis(butenyl)carborane was prepared by the following reaction sequence.

$$C_4H_9Br + 2Li \longrightarrow C_4H_9Li + LiBr$$

$$2C_4H_9Li + HC\underset{B_{10}H_{10}}{-}CH \longrightarrow LiC\underset{B_{10}H_{10}}{-}CLi + 2C_4H_{10}$$

$$LiC \underset{\underset{B_{10}H_{10}}{}}{\overset{}{C}} Li + 2Br(CH_2)_2CH{=}CH_2 \longrightarrow CH_2{=}CH(CH_2)_2 C \underset{\underset{B_{10}H_{10}}{}}{\overset{}{C}} (CH_2)_2 CH{=}CH_2 + 2LiBr$$

The crude product (17.2 gm) was fractionally crystallized from methanol–water.

Fraction	Weight (gm)	Melting Point °C
1	0.5	66 – 68
2	6.0	66 – 68
3	4.0	60 – 63
4	Residual	Oil

The infrared spectra of all three fractions were identical but showed different relative intensities at 720 and 910 cm^{-1}. (See Figure 2 for the infrared spectrum of Fraction 3) A semi–quantitative comparison of the ratio of the optical density of the peak at 910 cm^{-1} (CH$_2$ out–of–plane deformation of the methylene of the –CH=CH$_2$ group) to the optical density of the peak at 720 cm^{-1} (carborane cage) with that of the comparable ratio from the spectrum of 1-(3-butenyl)carborane showed the expected enhancement.

Material	$\dfrac{910 \text{ cm}^{-1} \text{ Optical Density}}{720 \text{ cm}^{-1} \text{ Optical Density}}$
Butenylcarborane	1.0
bis(3-butenyl)carborane (Fraction #1)	6.0
bis(3-butenyl)carborane (Fraction #2)	3.7
bis(3-butenyl)carborane (Fraction #3)	4.5

Based on these results, Fraction 1 is probably the pure bis(butenyl)carborane. This will be confirmed by elemental analysis. Fractions 2 and 3 will be purified further by recrystallization. Fraction 4 may be distilled. The most

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likely impurity in the product would be monobutenylcarborane resulting from reaction of monolithiocarborane with the bromobutene. The infrared spectra did not conclusively show the absence of a monosubstituted carborane. However, the peak at 3070 cm^{-1} and shoulder at 3085 cm^{-1} in the spectrum of monobutenylcarborane have become a shoulder and peak respectively in all three fractions of the bis(butenyl)carborane product. These absorptions are attributed to the C–H stretch of the methylene of the –CH=CH$_2$ group (3085 cm^{-1}) and the C–H stretch of carborane (3070 cm^{-1}). This trend then, is in the order that would be expected for the spectrum of the disubstituted carborane. In addition, the B–H stretch at 2585 cm^{-1} in the spectrum of the monobutenylcarborane has been split into a doublet in the spectra of all three fractions isolated in the bisbutenyl preparation (2570 and 2600 cm^{-1} – peaks of about equal intensity.)
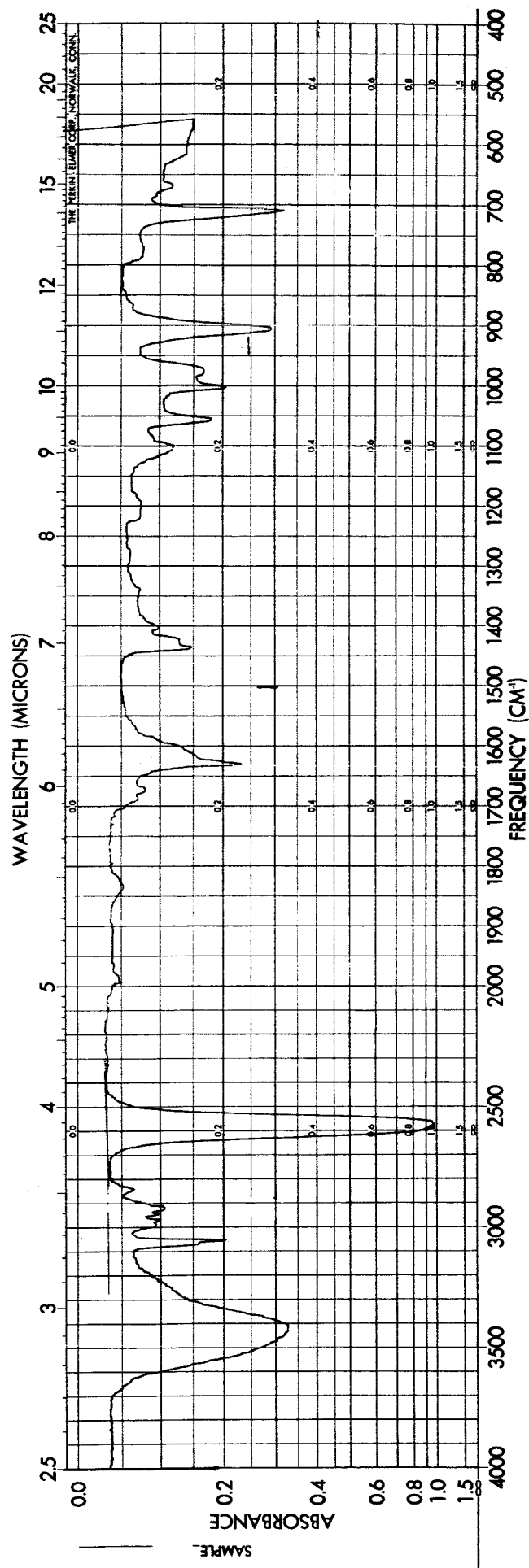
FIGURE 1

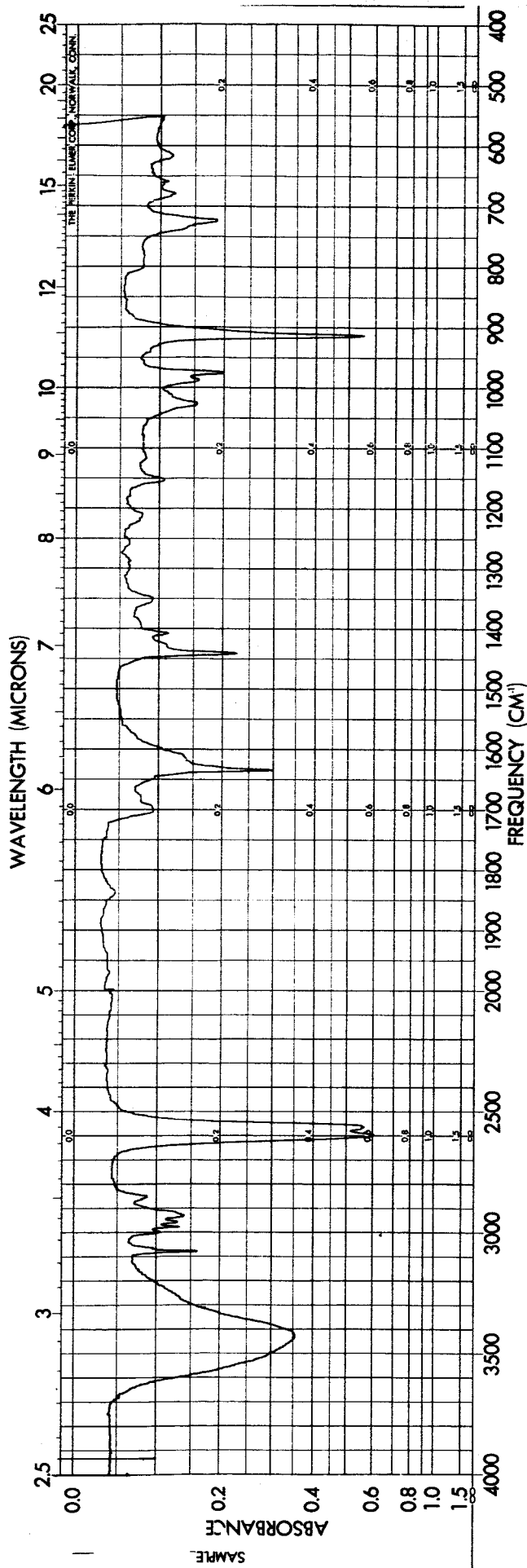INFRARED SPECTRUM OF 1-(3-BUTENYL)CARBORANE

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FIGURE 2

INFRARED SPECTRUM OF CRUDE 1,2-BIS(3-BUTENYL)CARBORANE

3. FUTURE WORK

Efforts will continue to be concentrated on Phase I, synthesis of alkenylcarborane and dialkenylcarborane intermediates and Phase II, synthesis of carborane-epoxy monomers.

1. The crude 1,2-bis(3-butenyl)carborane now on-hand will be purified by fractional crystallization, and its composition and purity will be demonstrated by elemental analysis.

2. An investigation will be made of the reaction of purified 1-(3-butenyl)-carborane with several common expoxidizing agents.

3. Similar epoxidation studies will then be initiated on the bisbutenylcarborane.

4. Additional quantities of carborane will be synthesized using decaborane and other intermediates previously prepared and reported in this Quarterly. The availability of a continuing supply of carborane is necessary for the preparation of alkenylcarboranes.

5. We have selected epoxyhexylcarborane as the next monomer to be synthesized and studied. Monolithiocarborane will be condensed with 6-bromo-1-hexene to prepare 1-(5-hexenyl)carborane.

Phase III and Phase IV, polymerization studies and adhesive bond property evaluation, are to be undertaken as epoxy materials become available.

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4. EXPERIMENTAL

A. Preparation of 6,9-bis(acetonitro)decaborane (BAND)

In a typical preparation, 300 gm of crude decaborane was added with stirring to 1500 ml of chromatoquality acentronitrile. The resulting suspension was filtered, and the residue was discarded. The decaborane – acetonitile solution was transferred to a three liter flask equipped with a mechanical stirrer, thermometer and reflux condensor. The flask was heated at 80-84°C for 4 1/2 hours, during which time a yellow solid formed. The mixture was cooled and the solid product was collected on a Büchner funnel using No. 42 filter paper. The product was washed with several 100 ml portions of fresh acetonitrile and air-dried. A light-yellow product (BAND) was obtained. The filtrate, containing unreacted decaborane and BAND was used in place of fresh acetonitrile for a subsequent run. This reuse of filtrate is reflected in the percent conversion of decaborane to BAND as shown in the following table:

Batch	$B_{10}H_{14}$ Used (gm)	BAND Obtained (gm)	% Conversion
1	300	330	67
2*	300	432	88
3	193	210	67
4*	300	385	78
5*	300	394	80
6*	300	397	81

*Using mother liquid from previous batch.

B. Preparation of 1,2-bis(acetoxymethyl)carborane (BAMC)

In a typical preparation, a mixture of 175 gm BAND, 151 gm of 1,4-bis(acetoxy)butyne -2 and one liter of benzene was heated in a three liter flask equipped with a mechanical stirrer, thermometer and reflux condensor. The mixture was refluxed at 82-85°C for 20 to 24 hours. The resulting suspension was cooled and Büchner - filtered using Number 42 filter paper. Benzene-insoluble "B-solids" retained on the filter paper were destroyed by reaction with methanol. The benzene solvent was removed from the brown filtrate on a vacuum rotary evaporator at 40-45°C. The dark brown semi-solid remaining in the flask was agitated with one liter of pentane. The suspension was allowed to settle, and the supernatant liquid was gravity-filtered to give a light yellow solution. The solution was cooled to -80°C, and the resulting solid (crude BAMC) was filtered by suction. The residual brown solids were treated with fresh 500 ml portions of pentane until no appreciable amount of solid appeared when the filtered liquid was cooled to -80°C. The brown pentane-insoluble "B-solids" were destroyed as described above. The combined off-white product was usually a semi-solid at room temperature. (The reported melting point of BAMC is 42-43°C [5].) Possible impurities are "B-solids" and unreacted butyne. BAND is relatively insoluble in pentane. After standing for several days, a small portion of the crude solid would not re-dissolve in fresh pentane. The purest product was obtained by adding enough fresh pentane to dissolve all but the most insoluble material, filtering, cooling to -80°C, filtering, washing the precipitate with cold fresh pentane and suction drying. The product obtained was white and melted at 38-42°C. Conversions based on starting BAND are listed below:

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Batch	BAND Used (gm)	BAMC Obtained (gm)	% Conversion
1	175	100	40
2	175	99	39
3	175	154	62
4	175	100	40

C. Preparation of 1,2-Bis(hydroxymethyl)carborane (BHMC)

Gaseous hydrogen chloride was passed into a solution of 250 gm of BAMC in 1.3 liters of methanol. The solution was refluxed for four hours with a continuous stream of hydrogen chloride bubbling through the solution. During this treatment, the solution turned dark brown. Removal of the solvent on a vacuum rotary-evaporator at 30-35°C gave a moist brown solid (214 gm - theoretical 177 gm). Decolorization with charcoal in hot toluene and recrystallization from toluene - heptane had no appreciable effect on the color. However, recrystallization from cyclohexane yielded a white product whose infrared spectrum was essentially identical to that of a previously authenticated sample of BHMC.

D. Preparation of Carborane

In a typical preparation, a suspension of 20.3 gm (0.100 moles) of 1,2-bis(hydroxymethyl)-carborane in 200 ml of 20% aqueous potassium hydroxide was stirred at 20°C. Potassium permanganate (48.2 gm-0.273 moles) was slowly added over a 2-2.5 hour period. An initial deep green color (MnO_4^{2-}) was observed which gave way to a brown suspension (MnO_2 and carborane). The suspension was stirred for an additional hour, cooled to 0°C, and acidified with excess concentrated hydrochloric acid. Several ml of ethyl ether were

added to break the resulting foam. In order to convert MnO_2 to Mn^{2+}, a solution of

3 gm of $NaHSO_3$ (0.30 mole – an excess of the amount needed for complete reaction) in

150 ml of water was slowly added to the acidified mixture. The resulting white suspension

was filtered, and the solid was washed with water and vacuum dried at room temperature.

Recrystallization from a 1-butanol-heptane mixture gave 8.2 gm of product (representing a

57% conversion of BHMC to carborane). The infrared spectrum of the product was identical

to that of carborane.

E. Purification of 1-(3-butenyl)carborane

Attempts to remove a liquid impurity from a crude shelf sample of 1-(3-butenyl)carborane

by vacuum sublimation and by recrystallization from cyclohexane and heptane were un-

successful. Crystallization of a 5.0 gm sample from methanol-water followed by vacuum

drying at room temperature gave 4.1 gm of a white solid. The melting point of 42-44°C

compared favorably with the reported melting point for 1-(3-butenyl)carborane of 45-46°C.[2]

The infrared spectrum of the purified material is found in Figure 1.

F. Preparation of 1,2-Bis(3-butenyl)carborane

Lithium wire was scraped free of oxide coating and weighed under mineral oil (2.7 gm =

0.39 moles). The wire was cut into small pieces and dropped into a three-necked flask

containing 150 ml of anhydrous ethyl ether. The flask was equipped with a nitrogen flow

inlet-thermometer combination, stirrer and dropping funnel. Bromobutane (27.3 gm = 0.20

moles) was added dropwise over a two hour period to the flask maintained at 0-10°C. The

resulting milky solution contained several pieces of unreacted lithium wire. Carborane

(11.5 gm, 0.08 moles) was dissolved in 150 ml of anhydrous ether and added slowly to the

flask again maintained at 0°C over a half-hour period. Solid dilithiocarborane precipitated and a gas (butane) was evolved. The thermometer-nitrogen flow inlet combination was replaced with a condensor, and the mixture was heated to reflux. Over a five minute period, 4-bromo-1-butene (28.7 gm - 0.21 moles) was added to the refluxing solution. The mixture was refluxed for an additional two hours, cooled to room temperature and poured into 200 ml of water. Some reactivity was observed that was probably due to unreacted lithium metal or lithiocarborane. The ether layer was separated, dried over magnesium sulphate, and solvent was removed on a rotary vacuum evaporator at 60°C. At room temperature, the product (17.2 gm) was a wet solid. The product was dissolved in 100 ml of methanol at room temperature and fractionally crystallized by addition of water. Each fraction was vacuum dried to constant weight.

Fraction	H_2O added (ml)	Product (gm)	M.P.°C
1	1	0.5	66-8
2	5	6.0	66-8
3	20	4.0	60-3
4	20	0.1	

Fraction 4 was combined with Fraction 3 and infrared spectra of all three fractions were recorded. The addition of 100 ml of methanol to the final cloudy filtrate partially cleared the suspension and gave an oil on the bottom of the flask. The contents of the flask were saved for future study.

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