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Aerospace Research Center

MATERIALS DEPARTMENT

HIGH TEMPERATURE STABLE CARBORANE ADHESIVES

CONTRACT NASA 9 - 5527

Second Quarterly Progress Report

by

Dr. Robert Barnes

Submitted to:

National Aeronautics and Space Administration
Manned Spacecraft Center
2101 Webster-Seabrook Road,
Houston, Texas.

[redacted]

June 20, 1966

GENERAL
PRECISION
AEROSPACE
Little Falls, New Jersey

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2101 Webster-Seabrook Road,
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Approved: Daniel Grafstein
Daniel Grafstein
Principal Staff Scientist
Manager, Materials Department

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RESEARCH CENTER
AEROSPACE GROUP
GENERAL PRECISION, INC.
LITTLE FALLS, NEW JERSEY

ABSTRACT

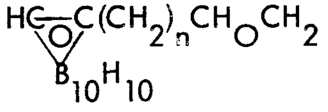
CONTRACT NASA 9-5527

This is the second 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 March 21, 1966 to June 20, 1966.

During the second quarter, progress was noted in the following areas:

1. During and Polymerization Studies (Phase III)

A preliminary evaluation was made of the polymerization characteristics of the epoxy materials prepared during the period. Epoxybutylcarborane has been successfully polymerized in the presence of DMP-30 catalyst at a temperature of 85-90°C. Under these conditions, the liquid epoxy sets to a non-flowing viscous liquid. The polymer is a very brittle solid at room temperature. This result shows that the oxirane ring in the series

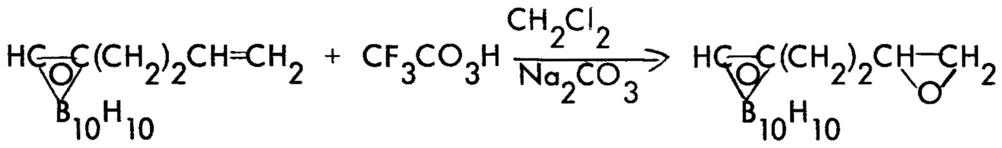


where n= 2 is opened under relatively mild conditions. The result is encouraging and indicates that application studies should proceed smoothly.

2. Synthesis of Carborane-epoxy Monomers (Phase II)

Epoxybutylcarborane was prepared by the following reaction route

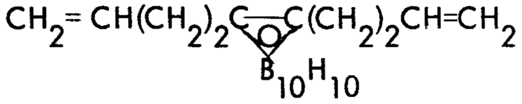
$$(CF_3CO)_2O \xrightarrow{H_2O_2\ (90\%)} CF_3CO_3H$$

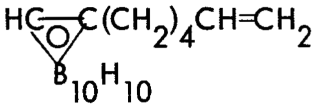


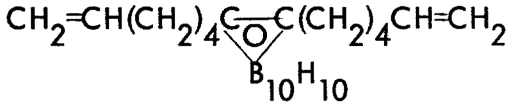
A total of 22.4 gm of the epoxy monomer was prepared in five batches.

3. Synthesis of Alkenylcarborane Intermediates (Phase I)

Progress was made toward the synthesis of the following monoalkenylcarboranes and dialkenylcarboranes







The following materials were synthesized to assure a supply of alkenylcarborane intermediates.

Material	Number of Batches	Amount, grams
1,2-bis(acetoxymethyl)carborane	2	190
1,2-bis(hydroxymethyl)carborane	1	119
carborane	7	62

ADMINISTRATIVE INFORMATION

This 12-month program is being sponsored by the NASA-Manned Spacecraft Center, Houston, Texas under Contract NASA 9-5527, Control No. P.R. No. 5320022. This Quarterly report covers the period from March 21, 1966 through June 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. Mr. William Benko aided in the preparation of several of the intermediate compounds. Infrared spectra were obtained with the assistance of Mr. Lawrence Flint and Mr. Clifford Whitmore.

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I. INTRODUCTION

The object of this program is the synthesis of 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.

Aside from the problem of thermal stability, conventional epoxies offer an unlimited scope of modification and application possibilities. However, the best epoxy systems, such as those derived from bis-phenol A, are not serviceable above 350°F. Combined epoxy phenols are very versatile adhesives and are serviceable to 350°F continuously. They retain satisfactory strength for short exposures up to 500°F. One solution to this dilemma is to try to incorporate a group into the system which serves 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.

Several research groups have concentrated recently on the synthesis of high-temperature - stable polymers by the incorporation of carborane and neocarborane units into polymer structures with other groups(1)*. The increased thermal stability of these polymers over conventional systems 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.

During the first quarter (2), efforts were directed toward 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

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* References are given at the end of this report.

of decaborane in a stepwise fashion to carborane. The hitherto unreported dialkenylcarborane, 1,2-bis(3-butenyl)carborane,was prepared by the reaction of dilithiocarborane with 4-bromo-1-butene. As described in the next section, during the current quarter the program progressed into a study of the reactivity of epoxyalkylcarboranes.

II. DISCUSSION

A. Technical Approach

The project has been divided into the following four phases:

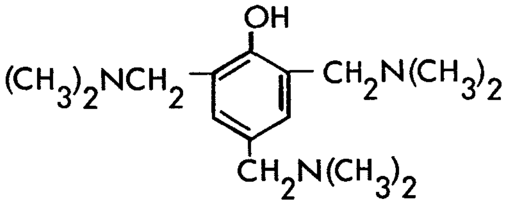
I. Synthesis of alkenylcarborane and dialkenylcarborane intermediates.
II. Synthesis of carborane-epoxy monomers.
III. Curing and polymerization studies.
IV. Adhesive bond property evaluation.

The major portion of the effort during the present quarter was devoted to Phase I and II. In addition, highly encouraging results were obtained in a preliminary evaluation of the polymerization of a carborane-epoxy (Phase III).

B. Technical Progress

1. Polymerization of 4-(carboranyl)-1-butene oxide

An initial examination was made of the polymerization characteristics of the monobutenylcarborane epoxide, prepared as described in the following section and used without further purification. The catalyst chosen to initiate the polymerization was DMP-30; tris(dimethylaminomethyl)phenol.



The melting point of the epoxybutenylcarborane of 60-63°C dictated that a higher temperature would have to be used for a homogeneous polymerization. Accordingly, one gram samples of the epoxy were heated at 80-90°C. With 20 drops of catalyst, the epoxy turned to a non-flowing viscous liquid in 30 minutes. With 5 drops of catalyst, the same consistency was obtained within a one hour period. Brittle solids were obtained when the samples were cooled to room temperature.

The infrared spectra of the polymerized materials were difficult to interpret because of their diffuse nature and the presence of absorption bonds attributable to the catalyst. Both spectra contained a shoulder at 2540 cm^{-1} associated with the B-H stretching frequency at 2580 cm^{-1}. This shoulder was weaker in the system using 5 drops of catalyst. The spectrum of the unpolymerized epoxy contained a peak at 860 cm^{-1} which was attributed to the oxirane linkage. The ratio of the peak at 720 cm^{-1} (carborane cage) to the epoxy peak at 860 cm^{-1} had increased as expected on treatment with the catalyst, as is shown below.

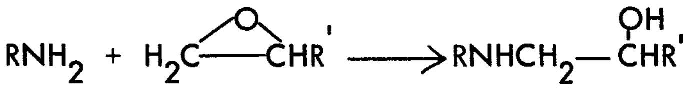
Material	$\frac{720\ \text{cm}^{-1}\ \text{Optical Density}}{860\ \text{cm}^{-1}\ \text{Optical Density}}$
butenylcarborane epoxide	1.58
catalytically heated	3.25

There were no other pertinent features in the spectra that could be used to determine the extent of polymerization.

The stability of the uncatalyzed epoxy was then investigated. There was no visible change in viscosity upon heating at 85-90°C for one hour, and an infrared spectrum of the resulting solid was identical to the starting material.

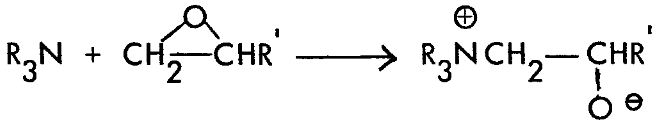
An attempt was made to determine if the appearance of a shoulder or the B-H stretching frequency in the infrared spectrum of the polymer was due to reaction of the catalyst with the carborane cage. Simple carboranyl compounds adduct with certain strong primary amine bases as well as undergoing competing degradation reactions. In the former, the typical cage band at 714 cm^{-1} disappears and the BH absorption shifts to 2500 cm^{-1} (3). To test the possible effect of catalyst on the carborane cage, a sample of monobutenylcarborane was heated at 85-90°C in the presence of the catalyst. Again, there was no visible change in the viscosity of the sample of 85-90°C. An infrared spectrum of the "wet" solid at room temperature was essentially identical to the superposition of the spectra of the individual specie. Some broadening of the BH absorption had occurred but there was no evidence of a peak shift or the appearance of a shoulder. This interpretation indicates that attack on the carborane cage did not occur to an appreciable extent.

The choice of tris(dimethylaminomethyl)phenol as the curing agent was based on several factors. First, in order to limit the introduction of organic moieties into the cured system in any large amount, a catalytic system was chosen over that involving a reactive hardener. A reactive hardener containing an active hydrogen (e.g. a primary amine) would enter into the polymerization reaction in the following manner:



$$RNH_2 + H_2C\overset{O}{\frown}CHR' \longrightarrow RNHCH_2-\overset{OH}{C}HR'$$

The products of these reactions are secondary alcohols. However, in this case, these groups do not combine with other epoxides(4). They do, however, stimulate the remaining amine to react more quickly with other epoxide linkages. In contrast to the use of a reactive hardener, catalytic curing system (e.g. tertiary amines) cure in the following fashion(5).



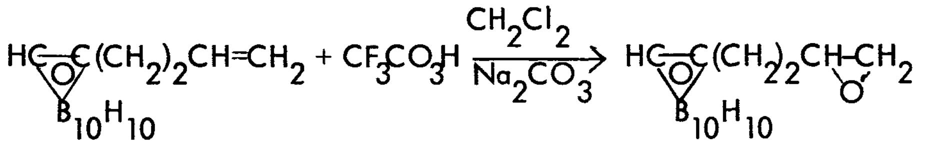
$$R_3N + CH_2\overset{O}{\frown}CHR' \longrightarrow R_3\overset{\oplus}{N}CH_2-\underset{O^{\ominus}}{C}HR'$$

The negative portion of the molecule (anion) then proceeds to attack another epoxide linkage etc. This results in a very long chain system. In this case, the number of molecules of catalyst needed to initiate polymerization is very limited.

The second determining factor in the choice of tris(dimethylaminomethyl)phenol as the catalyst was the nature of the reagent itself. The substance is considered to be one of the most reactive catalysts since it contains three tertiary nitrogen atoms. In addition, the phenolic hydroxymethyl group is considered to have a certain accelerating action. At the start of this project, there was some concern as to the deactivating effect of the carborane nucleus on the reactivity of the epoxy linkage. A strong catalyst was chosen to determine whether the system was, indeed, worth pursuing. As is shown here, the linkage is readily opened by a strong catalyst under moderate conditions. Work to be performed in the next period, as described in a following section, will be concerned with an elaboration of the epoxy reactivity and the development of optimum polymerization conditions.

2. Preparation of 4-(carboranyl)-1-butene oxide

Using the procedure of Grafstein and co-workers(3), the epoxybutenylcarborane was prepared according to the following equation:



$$\underset{B_{10}H_{10}}{HC\!-\!C}(CH_2)_2CH{=}CH_2 + CF_3CO_3H \xrightarrow[Na_2CO_3]{CH_2Cl_2} \underset{B_{10}H_{10}}{HC\!-\!C}(CH_2)_2\underset{O}{CH\!-\!CH_2}$$

A total of 22.4 gm of the epoxy monomer was prepared in five batches. Batch sizes were limited to that described in this report until more experience was gained in handling the 90% hydrogen peroxide necessary for the preparation of trifluoroperacetic acid. This work demonstrates the convenience and ease of using 90% hydrogen peroxide as an epoxidation agent for the carborane system. The reaction proceeds smoothly, and no problems were encountered. Naturally, adequate safety precautions were observed.

The by-product in the above system is trifluoroacetic acid which, in the absence of basic media, attacks the epoxy ring to give the hydroxy trifluoroacetate.(3) Trifluoroperoacetic acid also reacts with sodium carbonate but at a much slower rate than the normal acid itself. The peracid reacts much more rapidly with olefins than it does with sodium carbonate. For these reasons, very high yields of epoxy derivatives are obtained with trifluoroperacetic acid.

The infrared spectrum of the epoxybutenylcarborane prepared in this work was recorded as a KBr pellet and was compared to that of the monobutenylcarborane starting material. In the latter compound, the ratio of the optical density of the peak 910 cm^{-1} (out-of-plane deformation of the methylene of the $-CH=CH_2$ group(6)) to the optical density of the peak at 720 cm^{-1} (carborane cage(7)) is 1:1. The corresponding ratio in the spectrum of the epoxy was 0.53:1, showing that a major portion of the alkenylcarborane had reacted. However, a reference quoted in Bellamy lists a bond near 910 cm^{-1} which is characteristic of epoxy compounds (8). This interference suggests that even more of the alkylcarborane has reacted than indicated by the above ratio. Peaks in the spectrum of the epoxy but not in that of the alkene, appear at 830, 850, 1255, and 3000 cm^{-1}. According to Bellamy other characteristic absorption are found in the 1260-1240 cm^{-1} region and in the 830 cm^{-1} region. The region of the C=C stretching vibration (1660-1640 cm^{-1}) is partially obscured due to the background of the KBr pellet. However, a peak at 1640 cm^{-1} in the spectrum of the butenylcarborane appears to have disappeared in the spectrum of the epoxy derivative. Very good agreement was found of the m.p. (60-63°C) with that reported in the literature (60-62°C)(3).

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

The preparation of the first quantity of this material was described in Quarterly Progress Report Number 1.(2) The solid isolated as four solid fractions was combined and again fractionally crystallized from methanol-water. An elemental analysis of a fraction representing 50% of the total product was in excellent agreement with the theoretical values.

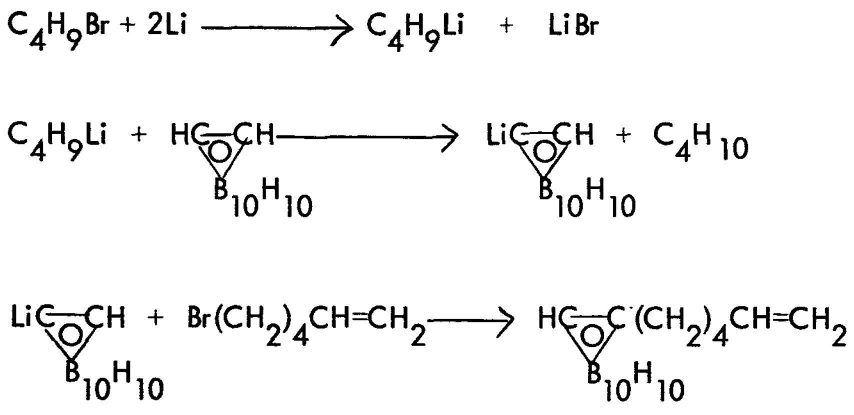
Calcd. for $B_{10}C_{10}H_{24}$: B, 42.8; C, 47.7; H, 9.5

Found: B, 42.4; C, 48.2; H, 9.5

A reaction, similar to that described in the previous report, was carried out using a hexane solution of butyllithium in hexane. The product obtained from 0.21 moles of butyllithium and 0.08 moles of carborane was recrystallized from methanol-water. Four fractions gave a total of 10.9 gm of product representing a theoretical conversion of 55% of reactant to desired product. Melting points and infrared spectra of the fractions remain to be obtained. Preliminary results indicate that the reaction proceeded normally.

4. Preparation of 1-(5-hexenyl)carborane

The following reaction sequence was undertaken to prepare the desired material



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

$$C_4H_9Li + HC\underset{B_{10}H_{10}}{\overset{O}{—}}CH \longrightarrow LiC\underset{B_{10}H_{10}}{\overset{O}{—}}CH + C_4H_{10}$$

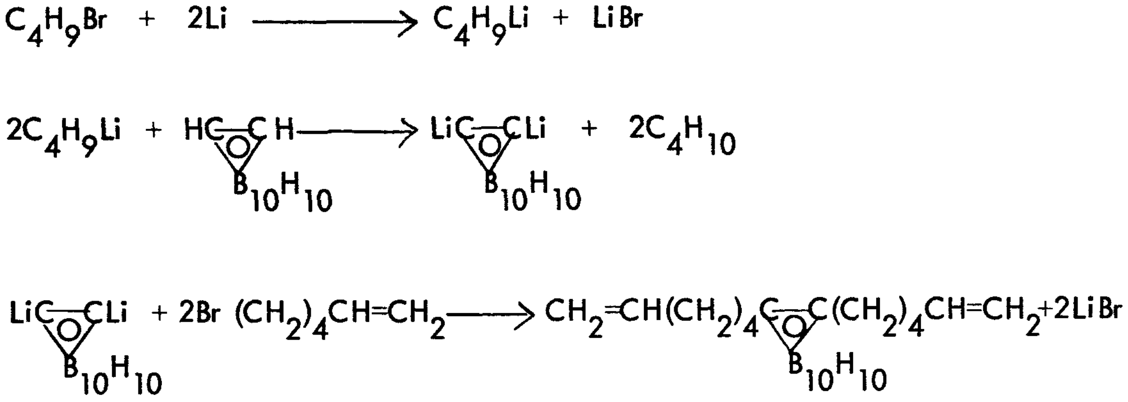
$$LiC\underset{B_{10}H_{10}}{\overset{O}{—}}CH + Br(CH_2)_4CH{=}CH_2 \longrightarrow HC\underset{B_{10}H_{10}}{\overset{O}{—}}C(CH_2)_4CH{=}CH_2$$

An attempted recrystallization of the hexenylcarborane product from methanol-water did not give a solid product. This suggests that the hitherto unreported monohexenylcarborane, like hexylcarborane, is a liquid at room temperature and will have to be purified by distillation. The crude product, after removal of the methanol-water solvent, was saved for further study.

An additional quantity of crude product was obtained using a hexane solution of butyllithium. Pending an infrared analysis of the sample, the product will be combined with the previously obtained sample, and the combined material will be fractionally distilled under vacuum.

5. Preparation of 1,2-bis(5-hexenyl)carborane

The following reaction sequence was investigated for the preparation of bis(hexenyl)-carborane.



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

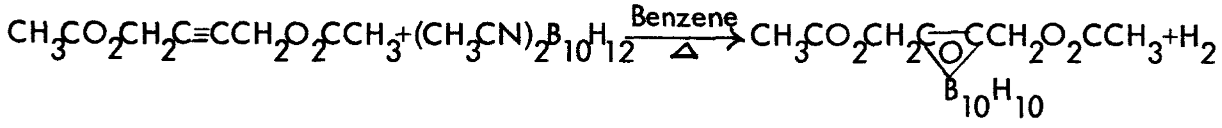
$$2C_4H_9Li + \underset{B_{10}H_{10}}{HC{-}CH} \longrightarrow \underset{B_{10}H_{10}}{LiC{-}CLi} + 2C_4H_{10}$$

$$\underset{B_{10}H_{10}}{LiC{-}CLi} + 2Br(CH_2)_4CH{=}CH_2 \longrightarrow CH_2{=}CH(CH_2)_4\underset{B_{10}H_{10}}{C{-}C}(CH_2)_4CH{=}CH_2 + 2LiBr$$

However, very little of the dilithiocarborane appeared to react, and subsequent treatment of the reaction mixture with water showed that "activity" remained. Separation of the ether extract and subsequent removal of solvent yielded a yellow liquid. The liquid must still be purified. The infrared spectrum, should indicate whether the desired product was formed.

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

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

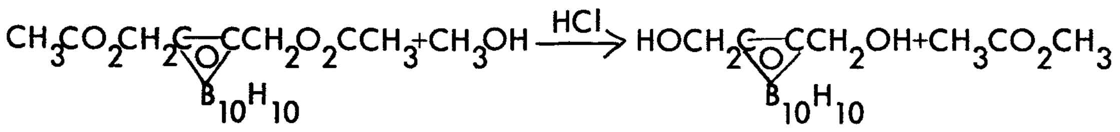


$$CH_3CO_2CH_2C\equiv CCH_2O_2CCH_3+(CH_3CN)_2B_{10}H_{12}\xrightarrow[\Delta]{Benzene}CH_3CO_2CH_2\underset{B_{10}H_{10}}{C\!-\!C}CH_2O_2CCH_3+H_2$$

Two 175 gm batches (Numbers 5 and 6) of 6,9-bis(acetonitrilo)decaborane (BAND) were converted to BAMC. A total of 190gm of BAMC was obtained for an over-all conversion of reactant BAND to product of 39%.

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

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

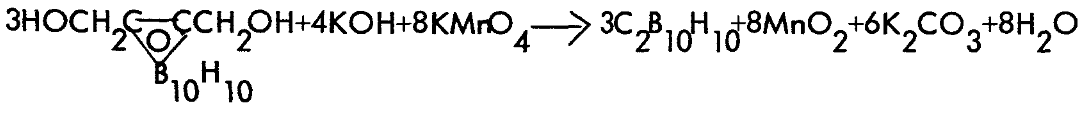


$$CH_3CO_2CH_2\underset{B_{10}H_{10}}{C\!-\!C}CH_2O_2CCH_3+CH_3OH\xrightarrow{HCl}HOCH_2\underset{B_{10}H_{10}}{C\!-\!C}CH_2OH+CH_3CO_2CH_3$$

A total of 250 gm of BAMC (Batch number 2) was treated in the above manner. Recrystallization from water gave 119 gm of a pure white solid (62% conversion based on reactant BAMC).

8. Preparation of Carborane

The preparation of carborane was carried out according to the following equation:



$$3HOCH_2\underset{B_{10}H_{10}}{C\!-\!C}CH_2OH+4KOH+8KMnO_4\longrightarrow 3C_2B_{10}H_{10}+8MnO_2+6K_2CO_3+8H_2O$$

A total of 62.1 gm of carborane was obtained from seven reactions (Batches 3 - 9). This quantity represents an average conversion of 62% of starting material to desired product.

III. FUTURE WORK

Efforts during the next six month period will be concentrated on Phase III, curing and polymerization studies and Phase IV adhesive bond property evaluation. In addition, work will be continued on Phase I, synthesis of alkenylcarborane and dialkenylcarborane intermediates and Phase II, synthesis of carborane-epoxy monomers.

1. The polymerization characteristics of the carborane-epoxy monomers will be studied as a function time, temperature and catalyst. Catalysts on hand are DMP-30 (described earlier), BF_3 monoethylamine, dimethylaminoethanol, diethylaminoethanol and N, N-dimethylbenxylamine.

2. As the carborane-epoxy monomers become available in quantity, studies will be initiated to evaluate their usefulness as adhesives. Thermal stability tests will be made on the raw polymer at 600° to 1000°F in air. An evaluation will be made of the shelf life (stability of the epoxy in the absence of catalyst) and room temperature pot life (time during which the blended epoxy-curing agent remains useable).

3. The alkenylcarborane and dialkenylcarborane intermediates on hand will be characterized. Reactions will be performed to assure an adequate supply of carborane for synthesis of additional supplies of alkenylcarboranes.

4. Epoxy derivatives of dibutenylcarborane, monohexenylcarboarne will be synthesized. The physical properties and chemical reactivity of these compounds will be investigated and correlated to the number of methylene groups separating the carborane nucleus from the oxirane ring.

IV. EXPERIMENTAL

A. Polymerization of 4-(carboranyl)-1-butene oxide

The catalyst used for the preliminary investigation was DMP-30; tris (dimethylaminomethyl) phenol. One gram samples of the epoxy were heated in test tubes in a water bath held at 85-90°C. With 20 drops of catalyst, the epoxy turned to a non-flowing viscous liquid in 30 minutes. With 5 drops of catalyst, the same consistency was obtained within a one hour period.

The thermal stability of the uncatalyzed epoxy was then investigated. Also the stability of the carborane cage was tested in the presence of DMP-30. One gram quantities of the following compounds were heated in closed test tubes to prevent contact of the enclosed materials with water vapor.

1. epoxybutylcarborane + 5 drops DMP-30
2. epoxybutylcarborane
3. monobutenylcarborane + 5 drops catalyst

The samples were heated for one hour in a water bath held at 85-90°C. As expected, system #1 set to a non-flowing viscous liquid . Systems #2 and #3 (monobutenylcarborane melts at 42-44°C) remained free-flowing liquids. On cooling, all three systems solidified, #1 and #2 to brittle solids and #3 to a "wet" solid. Infrared spectra were recorded on all three samples.

B. Preparation of 4-(carboranyl)-1-butene oxide

Trifluoroperacetic acid was prepared in the following manner. Twenty ml of methylene chloride was added to 1.1 ml (0.04 moles) of 90% hydrogen peroxide in an open beaker cooled by ice water. A total of 5.65 ml (0.04 moles) of trifluoroacetic anhydride was added to the above solution with stirring over a ten minute period. Stirring was continued for another ten minutes, after which the solution was transferred to a dropping funnel. A mixture of 30 ml. of methylene chloride, 12.0 gm of sodium carbonate and 5.0 gm of 1-(butenyl)carborane was placed in a 3-necked round bottom flask. The flask was equipped with a mechanical stirrer, reflux condensor (using water passed through an ice-water bath), and the dropping funnel from above. The solution of trifluoroperacetic acid was added dropwise over a 90 minute period. During this time, the temperature of the reactions was maintained below reflux by the use of an ice-water bath. After the addition was completed, the mixture was refluxed for 30 minutes. Following the reflux period, reaction of a drop of the supernatant liquid to starch-iodide paper was negative indicating the absence of peroxides. Gravity filtration of the reaction mixture followed by removal of solvent from the filtrate on a rotary evaporator gave 4.1 gm of a white solid. The melting point of the solid was 60-63°C (lit 60-62°C (3)). The infrared spectrum of the solid, recorded as a KBr pellet, indicated that epoxy formation had occurred. The reaction was repeated four times in an identical fashion to give a total accumulated crude product of 22.4 gm.

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

The material isolated in the previous Quarterly Report as four solid fractions was combined (10.6 gm) and again fractionally crystallized from methanol-water.

Fraction	H_2O added (ml)	Product (gm)	M. P. °C
II-1	3	0.6	71-73
II-2	5	5.2	70-72
II-3	20	3.3	69-71
II-4	20	0.4	58-64
II-5	Rinco off solvent	oil brown	

An elemental analysis of fraction II-2, representing 50% of the total product, was in excellent agreement with the theoretical values.

Calcd. for $B_{10}C_{10}H_{24}$: B, 42.8; C, 47.7; H, 9.5

Found: B, 42.4; C, 48.2; H, 9.5

A reaction, similar to that described in the previous Quarterly Report, was carried out using a solution of butyllithium in hexane. A slight excess of 1.6 M butyllithium solution (135 ml or 0.21 moles of BuLi) was transferred to a dropping funnel in a nitrogen-filled glove bag. The solution was added over a 15 minute period, with stirring, to 11.5 gm (0.08 moles) of carborane dissolved in 75 ml of anhydrous ether contained in a round bottom reaction flask. During the addition, a nitrogen flow was maintained over the system, and the flask was cooled with an ice-water bath. After the addition was complete the suspension of heavy white solid was stirred at room temperature for about one hour. Under nitrogen pressure, the bulk of the solution was forced out of the flask through a specially fitted glass tube with a glass wool plug to prevent loss of solid dilithiocarborane. About 75 ml of anhydrous ether was added to the system with stirring to wash the solid. The bulk of the solution was removed, and the procedure was repeated. About 100 ml of anhydrous ether was added, and the system was heated to reflux. A weighed quantity of 4-bromo-1-butene (27.0 gm=0.2 moles) was added to the system over a 10 minute period. After a two hour reflux period, the white solid had completely disappeared leaving a light brown solution. The reaction mixture was poured into 200 ml of water and thoroughly mixed. The ether layer was separated and dried with magnesium sulphate. The crude product, obtained from the removal of ether solvent on a rotary evaporator, was fractionally recrystallized from methanol-water. The final solution was evaporated on a rotary evaporator at room temperature and gave a brown oil.

Fraction	H_2O added (ml)	Product (gm)
1	15	3.3
2	10	4.6
3	20	2.4
4	10	0.6
5		oil

The samples were submitted for infrared analysis. Results are pending.

D. Preparation of 1-(5-hexenyl)carborane

Lithium wire was scraped free of oxide coating and weighed under mineral oil. The wire (1.4 gm = 0.20 moles) 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, mechanical stirrer and dropping funnel. Bromobutane (13.7 gm = 0.10 moles) was added dropwise over a 30 minute period to the flask maintained at 0-10°C. After an additional one hour of stirring, the resulting solution contained several pieces of unreacted lithium wire. Under nitrogen pressure, the bulk of the solution was forced out of the flask through a specially filtered glass tube with a glass wool plug. About 100 ml of fresh ether was added to the flask, and the butyllithium/ether solution was collected under nitrogen in an additional funnel. This solution was slowly added, at 0°, to another flask containing carborane (14.4 gm=0.1 moles) dissolved in 75 ml of anhydrous ethyl ether. The homogeneous solution containing monolithiocarborane was brought to reflux and 16.3 gm (0.01 moles) of 6-bromo-1-hexene was added over a 15 minute period. After a 90 minute reflux period, the solution was poured into water and thoroughly mixed. The ether layer was separated, dried with magnesium sulphate and evaporated to constant weight on a Rinco Rotary Evaporator.

An attempt to recrystallize the resulting yellow liquid from methanol water was unsuccessful. The crude product, after removal of the methanol-water solvent, was saved for further study.

The preparation was repeated using a hexane solution of butyllithium. Under a nitrogen atmosphere, 60 ml of a 1.6 molar solution (0.096 moles C_4H_9Li was added over a 30 minute period to 14.4 gm (0.1 moles) of carborane dissolved in 150 ml of ethyl ether. The temperature of the flask was maintained at about $10^{\circ}C$ during the course of the addition. Some white solid was present in the resulting brown solution. An additional 50 ml of ethyl ether was added and the solution was heated to reflux without a nitrogen flow. Over a 15 minute period, 13.6 ml (0.1 moles) of 6-bromo-hexene-1 was slowly added. The system cleared to a yellow solution as refluxing was continued for an additional one and a half hours. The solution was cooled to room temperature and poured into 200 ml of water. The ether layer was separated, dried over $MgSO_4$ and evaporated to constant weight on a Rinco Rotary Evaporator. The resulting yellow oil contained a small amount of white solid. The sample was saved for future study.

E. Preparation of 1,2-bis(5-hexenyl)carborane

The procedure for the preparation of this material is the same as that used for the preparation of the corresponding butenyl compound. The amounts of materials used are as follows: carborane; 14.4 gm (0.1 moles); butyllithium in hexane solution 1.6M, 150 ml (0.24 moles); 6-bromo-1-hexene, 27 ml (0.198 moles). However, very little of the dilithiocarborane appeared to react when the bromohexene was added to the ether slurry. Addition of another 10 ml of the bromide caused no observable change. Substantial "activity" was noticed when the slurry was poured into water. The ether layer was separated, dried over magnesium sulphate, and evaporated to constant weight on a Rinco Rotary Evaporator. The resulting pale yellow liquid was saved for future work.

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

The procedure for the preparation of the material is found in the previous Quarterly Report #1. Conversions based on starting BAND - 6,9-bis(acetonitrilo)decaborane - are listed below:

Batch	BAND Used (gm)	BHMC Obtained (gm)	% Conversion
5	175	86	35
6	175	104	42

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

One 250 gm batch of BAMC was treated with methanol in the presence of gaseous hydrogen chloride as described in the previous Quarterly Report #1. The crude product was isolated by reducing the volume of the methanol solution to about 3/4 liter by boiling at atmospheric pressure followed by the addition of one liter of water. The resulting solid was Buchner filtered and washed with water. No additional solid was obtained when additional water was added to the filtrate. The air dried solid (178 gm) was light brown in color and had a characteristic "burnt" odor. Recrystallization from water gave 119 gm of a white odorless solid (62 percent conversion based on reactant BAMC).

H. Preparation of Carborane

A total of 62.1 gm of carborane was obtained from seven reactions starting with 20.3 gm portions of BHMC using the procedure outlined in the previous Quarterly Report. This quantity represents an average conversion of 62 percent of starting material to desired product. Visual observation and infrared spectral evidence showed that this carborane was of the highest purity yet obtained. This success is probably due to the high purity of reactant BHMC and the utmost care taken to insure complete reaction in the oxidation step.

REFERENCES

1. USNASL-910-P-IJ, October 28, 1964; Papetti, S. and Heying, T.L. *Inorg.Chem.*, 3, 1448 (1964), Olin Matheson Co. Status Reports, Contract Nonr 3395(00), Project NR 356-431; Thiokol Chemical Corp., RMD 5040-SR-2, Contract Nobs 90065, Task 1000, April 1964.

2. General Precision, Inc., Quarterly Progress Report No. 1, Contract NASA9-5527, April 15, 1966.

3. D. Grafstein et al., *Inorg. Chem.* 2, 1120 (1963).

4. I. Skeist, *Epoxy Resins*, Reinhold Publishing Corporation, New York, 1958, p. 24.

5. H. Lee and K. Neville, *Epoxy Resins*, McGraw-Hill Book Company, Inc., New York, 1957, p. 31.

6. J. P. Phillips, *Spectra-Structure Correlation*, Academic Press, New York, 1964.

7. R. Alexander and H. Schroeder, *Inorg. Chem.*, (2), 1107 (1963).

8. L. Bellamy, *The Infrared Spectra of Complex Molecule*, John Wiley & Sons, Inc., New York, 2nd ed., 1962, p. 119.