

RMD Report 5065-Q7
Contract No. DA-11-070-AMC-852 (W)

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CARBORANE - SILOXANE ELASTOMERS

Report Period: 19 August through 18 November 1966

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REACTION MOTORS DIVISION
DENVER, NEW JERSEY

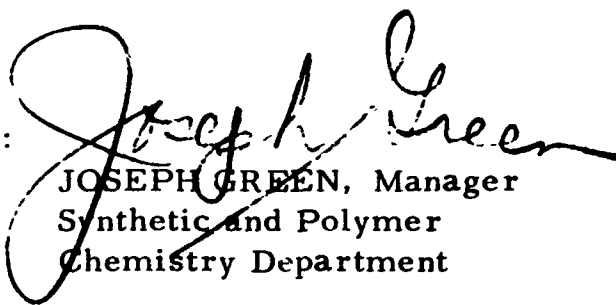
CARBORANE SILOXANE ELASTOMERS

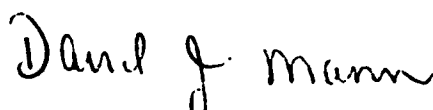
RMD Report 5065-Q7

Contract No. DA-11-070-AMC-852(W)

Report Period: 19 August through 18 November 1966

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FOREWORD

This report was prepared by Thiokol Chemical Corporation, Reaction Motors Division under U.S. Army Contract No. DA-11-070-AMC-852(W). It covers work done in the seventh quarter of the program during the period 19 August through 18 December 1966. Mr. Z. T. Ossefort of Rock Island Arsenal is the Project Engineer. Contributors at Thiokol are: Mr. Nathan Mayes (Principal Scientist) and Mr. Alan Jackson. The program is under the general direction of Mr. Joseph Green.

ABSTRACT

The synthesis of polymer of structure
$$-\text{Si} \begin{array}{c} \text{CH}_3 \\ | \\ \text{CB}_{10}\text{H}_{10} \\ | \\ \text{CH}_3 \end{array} \text{C}(\text{CF}_2)_5 \text{CB}_{10}\text{H}_{10} \text{C} \begin{array}{c} \text{CH}_3 \\ | \\ \text{SiO} \\ | \\ \text{CH}_3 \end{array} -$$

has been outlined, and work toward the preparation of precursors was initiated.

A new method for the preparation of m-carborane was investigated and developed, and reactions leading to products that may have the desired structure,

$$\text{HCB}_{10}\text{H}_{10} \overset{\text{O}}{\parallel} \text{C} (\text{CF}_2)_3 \overset{\text{O}}{\parallel} \text{CB}_{10}\text{H}_{10} \text{CH},$$
 were conducted.

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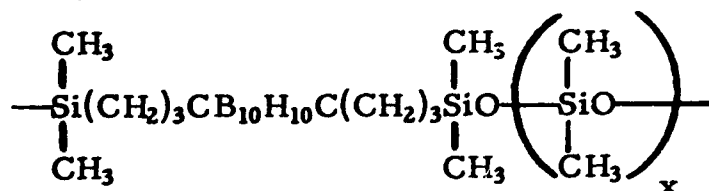
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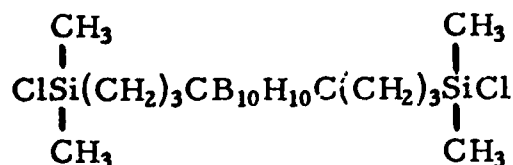
I. INTRODUCTION

The objective of this program is the synthesis of thermally stable carborane siloxane elastomers. The initial approach toward this objective was the preparation of polymer structure I*, where $x = 0, 1, \text{ and } 2$.

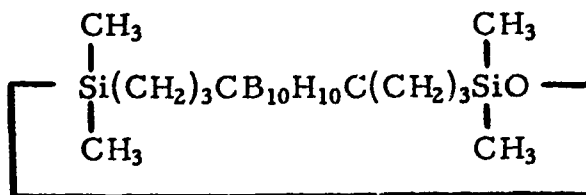


I

This approach led to the preparation of several precursors and monomers including



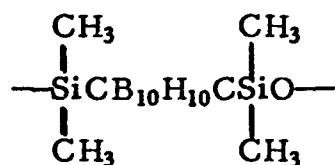
and



both of which were polymerized to polymers of the desired structures. The polymers were obtained as gums of molecular weights 5000-8500 and higher. The higher polymers did not dissolve and molecular weights are not known, but these materials were tough elastomeric gums of apparently high molecular weight and demonstrated the flexibility of the polymer chain.

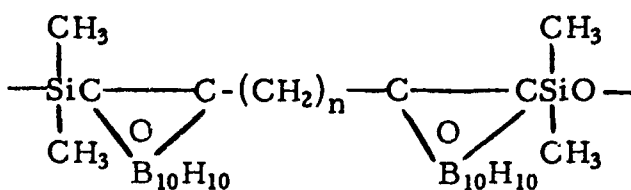
* -CB₁₀H₁₀C- denotes 1, 7-dicarboclovododecaborane commonly called:
m-carborane.

Examination of the polymer structure I ($x = 0$) for thermal and thermal oxidative stability showed stability in an inert atmosphere to 370°C (700°F) but decomposition in air at 240°C (465°F). These results indicated that carborane may have retarded the thermal rearrangements that polysiloxane chains normally undergo, but it did not inhibit oxidative attack on the silyl methyl groups. It has been determined in other work, however, that carborane does inhibit oxidative attack when the carborane is positioned adjacent to silicon as in structure II (Ref 1).



II

With the objective of obtaining a polymer that was both flexible and thermally stable, polymers of structure III* where $n = 3$ and 5 were prepared.

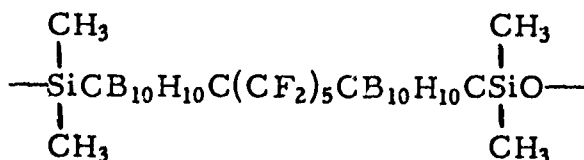


III

Where $n = 3$ the material had superior thermal oxidative stability but no flexibility.

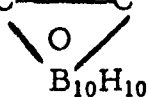
Where $n = 5$ the stability was poor and flexibility was marginal.

The approach presently being investigated is the preparation of polymer of structure IV. It is considered that the perfluoropentamethylene groups may



IV

* ---C---C is the symbol for o-carborane.

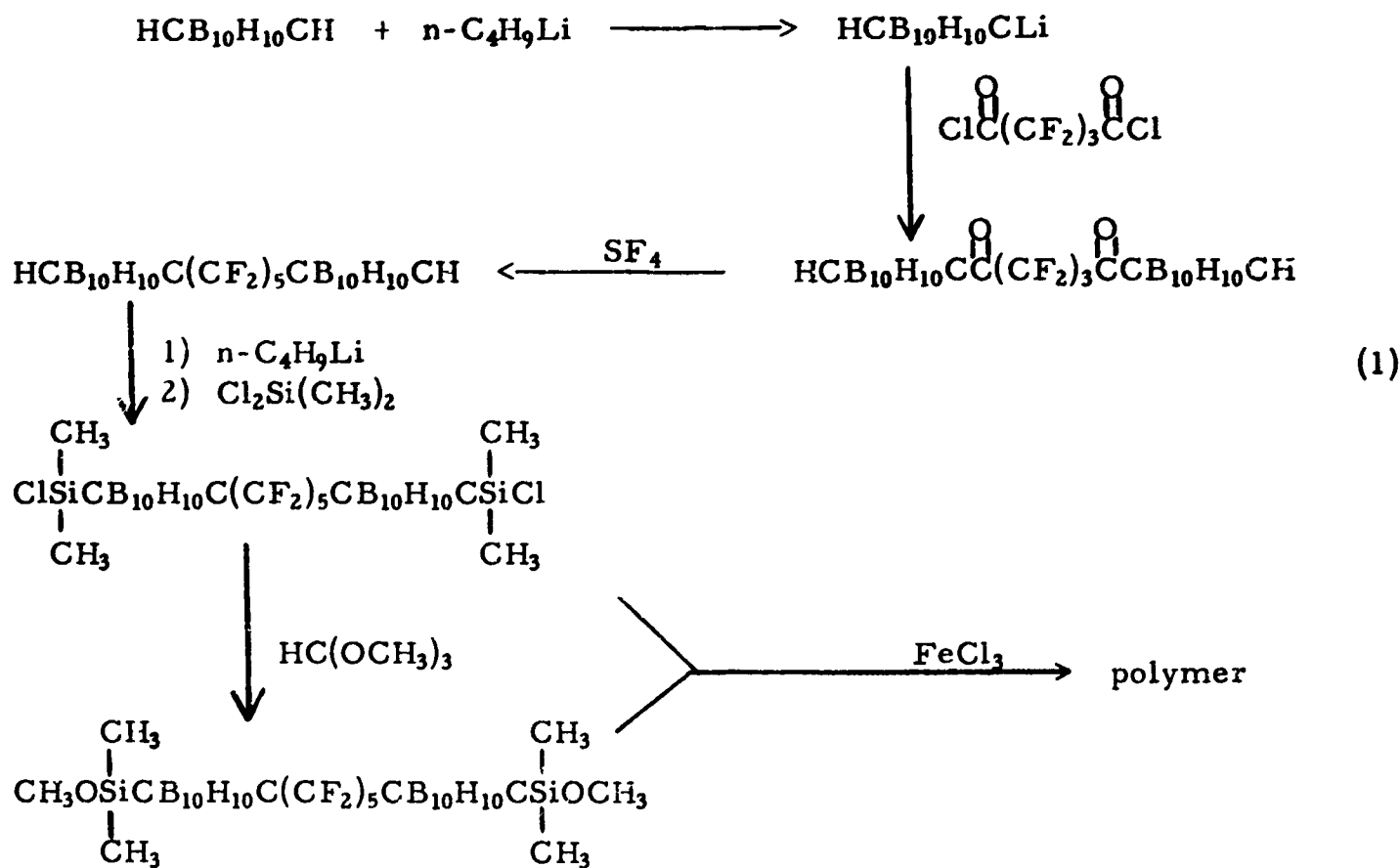


be thermally stable, flexible spacers for the carboranylsiloxy groups that already have demonstrated good thermal and thermal oxidative stability.

II. TECHNICAL PROGRESS

A. Synthesis of m-Carborane

The proposed polymer synthesis, as illustrated by the equations below, requires m-carborane as the starting material. m-Carborane, until now, has



been synthesized only by thermal isomerization of o-carborane. The synthesis that has been employed for o-carborane is a multistep process involving the reaction of decaborane with butynediacetate, hydrolysis of that product to a diol, and oxidation of the diol to o-carborane (Ref 2). With the objective of avoiding this lengthy synthesis, we have investigated the preparation m-carborane by the one-step pyrolysis of an available material, isopropyl-o-carborane.

The pyrolysis of isopropyl-o-carborane was studied using an apparatus consisting of a 200 ml. Pyrex flask in which the isopropyl-o-carborane is vaporized, a quartz tube (18 x 1 in.) which is heated by a furnace and through which the vapors pass, and a Pyrex collection flask in which the vapors are condensed. The apparatus is first thoroughly flushed with nitrogen and then the carborane compound is heated at 270-280°C with a metered flow of nitrogen to carry the vapors into the heated tube.

The initial experiments, conducted with an unpacked tube at 600-725°C determined that pyrolysis did yield m-carborane as a product; however, the conversion was low under the conditions employed. In subsequent experiments the use of a packed tube (quartz fragments as packing), a low nitrogen flow (20 ml./min.), and a tube temperature (outside wall) of 670°C has increased the conversion to 50% at a throughput of 14 g/hour. The carborane is obtained in a mixture with some brown unidentified byproduct from which the carborane is separated by sublimation. The conversion figure is for the crude sublimed product which may be purified with small loss by recrystallization from acetic acid. Recrystallized product melts at 66-70°C, and an infrared spectrum of the product indicates that it is pure m-carborane.

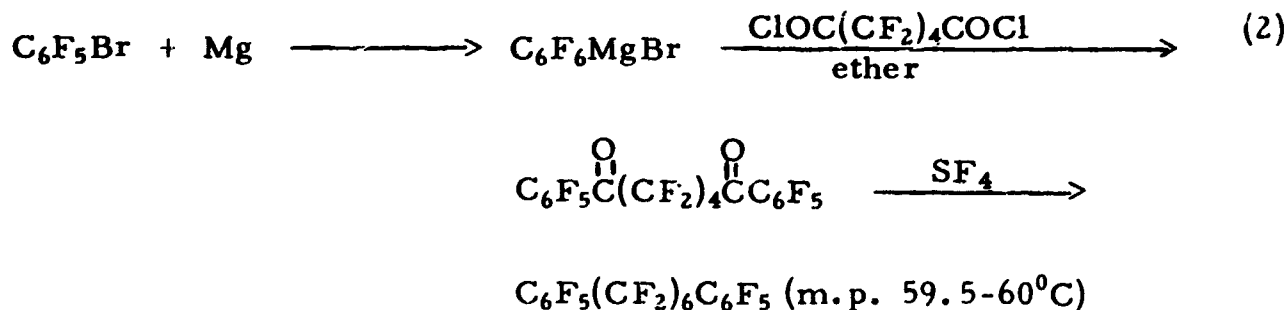
A sample of the volatile byproduct of the pyrolysis was collected at liquid nitrogen temperature and analyzed by infrared spectroscopy. The spectrum was identical to that of methane and indicated the presence of no other hydrocarbons. This suggests that methyl radicals produced in the pyrolysis are more able to combine with hydrogen radicals than with other methyl or alkyl radicals and

suggests that there is an abundance of hydrogen radicals available for combination. These hydrogen radicals probably result from partial decomposition of carborane.

This is the first reported successful direct conversion of an alkyl-o-carborane to m-carborane. Using this process m-carborane may be prepared in two steps, starting from decaborane and progressing through one of the more easily prepared alkyl carboranes, as apposed to the previous multistep process.

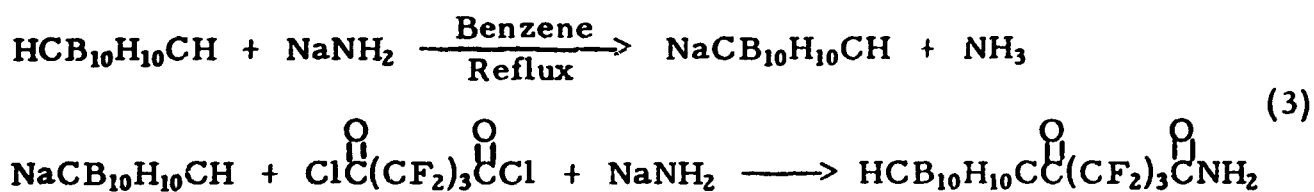
B. Synthesis of 1,5-Di-m-carboranylperfluoropentane

The synthesis of the subject compound is expected to parallel the recently reported synthesis of perfluoro-1,6-diphenylhexane, illustrated in equation 2 (Ref 3).



The parallel carborane reaction was first attempted using 1-sodio-m-carborane since it has been reported that o-carborane forms only a mono sodio derivative when treated with sodium amide in refluxing toluene (Ref 4). The reaction as attempted with m-carborane yielded a sodio derivative as evidenced by ammonia evolution. The second step of the reaction did not occur as expected. The reaction of sodio-m-carborane with acid chloride was largely incomplete and was complicated by the presence of sodium amide, which also reacted with

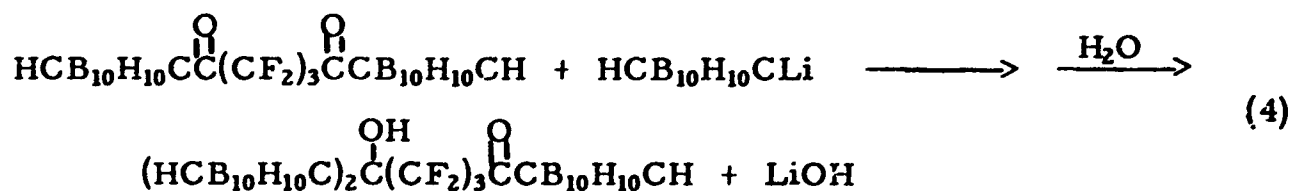
acid chloride. The major product obtained, after hydrolysis of the reaction mixture, was m-carborane, which resulted from hydrolysis of unreacted sodio-m-carborane. The only other product isolated was $\text{HCB}_{10}\text{H}_{10}\overset{\text{O}}{\parallel}\text{C}(\text{CF}_2)_3\overset{\text{O}}{\parallel}\text{CNH}_2$. The course of the reaction, as shown in equation 3, indicated that a more reactive metallo-carborane species was desirable, and elimination of other organo-metallic species from the reaction mixture was necessary.



For these reasons the reaction was next attempted with lithio-m-carborane which was prepared from n-butyllithium and excess m-carborane. An excess was used to insure formation of monolithio derivative and to minimize unreacted butyllithium. This reaction yielded two products after separation of excess m-carborane. An ether insoluble portion, representing 65% of the product, did not melt below 325°C and was partially soluble in acetone, methanol and acetic acid. It was fully soluble in dimethylformamide. The infrared spectrum (Fig. 1) exhibited absorption bands at 3.9 microns for BH of m-carborane, at 5.9 microns for ketone carbonyl, and in the 8-9 micron region for CF₂. The spectrum suggests the presence of the desired material; however, no means has been found for isolating this material.

An ether soluble portion melted with decomposition at 85-120°C. The infrared spectrum of this product (Fig. 2) was similar to the spectrum of the

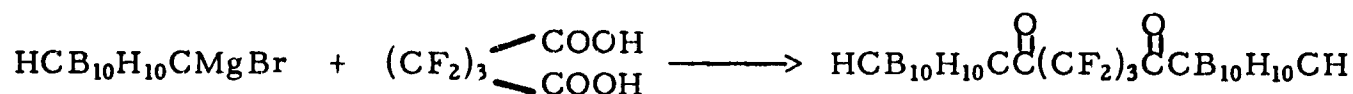
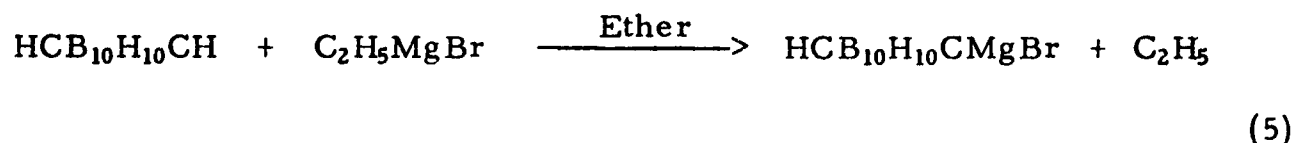
other product, except for bands at 5.78 microns and 5.98 microns, which are apparently due to different types of keto carbonyls. Both materials exhibit absorption bands in the region of 3.0-3.2 which may be for OH. This suggests that reaction, as illustrated in equation 4, may have occurred.



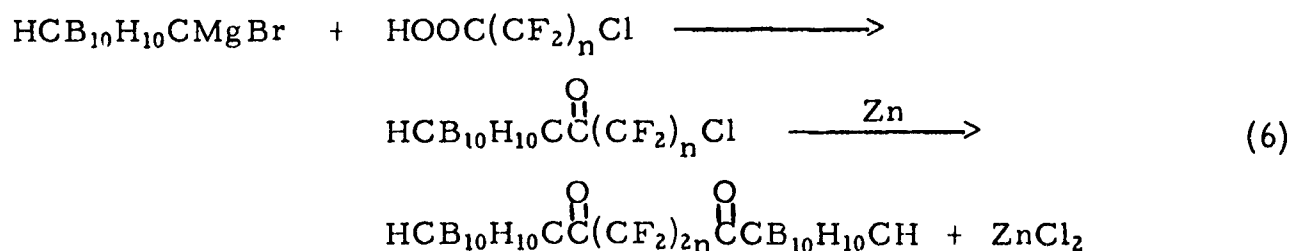
The products that have been obtained will be further characterized by elemental analysis to aid in identification; however, the reaction will also be investigated using a carborane Grignard reagent in an effort to eliminate the secondary reaction leading to alcohol formation.

III. DISCUSSION

The synthesis of perfluoroalkyl carborane siloxane polymers is to be preceded by the synthesis of a dicarboranylperfluoroalkane. The approach that has been chosen for this synthesis, namely through formation of a diketone and fluorination of that to a perfluoroalkyl, was considered most practical because a parallel synthesis for a perfluorodiphenylalkane has been described (Ref 3). The difficulties that are inherent in the preparation of analogous carborane derivatives are recognized, however, and other approaches to the carborane compound synthesis are being considered. Among these, the reaction of carborane Grignard reagent with perfluoroglutaric acid to diketo compound appears practical (eq. 5).



Another approach that employs monofunctional materials and eliminates the difficulties of polymer formation and formation of a number of possible side products is illustrated in equation 6.

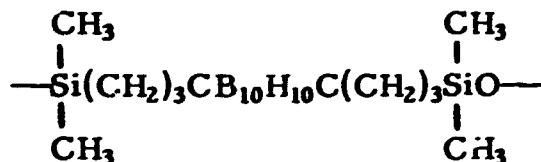


Here it is considered that the carbonyl will be so much more reactive toward the Grignard than is chlorine, that the compound is essentially monofunctional.

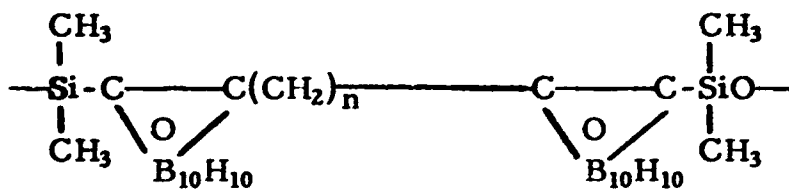
In the event that the desired dicarboranylperfluoroalkyldiketo compound is not obtained through the approaches already under investigation the above-described or similar synthesis will be investigated.

IV. SUMMARY

In previous work polymers of structures I and III were prepared and evaluated. None of these possessed the combination of properties necessary for



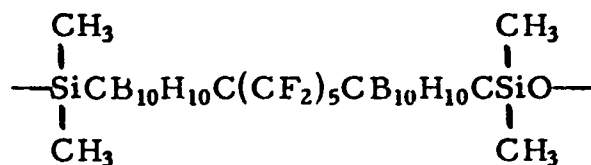
I



where n = 3 and 5

III

a thermally stable elastomer, and the work has now been directed toward the preparation of polymer of structure IV.



IV

Toward the preparation of precursors of structure IV, m-carborane was prepared by the pyrolysis of isopropyl-o-carborane at 670°C and the synthesis of 1,5-di-m-carboranylperfluoropentane was investigated. The latter involved reactions of sodio-m-carborane and lithio-m-carborane with perfluoroglutaryl chloride to obtain a diketo compound which might be fluorinated to the desired alkane. The results of the alkane synthesis are not yet definite and the investigation is continuing.

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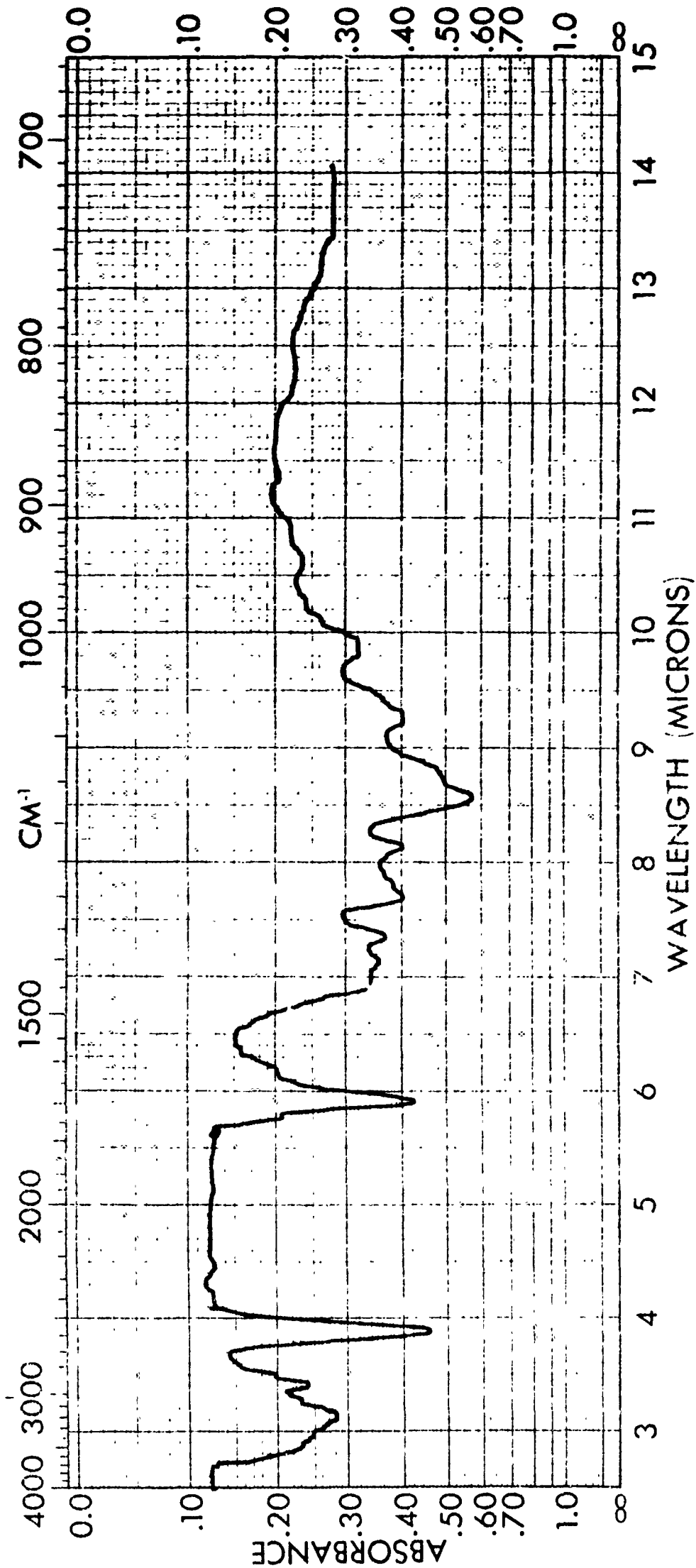


Figure 1. Infrared Spectrum of the Ether Insoluble Product of the Lithio-m-carborane/
Perfluoroglutaryl Chloride Reaction

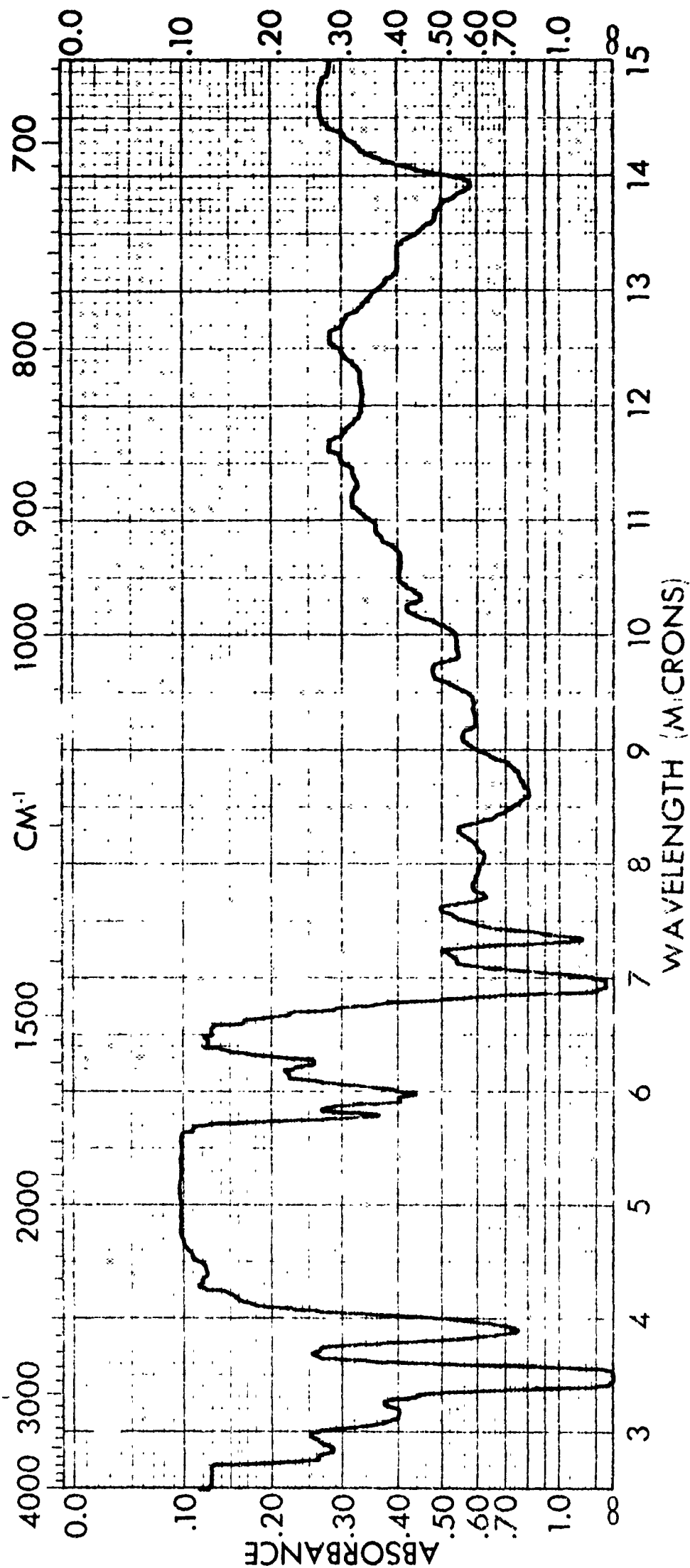


Figure 2. Infrared Spectrum of the Ether Soluble Product of the Lithio-m-carborane / Perfluoroglutaryl Chloride Reaction (Nujol Mull)

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13. ABSTRACT The synthesis of polymer of structure $\begin{array}{c} \text{CH}_3 \\ \\ \text{---SiCB}_{10}\text{H}_{10}\text{C}(\text{CF}_2)_5\text{CB}_{10}\text{H}_{10}\text{CSiO---} \\ \\ \text{CH}_3 \end{array}$ $\begin{array}{c} \text{CH}_3 \\ \\ \text{---} \\ \\ \text{CH}_3 \end{array}$ has been outlined, and work toward the preparation of precursors was initiated. A new method for the preparation of m-carborane was investigated and developed, and the reactions leading to products that may have the desired structure, $\text{HCB}_{10}\text{H}_{10}\text{C}(\text{CF}_2)_3\text{CCB}_{10}\text{H}_{10}\text{CH}$, were conducted.			

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KEY WORDS

m-Carborane
 di-m-Carboranylperfluoroalkane
 Thermally Stable Polymer

LINK A		LINK B		LINK C	
ROLE	WT	ROLE	WT	ROLE	WT

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