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AUBURN UNIV ALA DEPT OF CHEMISTRY
CARBORANE BURNING RATE MODIFIERS.(U)
MAR 78 W E HILL, F A JOHNSON

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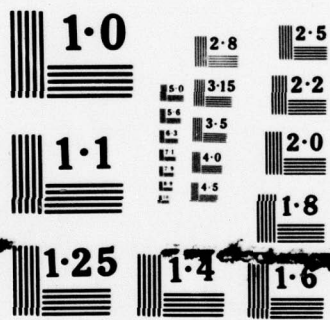
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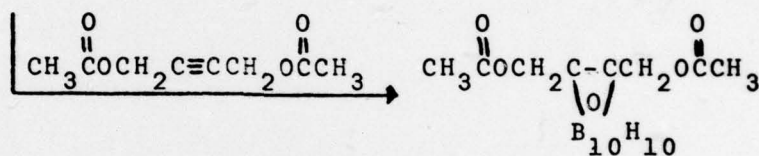
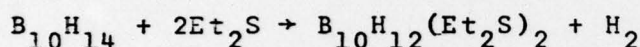
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I. Preparation of Starting Materials for Binder Addition Studies

Since the beginning of the contract extension year two explosions resulting in some property damage and no personnel injury have occurred. Both of these explosions took place when we attempted to prepare bis(acetoxymethyl)carborane(I) from $B_{10}H_{14}$ and 2-butyne-1,4-dioldiacetate utilizing the method reported in Inorganic Syntheses, Vol. XI, p. 19.



(I)

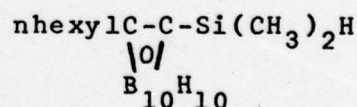
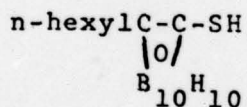
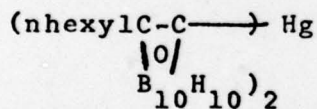
The first of these explosions occurred when volatiles were being removed in vacuo on a rotary evaporator after the reaction was completed. Gentle heat ($\sim 50^\circ$) was being applied. The second explosion occurred after the volatiles were removed and methanol was being added in very small portions to kill off reactive by-products in the preparation. The methanol was being added through a condenser column to the reaction products in 2-3 ml. portions. Vigorous refluxing occurred on each addition and as this reflux subsided somewhat, an additional 2-3 ml. of methanol would be added. After a total of approximately 25 ml. of methanol had been added, the reaction suddenly began to violently heat up and the explosion occurred.

Although we have performed this reaction several times in the past with no problems using the same procedure and personnel, our

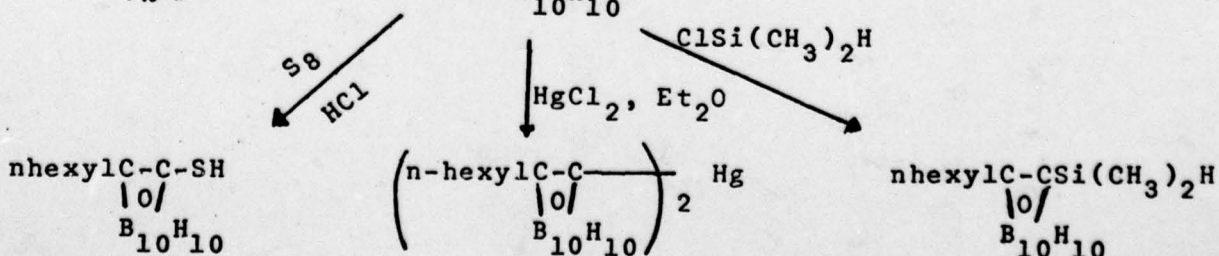
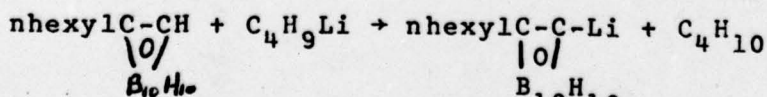
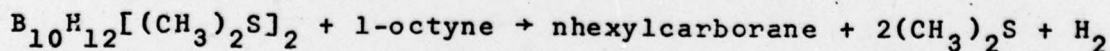
last two attempts have been unsuccessful. After a careful analysis of the probable cause of these explosions we found that in both instances we were using decaborane obtained from Redstone Arsenal in June, 1977. We were told by the Redstone Arsenal people that the decaborane we received had been stored in a magazine for a long time and the purity was unknown. We attempted to purify the decaborane by sublimation and by recrystallization from hexane. We feel, however, that the explosions resulted from some impurities that were not removed by these conventional purification routes. The identity of the main impurities in the decaborane is unknown. We are informing Redstone Arsenal of the potential hazard of this very old decaborane.

II. Synthesis and Characterization of n-hexylcarboranes Capable of Addition to C=C in Polybutadienes; \rightarrow p.3

During this report period we have synthesized the n-hexylcarborane derivatives I-III.



These have been synthesized by the following routes:



Compounds (I) and (II) are solids highly soluble in most organic solvents. Compound (IV) is a high boiling liquid.

The infrared spectrum of (II) shows the characteristic absorption due to the S-H stretching vibration at 2570cm^{-1} . The parent ion is observed in the mass spectrum. The proton nmr shows the characteristic absorptions of the hexyl side chain in the 1-2 ppm range.

The infrared spectrum of (IV) shows the characteristic absorption due to the Si-H vibration at 2240cm^{-1} . The proton nmr of the Si-H proton occurs as a septet.

III. Attachment of Carboranes to Polybutadiene Binders;

The attachment of the carborane derivatives to hydroxy-terminated polybutadiene (R45-M) has been studied. The addition was carried out by mixing the carborane and polybutadiene neat and heating to 90°C for 3 hours or by mixing the carborane and polybutadiene in methylene chloride, evaporating the solvent and heating at 90°C for about 3 hours. After the addition was complete the resulting polymer was extracted with boiling methylene chloride. It is of interest that no catalyst was needed for any of the additions with SH, Si-H, or carboranyl-Hg derivatives. Optimum addition of Si-H in particular might require catalyst and this point will be studied further. Treatment of the addition product of the mercury derivatives with HCl in diethylether cleaved the Hg mercury bond according to the following equation:

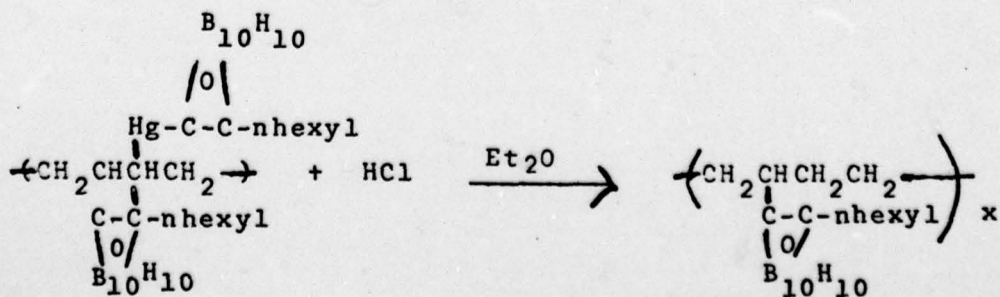


Table I lists the results of the addition. Examination of the table reveals that, under the conditions used to fix the carborane additive to the binder, much higher levels of incorporation of the SH moieties were observed. It should be pointed out that optimum conditions for the addition have not been studied. This is under study at the present time.

Clearly some improvement in the binder properties are observed with monofunctional carboranes. These cannot cross link polymer chains and therefore one would expect the polymer physical properties to be different from the cross-linked case.

It is perhaps a bit disappointing that the properties of the polymers containing n-hexyl derivatives were not significantly different than those of the corresponding methyl derivatives.

IV. Mechanism of Carborane Preparation

Recently we have devised a route to ortho-carboranes which by passes decaborane. However, this route still goes through the key intermediate, $B_{10}H_{12}[(CH_3)_2S]_2$. A raw material cost analysis of our process indicates that $B_{10}H_{12}[(CH_3)_2S]_2$ would cost \$27.91/lb. This process is summarized in the following scheme.

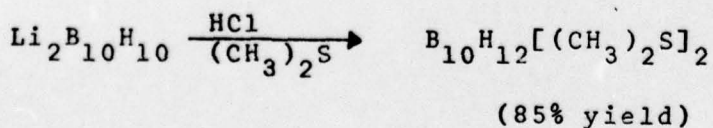
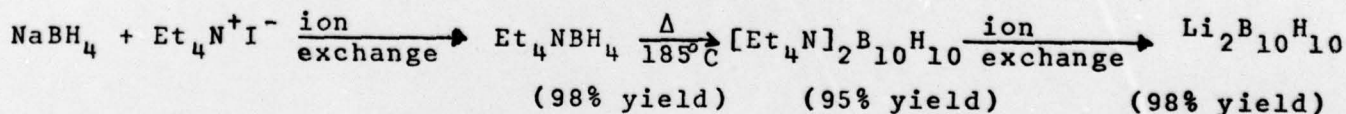


TABLE I

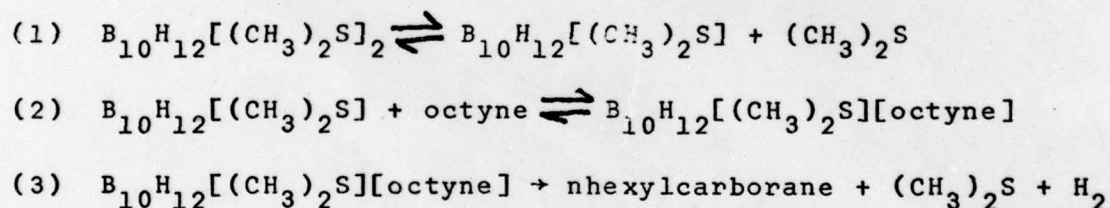
INCORPORATION OF CARBORANE ADDITIVES INTO HYDROXY-TERMINATED POLYBUTADIENE BINDER (A)

CARBORANE	POLYMER STATE	%, INCORPORATION (B)
$\begin{array}{c} \text{HSC-C-SH} \\ \quad / \\ \text{O} \\ \text{B}_{10}\text{H}_{10} \end{array}$	ORANGE-YELLOW, HARD SOLID	97%
$\begin{array}{c} \text{CH}_3\text{C-C-SH} \\ \quad / \\ \text{O} \\ \text{B}_{10}\text{H}_{10} \end{array}$	YELLOW, HARD SOLID	95%
$\begin{array}{c} \text{N-HEXYL-C-C-SH} \\ \quad / \\ \text{O} \\ \text{B}_{10}\text{H}_{10} \end{array}$	HARD YELLOW SOLID	93%
$\begin{array}{c} \text{CH}_3\text{C-C-SiH(CH}_3)_2 \\ \quad / \\ \text{O} \\ \text{B}_{10}\text{H}_{10} \end{array}$	LIGHT YELLOW, GUM	54%
$\begin{array}{c} (\text{CH}_3)_2\text{Si(H)C-C-SiH(CH}_3)_2 \\ \quad / \\ \text{O} \\ \text{B}_{10}\text{H}_{10} \end{array}$	LIGHT YELLOW, SOLID	52%
$\begin{array}{c} \text{CH}_3 \\ \\ \text{N-HEXYL-C-C-Si-H} \\ \quad / \quad \\ \text{O} \quad \text{CH}_3 \\ \text{B}_{10}\text{H}_{10} \end{array}$	LIGHT YELLOW GUM	55%
$\begin{array}{c} (\text{CH}_3\text{C-C-})_2 \text{ Hg} \\ \quad / \\ \text{O} \\ \text{B}_{10}\text{H}_{10} \end{array}$	TAN, SOLID	35%
$\begin{array}{c} (\text{N-HEXYL)C-C-})_2 \text{ Hg} \\ \quad / \\ \text{O} \\ \text{B}_{10}\text{H}_{10} \end{array}$	YELLOW-BROWN, GUM	25%

(A) Mixed in CH_2Cl_2 or neat, heated to 90°C for 3 hrs.(B) Based on polymer product of 1:1 adduct, carborane to $(\text{CH}_2\text{CH=CHCH}_2)$ unit.

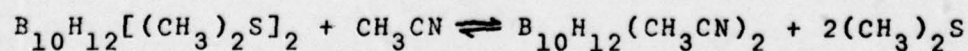
It is important to note that this process utilizes ~75% of the starting boron in the final product. However, conversion of $B_{10}H_{12}[(CH_3)_2S]_2$ to n-hexylcarborane can only be accomplished in yields of ~40%. Thus the raw material cost of hexylcarborane per pound is \$111.12. This is a slight improvement over the raw materials cost of n-hexylcarborane from the toxic $B_{10}H_{14}$ as reported by the U.S. Army Missile Command Propulsion Lab at Redstone Arsenal. Their cost was \$115/lb.

Since the new contract year we have continued to look at the kinetics of carborane formation with a goal of improving the yield of n-hexylcarborane from $B_{10}H_{12}[(CH_3)_2S]_2$. Our earlier kinetic studies reported during the last contract year suggested that the reaction proceeds via dissociation of $B_{10}H_{12}[(CH_3)_2S]_2$ to the mono-ligand adduct according to the following mechanism:



Our first approach in the new contract year has been to try and understand more about steps 1 & 2.

Another intermediate utilized in carborane synthesis has been $B_{10}H_{12}(CH_3CN)_2$. The Lewis bases $(CH_3)_2S$ and CH_3CN have very different properties and yet yields of ortho-carborane utilizing either adduct are about the same. We have studied the equilibrium of the following reaction:



Results of this study are summarized in Table II.

TABLE II

Equilibrium Constants as a Function of Temperature for the Exchange of $(\text{CH}_3)_2\text{S}$ by CH_3CN .

Temp, °K	K
302.11	2.24×10^{-2}
303.03	2.29×10^{-2}
307.69	2.48×10^{-2}
314.46	2.79×10^{-2}
321.54	3.16×10^{-2}
322.58	3.31×10^{-2}

From this data ΔH for the reaction may be calculated and was found to be + 2.6 kcal/mole. This suggests that the adduct $\text{B}_{10}\text{H}_{12}(\text{CH}_3\text{CN})_2$ is less stable than the corresponding $\text{B}_{10}\text{H}_{12}[(\text{CH}_3)_2\text{S}]_2$. Since dissociation is the first step in formation of orthocarborane, it's somewhat surprising that yields with $\text{B}_{10}\text{H}_{12}(\text{CH}_3\text{CN})_2$ are no better than those of $\text{B}_{10}\text{H}_{12}[(\text{CH}_3)_2\text{S}]_2$. However, $\text{B}_{10}\text{H}_{12}(\text{CH}_3\text{CN})_2$ is much less soluble than the sulfide and this may well complicate the overall process.

We are continuing to look at other bases and have begun a study to determine ΔH^\ddagger for the conversions of $\text{B}_{10}\text{H}_{12}\text{L}_2$ to orthocarboranes where L is a variety of bases. It should be noted that our earlier kinetic studies showed much better yields of carborane when ΔH^\ddagger for the reaction was high.

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