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Office of Naval Research  
800 North Quincy Street  
Arlington, VA 22217

Attention: Dr. R. S. Miller (Code 1132P)

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S H D

Subject: Sixth Quarterly Summary of Progress on  
Contract "Synthesis of Energetic Binders"  
Covering Period 01 April to 30 June 1988  
Contract N00014-86-C-0164

Dear Dr. Miller:

Enclosed is our paper presented at the 1988 AIAA meeting held in Boston, which serves at the subject report.

THE SYNTHESIS OF CARBORANE-OXETANE MONOMERS  
AND THEIR POLYMERIZATION

Introduction and Background

Modern rocket propellants, gun propellants, and explosives are an adaptation of the basic concept of a formulation consisting of a solid oxidizer and fuel held in a polymeric matrix. To aid in the processibility, energy and ballistic performance, other components are often added (plasticizers and burn rate additives). Over the past decade, as mission objectives increased, the formulation chemist has been forced to consider higher performance requirements. This was initially met by increased solids loadings, but it was soon found that there were limits to this approach.

Next came a thrust to synthesize oxidizers with higher performance potential, a field of research that is continuing, but as expected, these new ingredients tend to lead to higher vulnerability to unscheduled detonation. One other approach was to consider replacing the nonenergetic polymeric binder with a polymer that could contribute energy to the formulation. If one considers that 8 to 20% of a given formulation contains a polymer that does not contribute any energy, oxidizer, or fuel value to the formulation, then instant and significant performance increases can be expected. Nitrocellulose has been used as a "binder", but extreme vulnerability to catastrophic initiation is unacceptable in today's propellants.

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In 1978, we embarked on a research effort to synthesize energetic polymeric binders specifically designed for propellant applications. Our approach has always been to synthesize energetic monomers, then by suitable polymerization techniques, obtain energetic polymers. Within a short period of time, we decided to concentrate on the cyclic ether, oxetane, class of monomers that could be synthesized relatively easily, undergo controlled polymerization, and produce a polyether that would be expected to exhibit superior mechanical properties. The concept of preparing, with azide pendant functionality, an energetic polyether glycol was later demonstrated.<sup>2,3</sup> During this time, a modified cationic polymerization technique was developed, which allowed the synthesis of polymers to predetermined molecular weight and functionality, and the concept of energetic polyoxetanes was presented.<sup>4</sup> Further work has now resulted in nitrate ester, nitramine polymers,<sup>5,6</sup> copolymers,<sup>7</sup> and recently nitro, cubane and carborane polymers.<sup>8</sup> The latter is the subject of this paper.

### Discussion and Results

Boron or boron compounds have been used as a burning rate modifier and as a metal fuel source in solid propellant motors. Migration of these chemicals in the propellant grain is a continuous and serious problem. We proposed that a urethane curable polyether glycol with a carboranyl functionality would solve migration problems. Oxetane-carboranes (Figure 1) would be good candidates as monomers for these carboranyl pendant polymers. These monomers could be homopolymerized or co-polymerized with other oxetanes for specific properties. This paper describes the synthesis, characterization, and polymerization of oxetane-carborane monomers.

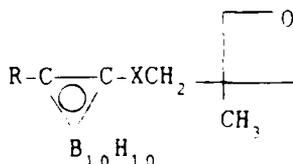
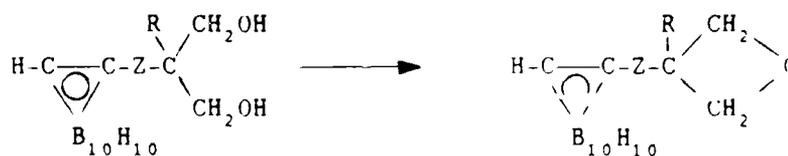


Figure 1

### Synthesis Approaches

We have identified three general approaches to the synthesis of a carborane-oxetane molecule. One general method was to start with a carborane cage with an alkyl chain substituted such that an oxetane ring could be formed by subsequent reaction. Scheme I shows one such example of this approach, cyclization of dihydroxyalkylcarborane. However, as Searles reported<sup>10</sup>, oxetanes are produced by a variety of methods, but most are quite limited in scope. We decided that this approach held the least chance of success.

Scheme I

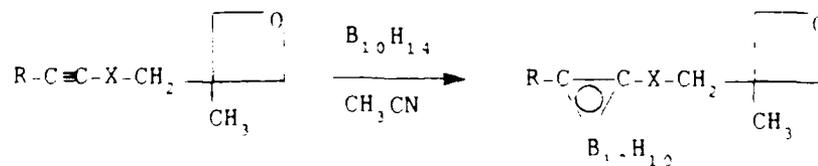


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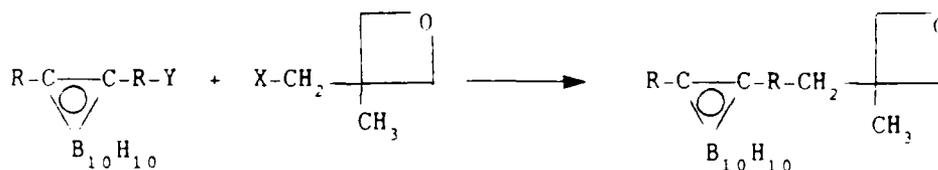
A second approach was to react an alkyne-oxetane with decaborane, Scheme II. Applying this approach to the simplest case, 3-propynyloxymethyl-3-methyloxetane, gave no product. At this time it is thought that decaborane is a strong enough Lewis acid that it is capable of catalyzing the polymerization of the oxetane.

Scheme II



A third approach was to combine a preformed carborane with a preformed oxetane ring, Scheme III. This could be done in a variety of ways. We have proposed three methods for this scheme: using a Grignard reagent, using an organolithium reagent, or using the Williamson-Ether synthesis. Most of our work so far has been with the Williamson-Ether synthesis.

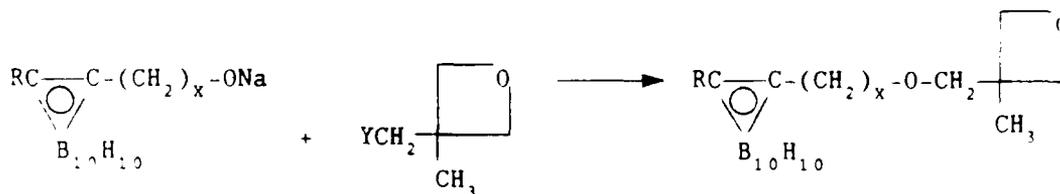
Scheme III



Williamson-Ether Synthesis

Our first approach was to react an alkyl sodium alcoholate derivative of carborane with an oxetane, Scheme IV.

Scheme IV

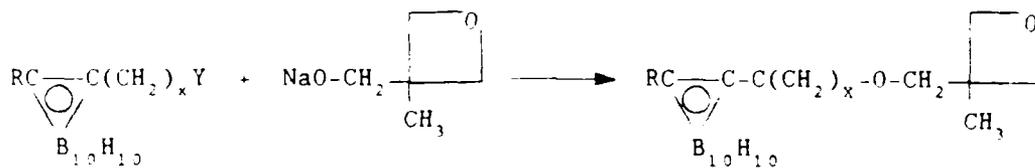


	<u>1</u>		<u>2</u>		<u>3</u>		
1a	R H	X I	2a	Y I	3a	R H	X I
b	CH <sub>3</sub>	3	b	Tos	b	CH <sub>3</sub>	
			c	Br			

One report<sup>11</sup> of the preparation of ethers from 1a used interphase catalyst conditions. Using these conditions with 2c gave no indication that 3a was formed in any but trace amounts. Also, no significant amount of product was detected when 1a was reacted with 2a-c using nonpolar aprotic solvent (dioxane or THF) or using polar aprotic solvents (DMF or HMPA). Lengthening the alkyl chain (X = 2 or 3) did not significantly modify the strong inductive (-I) effect of the carborane ring. These reactions merely degraded the carborane ring. Nucleophilic reactants of sufficiently high basicity will degrade the carborane nucleus, initially forming the (3)-1,2-dicarbaundecaborane.<sup>12</sup>

Next we looked at the reverse Williamson-Ether reaction, which is the reaction of the sodium salt of 3-hydroxymethyl-3-methyloxetane with a carborane, Scheme V.

Scheme V



	X	Y	R		X	R
4a	1	Br	H	6a	2	H
b	1	Tos	H	b	3	CH <sub>3</sub>
c	2	Tos	H			
d	2	Br	H			
e	3	Tos	CH <sub>3</sub>			
f	3	Br	CH <sub>3</sub>			
g	3	Cl	CH <sub>3</sub>			

This scheme has the advantage that the leaving group is not on the oxetane. Oxetane is a neopentyl type system which is typically resistant to nucleophilic substitution. A disadvantage to this method would be base-induced elimination when X = 2 or greater.

The reaction of 5 with 4a using dioxane or hexamethylphosphoramide (HMPA) as solvent gave no desired ether. With mild heat, only degraded products which are water soluble were obtained. This is consistent with the literature<sup>12,13</sup> that reports 1-halomethylcarboranes are extremely inert to nucleophilic replacement reaction. Reaction of ethyl carboranes, 4c and 4d, also gave little or no product. The major product was 1-vinylcarborane. A small amount of crude 6a was isolated when the ethylbromocarborane, 4d, was reacted with 5 in DMF.

Finally, the reaction of 5 with 4e in HMPA afforded 6b as a minor product; the elimination product 7 was the major product. Table 1 shows the effect of solvent on the reaction of 5 with 4e (at 5-10°C for 60 min). In the less polar solvent, THF, the reaction was very slow and then stopped after several hours. Adding HMPA increased the rate but did not seem to change the molar ratio of coupling product to elimination product. DMF gave similar results. This

increased reaction could be due to increased stability of the reaction intermediate in the dipolar-aprotic solvents or because 5 is more soluble in these solvents.

The effect of different leaving groups on the carborane is shown in Table 2. The bromopropylcarborane (4f) gave about the same molar ratio of coupling to elimination product as the tosyl derivative (4e); however, a different elimination product, 8, is produced along with some 7. These results are similar using DMF as the solvent with 8 being the major by-product. The chloropropylcarborane (4g) gave very little coupling, and the major elimination by-product was again 7.

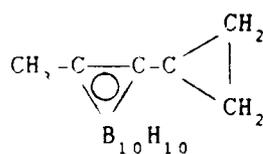
TABLE 1. EFFECT OF CHANGING SOLVENT ON REACTION OF METHYL-TOSYLPROPYLCARBORANE AND HMMO (5-10°C/60 min)

Solvent	Percent Starting Material Remaining	Yield Mole Percent	
		Coupling	<u>7</u> Elimination
HMPA	0	90	10
HMPA/THF (17/100)	1	60	40
HMPA/THF (10/100)	20	55	45
THF	90	50	50
DMF	20	65	35

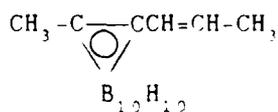
TABLE 2. EFFECT OF CHANGING LEAVING GROUP ON METHYL-PROPYLCARBORANE (5-10°C/60 min)

Solvent is HMPA/THF (10/100)

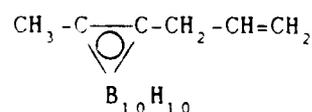
Leaving Group	Percent Starting Material Remaining	Yield Mole Percent		
		Coupling	Elimination	
			<u>7</u> Cyclopropyl	<u>8</u> Propenyl
OTs ( <u>4e</u> )	20	45	55	0
Br ( <u>4f</u> )	2	40	7	53
Cl ( <u>4g</u> )	60	10	85	5



7



8

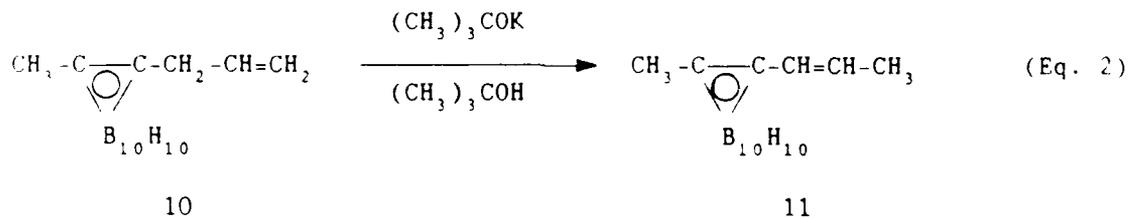


9

The structures of the elimination products 7 and 8 are quite surprising. An expected structure would be 9, which would result from an E1 carbanion mechanism described by Bunnett<sup>14</sup>, Eq. 1.



The strong inductive (-I) effect of the carborane ring must stabilize the shift of the carbanion next to the ring. This type of allyl isomerization was reported by Zakharkin, et al.<sup>15</sup> He found that 1-allylcarborane (10) would completely isomerize to trans-1-propenylcarborane (11) with (CH<sub>3</sub>)<sub>3</sub>COK in (CH<sub>3</sub>)<sub>3</sub>COH, Eq. 2.

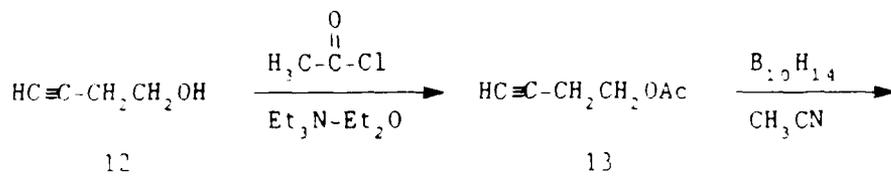


The mechanism for the formation of the cyclopropyl elimination product is unclear, but it is likely that the acidic proton next to the carborane nucleus is removed first and the resulting anion displaced the tosylate.

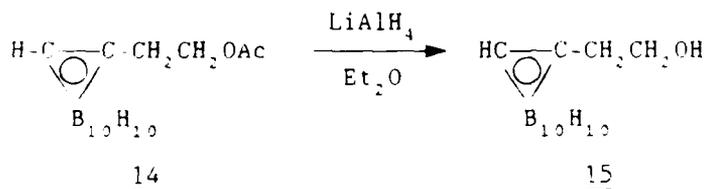
#### Preparation of Oxetanes and Carboranes

3-Hydroxymethyl-3-methyloxetane (HMMO) was the starting oxetane used in this work. Our procedure has been described previously.<sup>16</sup> The tosyl derivative was prepared by the addition of p-toluenesulfonyl chloride to HMMO using pyridine as solvent and acid scavenger.<sup>9</sup> 3-Bromomethyl-3-methyloxetane was prepared in high yield by the action of lithium bromide on TMMO in DMF.<sup>9</sup> The reaction of sodium iodide with 3-chloromethyl-3-methyloxetane (CMMO) in DMF gave 3-iodomethyl-3-methyloxetane.<sup>9</sup> CMMO was prepared from HMMO using triphenylphosphine and carbon tetrachloride.<sup>8</sup> The alkyne-oxetane, 3-propynloxy-methyl-3-methyloxetane was prepared from the sodium salt of HMMO and propargyl bromide in DMF.<sup>9</sup>

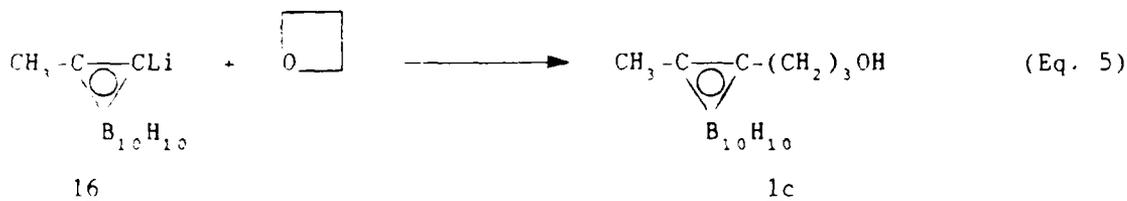
Carborane<sup>17-20</sup> and 1-methylcarborane<sup>21</sup> were used to make most of the carboranes used in this work. Exceptions were 1a which was made from propargylalcohol and decaborane<sup>22</sup> and 4a which was made from propargylbromide and decaborane.<sup>18,21,22</sup> Also, the starting material for hydroxyethylcarborane (15) was the acetylated 3-butyn-1-ol (13). Although the literature report<sup>22</sup> used an acid hydrolysis to give 15 from 14, reduction of 14 with lithium aluminum hydride gave 15 in better yields, Eq. 4.



(Eq. 4)



Preparation of 1-methyl-2(propanol)carborane, 1c, has been reported.<sup>16,22</sup> A more convenient method proved to be the reaction of lithium methyl carborane, 16, with oxetane (Eq. 5).



The tosylates of the carboranyl alcohols were prepared using toluene-sulfonylchloride in methylene chloride with pyridine or triethylamine as base. In the synthesis of 4e, 1-(3-chloropropyl)-2-methylcarborane was isolated as a side product. The side reaction was minimized by using an excess of triethylamine and cold reaction conditions. It is assumed that this chlorination side reaction accompanied all tosylation reactions although the unknown side products that were seen were never characterized.

Synthesis of bromoethylcarborane (4d) from 1-bromo-3-butyne has been reported.<sup>22</sup> However, we prepared 4d from the tosylate (4c) and lithium bromide in DMF. The simplest preparation of 1-(3-bromopropyl)-2-methylcarborane (4f) was from the alcohol (1c) using hydrobromic-sulfuric acid. Triphenylphosphine/bromine in chloroform also gave high yields, but isolation was more difficult. The literature<sup>23</sup> procedure for preparing 4f reacts the alcohol with phosphoroustribromide, but using  $\text{PBr}_3$  in toluene gave a crude product which was only 50% 4f. Triphenylphosphine in carbon tetrachloride gave the chlorocarborane 4g from the alcohol 1c.

#### Preparation of Carborane/Oxetane Polymers

The model monomer 1,2-Dicarbododecaborane(12)-1-methyl-2[3-((3-methyl-3-oxetanyl)methoxy)propyl], [Carbox], was subjected to conditions that induce cationic initiation of other oxetane monomers.<sup>4,5</sup> Our more recent work on the

initiator formed by prereacting bis-cumylchloride with silver antimony hexafluoride<sup>2+</sup> was found to readily polymerize carbox in a controlled manner. Quantities of polymer have been produced and are being subjected to exhaustive analysis. Initial results indicate that the carboranyl group is thermally stable even above the depolymerization temperature of the polymer and should result in fulfilling the objectives of our program.

### Conclusions

We have demonstrated that a polyether prepolymer can be synthesized that contains a carboranyl (boron cage) pendant group attached to each monomer repeating unit. The polymer is readily prepared by the cationic initiation of an oxetane monomer with a carborane functionality in the 3 position.

A model monomer was successfully synthesized by the Williamson-Ether synthesis of suitably substituted carborane coupled with an oxetane. Alternate methods (general) have and will continue to be investigated.

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### Experimental

#### 1-Ethanol-1,2-dicarbododecaborane(12) (1b)

A 3-liter, 3-necked, round-bottom flask equipped with a mechanical cone-driven stirrer, nitrogen gas inlet, and reflux condenser was charged with  $\text{LiAlH}_4$  (14 gm, 0.366 mol) and 500 ml anhydrous ethyl ether. The flask was cooled to Ca.  $4^\circ\text{C}$  in an ice-water bath. To this mixture the 1-ethanol-1,2-dicarbododecaborane(12)acetate (85 gm, 0.366 mol) in 500 ml of anhydrous ethyl ether was added dropwise via a pressure-equalizing addition funnel. The gray mixture was left to stir overnight, approximately 12 hours, at room temperature. The excess  $\text{LiAlH}_4$  was destroyed with dropwise addition of water-methanol (50-50) in a cold ice bath. When the excess  $\text{LiAlH}_4$  was fully destroyed, the mixture turned from milky yellow to white.  $\text{HCl}$  was carefully added until the solution turned clear. The two layers were separated and the aqueous layer extracted two times with ether. The combined ethereal layers were then extracted with 500 ml of water and dried over  $\text{MgSO}_4$ . Rotary evaporation of the ether gave a yellow syrup. High purity product was obtained via allembic distillation at  $120^\circ\text{C}$  under approximately 0.02 mm Hg.

#### 1-Ethanol-1,2-dicarbododecaborane(12)acetate (13)

A 3-liter, 3-necked, round-bottom flask, equipped with a water-cooled reflux condenser, nitrogen gas inlet, and a mechanical cone-driven stirrer, was charged with freshly sublimed decaborane (125 gm, 1 mol) and 1.0 liter distilled benzene. When the decaborane was dissolved, distilled  $\text{CH}_3\text{CN}$  (100 ml, 1.5 mol) was added under  $\text{N}_2$ . The reaction solution was heated at gentle reflux with stirring for 1.5 hours. Solid formation is evident, indicating

$B_{10}H_{12}(CH_3CN)_2$  formation. Distilled butynacetate (130 gm, 1.2 mol), containing a small amount of phenothiazine or hydroquinone, was added to the reaction solution via a pressure-equilizing addition funnel over 2 hours and refluxed for 16 hours.

The reaction flask was allowed to cool to room temperature and the workup was done in air. The reaction solution was added to a separatory funnel containing 700 ml iced 10% aqueous KOH and 500 ml pentane. The organic layer was washed twice with 500 ml 10% KOH. The combined aqueous layer was washed with 10% KOH and then with distilled water until the pH of the aqueous layer was neutral. The organic layer was dried over  $MgSO_4$  and evaporated with the help of a rotary evaporator. The remaining solvent is evacuated using a pump to give a yellow syrup. The crude product was used as is in the reduction step to give the alcohol. The carboranylethylacetate could be purified by recrystallization from heptane. The product collected in this fashion weighed 120 gm, 50%.

### 3-Butyn-1-ol Acetate (12)

A 3-liter, 3-necked, round-bottom flask equipped with a water reflux condenser, nitrogen gas inlet, and a mechanical cone-driven stirrer was charged under dry  $N_2$  with one liter anhydrous ethyl ether, 100 gm (1.42 mol) 3-butyn-1-ol and triethylamine (300 ml, 2.1 mol). The reaction solution was stirred and chilled to about 4°C in an ice-water bath. Acetyl chloride (120 gm, 1.7 mol) was added dropwise under  $N_2$  via a pressure-equilizing addition funnel to the chilled reaction solution. Solid formation was evident. The reaction solution was stirred for 16 hours with concomitant slow warming to room temperature. Stirring was stopped and the workup was carried out in air. The mixture was washed twice with 10% Aqueous KOH. The combined aqueous layer was back-extracted with 400 ml ether. The combined organic layers were then washed with distilled water until the water layer was pH neutral. Dilute HCl may be added if necessary. The organic layer was dried over  $MgSO_4$  and filtered through a Buchner funnel. The volume of the organic layer was reduced to a minimum in a rotary evaporator using a water aspirator and then under a vacuum pump. Purification was accomplished via allembic distillation at high vacuum, approximately 0.02 mm Hg, and room temperature.

### 1-Propanol-2-methyl-1,2-dicarbododecaborane(12) (1c)

1-Methyl-1,2-dicarbododecaborane (12) (41 gm, 0.25 mol) and 250 ml of distilled ethyl ether were placed in a 1000 ml oven dried Slenck line round-bottom flask equipped with a reflux condenser, nitrogen gas inlet, and a magnetic bar. A mechanical stirrer produces better results. The solution was cooled in an ice bath for about half an hour before butyllithium (128 ml, 0.25 mol, 1.5 M) was introduced dropwise via a cannula. The solution turned cloudy as the lithiomethylcarborane precipitated out of solution. The mixture was stirred at room temperature overnight.

The mixture was cooled again in an ice bath and trimethylene oxide (16.7 ml, 0.25 mol) introduced dropwise via cannulation. The cloudy mixture turned clear yellow. The reaction mixture was stirred for two hours at room temperature and refluxed for two more hours. The thick yellow sludge that was formed was cooled in ice again and dilute HCl added until the sludge was in

solution. The ethereal layer was recovered in a separatory funnel, washed three times with distilled water, and dried over magnesium sulfate. Evaporation of the ethereal layer gave a brownish solid. The product was recrystallized from hexanes. High purity material can be obtained from three recrystallizations to give 34 gm (63%) product.

#### 3-Iodomethyl-3-methyloxetane (2a)

To a mixture of 231 gm (0.88 mol) of 3-(p-toluenesulfonyloxy)methyl-3-methyloxetane and 1200 ml of dimethylformamide was slowly added 200 gm (1.33 mol) of sodium iodide. The reaction mixture was heated to 60°C for 30 min and then cooled to room temperature. The reaction was quenched with one liter of water and this mixture was extracted twice with 200 ml of methylene chloride. The organic layer was washed twice with dilute sodium thiosulfate and once with water. The organic layer was dried over magnesium sulfate and then the solvent was removed *in vacuo*. Distillation of the crude product gave 143 gm (80% yield) distilling at 74°C and 9mm.

#### 3-(p-Toluenesulfonyloxymethyl)-3-methyloxetane (2b)

A solution of 612 gm (6 mol) of 3-hydroxymethyl-3-methyloxetane in 800 ml pyridine, in a 5 liter, three-neck flask, was cooled to -10°C. With vigorous stirring, 1364 gm (7 mol) of p-toluenesulfonyl chloride in 700 ml of pyridine was added slowly. The rate of addition was maintained so that the contents of the flask were kept below -5°C. Upon complete addition, the solution temperature was held at -5°C for 30 min, then allowed to come to room temperature and held there at least 2 hr. The contents of the flask were then quenched by pouring into 10 liters of ice water while the ice water bath was stirring vigorously. The resultant solid was filtered off, washed four times with ice water, and dried in the air. The required product was obtained in 88% yield and 98% purity.

#### 3-Bromomethyl-3-methyloxetane (2c)

Into a 3-liter, 3-neck flask, equipped with a stirrer, reflux condenser, and thermometer, were placed 688 gm (2.69 mol) of 3-(p-toluenesulfonyl)-methyl-3-methyloxetane and 700 ml of DMF. To the mixture was slowly added 257 gm (2.96 mol) of lithium bromide, and the mixture was stirred one hour at 78°C. The reaction mixture was filtered to remove precipitated lithium tosylate and then diluted with one liter of water. After extracting twice with 500 ml of methylene chloride, the aqueous layer was diluted with 500 ml of water and extracted twice more with 300 ml of methylene chloride. The organic layers were combined and dried over magnesium sulfate. The solvent was removed *in vacuo* and the crude product distilled. The yield of monomer distilling at 53°C and 2 mm was 379 gm (85% yield).

#### 1-Methanol-1,2-dicarbadodecaborane(12), p toluenesulphonate (4b)

To a solution of 3.48 gm (0.02 mol) of 1-methanol-1,2-dicarbadodecaborane, 4.19 gm (0.022 mol) of p-toluenesulfonyl chloride, and 40 ml of methylene chloride cooled to 5°C with an ice bath, was added a solution of 1.94 gm (0.022 mol) of pyridine over 15 minutes. The ice bath was removed and the reaction was allowed to warm to room temperature. After 5 hr the reaction was

poured into 100 ml of cold water to which 2 ml of concentrated hydrochloric acid had been added. The methylene chloride layer was separated and washed with water and then 50% saturated sodium bicarbonate. The methylene chloride layer was dried over magnesium sulfate and solvent removed in vacuo to give 6.7 gm of crude product as a colorless oil. This crude product contained product and both starting materials by GC analysis.

The crude product was passed through an alumina column with ethyl acetate and then fractionated through a silica gel column with hexanes-chloroform (50:50) to give 1.4 gm of white semisolid. Recrystallization from 25 ml of cyclohexane gave 1.0 gm (15% yield) of a white solid, m.p. 112-113°C. Analysis calculated for  $C_{13}H_{20}B_{10}O_3S$  was C, 35.56; H, 6.14. Found: C, 36.81; H, 6.44. NMR and FT-IR spectra agree with this structure.

#### 1-Ethanol-1,2-dicarbadodecaborane(12), p-toluenesulfonate (4c)

A solution of 1.88 gm (0.010 mol) of 1-ethanol-1,2-dicarbadodecaborane, 2.09 gm (0.011 mol) of p-toluenesulfonylchloride, 2.22 gm (0.022 mol) of triethylamine, and 45 ml of methylene chloride was stirred for 12 hours at 5°C. Another 1.11 gm (0.011 mol) of triethylamine was added and the reaction stirred another 4.5 hours. The reaction was extracted once with 50 ml of water, once with 50 ml of 1 N hydrochloric acid, and once with 50 ml of saturated sodium chloride. The organic layer was dried over magnesium sulfate and then the solvent was removed in vacuo to give 3.3 gm of a white semi-solid. The crude product was recrystallized from 40 ml cyclohexane to give 2.54 gm (74% yield) of white solid, m.p. 108-110°C. Analysis calculated for  $C_{13}H_{20}B_{10}O_3S$  was C, 38.58; H, 6.48; B, 31.57; S, 9.36. Found: C, 38.48; H, 6.62; B, 31.57; S, 9.36. NMR and FT-IR spectra agree with this structure.

#### 1-Methyl-2-propanol,1,2-dicarbadodecaborane(12), p-toluenesulfonate (4e)

A solution of 10.69 gm (0.0495 mol) of 1,2-dicarbadodecaborane-(12)-1-methyl-2-propanol, and 100 ml of methylene chloride was cooled to 5°C and then 8.76 gm (0.0866 mol) of triethylamine and 10.34 gm (0.0544 mol) of p-toluenesulfonyl chloride were added. The reaction temperature rose to 9°C before cooling again to 5°C. After 6 hr at 5°C another 2.19 gm (0.0217 mol) of triethylamine was added and the reaction stirred another 3 hr. The reaction was quenched with 100 ml of water. The organic layer was washed with 100 ml of 1 N hydrochloric acid and then 100 ml of saturated sodium chloride, and then dried over magnesium sulfate. The drying agent was removed, the solvent evaporated in vacuo to give 18.84 gm of a white solid. Recrystallization from 250 ml of cyclohexane gave 12.6 gm of product, m.p. 105-106°C. Partial evaporation gave a second crop of 1.5 gm. Both crops were pure by thin layer chromatography (silica gel:methylene chloride). Analysis calculated for  $C_{13}H_{26}B_{10}O_3S$  is C, 42.14; H, 7.07; B, 29.18; S, 8.65. Found: C, 42.04; H, 7.18; B, 29.56; S, 8.91. NMR and FT-IR spectra agree with this structure.

#### 1-(2-Bromoethyl)-1,2-dicarbadodecaborane(12) (4d)

To a solution of 18.0 gm (0.05 mol) of 1-ethanol-1,2-dicarbadodecaborane-(12)-p-toluenesulfonate and 65 ml of dimethylformamide was slowly added 6.5 gm (0.075 mol) of lithium bromide and then the reaction was heated at 80°C for 3 hours. The reaction was diluted with water and extracted several times with

hexanes. The combined hexanes layers were then washed three times with water, dried over magnesium sulfate, and then the solvent was removed by evaporation to give 11 gm (86% yield) of crude product. The crude solid was passed through a silica column, eluting with hexanes/chloroform (7/3). A sample for elemental analysis was obtained by sublimation, m.p. 111-112°C. Analysis calculated for  $C_4H_{15}B_3Br$  was C, 19.13; H, 6.02; B, 43.04; Br, 31.81. Found: C, 19.24; H, 6.01; B, 42.68; Br, 31.82. The NMR and FT-IR confirmed this structure.

#### 1-(3-Bromopropyl)-2-methyl-1,2-dicarbadoecaborane (4f)

##### Method A

A mixture of 4.32 gm (0.02 mol) of 1-propanol-2-methyl-1,2-dicarbadoecaborane, 34.4 gm (47%, 0.2 mol) of hydrobromic acid, and 4.0 gm (0.04 mol) of concentrated sulfuric acid was heated to 125°C. The reaction temperature was maintained between 125 and 130°C allowing water and some hydrobromic acid to distill as more hydrobromic acid was added. After 3 hours, GC analysis showed only a trace of starting material remaining. Weight of distillate was 13.3 gm and weight of acid added was 5.0 gm. The reaction was cooled and the crude product was collected by filtration, washed with water, and air dried to give 4.91 gm of solid. The crude product was recrystallized from ethanol-water and vacuum dried to give 4.57 gm (81% yield) of white solid, m.p. 47-48°C (lit. m.p. is 46-47°C).

##### Method B

Into a 500-ml, 3-neck flask, fitted with a thermometer and nitrogen inlet tube, were placed 9.5 gm (0.036 mol) of triphenylphosphine, 6.0 gm (0.028 mol) of 1,2-dicarbadoecaborane(12)-1-methyl-2-propanol, and 50 ml DMF. Then, 5.8 gm (0.036 mol) of  $Br_2$ , diluted in 40 ml DMF was slowly added to the flask while the reaction was kept below 50°C. After one hour stirring, the DMF solution was extracted with hexanes. The hexanes layer was then washed three times with water and dried over magnesium sulfate. The solvent was then removed by evaporation, leaving a crystalline crude product, which was recrystallized from EtOH- $H_2O$  to give a pure product, m.p. 48-49°C. Analysis calculated for  $C_4H_{13}B_3Br$  was C, 25.81; H, 6.86; B, 38.72; Br, 28.62. Found: C, 26.38; H, 6.91; B, 38.55; Br, 28.88. A second crop was obtained by reducing the volume of the filtrate. Combined yield was 5.2 gm (67%).

#### 1-Methyl-2-(3-chloropropyl)-1,2-dicarbadoecaborane (4g)

Azeotropically dry 50 ml of carbon tetrachloride by heating to boiling for 10 minutes, and then cool to room temperature. Triphenylphosphine (4.0 gm, 0.0184 mol) and 1-propanol-2-methyl-1,2-dicarbadoecaborane(12) (4.8 gm, 0.0181 mol) was added and the reaction was heated cautiously to 65°C. After no vigorous exotherm occurred, the reaction was heated to 80°C and kept at 80°C for five hours. The cooled reaction was filtered and the solvent was removed by evaporation. The crude product was passed through a silica gel column, eluting with methylene chloride/hexanes (1/1 vol/vol). Recrystallization from ethanol gave 2.5 gm (66% yield) of white solid, m.p. 58-59°C. Analysis calculated for  $C_4H_{13}B_3Cl$  was C, 30.70; H, 8.16; B, 46.05; Cl, 15.10. Found: C, 30.96; H, 8.38; B, 46.12; Cl, 14.86. The NMR and FT-IR spectra confirm this structure.

1,2-Dicarbododecaborane(12)-1-methyl-2-[3-((3-methyl-3-oxetanyl)methoxy)propyl]

To a solution of 0.56 gm (0.005 mol) of 3-hydroxymethyl-3-methyloxetane and 25 ml of hexamethylphosphoramide was added over 10 min 0.24 gm of sodium hydride (60% in mineral oil, 0.006 mol). After stirring 30 min, 1.78 gm (0.005 mol) of 1,2-dicarbododecaborane(12)-1-methyl-2-propanol, p-toluene-sulfonate, was added in one portion, and the reaction temperature rose to 35°C. After 20 min all solids dissolved giving a dark orange solution. The reaction was stirred another 40 min.

A solution of the crude reaction mixture and 50 ml of ether was extracted twice with 50 ml of water and dried over magnesium sulfate. The ether was removed in vacuo to give 1.0 gm of light brown oil containing two components by thin layer analysis. These components were separated by column chromatography (silica gel:hexane/CH<sub>2</sub>Cl<sub>2</sub>). The more polar component (0.33 gm) was the title compound and could not be induced to crystallize because of a small contamination with mineral oil. A sample isolated from another reaction melted at 43-45°C. The NMR and FT-IR spectra agreed with this structure.

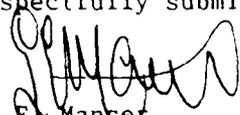
References

1. G. E. Manser, D. L. Ross, and J. M. Guimont, Summary Report, ONR Contract N00014-79-C-0525, August 1980.
2. G. E. Manser and D. L. Ross, Summary Report, ONR Contract N00014-79-C-0525, October 1981.
3. G. E. Manser and D. L. Ross, Final Report, ONR Contract N00014-79-C-0525, September 1982.
4. G. E. Manser, U.S. Patent 4,393,199, July 1983.
5. G. E. Manser, U.S. Patent 4,483,978, November 1984.
6. G. E. Manser, R. W. Fletcher, and M. R. Knight, Final Report, ONR Contract N00014-82-C-0800, July 1985.
7. G. E. Manser and R. W. Fletcher, U.S. Patent 4,707,540, November 1987.
8. G. E. Manser, R. W. Fletcher, and M. R. Knight, Final Report, ONR Contract N00014-84-C-0295, June 1985.
9. G. E. Manser, L. S. Newton, and H. W. Cheung, Summary Report, ONR Contract N00014-86-C-0164, January 1988.
10. S. Searles, Jr., "Oxetanes", Heterocyclic Compounds: Three- and Four-Membered Rings, Part Two, Interscience Publishers, New York, 1964.
11. L. A. Churkina, T. D. Zvereva, I. A. Shingel, and Yu. A. Ol'dekop, Vestsi Akad. Navuk BSSR. Ser Khim. Navuk, 1982 59-66.

12. R. N. Grimes, Carboranes, Academic Press, New York, 1970.
13. L. I. Zakharkin, V. S. Kozlova, S. A. Babich, J. Gen. Chem. USSR (Engl. Transl.) 1975, 44 1858, Zh. Obshch. Khim. 1974, 44 1891-1902.
14. J. F. Bunnett, Angew. Chem. Intn. Ed. 1 225-235 (1962).
15. L. I. Zakharkin, and N. N. Ivanova, Izv. Akad. Nauk. SSSR, Ser. Khim. 1975 2594-2596 (Engl. Transl.) 1975, 2481-3.
16. R. D. Campbell and N. H. Cromwell, J. Am. Chem. Soc. 79 3455-6 (1957).
17. T. L. Heying, J. W. Ager, Jr., S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, Inorg. Chem. 2 1089 (1963).
18. M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, Inorg. Chem. 2 1111 (1963).
19. L. I. Zakharkin, V. I. Stanko, V. A. Brattsev, Yu. A. Chapovskii, A. I. Klemova O. Yu. Okhlobysten, and A. A. Ponomarenko, Dokl Akad Nauk SSSR 15 5 1119 (1964).
20. L. I. Zakharkin, V. I. Stanko, V. A. Brattsev, Yu. A. Chapovskii, and Yu. T. Struchkov, Izv. Akad. Nauk SSSR, Ser. Khim. 2069 (1963).
21. E. L. Muetterties, Ed., Inorg. Syntheses, 10, 100 (1967).
22. L. I. Zakharkin, V. A. Brattsev, and V. I. Stanko, Zh. Obshch. Khim. 36 886 (1966). CA 65:10603h.
23. L. I. Zakharkin, A. V. Kazantsev, and L. E. Litovchenko, J. Gen. Chem. USSR (Engl. Transl.) 1975, 43, 2379-86. Zh. Obshch. Khim. 1975 43, 2394-2402.
24. G. E. Manser and R. W. Fletcher, "Energetic Thermoplastic Elastomer Synthesis", International Society for Optical Engineering Optoelectronics and Laser Application 88 Meeting, Los Angeles, CA, January 1988.

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