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CARBORANE BURNING RATE MODIFIERS.(U)
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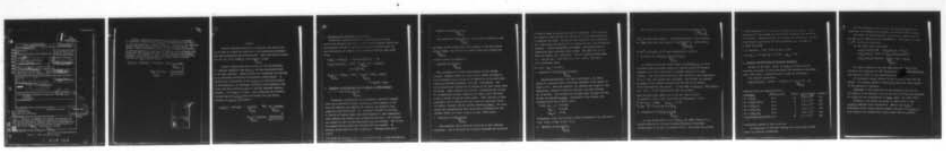

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Several carborane derivatives containing side chains that can be used to attach the carborane to the polybutadiene backbone have been synthesized and characterized. These derivatives contain the S-H, OH, Si-H, $P(MMe_2)_2$, and Hg-C-C-H groups.

$B_{10}H_{10}$

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Kinetic studies have been carried out and the mechanism of carborane formation from $B_{10}H_{12}L_2$ has been postulated based on the data obtained. Highest yields of o-carboranes are obtained using acetylenes containing electronegative substituents. In general, best utilization of the $B_{10}H_{12}L_2$ on hand would consist of the preparation of carboranes containing electronegative side chains and then converting these to desired compounds whenever possible. For example, to make n-hexyl carborane the following reaction may use $B_{10}H_{12}L_2$ more efficiently than the direct reaction of $B_{10}H_{12}L_2$ with octyne.

$$B_{10}H_{12}L_2 + HC{\equiv}CCH_2Br \rightarrow HC{-}CCH_2Br \xrightarrow{Mg} HC{-}CCH_2MgBr$$

$$\begin{array}{l} HC{-}CCH_2MgBr \\ \quad\backslash O / \\ \quad\ B_{10}H_{10} \end{array} \xrightarrow{CH_3(CH_2)_4Br} \begin{array}{l} HC{-}C{-}(CH_2)_5CH_3 \\ \quad\backslash O / \\ \quad\ B_{10}H_{10} \end{array}$$

Summary

Several carborane derivatives containing side chains that can be used to attach the carborane to the polybutadiene backbone have been synthesized and characterized. These derivatives contain the S-H, OH, Si-H, $P(NMe_2)_2$, and Hg-C(O)$B_{10}H_{10}$-C-H groups.

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$$B_{10}H_{12}L_2 + HC{\equiv}CCH_2Br \rightarrow HC(O)B_{10}H_{10}CCH_2Br \xrightarrow{Mg} HC(O)B_{10}H_{10}CCH_2MgBr$$

$$HC(O)B_{10}H_{10}C\text{-}(CH_2)_5CH_3 \xleftarrow{CH_3(CH_2)_4Br} HC(O)B_{10}H_{10}CCH_2MgBr$$

A. Synthesis and Procurement of Materials

Decaborane, hydroxy-terminated polybutadiene and curing agents were obtained from the U.S. Army Missile Command, Huntsville. Approximately 300 gms of ortho-carborane, the starting point for most derivatives of interest, were prepared using the route shown below:

$$B_{10}H_{14} + 2(C_2H_5)_2S \rightarrow B_{10}H_{12}[(C_2H_5)_2S]_2 + H_2$$

$$B_{10}H_{12}[(C_2H_5)_2S]_2 + RC{\equiv}CR \rightarrow RC\underset{B_{10}H_{10}}{\overset{O}{\backslash/}}CR + H_2 + 2(C_2H_5)_2S$$

$$(R = CH_3\overset{O}{\overset{\|}{C}}\text{-}OCH_2)$$

$$RC\underset{B_{10}H_{10}}{\overset{O}{\backslash/}}C\text{-}R + 8KMnO_4 + 10KOH \rightarrow H\text{-}C\underset{B_{10}H_{10}}{\overset{O}{\backslash/}}C\text{-}H + 8MnO_2 + 6K_2CO_3$$

$$+ 6CH_3COOK + 8H_2O$$

B. Synthesis of Derivatives for Attachment to HTPB Polymers.

1. Synthesis of $Hg(-C\underset{B_{10}H_{10}}{\overset{O}{\backslash/}}C\text{-}H)_2$

o-Carborane (0.028 moles) was dissolved in 100 mls of diethyl ether and 0.028 moles of butyl lithium was added dropwise at 0°C. After the addition was complete the reaction was warmed to room temperature and stirred for 1 hr. Mercuric chloride (0.014 moles in 100 mls of diethyl ether) was added dropwise at room temperature; after addition the reaction was refluxed for one hour. The reaction was allowed to cool to room temperature and was filtered. The solvent was removed and the solid was extracted with hot pentane. On coolinga white solid (5.3 gms.) separated. (decomposition point, 172°C).

I.R. peaks of interest: 3.85μ (B-H stretch) 13.90 μ (cage deformation)

2. Synthesis of $HSCH_2C\text{-}C(O)B_{10}H_{10}CH_2SH$

The reaction of $BrCH_2C\text{-}C(O)B_{10}H_{10}CH_2Br$ and thiourea followed by base hydrolysis of the residue gave small amounts of the bis-sulfide $HSCH_2C\text{-}C(O)B_{10}H_{10}CH_2SH$. Due to the low overall yield this reaction was avoided in favor of synthesis 3.

3. Synthesis of $HSC\text{-}C(O)B_{10}H_{10}SH$

This procedure is a slight modification of that already reported. Powdered sulfur (1.6 gms, 0.05 g atoms) was added in small increments over a period of 10 minutes to an ice-cold ether solution of dilithio-carborane (3.61 gms, 0.025 moles). The yellow solution was stirred for 25 minutes at 0°C and a white solid was formed. After removing the ice-bath, the mixture was stirred for an additional 25 mins, cooled to 0°C again, and 0.080 moles of HCl in 50 mls of H_2O was added slowly. After stirring at room temperature for 15 minutes the ether layer was separated, dried over $MgSO_4$, filtered, and the solvent removed <u>in vacuo</u>. The crude product was recrystallized from low boiling petroleum ether and sublimed [180°C (0.5 torr] to give 5.0 gms. (≥90% yield).

4. Synthesis of $HOCH_2C\text{-}C(O)B_{10}H_{10}CH_2OH$

This synthesis was carried out similarly to that reported previously. 45g (0.08 moles) of potassium hydroxide was dissolved

in 50ml of water and mixed with 340 ml of methanol. This solution was cooled to 20°C and 45g (0.16 moles) of 1.2-bis-(acetoxymethyl)-o-carborane was added. The mixture was stirred at room temperature for 2 hours, then was poured into 1.7 liters of water and neutralized with HCl. A white precipitate was formed. The precipitate was washed with water and dried under vacuum. The yield was 32.3 g (99%) of product (m.p. 302-303°C). The i.r. spectrum shows peaks at: 3.0μ (OH st.), 3.85 μ(B-H st.), 9.4 - 10.4μ (B-H def.), 13.9 μ(carborane cage).

^1H n.m.r: δ_{CH_2} = 4.3 pp.m.

5. Synthesis of $H(CH_3)_2SiC\text{-}C\text{-}Si(CH_3)_2H$ (O bridge, $B_{10}H_{14}$)

Dimethylchlorosilane, 6.05 gms (0.064 moles), was added slowly to a stirred slurry of dilithio-carborane (0.031 moles) in ether at 0°C. After the addition, the reaction was warmed to room temperature, allowed to stand for one hour, and then refluxed for 30 minutes. The solution was filtered under nitrogen and the solvent was removed <u>in vacuo</u>. Extraction of the residue with petroleum ether gave a white solid.

^1H nmr, δ_{Si-H} = 4.22 ppm

δ_{CH_3} = 0.35 ppm

J_{CH_3-H} = 4.8 Hz

IR Spectrum, 3.38μ (C-H stretch) 3.85μ(B-H stretch) 4.61μ (Si-H st.); 7.1μ; 7.95μ; 11.80μ; 12.35μ; 13.9μ

6. Synthesis of $H_2Si(C\text{-}C\text{-}H)_2$ (O bridge, $B_{10}H_{10}$)

The reaction of lithio-carborane with $SiCl_4$ gave $\left(HC\text{-}C\begin{smallmatrix}\diagup O \diagdown \\ B_{10}H_{10}\end{smallmatrix}\right)_2$ $SiCl_2$ as previously reported. Attempted reduction of the chloride by $LiAlH_4$ gave only trace amounts of $H_2Si\left(C\text{-}C\text{-}H\begin{smallmatrix}\diagup O \diagdown \\ B_{10}H_{10}\end{smallmatrix}\right)_2$ identified by by the ^1H nmr signal at 4.35 ppm characteristic of Si-H.

7. Synthesis of $[(CH_3)_2N]_2P\text{-}C\begin{smallmatrix}\diagup O \diagdown \\ B_{10}H_{10}\end{smallmatrix}C\text{-}P[N(CH_3)_2]_2$

A solution of 9.8 gms (0.063 moles) of $ClP[N(CH_3)_2]_2$ in 15 ml of diethyl ether was slowly added to a stirred slurry of dilithio-carborane (4.5 gms, 0.031 moles) in diethyl ether at 0°C under nitrogen. The light brown slurry was then stirred at room temperature for 1.5 hours and refluxed for 30 minutes. The solvent was removed in vacuo and the residue extracted with 200 mls of hot hexane. After concentration and cooling , 7.5 gms (64%) of $B_{10}H_{10}C_2[(CH_3)_2N]_2P]_2$, m.p. 114.5 - 117.5°C precipitated from the solution.

Mass spectrum gives parent ion at 381 amu (380.2 calc'd.)

IR spectrum: 3.46μ; 3.85μ; 10.35 (due to $PNMe_2$ group); 13.90μ.

^1H nmr: δ_{CH_3} = 2.8ppm $J_{P\text{-}CH_3}$ = 5.2 Hz

^{31}P nmr: δP = 107.59 ppm from H_3PO_4

8. Synthesis of $[(CH_3)_2N]_2P\text{-}C\begin{smallmatrix}\diagup O \diagdown \\ B_{10}H_{10}\end{smallmatrix}C\text{-}P\phi_2$

6.2 gms (0.040 moles) of $Cl\text{-}P(NMe_2)_2$ was added dropwise to a stirred solution of 1-lithio-2-diphenylphosphino-o-carborane (0.040 moles) in 100 mls. of benzene at 6°C. The slurry was stirred

it room temperature for 1 hour and refluxed for 20 minutes. After evaporation of the solvent the residue was extracted with 400 ml of hot n-hexane. Concentration of the extract and cooling the solution yielded white crystals of the desired product, m.p. 137-140 °C, in about 50% yield.

I.R. spectrum: 3.85μ; 6.98μ; 10.40μ; 13.90μ.

H nmr δ_{CH_3} = 2.79 ppm; δ_{ϕ} = 7.5 ppm; J_{PCH_3} = 9 Hz

C. Kinetics and Mechanism of Carborane Formation

Because of the small amount of $B_{10}H_{14}$ available and the generally low yield of ortho-carboranes from acetylenes containing alkyl side chains, a detailed kinetic study was undertaken.

The reaction studied was:

$$B_{10}H_{12}[I(CH_3)_2S]_2 + RC{\equiv}CR' \rightarrow 2(CH_3)_2S + R - C\underset{B_{10}H_{10}}{\overset{O}{\backslash\,/}}C - R' + H_2$$

Important data are summarized below:

Acetylenes	$\Delta H^{\neq}$ (kcals/mole)	$\Delta S^{\neq}$ (eu)	Rate Constant Sec^{-1}, 37°C	Yields, %
$HC \equiv CCH_2Br$	36.1	40	1.04×10^{-4}	~90
$HC \equiv CCH_2OC(O)CH_3$	34.9	34	4.35×10^{-5}	~85
$HC \equiv C(CH_2)_3Cl$	26.6	6	1.80×10^{-5}	~50
$HC \equiv C(CH_2)_2CH_3$	26.4	6	3.35×10^{-5}	~30
$HC \equiv C(CH_2)_5CH_3$	24.8	0	2.62×10^{-5}	~30
$CH_3C(O)OCH_2{\equiv}CCH_2OC(O)CH_3$	33.4	29	5.2×10^{-5}	~85

Conclusions reached in this study are:

(1) Acetylenes of the type $HC{\equiv}CCH_2X$ give much higher yields when X is electron withdrawing.

(2) Side products in the reaction of $B_{10}H_{12}[(CH_3)_2S]_2$ with acetylenes are hydroboration products with high molecular weight.

(3) Yields of ortho-carboranes are directly proportional to the Taft polar substituent constant σ^* for X. The higher the value of σ^*, the better the yield.

(4) Data best fits a mechanism:

$$B_{10}H_{12}[(CH_3)_2S]_2 \rightleftharpoons B_{10}H_{12}(CH_3)_2S + (CH_3)_2S$$

$$B_{10}H_{12}(CH_3)_2S + HC\equiv C\text{-}R \rightarrow B_{10}H_{12}[(CH_3)_2S][HC\equiv CR]$$

$$B_{10}H_{12}[(CH_3)_2S][HC\equiv C\text{-}R] \rightarrow HC\text{-}C\text{-}R + H_2 + (CH_3)_2S$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \backslash O/$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad B_{10}H_{10}$$

(5) Steric factors do not seem especially important since yields of the carborane and $\Delta S^{\neq}$ values using $CH_3C(O)OCH_2C\equiv CCH_2OC(O)CH_3$ are similar to those of mono-substituted acetylenes.

(6) Functional groups adjacent to the C≡C group give very low yields. For example, $HC\equiv C\emptyset$ or $HC\equiv COC(O)CH_3$ gave only trace amounts of the appropriate carborane.

Subsequent to the submission of this proposal and prior to the funding of the proposal, some of the data given here was reported in a paper by the investigators in Inorg. Chem., 14, 1244 (1975).

Attempts to use amines and ethers as Lewis bases in the $B_{10}H_{12}L_2$ complexes were unsuccessful. Amines give $B_{10}H_{10}^{-2}$ derivatives while ethers undergo complex reactions with $B_{10}H_{14}$ to give alcohols and unidentified complex boron hydride products.