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CHEMICALS GROUP, NEW HAVEN, CONNECTICUT 06504

Icosahedral Carboranes. X. Carborane Bis(sulfenyl chlorides) as Polymer Intermediates[1-3]

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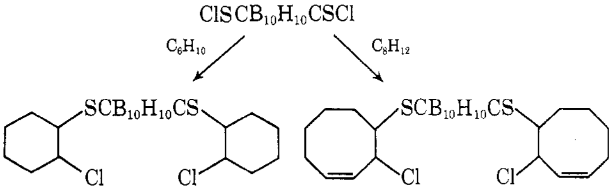
Icosahedral carborane bis(sulfenyl chlorides) could be readily obtained from the respective C,C′-dimercaptocarboranes by direct chlorination. The *meta* and *para* representatives were found to be suitable as difunctional polymer intermediates. Their conversion to polysulfides was achieved by condensation with the respective C,C′-dilithiocarboranes. *m*-$B_{10}H_{10}C_2(SCl)_2$ also formed a polydisulfide by a variety of means. In addition, both *m*- and *p*-$B_{10}H_{10}C_2(SCl)_2$ were oxidized to the corresponding bis(sulfonyl chlorides). Furthermore, nucleophilic displacement reactions of *m*-$B_{10}H_{10}C_2(SCl)_2$ as well as its addition to olefins are described.

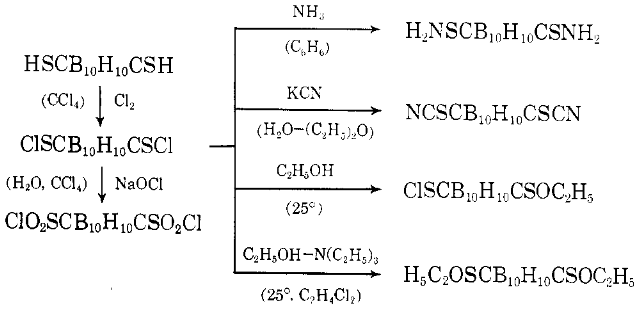
During recent years the preparation of thermally stable polymers, containing as building blocks carboranes having a $B_{10}C_2$ skeleton with the carbon atoms in *meta* configuration, has received considerable attention. For example, polymers were developed in which these icosahedral nuclei are linked *via* dimethylsiloxy groups[4,5] or single atoms such as carbon,[6] phosphorus,[7] tin,[8,9] germanium,[10,11] lead,[10,11] and mercury.[12] The polymer formed including the latter element is unique in that there are no substituents on the bridging atom.

For the synthesis of a similar polymer but having a nonmetallic bridging atom without substituents, namely, sulfur, 1,7-dimercapto-*m*-carborane[1] has now been found to be a convenient starting material. It could be readily converted into the corresponding bis(sulfenyl chloride) by direct chlorination utilizing the general procedure of Schneider.[13] The respective *o*-dithiol underwent the same reaction, but derivative and polymer chemistries of *o*-$B_{10}H_{10}C_2(SCl)_2$ were not pursued because of the observed instability of the starting material and the anticipated lack of ability to enter into polymerization reactions due to preferential formation of five-membered exocycles.

m-$B_{10}H_{10}C_2$ $(SCl)_2$ is a readily distillable liquid, stable to ordinary light (or short exposure to uv light) and stable to atmospheric moisture as well as concentrated sulfuric acid. In a study of its general activity, it was found to add easily in methylene chloride to olefins such as cyclohexene and 1,3-cyclooctadiene. In the latter case, each sulfenyl chloride group reacted with one 1,3-diene through 1,2 Markovnikov addition.[14]



To prove the susceptibility of the chlorine atoms to nucleophilic displacement, *m*-$B_{10}H_{10}C_2(SCl)_2$ was derivatized to its bis(sulfenamine), bis(thiocyanate), and bis(ethylsulfenate). The formation of the latter compound with ethanol at room temperature required the presence of triethylamine; without this scavenger, the replacement of only one chlorine by an ethoxy group occurred. On oxidation with aqueous NaOCl, it was transformed to *m*-$B_{10}H_{10}C_2(SO_2Cl)_2$, a compound stable to air and boiling water.



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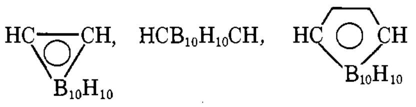
[1] Preceding communication: H. D. Smith, Jr., C. O. Obenland, and S. Papetti, *Inorg. Chem.*, **5**, 1013 (1966).

[2] Presented at the 100th Meeting of the German Chemical Society, Berlin, Sept 1967; *Angew. Chem.*, **79**, 1017 (1967); *Angew. Chem. Intern. Ed. Engl.*, **6**, 997 (1967).

[3] Nomenclature of the *closo* boron–carbon hydrides was discussed by R. Adams, *Inorg. Chem.*, **2**, 1087 (1963), and appropriate rules approved by the Council of the American Chemical Society are presented in *Inorg. Chem.*, **7**, 1945 (1968). The terms *o*-, *m*-, and *p*-carborane are used to designate 1,2-, 1,7-, and 1,12-dicarba-*closo*-dodecaborane. In accord with current practice, the following symbols are employed for representation of these isomers



[4] S. Papetti, B. B. Schaeffer, A. P. Gray, and T. L. Heying, *J. Polymer Sci., A-1*, **4**, 1623 (1966).

[5] H. Schroeder, O. G. Schaffling, T. B. Larchar, F. F. Frulla, and T. L. Heying, *Rubber Chem. Technol.*, **39**, 1184 (1966).

[6] J. R. Reiner, R. P. Alexander, and H. Schroeder, *Inorg. Chem.*, **5**, 1460 (1966).

[7] R. P. Alexander and H. Schroeder, *ibid.*, **5**, 493 (1966).

[8] S. Bresadola, F. Rossetto, and G. Tagliavini, *Chem. Commun.*, 623 (1966).

[9] H. Schroeder, S. Papetti, R. P. Alexander, J. F. Sieckhaus, and T. L. Heying, paper presented at the 3rd International Symposium on Metal Organic Chemistry, Munich, Sept 1967; *Inorg. Chem.*, **8**, 2444 (1969).

[10] S. Bresadola, F. Rossetto, and G. Tagliavini, *Chim. Ind.* (Milan), **49**, 531 (1967).

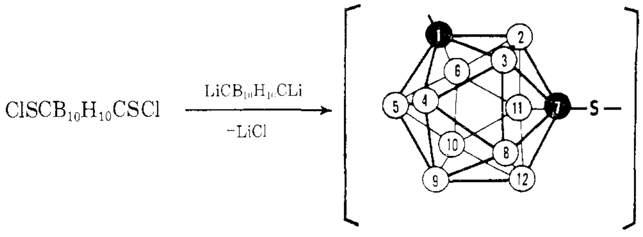
[11] S. Bresadola, F. Rossetto, and G. Tagliavini, *European Polymer J.*, **4**, 75 (1968).

[12] S. Bresadola, F. Rossetto, and G. Tagliavini, *Chim. Ind.* (Milan), **50**, 452 (1968).

[13] E. Schneider, *Chem. Ber.*, **84**, 911 (1951).

[14] This type of addition contrasts previous work and is in accordance with findings of W. H. Mueller and P. E. Butler, *Chem. Commun.*, 646 (1966), on methane- and benzenesulfenyl chloride.

Because of its difunctionality and nonadjacent position of the carbon atoms, *m*-$B_{10}H_{10}C_2(SCl)_2$ is ideally suited as a polymer intermediate. Its conversion into a polysulfide was achieved by condensation with *m*-$B_{10}H_{10}C_2Li_2$ in ether resulting in a mixture of linear polymers containing up to about 30 repeating units.

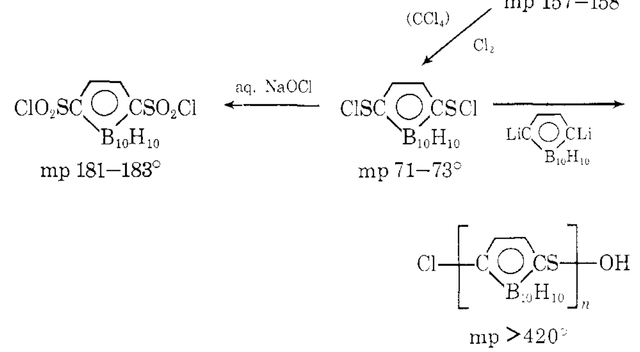


mp 219–222°

The corresponding polydisulfide, $(\text{-S-CB}_{10}H_{10}\text{C-S-})_x$, was prepared by treatment of *m*-$B_{10}H_{10}C_2(SCl)_2$ with refluxing ethanol. This reaction is presumed to proceed through *m*-$B_{10}H_{10}C_2(SCl)(SOC_2H_5)$, which could be isolated and which apparently reacts *via* a complex reaction path similar to that proposed by Douglass and Koop[15] for the methanolysis of methanesulfenyl chloride. Of all possible products formed in this reaction, only the least polar, namely, the disulfide polymer, precipitates from solution. It was also obtained by the reaction of *m*-$B_{10}H_{10}C_2(SLi)_2$ with chlorine in cold hexane or by reaction of *m*-$B_{10}H_{10}C_2Li_2$ with sulfur dichloride.

The polythiolsulfinate, $(\text{-S-CB}_{10}H_{10}\text{C-S(O)-})_x$, was formed by refluxing *m*-$B_{10}H_{10}C_2(SCl)_2$ in water. The structure was ascertained by elemental, molecular weight, and infrared analyses. In the ir spectrum, the $S \rightarrow O$ absorption appears as a strong singlet at 8.80 μ, while one would expect the respective thiolsulfonate to absorb at two positions as has been shown for various thiolsulfonates.[16] In this regard, the asymmetric and symmetric vibrations of the SO_2 group of *m*-$B_{10}H_{10}C_2(SO_2Cl)_2$ were found at 7.15 and 8.45 μ, respectively.

Since all of these *m*-carborane-based polymers exhibited melting points below the temperature level hoped for, we were prompted to extend this work to include the *p*-carborane isomer. Starting from its dilithio salt, a similar series of reactions was conducted culminating in poly-*p*-carboranylene sulfide



This product, also a crystalline solid, starts to soften only above 420°. It is insoluble in common organic solvents thus preventing determination of its molecular weight. An even more stable polymer should be expected from the respective bis(sulfonyl chloride) which was obtained in good yield by oxidation of *p*-$B_{10}H_{10}C_2(SCl)_2$. However, treatment with *p*-$B_{10}H_{10}C_2Li_2$ resulted only in a lithium–chlorine exchange; the same type of reaction was observed between *m*-$B_{10}H_{10}C_2(SO_2Cl)_2$ and *m*-$B_{10}H_{10}C_2Li_2$. These results can be attributed to the stability of the resulting disulfonylcarborane dianions and are not so surprising since a similar halogen–lithium interconversion has been reported recently[17] in the reaction of benzylsulfonyl halide with phenyllithium.

Experimental Section[18]

Starting Materials.—Crude *o*-carborane[19] was recrystallized from petroleum ether (bp 65–110°) for experimental use; *m*-carborane was prepared from crude *o*-carborane *via* a continuous-flow process[20] and refined by vacuum sublimation; *p*-carborane was made by the same flow process[20] but purified by elution chromatography on basic alumina.[21]

Chlorination of C,C′-Dimercaptocarboranes. 1,7-Bis(chlorosulfenyl)-*m*-carborane.—A solution of 31.26 g (0.15 mol) of 1,7-bis(mercapto)-*m*-carborane in 300 ml of CCl_4 was cooled to −20° and stirred mechanically under a nitrogen sweep. To this solution, maintained at −20 to −15°, was added over a 90-min period a solution of 23.40 g (0.33 mol) of chlorine in 200 ml of CCl_4. The resulting solution was allowed to warm slowly to room temperature and then allowed to stand under nitrogen overnight. Evaporation of the solution yielded an orange residue (41.4 g) that was vacuum distilled to yield 32.59 g (78%) of *m*-$B_{10}H_{10}C_2(SCl)_2$, bp 97–98° (0.17 mm), $n^{25}D$ 1.6172. The mass spectrum shows the expected molecular ion group centered around *m/e* 277 and a fragmentation pattern compatible with the assumed formula. The ir spectrum is very simple with only three major absorptions due to B–H stretching (3.79 μ), B–H deformation (9.2 μ), and cage vibration (13.76 μ). *Anal.* Calcd for $C_2H_{10}B_{10}Cl_2S_2$ (277.25): C, 8.66; H, 3.61; B, 38.99; Cl, 25.58; S, 23.13. Found: C, 9.11; H, 3.79; B, 38.89; Cl, 25.60; S, 22.50.

Similarly, the isomeric *o*-$B_{10}H_{10}C_2(SCl)_2$ was obtained as a yellow solid and purified by recrystallization from acetonitrile; mp 79–80°. To avoid decomposition, the product was stored in the cold under nitrogen. *Anal.* Found: C, 8.63; H, 3.65; B, 38.71; Cl, 25.32; S, 23.22.

The same procedure was used to prepare *p*-$B_{10}H_{10}C_2(SCl)_2$ which was purified by vacuum sublimation; mp 71–73°. *Anal.* Found: C, 9.18; H, 3.78; B, 39.32; Cl, 24.32; S, 22.30.

Oxidation of C,C′-Bis(chlorosulfenyl)carboranes. 1,7-Bis(chlorosulfonyl)-*m*-carborane.—A solution of 92.4 g (0.33 mol) of *m*-$B_{10}H_{10}C_2(SCl)_2$ in 1000 ml of CCl_4 was stirred mechanically under nitrogen. To this solution, maintained at 25–28°, was added 2300 g (*ca.* 1.65 mol) of 5% aqueous sodium hypochlorite

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(15) J. B. Douglass and D. A. Koop, *J. Org. Chem.*, **27**, 1398 (1962).

(16) S. S. Block and J. P. Weidner, *Appl. Spectry.*, **20**, 73 (1966).

(17) Y. Shirota, T. Nagai, and N. Tokura, *Tetrahedron*, **23**, 639 (1967).

(18) Melting points are uncorrected (Mel-Temp apparatus); elemental analyses were by the Olin Microchemical Section under the supervision of Dr. R. C. Rittner; the mass spectra were obtained and interpreted by H. Hoberecht; ^1H nmr spectra were recorded by Dr. J. S. Babiec; the molecular weights were determined using a Mechrolab vapor pressure osmometer, Model 301. Measurements in each case were conducted at four different concentrations ranging between 5 and 25 g/l.

(19) We thank Mr. R. W. Blundon for preparing a continuing supply of both *o*- and *m*-carborane for this research.

(20) S. Papetti, C. Obenland, and T. L. Heying, *Ind. Eng. Chem., Prod. Res. Develop.*, **5**, 334 (1966).

(21) J. F. Sieckhaus, N. S. Semenuk, T. A. Knowles, and H. Schroeder, *Inorg. Chem.*, **8**, 2452 (1969).

("Clorox") over a 60-min period. The stirring was continued for 2 more hr, at which time the yellow color had completely disappeared. The CCl_4 layer was then separated from the water layer, washed with water, and dried over sodium sulfate. Evaporation yielded 108.7 g of a soft, white solid that was recrystallized from low-boiling petroleum ether to yield 77.7 g (68%) of pure *m*-$B_{10}H_{10}C_2(SO_2Cl)_2$, mp 62–63°. The ir spectrum shows both asymmetric and symmetric SO_2 stretching at 7.15 and 8.45 μ, respectively. *Anal.* Calcd for $C_2H_{10}B_{10}Cl_2O_4S_2$ (341.23): C, 7.04; H, 2.95; B, 31.68; Cl, 20.78; S, 18.79. Found: C, 7.21; H, 2.98; B, 31.93; Cl, 20.6; S, 18.55.

The crude **1,2-bis(chlorosulfonyl)-*o*-carborane** was obtained in the same manner as the *meta* isomer. Like its precursor, it was stable only at low temperature and was difficult to purify. The product did show the characteristic sulfonyl chloride absorption in the infrared spectrum.

The respective *para* isomer, *p*-$B_{10}H_{10}C_2(SO_2Cl)_2$, was obtained in a similar fashion and purified by recrystallization from a heptane–benzene mixture; mp 181–183°. *Anal.* Found: C, 7.39; H, 3.23; B, 31.42; Cl, 20.88; S, 18.87.

1,7-Bis(sulfenamino)-*m*-carborane.—Ammonia was passed into a stirred solution (150 ml of benzene) of *m*-$C_2B_{10}H_{10}(SCl)_2$ (5.54 g, 0.02 mol). Ammonium chloride precipitated and the temperature rose to 45°. After 15 min, the suspension was filtered, and the filtrate was evaporated. The resulting liquid residue (4.3 g) was vacuum distilled to yield 2.56 g (45%) of *m*-$B_{10}H_{10}C_2(SNH_2)_2$, a colorless liquid, bp 120–123° (0.15 mm), u^{25}D 1.6296. In the ir spectrum NH_2 stretching appears as a doublet at 2.8 and 2.9 μ and NH_2 deformation appears at 6.3 μ. *Anal.* Calcd for $C_2H_{14}B_{10}N_2S_2$ (238.38): C, 10.08; H, 5.92; B, 45.35; N, 11.76; S, 26.90. Found: C, 10.07; H, 5.98; B, 45.74; N, 11.86; S, 26.60.

Similarly prepared were the **1,7-bis(thiocyanato)-*m*-carborane** (mp 68–69°, 54% yield) from the reaction with KCN in a water–ether mixture and the **1,7-bis(ethoxythio)-*m*-carborane** (bp 114–116° (0.15 mm), n^{25}D 1.5521, 36% yield) by reaction with a slight excess of ethanol and triethylamine in ethylene dichloride. *Anal.* Calcd for $C_4H_{10}B_{10}N_2S_2$ (258.38): C, 18.59; H, 3.90; B, 41.84; N, 10.84; S, 24.82. Found: C, 18.58; H, 3.95; B, 41.74; N, 10.79; S, 24.7. In the ir spectrum SCN stretching occurs at 4.65 μ. Calcd for $C_6H_{20}B_{10}O_2S_2$ (296.46): C, 24.31; H, 6.80; B, 36.47; S, 21.63. Found: C, 24.62; H, 6.70; B, 35.96; S, 21.35.

1,12-Bis(mercapto)-*p*-carborane.—*p*-$B_{10}H_{10}C_2Li_2$ was prepared in the conventional fashion by addition of 280 ml (0.44 mol) of 16% *n*-butyllithium solution (hexane) to a solution of 28.84 g (0.20 mol) of *p*-carborane in 60 ml of diethyl ether. After inverse filtration, the lithio salt was suspended in 200 ml of ether and added to a cooled suspension of 12.82 g (0.40 mol) of sulfur in ether, with the temperature being maintained at 5–15° during addition. After completion of addition, the temperature was allowed to rise to 25° and then to 32–35° for 2 hr. The reaction mixture was then hydrolyzed in the cold with dilute HCl. The resulting suspension was filtered (precipitate a polydisulfide), and the ether portion of the filtrate was evaporated to yield 16.6 g of residue. Sublimation of this residue (120–155° (0.2 mm)) yielded 11.2 g of only partially purified product which, for analytical purposes, was recrystallized from hexane; mp 157–158°. *Anal.* Calcd for $C_2H_{12}B_{10}S_2$ (208.4): C, 11.53; H, 5.80; B, 51.89; S, 30.78. Found: C, 12.13; H, 5.78; B, 52.0; S, 30.74.

Addition of 1,7-Bis(chlorosulfenyl)-*m*-carborane to olefins.

1,7-Bis(2-chlorocyclohexylthio)-*m*-carborane.—A solution of cyclohexene (1.64 g, 0.02 mol) in 20 ml of methylene chloride was added to a solution of *m*-$B_{10}H_{10}C_2(SCl)_2$ (2.77 g, 0.01 mol) in 30 ml of CH_2Cl_2. After stirring at ambient temperature for 7 days (168 hr), some yellow coloration still remained. The solvent was removed to yield 4.4 g of residual yellow oil which was redissolved in 10 ml of CH_2Cl_2 and column chromatographed on basic alumina (Merck). The second fraction (1.75 g, 40%) proved to be pure product. *Anal.* Calcd for $C_{14}H_{30}B_{10}Cl_2S_2$ (441.6): C, 38.04; H, 6.85; B, 24.48; Cl, 16.05; S, 14.52. Found: C, 38.15; H, 6.91; B, 25.13; Cl, 14.18; S, 14.62.

1,7-Bis(2-chloro-3-*cyclo*-octenylthio)-*m*-carborane.—To a stirred solution of *m*-$B_{10}H_{10}C_2(SCl)_2$ (2.77 g, 0.01 mol) in CH_2Cl_2 (30 ml) was added a solution of 1,3-*cyclo*-octadiene (1.08 g, 0.01 mol) in CH_2Cl_2 (20 ml). After 4 days (96 hr), all color had disappeared. The solvent was removed by evaporation, and the residue was recrystallized from a benzene–heptane mixture to give 1.8 g of adduct, mp 149–151°. The structure was confirmed by vpc, molecular weight determination, and nmr analysis. The proton spectrum showed C–H(S) resonance at 3.17 ppm and C–H(Cl) resonance at 4.46 ppm. Confirmation of the coupling of these two resonances, hence 1,2 addition, was obtained by frequency sweep decoupling, which also established 1,2 Markovnikov addition by coupling of the C–H(Cl) resonance with the adjacent olefinic proton. *Anal.* Calcd for $C_{18}H_{34}B_{10}Cl_2S_2$: C, 43.80; H, 6.94; B, 21.90; Cl, 14.36; S, 12.99; mol wt, 493.7. Found: C, 43.90; H, 6.70; B, 22.03; Cl, 14.25; S, 12.90; mol wt, 481.

Poly-*m*-carboranylene Sulfide.—*m*-$B_{10}H_{10}C_2Li_2$ was prepared under nitrogen by the addition of a solution of 14.4 g (0.1 mol) of *m*-carborane in 400 ml of diethyl ether to a hexane solution of *n*-butyllithium (140 ml, 0.221 mol of 1.6 *M* solution). An additional 400 ml of hexane was added, and the salt was isolated by inverse filtration and then suspended in 400 ml of diethyl ether. To the well-stirred suspension was added a solution of 25 g (0.09 mol) of *m*-$B_{10}H_{10}C_2(SCl)_2$ in 200 ml of ether. The addition time was 15 min, and the temperature was maintained below 10°. After stirring at 23–30° for 60 min, the white suspension was cooled and hydrolyzed with aqueous HCl. The suspension was filtered, and the precipitate was washed with water and ether and dried *in vacuo* to yield 16.4 g (53%) of crude polymer. A portion of this polymer was recrystallized from *o*-xylene to yield a white product (mp 219–222°) of molecular weight 5391 (osmometry), which corresponds to about 30 repeating units. *Anal.* Calcd for $Cl(CB_{10}H_{10}CS)_{30}Cl$ (5299.2): C, 13.60; H, 5.71; B, 61.20; Cl, 1.34; S, 18.15. Found: C, 13.54; H, 5.60; B, 57.81; Cl, 2.07; S, 17.7.

Poly-*p*-carboranylene Sulfide.—To a slurry of 0.05 mol (from 7.2 g of *p*-carborane) of *p*-$B_{10}H_{10}C_2Li_2$ in 200 ml of diethyl ether, maintained at 10° under nitrogen, was added a solution of *p*-$B_{10}H_{10}C_2(SCl)_2$ (12.5 g, 0.045 mol) in 200 ml of ether. Following the procedure used in the *meta* series, a colorless precipitate (7.5 g) was isolated which had the expected ir spectrum for a polysulfide terminated by a hydroxy group. The polymer was high melting (>420°) and could not be rigorously purified because of lack of solubility; impurities were extracted with refluxing *o*-xylene. *Anal.* Calcd for $Cl(SCB_{10}H_{10}C)_{30}OH$: C, 13.65; H, 5.75; B, 61.42; Cl, 0.67; S, 18.19. Found: C, 12.98; H, 5.52; B, 60.32; Cl, 1.19; S, 20.3.

Poly-*m*-carboranylene Disulfide. (1) From 1,7-Bis(chlorosulfenyl)-*m*-carborane and Ethanol.—A total of 5.54 g (0.02 mol) of *m*-$B_{10}H_{10}C_2(SCl)_2$ was refluxed in 100 ml of absolute ethanol for 6 hr. Upon cooling, the suspension was filtered, and a portion of the precipitate (2.30 g, 39%) was recrystallized from chloroform to yield a white solid, mp 308–310°. In a separate experiment, the same polymer was prepared, but recrystallized from *o*-xylene, mp 307–310°. The molecular weight found by osmometry was 1771. *Anal.* Calcd for $H_5C_2O(SCB_{10}H_{10}S)_8O$-$C_2H_5$ (1740.8): C, 13.80; H, 5.21; B, 49.68; S, 29.47. Found: C, 13.93; H, 5.19; B, 48.4; S, 29.0.

(2) From 1,7-Bis(lithiomercapto)-*m*-carborane and Chlorine.—*m*-$B_{10}H_{10}C_2(SLi)_2$ was prepared from 10.42 g (0.05 mol) of the dimercaptan dissolved in 150 ml of diethyl ether and 62.5 ml (0.10 mol) of 1.6 *M* *n*-butyllithium solution (in hexane). After inverse filtration, *m*-$B_{10}H_{10}C_2S_2Li_2$ was suspended in 300 ml of petroleum ether (bp 30–60°). With the temperature maintained at -20 to 15° and a nitrogen sweep, chlorine gas was passed into the suspension at a moderate rate. After about 2 hr, an exotherm and considerable formation of HCl were noticed. Continued cooling and more nitrogen purging finally removed all further HCl from solution. The suspension was filtered and a total of 5.6 g of precipitate was isolated. After washing with water to a negative halide test and recrystallization from *o*-xylene, a total of 2.2 g of polydisulfide was isolated; mp 315–317°. *Anal.* Calcd for $Cl(SCB_{10}H_{10}CS)_{12}Cl$: C, 11.31; H, 4.75; B, 50.94; Cl, 2.78; S, 30.21. Found: C, 12.72; H, 5.01; B, 50.37; Cl, 2.86; S, 28.2.

(3) **From Dilithio-*m*-carborane and Sulfur Dichloride.**—A slurry of 0.1 mol (from 14.4 g *m*-carborane) of *m*-$B_{10}H_{10}C_2Li_2$ in 200 ml of diethyl ether was added slowly to a solution of SCl_2 (22.7 g, 0.22 mol) in ether (100 ml) while the temperature was maintained at −10°. After the addition was complete, the reaction mixture was stirred at ambient temperature for 60 min and then hydrolyzed with ice water. The suspension was filtered and the precipitate was dried *in vacuo*. This material was recrystallized from ethylene dichloride to yield 7.0 g (34%) of a white product (mp 231–233°) of molecular weight 1265 (osmometry), which corresponds to 6 repeating units. *Anal.* Calcd for $Cl(SCB_{10}H_{10}CS)_6Cl$ (1309): C, 11.01; H, 4.62; B, 49.58; S, 29.38; Cl, 5.41. Found: C, 11.59; H, 4.89; B, 50.11; S, 28.20; Cl, 5.42.

Poly-*m*-carboranylene Thiolsulfinate.—A total of 5.54 g (0.02 mol) of *m*-$B_{10}H_{10}C_2(SCl)_2$ was suspended in 50 ml of water, first refluxed periodically over a 4-hr period, and then kept at room temperature for another 20 hr. Next, the suspension was filtered, and the residue was washed successively with water and ether and dried *in vacuo* to yield 4.70 g (100%) of a white polymer. Recrystallization of a portion of this product from benzene–heptane yielded pure $Cl[SCB_{10}H_{10}CS(O)]_{11}Cl$, mp 281–285°. The molecular weight found by osmometry was 2525. *Anal.* Calcd for $Cl[SCB_{10}H_{10}CS(O)]_{11}Cl$ (2516.6): C, 10.50; H, 4.41; B, 47.25; Cl, 2.82; S, 28.03. Found: C, 11.03; H, 4.68; B, 47.84; Cl, 2.3; S, 27.72.

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Icosahedral Carboranes. XI. Germanium and Tin Derivatives of *o*-, *m*-, and *p*-Carborane and Their Polymers[1-3]

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The dilithio salts of *o*-, *m*-, and *p*-carborane were allowed to react with selected chloro derivatives of germanium and tin. In the germanium series, disubstituted *o*-carborane derivatives were formed as in the similar silicon chemistry, but the germanium *m*- and *p*-carborane products obtained were mixtures of disubstituted monomers and related polymers. In analogous reactions of the *m*- and *p*-dilithio salts with various substituted dichlorotin derivatives, it was found that the tendency toward polymerization is much more pronounced although the substituents still have a marked influence on the type of product formed. With regard to preparing high-melting linear polymers, homopolymers based on *p*-carborane nuclei linked by tin with softening points up to 420° could be obtained; in addition, related random copolymers having melting ranges between 350 and 400° were prepared.

A prime objective of this research program has been the incorporation of the $B_{10}C_2$ carborane nuclei into the backbone of essentially inorganic polymers. To this end, we have conducted studies to determine which elements or groups of elements are most suitable for linking these icosahedra. Our recent success with either dimethylsiloxy groups[4,5] or carbon,[6] phosphorus,[7] and sulfur bridges[1] prompted extension of this work to other elements, and the results wherein germanium and tin derivatives were explored are reported here.

Until this investigation was nearly completed, no such derivatives had been described. Recently, however, the syntheses of several series of such monomers[8,9] and polymers[10-13] based on *o*- and *m*-carborane but not the *para* species have been reported. Consequently, *o*- and *m*-carborane derivatives will be de-

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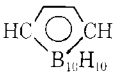
[1] Preceding communication: N. S. Semenuk, S. Papetti, and H. Schroeder, *Angew. Chem., Intern. Ed. Engl.*, **6**, 997 (1967); *Inorg. Chem.*, **8**, 2441 (1969).

[2] Presented at the 3rd International Symposium of Metal Organic Chemistry, Munich, Sept 1967.

[3] Nomenclature of the *closo* boron–carbon hydrides was discussed by R. Adams, *Inorg. Chem.*, **2**, 1087 (1963), and appropriate rules approved by the Council of the American Chemical Society are presented in *Inorg. Chem.*, **7**, 1945 (1968). The terms *o*-, *m*-, and *p*-carborane are used to designate 1,2-, 1,7-, and 1,12-dicarba-*closo*-dodecaborane. In accord with current practice, the following symbols are employed for representation of these isomers

$HCB_{10}H_{10}CH$,



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