for 2 hr at 150°, 1 hr at 200°, and then for 2 hr at 260°. When the tube was opened at ambient temperature, there was sufficient gas pressure to cause mechanical failure and loss of the gas. The viscosity of the material had increased markedly. An additional 0.0080 g of the same catalyst was added and the mixture was similarly reheated at 215° for 7 hr. The residual material at ambient temperature was a yellow glass which became a viscous liquid at 80–85°. An infrared spectrum showed a decrease in the relative intensity of the C=C stretching mode at 1644 $\text{cm}^{-1}$, and the entire spectrum showed a considerable loss of resolution indicating restricted molecular motion characteristic of polymeric species.

$\alpha,\alpha'$-Azobisisobutyronitrile, 0.0310 g, was dissolved in a solution of about 6 g of *sym*-P-(triallyltrimethyl)cyclotriborphosphane (I) and 6 g of *o*-xylene. The mixture was heated in an inert atmosphere at 125° for 2 hr, during which time a small amount of noncondensable gas was evolved (nitrogen from decomposition of the catalyst). The viscosity of the solution remained unchanged, and on removal of most of the xylene, a mobile liquid remained.

**Acknowledgments.**—The authors wish to thank Dr. Frederick F. Caserio, Jr., and Messrs. LeVern D. Freeman and Gordon F. Dierks for preliminary experiments, Mrs. Nancy J. Naumann for helpful interpretations of infrared spectra, Messrs. Kent A. Smitheman, Karl H. Sterner, and M. Eugene Persons for analyses, Mr. Danford E. Clark for molecular weight determinations, and Dr. Marvin H. Goodrow for helpful discussions. Finally, we are indebted to Mr. Harley J. Rockoff for first synthesizing 3-dimethylaminopropylmethylphosphine and Mr. Francis X. Maggio for the preliminary experiments on polymerization of *sym*-P-(triallyltrimethyl)cyclotriborphosphane (I).

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CONTRIBUTION FROM THE OLIN RESEARCH CENTER,
CHEMICALS DIVISION, NEW HAVEN, CONNECTICUT

# A New Series of Organoboranes. IX. The Preparation and Some Reactions of Sulfur–Carborane Derivatives[1]

BY H. D. SMITH, JR., C. O. OBENLAND, AND S. PAPETTI

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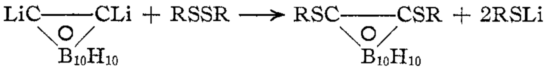
The first examples of sulfur derivatives of *o*- and *m*-carborane are reported and the preparative reactions have been extended to include various B-bromocarboranes. Some chemistry of these derivatives is described including the preparation of an inner complex of nickel.

Although a considerable number of *o*- and *m*-carborane[2] derivatives have been reported,[3] there is no mention of a compound in which a group VI element is linked directly to the carborane nucleus.

It was logical to expect that this series of compounds should be capable of existence since the nature of the group VI congeners, in general, and sulfur in particular, should permit facile attachment by methods previously reported.[4]

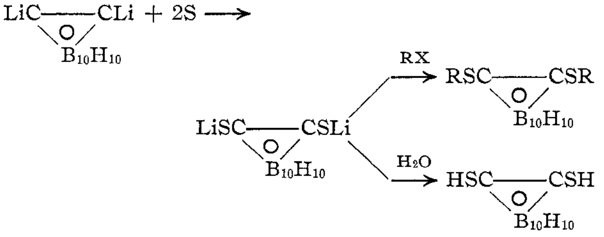
First attempts to establish a sulfur–carborane bond were based on the metathesis of dilithio-*o*-carborane with sulfur dichloride. Although the reaction was conducted under various conditions, no monomeric compounds were isolated. Instead, low molecular weight polymeric materials containing a disulfide linkage were obtained.

The next reactions attempted the cleavage of organic disulfides according to eq 1. The desired reaction



$$\underset{\mathrm{B_{10}H_{10}}}{\mathrm{LiC{-}{-}CLi}} + \mathrm{RSSR} \longrightarrow \underset{\mathrm{B_{10}H_{10}}}{\mathrm{RSC{-}{-}CSR}} + 2\mathrm{RSLi} \qquad (1)$$

occurred with the dilithio salts of both *o*- and *m*-carborane to give the bis(thioethers) in excellent yields. The mechanism is presumed to be a bimolecular nucleophilic substitution on sulfur by the carboranyl carbanion. Subsequently, the same product was isolated from the reaction of the dilithio carboranes with elemental sulfur followed by treatment of the intermediate salt with an alkyl halide (eq 2). Hydrolysis of the intermediate resulted in the bis(mercapto) derivative (eq 3). The reaction was shown to be general in that the boron-substituted mono-, di-, and tribromocarboranes[5] were converted to the corresponding derivatives.



$$\underset{\mathrm{B_{10}H_{10}}}{\mathrm{LiC{-}{-}CLi}} + 2\mathrm{S} \longrightarrow \underset{\mathrm{B_{10}H_{10}}}{\mathrm{LiSC{-}{-}CSLi}} \xrightarrow{\mathrm{RX}} \underset{\mathrm{B_{10}H_{10}}}{\mathrm{RSC{-}{-}CSR}} \qquad (2)$$

$$\underset{\mathrm{B_{10}H_{10}}}{\mathrm{LiSC{-}{-}CSLi}} \xrightarrow{\mathrm{H_2O}} \underset{\mathrm{B_{10}H_{10}}}{\mathrm{HSC{-}{-}CSH}} \qquad (3)$$

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[1] Preceding communication: P. Alexander and H. Schroeder, *Inorg. Chem.*, **5**, 493 (1966).

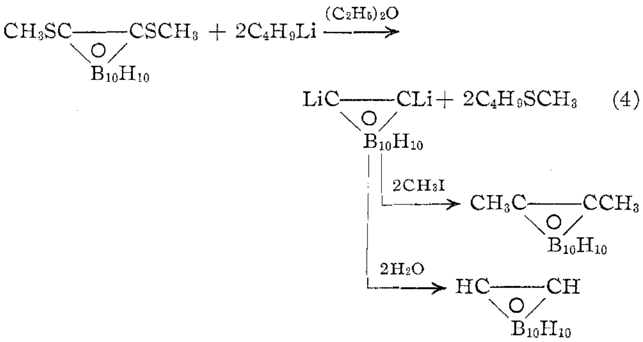
[2] We use the terms *o*- and *m*-carborane to refer to 1,2- and 1,7-dicarbaclovododecaborane, respectively. The basic nomenclature of the clovo boron–carbon hydrides is discussed by R. Adams, *Inorg. Chem.*, **2**, 1087 (1963).

[3] See pertinent references in the review by V. I. Stanko, Yu. A. Chapovskii, V. A. Bratsev, and L. I. Zakharkin, *Usp. Khim.*, **34**, 1011 (1965), and references therein.

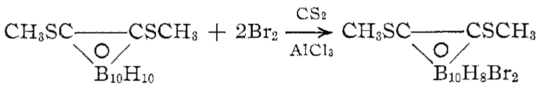
[4] For example, see S. Papetti and T. L. Heying, *Inorg. Chem.*, **2**, 1105 (1963).

[5] H. D. Smith, T. A. Knowles, and H. A. Schroeder, *ibid.*, **4**, 107 (1965); J. A. Potenza, W. N. Lipscomb, G. D. Vickers, and H. Schroeder, *J. Am. Chem. Soc.*, **88**, 628 (1966).

Since the carborane nucleus is highly electronegative,[6,7] it was suspected that it would affect reactions involving an attack at the sulfur atoms now bound directly to them. This proved to be the case as illustrated by the action of butyllithium. In contrast to the facile metalation of alkyl or mixed alkyl–aryl sulfides, the reaction of *o*-carborane-1,2-bis(methyl thioether) with *n*-butyllithium resulted in the cleavage of the carborane–sulfur bond according to eq 4.

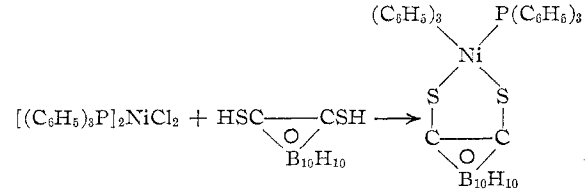

(4)

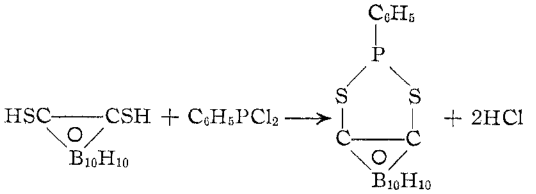
Another reaction typical of organic sulfides is the facile formation of addition compounds with chlorine or bromine.[8] In contrast, no reaction was observed when *o*-carborane-1,2-bis(methyl thioether) and the corresponding *meta* derivative were refluxed with bromine in carbon tetrachloride or carbon disulfide. Addition of aluminum chloride in the latter case gave rise to substitution on the carborane nucleus with still no evidence of attack of the sulfur atom (eq 5). Treatment of the same compounds with chlorine under various conditions had no effect.


(5)

$$\underset{B_{10}H_{10}}{CH_3SC\text{—}CSCH_3} + 2Br_2 \xrightarrow[AlCl_3]{CS_2} \underset{B_{10}H_8Br_2}{CH_3SC\text{—}CSCH_3} \quad (5)$$

An extensive investigation of the reactions of the bis(mercapto)carboranes is in progress and will be reported in detail in subsequent publications. We can note at this time, however, that in the case of 1,2-bis(mercapto)-*o*-carborane there is the expected tendency for it to enter into reactions which will give products where the two carbon atoms of the *o*-carborane nucleus participate in a five-membered ring.[4,9,10] For example, it readily reacted with dichlorobis(triphenylphosphine)nickel(II) to give a nonionic, olive-green complex according to reaction 6 which had zero magnetic moment, indicating it to be square-planar in conformation. The bis(mercapto) compound also reacted readily with dichlorophenylphosphine according to reaction 7 to form the cyclic product shown. Although its mass spectrum indicates it to be monomeric as expected, in the vapor state, determinations of molecular weight in chloroform and benzene gave values equivalent to a dimer in solution. We are attempting to define the structure of the dimeric species.


(6)


(7)

## Experimental Section

**Materials.**—All reagents and solvents were used as received from the various commercial sources; *o*- and *m*-carborane and their brominated derivatives were prepared according to standard literature procedures.[5,11,12]

**Analyses and Properties.**—Melting points are uncorrected (Mel-Temp capillary tube apparatus); elemental analyses were by R. Rittner, R. Culmo, J. D. Giunta, and A. C. Mayer of the Olin Microchemical Section, and the results are presented in Table I.

**1,2-Bis(mercapto)-*o*-carborane (I).**—To an ice-cold, nitrogen-blanketed dilithio-*o*-carborane solution, prepared from 72.2 g (0.5 mole) of *o*-carborane and 64 g (1.0 mole) of *n*-butyllithium, was added 35 g (1.1 g-atoms) of powdered sulfur in small increments over a 10-min period. The resulting yellow solution was stirred for 30 min, during which time a white solid separated. The ice bath was removed and stirring continued for an additional 30 min. The flask was next cooled to 0°, and a solution of 1.5 moles of HCl in 300 ml of water was added at a moderate rate. After stirring at room temperature for 15 min, the ether layer was separated, dried over magnesium sulfate, and evaporated to dryness, yielding 104 g (100%) of crude bis(mercapto)-*o*-carborane, which was recrystallized from petroleum ether (30–60°) and then sublimed [180° (0.5 mm)].

**1,2-Bis(mercapto)polybromocarboranes.**—The procedure for the synthesis of the bis(mercapto)bromocarboranes was identical with that for I. The monobromo derivative (II) was recrystallized from petroleum ether (30–60°), while the tribromo compound (III) was recrystallized from a carbon tetrachloride–hexane mixture.

***o*-Carborane-1,2-bis(methyl thioether) (IV). (a) From Dimethyl Disulfide.**—To a dilithio-*o*-carborane solution (0.05 mole in 250 ml of ether) was added a solution of 9.4 g (0.1 mole) of dimethyl disulfide in 150 ml of ether. After stirring for 30 min, 50 ml of water was added and the ether layer was separated and dried over $MgSO_4$. The product was obtained on evaporation of the ether layer and recrystallized from petroleum ether (30–60°).

(b) **From the Dilithio Salt of 1,2-Bis(mercapto)*o*-carborane.**—The salt was prepared as described in the general procedure for the thiocarboranes. Instead of hydrolyzing with dilute hydrochloric acid an ether solution of methyl iodide was added, and the resulting yellow solution was evaporated to dryness. The residue was washed with water, dried over $P_2O_5$, and recrystallized from petroleum ether (30–60°). The product was identical with that prepared by method a.

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[6] See footnote 14 of S. Papetti, B. B. Schaeffer, H. J. Troscianiec, and T. L. Heying, *Inorg. Chem.*, **3**, 1444 (1964).

[7] M. F. Hawthorne, T. R. Berry, and P. A. Wegner, *J. Am. Chem. Soc.*, **87**, 4746 (1965).

[8] H. Gilman, "Organic Chemistry," Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1949, p 850.

[9] R. P. Alexander and H. Schroeder, *Inorg. Chem.*, **2**, 1107 (1963).

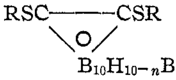
[10] H. D. Smith, Jr., *J. Am. Chem. Soc.*, **87**, 1817 (1965).

[11] 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).

[12] S. Papetti and T. L. Heying, *ibid.*, **3**, 1448 (1964).

TABLE I

TABULATION OF SULFUR–CARBORANE DERIVATIVES

| Compd | R | *n* | Mp, °C | Carbon, % Calcd | Carbon, % Found | Hydrogen, % Calcd | Hydrogen, % Found | Sulfur, % Calcd | Sulfur, % Found | Boron, % Calcd | Boron, % Found | Bromine, % Calcd | Bromine, % Found | Reaction types |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  $\underset{B_{10}H_{10-n}Br_n}{\mathrm{RSC{-}CSR}}$ | | | | | | | | | | | | | | |
| I | H | 0 | 265–267 | 11.53 | 11.77 | 5.76 | 5.80 | 30.80 | 29.98 | 51.90 | 51.91 | | | 2 |
| II | H | 1 | 138–140 | Mass spectral identification only | | | | | | | | | | 2 |
| III | H | 3 | 203–206 | Mass spectral identification only | | | | | | | | | | 2 |
| IV | $CH_3$ | 0 | 101–102 | 20.35 | 20.62 | 6.79 | 6.92 | 27.10 | 26.98 | 45.70 | 45.83 | | | 1, 3 |
| V | $CH_3$ | 2 | 181–183 | 12.20 | 12.38 | 3.55 | 3.69 | 16.25 | 16.05 | 27.40 | 27.43 | 40.60 | 41.0 | 1 |
| VI | $C_2H_5$ | 2 | 95–97 | 17.02 | 16.74 | 4.26 | 4.26 | 15.15 | 14.04 | | | 37.9 | 39.0 | 1 |
| VII | $C_6H_5CH_2$ | 0 | 102–104 | 49.60 | 49.50 | 6.18 | 6.23 | 16.50 | 16.50 | 27.80 | 27.94 | | | 1 |
| VIII | $C_6H_5$ | 0 | 189–191 | 46.60 | 46.57 | 5.55 | 5.49 | 17.85 | 17.76 | 30.00 | 30.07 | | | 1 |
| $RSCB_{10}H_{10}CSR$ | | | | | | | | | | | | | | |
| IX | H | 0 | 164–165 | 11.53 | 11.90 | 5.76 | 6.00 | 30.81 | 29.11 | 51.90 | 53.11 | | | 2 |
| X | $C_2H_5$ | 0 | *a* | 27.30 | 27.71 | 7.59 | 7.88 | 24.20 | 24.91 | 40.91 | 40.35 | | | 1 |
| XI | $CH_3C_6H_4$ | 0 | 131–132 | 49.45 | 49.69 | 6.17 | 6.30 | 16.50 | 16.32 | 27.88 | 27.79 | | | 1 |

[a] Bp 114° (0.1 mm).

**9,12-Dibromo-*o*-carborane-1,2-bis(methyl thioether) (V).**—A dilithiodibromo-*o*-carborane suspension was prepared by adding 6.4 g (0.1 mole) of *n*-butyllithium in 70 ml of hexane to a solution of 15.1 g (0.05 mole) of 9,12-dibromo-*o*-carborane in 150 ml of ether cooled to 5° and blanketed with dry nitrogen. To this suspension was added a solution of dimethyl disulfide in ether (9.4 g in 150 ml). The resulting solution was refluxed for 15–20 min and then evaporated to dryness. The residue was shaken with 100 ml of water and then extracted with hot benzene. The product was obtained by precipitating with petroleum ether and was recrystallized from hot benzene.

**9,12-Dibromo-*o*-carborane-1,2-bis(ethyl thioether) (VI).**—9,12-Dibromo-*o*-carborane (0.1 mole) in ether was added to a cooled (0–5°) solution of *n*-butyllithium (0.2 mole) in hexane. To the resulting white suspension was added 0.2 mole of diethyl disulfide in ether. Ten moles of water was added and the ether layer was separated, dried over magnesium sulfate, and evaporated to dryness, yielding a red oil. On shaking the oil with two portions of petroleum ether a tan solid was obtained which was recrystallized from hexane.

***o*-Carborane-1,2-bis(benzyl thioether) (VII) and *o*-carborane-1,2-bis(phenyl thioether) (VIII)** were obtained by the same general procedures as that described above for the methyl thioether (IV). The products were recrystallized from petroleum ether (30–60°).

**1,7-Bis(mercapto)-*m*-carborane (IX).**—A suspension of dilithio-*m*-carborane was prepared from 25 g (0.174 mole) of *m*-carborane, using the same procedure as previously described.[12] After washing with petroleum ether, the dilithio salt was slurried in ethyl ether and stirred rapidly at 5°, while 11.7 g (0.366 g-atom) of powdered sulfur was slowly added. The mixture was then stirred overnight at room temperature. About 200 ml of a 20% hydrochloric acid solution was then slowly added. The ether layer was separated and dried over anhydrous magnesium sulfate. Filtration and evaporation gave 31.8 g of light yellow solid. This was sublimed [130–150° (1–2 mm)] to give 19 g of a white sublimate, mp 161–163°, which was recrystallized from ethanol–water solution to give a white crystalline product.

***m*-Carborane-1,7-bis(ethyl thioether) (X).**—A solution of dilithio-*m*-carborane was prepared as above for IX from 6.4 g (0.1 mole) of *n*-butyllithium in 65 ml of hexane and 7.2 g (0.05 mole) of *m*-carborane in 100 ml of ether. A solution of 12.2 g of ethyl disulfide in 100 ml of ether was added. After stirring 45 min at room temperature, the contents of the reaction flask was poured into an aqueous solution of $HgCl_2$ (27.15 g in 1.5 l. of $H_2O$). The mixture was acidified and filtered, and the ether layer was separated and dried over $MgSO_4$. The product was obtained as a yellow oil on evaporation of the ether. Distillation under reduced pressure gave a colorless liquid boiling at 113° at 0.10 mm. The product was additionally identified by its mass spectrum.

***m*-Carborane-1,7-bis(*p*-tolyl thioether) (XI).**—A suspension of dilithio-*m*-carborane was prepared by the dropwise addition of an ethereal solution of 2.92 g (0.020 mole) of *m*-carborane to a hexane solution of butyllithium (0.04 mole; a 10% excess). After 1 hr of stirring at 10–15°, an equal volume of petroleum ether (30–60°) was added and the mixture was cooled to 0° and allowed to settle. The supernatant liquid was then withdrawn through a filter stick, and the white solid remaining was washed twice with fresh portions of petroleum ether. The solid was reslurried in ethyl ether for reaction. To this slurry was added 10 g (0.04 mole) of di-*p*-tolyl disulfide and the mixture was stirred for 2 hr, allowing the temperature to rise slowly to 20°. About 100 ml of water was then slowly added, and the ethereal layer was separated and dried over anhydrous magnesium sulfate. Filtration and evaporation of the ether solution gave 8.1 g of light yellow solid. This was recrystallized from ethyl ether to give a white crystalline product.

**Reaction of 1,2-Bis(mercapto)-*o*-carborane and Phenyldichlorophosphine; Compound XII.**—A solution of 1,2-bis(mercapto)-*o*-carborane (5.2 g) and phenyldichlorophosphine (4.5 g) was dissolved in 50 ml of chloroform and the solution heated to reflux. When the HCl evolution ceased, the product was evaporated to dryness. The residue was washed with low-boiling petroleum ether and recrystallized from benzene. Compound XII melted at 158–160°.

*Anal.* Calcd for $C_8H_{15}B_{10}PS_2$: C, 30.60; H, 4.77; B, 34.39; S, 9.85. Found: C, 30.29; H, 5.04; B, 34.38; S, 9.87.

**Reaction of 1,2-Bis(mercapto)-*o*-carborane with $NiCl_2[P(C_6H_5)_3]_2$; Compound XIII.**—A 1:2 molar ratio mixture of $NiCl_2 \cdot 6H_2O$ and $P(C_6H_5)_3$ in ethyl acetate was stirred for 30 min. Then 1,2-bis(mercapto)-*o*-carborane (1 molar equiv) in ethyl acetate was added. An olive-green precipitate separated which was filtered, washed with ether, and dried. The product melted at 250° and analyzed as compound XIII.

*Anal.* Calcd for $C_{38}H_{40}B_{10}NiP_2S_2$: C, 57.79; H, 5.07; B, 13.69; P, 7.85; S, 8.10. Found: C, 57.62; H, 5.20; B, 13.80; P, 8.06; S, 7.94.

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