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Organofunctional P-Substituted Cyclotriborphosphanes[1]

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3-Dimethylaminopropylmethylphosphine [bp 68° (32 mm)], prepared by reaction of 3-chloropropyldimethylammonium chloride and sodium methylphosphinide in liquid ammonia, on treatment with diborane yields either the mono- or the bis(borane) adduct. The former on pyrolysis forms, in better yield than the latter, *sym*-P-[tris(3-dimethylaminopropyl)trimethyl]cyclotriborphosphane, which was conveniently converted by methanolic hydrogen peroxide to *sym*-P-[trimethyltris(N-oxo-3-dimethylaminopropyl)]cyclotriborphosphane. This tris(amine oxide) derivative was thermally decomposed to yield *sym*-P-(triallyltrimethyl)cyclotriborphosphane, which on attempted epoxidation by monoperphthalic acid underwent rapid attack of the B–H bonds and probable destruction of the $(P-B)_3$ ring.

Introduction

Preparation of a polymer having essentially an inorganic backbone has provided a challenging and, in some instances, rewarding goal for chemists working with several different metalloid bonding systems.[3] One such effort has been directed toward heat-resistant materials based on the P–B bond. The first well-defined polymers based on the R_2PBR_2 unit were derivatives of the cyclotriborphosphane and cyclotetraborphosphane rings.[4] Later, employing tertiary amines as blocking groups, Wagner and Caserio[5] inhibited cyclization and prepared linear borphosphane polymers of moderate molecular weight.

Further investigations of these borphosphane compounds led to the syntheses of interesting derivatives involving substitution of functional groups on the boron atoms[6,7] and, in one instance, on the phosphorus atoms.[4] In the present paper examples of organofunctional P-substituted cyclotriborphosphanes are described. In particular, the derivative with an allyl group on each phosphorus atom appeared interesting as a compound which might either undergo addition polymerization by conventional means to produce a semiinorganic polymer or be useful in preparing other polymerizable compounds.

Results and Discussion

The previous approach to preparation of organo-P-substituted cyclotriborphosphanes has been thermally induced condensation polymerization of a secondary phosphine borane (*cf.* eq 1a). However, when the phosphine borane carries an unsaturated organic radical, polymerization may occur by addition of either B—H bonds[8] or P—H bonds[9] across the $C{=}C$ bond (eq 1b and 1c) as well as by P—B condensation. If the rate of P—B condensation were fast relative to the reactions involving additions across the double bond, an allyl-substituted cyclotriborphosphane might be obtained as the major product (eq 1a). To test this approach allylmethylphosphine (II) was prepared in low yield and found to be unstable with respect to polymerization probably by addition of P–H across the double bond. The polymerization rate was sufficiently slow, however, to allow formation of an unstable liquid borane adduct (III) (eq 2). The polymerization of the adduct proceeded very slowly at ambient temperature, presumably as indicated by one of the equations (1a, b, or c). No attempt was made to establish the course of reaction at ambient temperature but at elevated temperature hydroboration (eq 1b) is indicated by the amount of hydrogen formed and the absence of *sym*-P-(triallyltrimethyl)cyclotriborphosphane (I) in the product. The possibility of hydroboration of an allyl-substituted cyclotriborphosphane by a ring BH_2 group to give more complex polymeric products appears improbable under the reaction conditions used in view of the thermal stability of I prepared by the indirect method next described.

Formation of the allyl side chain subsequent to synthesis of the $(P-B)_3$ ring proved to be a satisfactory preparative method for P-allyl-substituted cyclotriborphosphanes.

3-Dimethylaminopropylmethylphosphine (IV), prepared by the reaction of 3-chloropropyldimethylammonium chloride and methylphosphinide ion in

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[3] K. R. Eilar and R. I. Wagner, *Chem. Eng. News*, **40**, No. 32, 138 (Aug 6, 1962).

[4] A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **75**, 3872 (1953), refer to these specific compounds as dimethylphosphinoborine trimer and tetramer. In this paper the name borphosphane is used together with the appropriate Greek prefixes to describe the structure unambiguously. This system is in essence the one used in an earlier paper (*cf.* footnote 2, ref 6) but using a name apparently more acceptable to a greater number of chemists than that previously proposed. The name borphosphane thus is proposed as the basis for a systematic nomenclature of related P–B compounds and not as just another trivial name for a ring system (*cf.* Ring Index, First Supplement No. 7740, which names $[H_2PBH_2]_3$ as borphosphane).

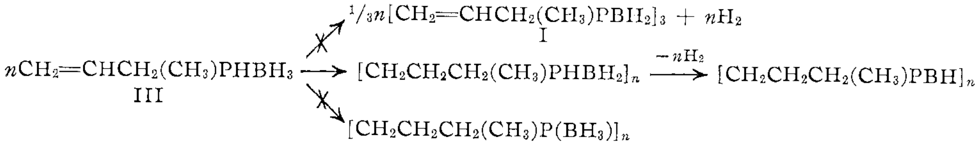
[5] R. I. Wagner and F. F. Caserio, Jr., *J. Inorg. Nucl. Chem.*, **11**, 259 (1959).

[6] M. H. Goodrow, R. I. Wagner, and R. D. Stewart, *Inorg. Chem.*, **3**, 1212 (1964).

[7] R. I. Wagner, F. F. Caserio, Jr., E. M. Evleth, Jr., L. D. Freeman, and R. D. Stewart, Abstracts of Papers presented at the 135th National Meeting of the American Chemical Society, Boston, Mass., April 1959, p 49-O.

[8] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

[9] A. R. Stiles, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **74**, 3282 (1952).



$$\underset{\text{III}}{nCH_2{=}CHCH_2(CH_3)PHBH_3} \xcancel{\nearrow} {}^1/_3n[\underset{\text{I}}{CH_2{=}CHCH_2(CH_3)PBH_2}]_3 + nH_2 \qquad (1a)$$

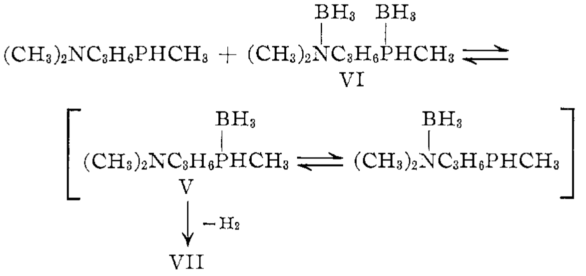
$$\underset{\text{III}}{nCH_2{=}CHCH_2(CH_3)PHBH_3} \longrightarrow [CH_2CH_2CH_2(CH_3)PHBH_2]_n \xrightarrow{-nH_2} [CH_2CH_2CH_2(CH_3)PBH]_n \qquad (1b)$$

$$\underset{\text{III}}{nCH_2{=}CHCH_2(CH_3)PHBH_3} \xcancel{\searrow} [CH_2CH_2CH_2(CH_3)P(BH_3)]_n \qquad (1c)$$

$$CH_2{=}CHCH_2Cl \xrightarrow[NH_3(l)]{CH_3PH^-} \underset{\text{II}}{CH_2{=}CHCH_2PHCH_3} \xrightarrow{{}^1/_2B_2H_6} \text{III} \qquad (2)$$

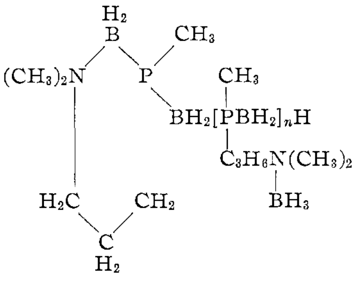
liquid ammonia (eq 3), absorbed either half-molar or equimolar amounts of diborane readily to form 3-dimethylaminopropylmethylphosphine mono(borane) (V) or bis(borane) (VI). The bis(borane) adduct served better as a solid derivative for characterization of IV than as an intermediate for *sym*-P-[tris(3-dimethylaminopropyl)trimethyl]cyclotriborphosphane (VII), which was obtained in relatively low yield by pyrolysis of VI followed by acid hydrolysis and neutralization of the tris(borane) adduct of VII. A possible explanation for the low yield of VII is that VI by intramolecular loss of hydrogen gives a cyclic compound (VIIIa) or by a combination of intra- and intermolecular loss of hydrogen a homologous series of cyclic terminated linear compounds (VIIIb) which inhibit cyclotriborphosphane formation. Such compounds would be expected to hydrolyze readily. An approximately equimolar mixture of VIIIa, VIIIb, and the tris(borane) adduct of VII is consistent with the observed "dimer" molecular weight of the crude pyrolyzate from VI and the quantity of VII finally isolated from the hydrolyzed mixture.

$$[(CH_3)_2NHC_3H_6Cl]^+Cl^- + 2CH_3PH^- \xrightarrow{NH_3(l)} \underset{\text{IV}}{(CH_3)_2NC_3H_6PHCH_3} + CH_3PH_2 + 2Cl^- \qquad (3)$$

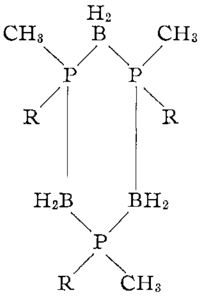


$$(CH_3)_2NC_3H_6PHCH_3 + \underset{\text{VI}}{(CH_3)_2\overset{BH_3}{N}C_3H_6\overset{BH_3}{P}HCH_3} \rightleftharpoons \left[\underset{\text{V}}{(CH_3)_2NC_3H_6\overset{BH_3}{P}HCH_3} \rightleftharpoons (CH_3)_2\overset{BH_3}{N}C_3H_6PHCH_3\right] \qquad (4)$$

$$\text{V} \xrightarrow{-H_2} \text{VII}$$



VIIIa, $n = 0$
VIIIb, $n = 1$



I, R = $-CH_2CH{=}CH_2$
VII, R = $-CH_2CH_2CH_2N(CH_3)_2$
IX, R = $-CH_2CH_2CH_2N(O)(CH_3)_2$
X, R = $-CH_2CHCH_2O$

In an attempt to avoid the undesirable side reaction and thereby increase the yield of VII markedly, the mono(borane) adduct (V) was pyrolyzed. Some solid in the liquid product initially formed was probably the bis(borane). On gentle heating the solid dissolved, suggesting the equilibrium (eq 4) which favors attachment of the BH_3 group to the phosphorus atom.[10,11] At higher temperatures elimination of hydrogen and formation of VII occurs. As was observed in the synthesis of linear polyborphosphanes,[5] pyrolysis of the secondary phospine borane (V), which contains an equivalent quantity of tertiary amine, yielded hydrogen at a much slower rate than the bis(borane) adduct (VII), which has no free amine. It is noteworthy that formation of linear polymer was not promoted. Although a small percentage of the cyclotetraborphosphane was expected,[4,5] none was observed.

Attempts to prepare a suitable derivative for purification of VII by fractional crystallization were difficult and unrewarding, probably because the material is a mixture of two trifunctional stereoisomers. The tris(quaternary methylammonium iodide) and the tripicrate formed oils while the tris(tetraphenylborate) and the tris(amine hydrochloride) formed seemingly colloidal solids on attempted recrystallization. Finally, VII was obtained pure by molecular distillation.

Selective oxidation of the amine groups in VII with methanolic hydrogen peroxide[12] to form *sym*-P-[trimethyltris(N-oxo-3-dimethylaminopropyl)]cyclotriborphosphane (IX) proceeded without complication. After evaporation of excess methanol, IX was heated to 150°, at which temperature it decomposed[13] to yield *sym*-P-(triallyltrimethyl)cyclotriborphosphane (I) with simultaneous release of bound methanol. Difficulty was encountered in decomposing all of the amine oxide groups, apparently because as one or two allyl groups are formed the volatility of the product increases, allowing it to escape from the hot zone. Residual amine oxide groups were decomposed in a closed system before the pure product (I) was isolated by molecular distillation.

Cram, Sahyun, and Knox[14] have reported a Cope elimination reaction at room temperature by allowing extremely hygroscopic solvents, like dimethyl sulfoxide, to remove the stabilizing protic material from the amine oxide, thus allowing decomposition to occur. One attempt was made to apply this method to the decomposition of IX, but for lack of time the reason for failure was not determined.

Attempted epoxidation of I with monoperphthalic acid to produce *sym*-P-[tris(2,3-epoxypropyl)trimeth-

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(10) R. A. Baldwin and R. M. Washburn, *J. Org. Chem.*, **26**, 3549 (1961).

(11) W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **3**, 164 (1956).

(12) A. C. Cope, *Org. Syn.*, **39**, 40 (1959).

(13) A. C. Cope, T. T. Foster, and P. H. Towle, *J. Am. Chem. Soc.*, **71**, 3929 (1949).

(14) D. J. Cram, M. R. V. Sahyun, and G. R. Knox, *ibid.*, **84**, 1734 (1962).

yl]cyclotriborphosphane (X) resulted in rapid attack of the B–H bonds and destruction of the ring with little effect on the unsaturated bonds as indicated by periodic infrared analyses.

Preliminary efforts were made to polymerize I itself. A Lewis acid type[15] of catalyst, boron trifluoride, used as its monoethylamine adduct in very small amount, apparently enhanced the thermal transformation of I from a mobile liquid to a glass. Comparison of the infrared spectra of the polymeric material and I showed the expected decrease in the relative intensity of the C═C bands while the intensities of the B—H bands appeared unchanged. In contrast, the free-radical initiator, α,α′-azobisisobutyronitrile, had little or no effect on I under polymerizing conditions which were, however, far less drastic than those used in the Lewis acid catalyzed polymerization.

Experimental Section

Standard high-vacuum apparatus and techniques were employed when necessary. The equipment used in the preparation of phosphines was similar to that previously described.[16] For distillation of high molecular weight products an A. F. Smith 2-in. rotary molecular still was used. All infrared spectra were obtained using a Perkin-Elmer Model 21 infrared spectrophotometer with NaCl optics. Molecular weights were determined using 0.05 *M* benzene solutions by the vapor pressure osmometric method[17] unless otherwise noted. All gas volumes are reported as measurements at standard temperature and pressure with corrections for water vapor included.

Preparation of Allylmethylphosphine (II).—Allylmethylphosphine was prepared by the addition of 18.6 g (0.24 mole) of allyl chloride to 250 ml of a refluxing liquid ammonia solution of sodium methylphosphinide, prepared from 5.3 g (0.23 g-atom) of sodium and a slight excess of methylphosphine.[16] Upon completion of the reaction, as indicated by decolorization of the orange solution, the product was separated from the reaction mixture by azeotropic distillation and mechanical separation of the two-phase distillate. Residual ammonia was removed by passing the vaporized product through a bed of anhydrous zinc sulfate suspended on glass wool at 0°. Fractional distillation through a vapor take-off column at −38° gave 4.61 g (0.052 mole, 22.5%) of allylmethylphosphine. The product was characterized by vapor density molecular weight, 87.5 (calcd 88.09) and infrared spectrum (cm^{-1}): (neat) 3080 m, 2980 m, 2920 m, 2830 w, 2274 vs, 1819 w, 1639 s, 1427 s, 1403 m, 1298 wsh, 1285 w, 1198 m, 1079 m, 992 vs, 937 s, 904 vs, 878 s, 837 w, 794 vw, 758 vw, 698 m, 677 m, 669 m. The following vapor tensions were observed [T (°C), P (mm)]: −30.8, 3.8; −22.8, 6.1; −12.5, 12.0; 0.0, 23.9; and 18.0, 62.8. These data determine the equation $\log P_{\mathrm{mm}} = 7.925 - 1786/T$, from which the boiling point was estimated to be 81° and the heat of vaporization 8.17 kcal/mole. The Trouton constant was calculated as 23.1 cal/deg-mole.

The instability of allylmethylphosphine was indicated not only by the low yield but by a nonvolatile, glassy residue remaining in the vessels from which it was distilled.

Preparation of Allylmethylphosphine Borane (III).—In order to minimize degradation induced by the exothermic formation of the borane adduct, 57.8 cc (2.58 mmoles) of diborane was introduced slowly into 0.4538 g (115.4 cc, 5.152 mmoles) of freshly distilled allylmethylphosphine (II) cooled to −78°. The liquid adduct was degassed at ambient temperature. The infrared spectrum showed the following bands (cm^{-1}): (neat) 3080 m, 2980 m, 2920 m, 2820 m, 2820 vw, 2385 vs, 2345 vssh, 2260 s, 2200 w, 2135 w, 1848 w, 1642 m, 1420 s, 1402 m, 1298 s, 1228 m, 1198 m, 1132 s, 1060 vs, 994 vs, 950 vvs, 910 vvs, 863 s, 818 vwsh, 804 m, 757 w, 748 w, 727 m, 689 vw. During 9.5 days the adduct increased in viscosity and finally became a slightly tacky solid. Infrared spectra obtained 2.5 and 9.5 days after synthesis were compared with the spectrum of the original adduct. The bands at 3080 (H_2C═ stretch) and 1642 cm^{-1} (C═C stretch) decreased in intensity while those at 2980 and 2920 cm^{-1} (resonance split H_2C—C═stretch) coalesced to a more intense band at 2930 cm^{-1}. New bands appeared in the spectrum at 1455 and 1383 cm^{-1} (asymmetric and symmetric CH_3—C deformation) and at 3515 and 3180 cm^{-1} (O—H stretch) suggesting some spurious interaction of atmospheric components.

Pyrolysis of Allylmethylphosphine Borane (III).—A 3.37-mmole quantity of freshly prepared allylmethylphosphine borane was heated in a sealed tube at 200° for 22 hr to give 74.3 cc (3.32 moles, 98.5%) of hydrogen, several milligrams of unidentified liquid which distilled from the mixture at 180°, and a nonvolatile polymeric residue about half of which was extracted by boiling benzene. Infrared spectra of both the benzene-soluble and -insoluble portions of the residue were poorly resolved but showed that no C═C bonds or P—H bonds remained and that hydrogen-bonded hydroxyl groups, presumably introduced during the extraction process, were present in abundance.

Preparation of 3-Dimethylaminopropylmethylphosphine (IV).—3-Chloropropyldimethylammonium chloride was first recrystallized from anhydrous 2-propanol and then melted and cast into cylindrical pellets of 5-mm diameter, 20–40 mm in length.

Anal. Calcd for $C_5H_{13}NCl_2$: N, 8.86. Found: N, 8.82.

Sodium methylphosphinide was prepared in 1.8 l. of freshly distilled anhydrous ammonia from 37.0 g (1.61 g-atoms) of sodium and excess methylphosphine. Pelletized 3-chloropropyldimethylammonium chloride, 139.8 g (0.884 mole, 10% excess), was added slowly to the refluxing solution from a nitrogen-swept tube used to prevent ammonolysis of the otherwise delinquescent solid. Regenerated methylphosphine was recovered from the azeotrope condenser.[16]

After the ammonia had volatilized and passed through a flare, 1.2 l. of water was added to dissolve the sodium chloride. The two-phase mixture was extracted with four 100-ml portions of *n*-hexane; the filtered and dried (20 hr over 75 g of anhydrous sodium sulfate) solution was then fractionally distilled to give 58.3 g (0.438 mole, 54.5%) of 3-dimethylaminopropylmethylphosphine, bp 68° (32 mm). The product, indicated by vapor phase chromatographic analysis to be 98.7% pure, was characterized by its infrared spectrum and the bis(borane) adduct described below. The infrared spectrum showed the following bands (cm^{-1}): (neat) 2948 vs, 2888 vssh, 2788 vs, 2275 vs, 1464 vs, 1429 s, 1377 m, 1348 w, 1289 m, 1263 s, 1228 m, 1196 m, 1164 w, 1149 w, 1125 w, 1098 m, 1062 m, 1041 s, 1018 s, 993 vs, 957 m, 887 m, 877 m, 849 m, 827 w, 780 m, 719 m, 692 m, 668 vw.

Preparation of 3-Dimethylaminopropylmethylphosphine Bis(borane) (VI).—To 42.8394 g (0.3216 mole) of 3-dimethylaminopropylmethylphosphine (IV) in a magnetically stirred 300-ml flask under a −78° reflux condenser, 7.213 l. (0.3220 mole, 100.1%) of diborane was added from the vacuum line during 5 hr to form 3-dimethylaminopropylmethylphosphine bis(borane), mp 57.5–59.5°. During addition of the diborane the temperature of the mixture was maintained just above that required to keep the mixture liquid (25–65°). The infrared spectrum showed the following bands (cm^{-1}): (KBr disk) 3025 w, 2975 w, 2380 vs, 2340 vssh, 2275 s, 2075 vw, 1480 m, 1468 m, 1440 vw, 1423 w, 1396 vw, 1335 vw, 1303 w, 1247 w, 1230 vw, 1198 m, 1168 vs, 1138 m, 1116 vw, 1069 vw, 1064 m, 1048 m, 1040 vw, 1014 m, 995 ssh, 990 s, 929 s, 878 m, 843 w, 810 w, 773 w, 748 m, 728 vw, 719 vw, 694 vw, 668 vw.

Anal. Calcd for $C_6H_{22}B_2NP$: C, 44.80; H, 13.79; B, 13.45; N, 8.71; P, 19.26; mol wt, 160.9. Found: C, 45.05; H, 13.22; B, 13.47; N, 8.67; P, 19.10; mol wt, 177 (vapor pressure osmometer), 173 (microbulliometric in benzene).

Pyrolysis of 0.6249 g (3.881 mmoles) of the bis(borane) adduct

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(15) C. E. Schildknecht, "Vinyl and Related Polymers," John Wiley and Sons, Inc., New York, N. Y., 1952, p 126.

(16) R. I. Wagner and A. B. Burg, *J. Am. Chem. Soc.*, **75**, 3869 (1953).

(17) J. J. Neumayer, *Anal. Chim. Acta*, **20**, 519 (1959).

(VI) in a sealed tube for 17.5 hr at 190–195° produced 87.4 cc (3.89 mmoles, 100%) of hydrogen which was collected by means of a Sprengel pump. Hydrolysis of the resultant semisolid with 6 ml of 6 *N* hydrochloric acid (about 100% excess) at 107° for 15 hr produced 268.9 cc (11.97 mmoles, 102.8%) of hydrogen.

Preparation of *sym*-P-[3-Dimethylaminopropyltrimethyl]cyclotriborphosphane (VII) from 3-Dimethylaminopropylmethylphosphine Bis(borane) (VI).—A 51.7584-g (0.3216 mole) quantity of VI was heated to 190–215° for 15 min, during which time 7.316 l. (0.3267 mole, 101.6%) of hydrogen as expected for borphosphane formation was evolved and measured with a wet test meter. No further hydrogen was evolved on heating for an additional 20 min. The product, presumed to be a low polymer of the unit $(CH_3)_2N(BH_3)C_3H_6(CH_3)PBH_2$, formed a viscous liquid on cooling.

Anal. Calcd for $(C_6H_{20}B_2NP)_3$: C, 45.36; H, 12.69; mol wt, 476.5. Found: C, 45.68; H, 12.48; mol wt, 299 (microebulliometric in benzene), 330 (vapor pressure osmometer).

The viscous liquid was refluxed for 2 hr with 170 ml of 8.5 *N* hydrochloric acid (1.445 moles, 50% excess) to hydrolyze the BH_3 groups, and the evolved hydrogen was measured with a wet test meter as 22.471 l. (1.003 moles, 105%). The solution was basified with 200 ml of 10.5 *M* sodium hydroxide, the resulting organic layer was extracted with four 200-ml portions of ether, and the combined extracts were dried at reflux over calcium hydride for 3 hr. After removal of the ether the crude liquid product was twice distilled in a rotary molecular still with a hot-wall temperature of 150° and once passed through the still at 80° to remove a minute amount of more volatile impurity. The small quantity, 14.3432 g (0.0330 mole, 31.3%) of *sym*-P-[trimethyltris(3-dimethylaminopropyl)]cyclotriborphosphane obtained indicated substantial loss of other material in the aqueous phase.

Anal. Calcd for $C_{18}H_{51}B_3N_3P_3$: C, 49.70; H, 11.82; N, 9.66; mol wt, 435.0. Found: C, 49.53; H, 11.57; N, 10.45; mol wt, 431 (vapor pressure osmometer). The infrared spectrum is consistent with the proposed structure: (neat) 2970 vs, 2895 vssh, 2800 vs, 2395 vs, 2360 vssh, 2220 w, 1692 w, 1466 vs, 1450 vssh, 1423 s, 1377 m, 1349 w, 1291 s, 1263 s, 1229 s, 1198 s, 1166 w, 1148 w, 1120 msh, 1109 s, 1099 msh, 1064 s, 1041 vs, 1018 vs, 990 s, 947 s, 904 ssh, 893 vs, 857 s, 800 s, 768 s, 730 s, 670 m.

Preparation of VII from 3-Dimethylaminopropylmethylphosphine Mono(borane) (V).—By absorption of 4.737 l. (0.2115 mole) of diborane by 56.4022 g (0.4230 mole) of 3-dimethylaminopropylmethylphosphine (IV) at ambient temperature a mixture of solid and liquid was produced. This slurry on heating to 60° was transformed into a free-flowing liquid which became quite glassy at approximately −70°. On further heating the liquid began to evolve hydrogen slowly at 183° and at a moderate rate at 195–224° for 7.5 hr to yield 9.96 l. (0.445 mole, 105%) as measured with a wet test meter. Purification of the crude liquid product by molecular distillation gave 49.7 g (0.114 mole, 80.9%) of *sym*-P-[tris(3-dimethylaminopropyl)trimethyl]cyclotriborphosphane, which was characterized by infrared analysis.

Preparation of *sym*-P-[Trimethyltris(N-oxo-3-dimethylaminopropyl)]cyclotriborphosphane (IX).—A 49.7-g (0.114 mole) quantity of *sym*-P-[tris(3-dimethylaminopropyl)trimethyl]cyclotriborphosphane (VII) in 600 ml of absolute methanol was mixed with 101.0 g (0.882 mole, 260% excess) of 30% hydrogen peroxide and allowed to stand at ambient temperature until it tested[12] colorless to phenolphthalein (40 hr required). Excess peroxide was destroyed by addition of about 0.7 g of platinum black[18] to the methanolic solution, which was stirred until oxygen evolution ceased (*ca.* 0.5 hr). The filtered solution was concentrated on a rotary evaporator under aspirator vacuum. The resulting viscous liquid, after several hours at 60–70° under high vacuum, became almost a glass and weighed 66.7 g (0.115 mole, 101% of $IX \cdot 3CH_3OH$). The infrared spectrum of the solvate showed the following bands (cm^{-1}): (neat) 3230 vsb, 3070 s, 2970 s, 2920 ssh, 2380 s, 2360 ssh, 2220 w, 1670 w, 1608 w, 1473 msh, 1460 m, 1426 m, 1400 vwsh, 1343 vw, 1328 vw, 1292 w, 1254 vw, 1223 w, 1184 w, 1145 w, 1108 w, 1062 m, 1038 m, 988 m, 953 m, 920 m, 894 m, 867 w, 819 vwb, 793 vw, 760 w, 744 vwb, 713 vwb, 671 vw. The presence of bound methanol was indicated by the strong broad absorption band at 3230 cm^{-1} (O–H stretching). The weak band at 1608 cm^{-1} was assumed to arise from the N–O stretching vibration.

Preparation of *sym*-P-(Triallyltrimethyl)cyclotriborphosphane (I).—Pyrolysis of the tris(amine oxide) (IX), prepared from 0.114 mole of VII and diluted with methanol to reduce the viscosity, was accomplished by passing the solution through a rotary molecular still operating at 660–675 mm pressure and a hot-wall temperature of 160–178°. The distillate and pyrolysis residue were combined and the procedure was repeated. The volatile components were removed under vacuum from the combined distillate and residue on a rotary evaporator at ambient temperature. N,N-Dimethylhydroxylamine was isolated from the trapped volatile products by high-vacuum fractional condensation and identified by infrared analysis. The mobile, yellow pyrolysate was passed through the same still at 0.005 mm and 150–165° to obtain a cloudy distillate and a viscous yellow residue which turned to a glass below the hot zone. Infrared analysis of the distillate indicated the presence of some residual amine oxide groups and thus the distillate was heated in a sealed tube for 1 hr at 150–160° to ensure completion of the pyrolysis. The distillate obtained on a final pass through the molecular still at 0.005 mm and 80–88° was 26.9 g (0.090 mole, 78.9%) of pure *sym*-P-(triallyltrimethyl)cyclotriborphosphane, which showed the expected infrared absorption bands (cm^{-1}): (neat) 3100 w, 3000 w, 2930 w, 2805 vw, 2400 vs, 2370 vssh, 2220 w, 1842 w, 1644 m, 1466 vw, 1423 m, 1400 w, 1292 m, 1194 m, 1109 m, 1067 m, 994 s, 934 m, 908 vs, 898 vs, 876 m, 826 m, 798 wb, 767 w, 725 s, 674 m.

Anal. Calcd for $C_{12}H_{30}B_3P_3$: C, 48.08; H, 10.09; mol wt, 299.8. Found: C, 48.04; H, 10.09; mol wt, 298 (vapor pressure osmometer).

Attempt to Prepare *sym*-P-[Tris(2,3-epoxypropyl)trimethyl]cyclotriborphosphane (X).—In a preliminary experiment excess ethereal monoperphthalic acid[19] was added rapidly to ethereal *sym*-P-(triallyltrimethyl)cyclotriborphosphane (I). The resulting exothermic reaction caused the ether to reflux vigorously, a result which was unexpected in light of reported[20] sluggish rates of epoxidation.

In a second experiment 261 ml of 0.264 *M* ethereal monoperphthalic acid (68.8 mmoles, 10% excess) was added at a rate of 50 ml/hr to a solution of 6.2632 g (20.88 mmoles) of *sym*-P-(triallyltrimethyl)cyclotriborphosphane (I) in 60 ml of ether. The course of the reaction was followed by changes in the infrared spectrum of the reaction mixture determined on aliquots which were taken from the initial solution and after addition of each 50 ml of acid solution. Only a small decrease in the relative intensity of the C═C stretching band at 1644 cm^{-1} was noted while the relative intensities of the B–H stretching frequencies at 2400 and 2370 cm^{-1}, the BH_2 deformation frequency at 994 cm^{-1}, and the BH_2 rocking frequency[21] at 674 cm^{-1} decreased progressively. Similar marked decreases in intensity were observed for the $P–C_2$ rocking and wagging bands[22] at 898 and 908 cm^{-1} (the strongest in the spectrum of I) and the first degenerate ring stretching frequency[20] at 725 cm^{-1}. The final solution was stirred for 65 hr, after which time it was observed that bands associated with monoperphthalic acid were absent although weak B—H and C═C absorption bands remained.

Polymerization of *sym*-P-(Triallyltrimethyl)cyclotriborphosphane (I).—Monoethylamine boron trifluoride, 0.0039 g, was dissolved in 0.513 g of *sym*-P-(triallyltrimethyl)cyclotriborphosphane, and the mixture was heated in an evacuated, sealed tube

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[18] V. Voorhees and R. Adams, *J. Am. Chem. Soc.*, **44**, 1397 (1922).

[19] H. Böhme, *Org. Syn.*, **20**, 70 (1940).

[20] D. Swern, *J. Am. Chem. Soc.*, **69**, 1692 (1947).

[21] A. B. Burg in a private communication indicated his assignments were established by appropriate band shifts in the spectra of $[(CH_3)_2PBH_2]_3$ and $[(CH_3)_2PBD_2]_3$.

[22] A. C. Chapman, *Trans. Faraday Soc.*, **59**, 806 (1963).

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 cm^{-1}, and the entire spectrum showed a considerable loss of resolution indicating restricted molecular motion characteristic of polymeric species.

α,α'-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.

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CONTRIBUTION FROM THE OLIN RESEARCH CENTER,
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A New Series of Organoboranes. IX. The Preparation and Some Reactions of Sulfur–Carborane Derivatives[1]

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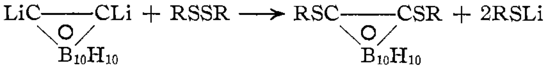
The first examples of sulfur derivatives of *o*- and *m*-carborane are reported and the preparative reactions have been extended to include various B-bromocarboranes. Some chemistry of these derivatives is described including the preparation of an inner complex of nickel.

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.

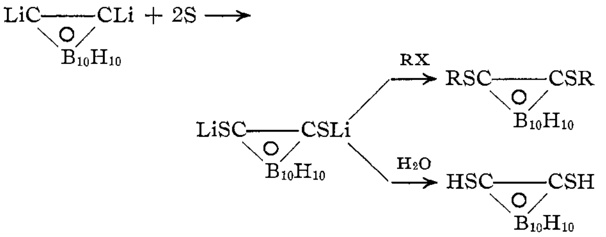
It was logical to expect that this series of compounds should be capable of existence since the nature of the group VI congeners, in general, and sulfur in particular, should permit facile attachment by methods previously reported.[4]

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 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.



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



$$\underset{\mathrm{B_{10}H_{10}}}{\underset{\diagdown\mathrm{O}\diagup}{\mathrm{LiC{-}{-}CLi}}} + 2\mathrm{S} \longrightarrow \underset{\mathrm{B_{10}H_{10}}}{\underset{\diagdown\mathrm{O}\diagup}{\mathrm{LiSC{-}{-}CSLi}}} \begin{cases} \xrightarrow{\mathrm{RX}} \underset{\mathrm{B_{10}H_{10}}}{\underset{\diagdown\mathrm{O}\diagup}{\mathrm{RSC{-}{-}CSR}}} & (2) \\ \xrightarrow{\mathrm{H_2O}} \underset{\mathrm{B_{10}H_{10}}}{\underset{\diagdown\mathrm{O}\diagup}{\mathrm{HSC{-}{-}CSH}}} & (3) \end{cases}$$

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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).