

Peak intensity measurements were rather imprecise, but at equilibrium, the reorganization mixture consists of approximately 25% neso groups, 50% end groups, and 25% middle groups.

Experimental

Apparatus.— F^{19} and P^{31} n.m.r. measurements were made on a previously described spectrometer system⁷ using a Varian Model V-4310 radiofrequency unit at 16.2 and 40.0 Mc. and a Model V-4311 radiofrequency unit at 24.3 Mc. Chemical shifts were measured with respect to CF_3COOH and 85% H_3PO_4 as reference standards using a tube interchange technique with audio side-band calibration of the field sweep. Upfield shifts are regarded as positive. Heteronuclear spin decoupling by double irradiation² was accomplished with a Varian spin decoupler, which provides a tunable excitation frequency at 37.6 Mc. for irradiation of F^{19} while one observes the P^{31} spectrum at 16.2 Mc. under low radiofrequency power.

Samples.— $P_2O_5Cl_2F_2$ was obtained as a pure liquid in a sealed test tube.⁸ Preliminary examination by low-resolution P^{31} n.m.r. showed that it was better than 99% compound I. The tube was opened in a drybox and the sample transferred to a precision 5-mm. n.m.r. tube for examination under higher resolution. The sealed n.m.r. tube was then finally heated in a thermostated bath at 50° for several days to effect reorganization. Repeat measurements after 2 months assured that equilibrium had been reached.

Acknowledgment.—Messrs. J. T. Yoder and G. C. Roth assisted in making some of the n.m.r. measurements.

(7) M. M. Crutchfield, C. F. Callis, R. R. Irani, and G. C. Roth, *Inorg. Chem.*, **1**, 813 (1962).

(8) The authors wish to thank Prof., Dr., Dr. Ing. E. h. A. Simon, Technische Hochschule, Dresden, for supplying us with an analyzed sample of $P_2O_5Cl_2F_2$. His average analytical data by two independent methods are as follows: *Anal.* Calcd.: P, 28.32; F, 17.36; Cl, 32.40; mol. wt., 218.9. Found: P, 28.76; F, 17.25; Cl, 32.29; mol. wt., 225 to 265.

CONTRIBUTION FROM THE ORGANICS DIVISION,
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Some Chemistry of Substituted Decaboranes

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Received June 29, 1963

Although considerable chemistry of decaborane has been established, very few reports of reactions of substituted decaboranes have appeared. Therefore we conducted an investigation to determine whether some of the reactions characteristic of decaborane could be applied to its derivatives and to more thoroughly examine some reactions previously described. For example, numerous preparations¹ and reactions² of $B_{10}H_{12}(\text{ligand})_2$ compounds have appeared but only recently has the first example of such a derivative of a substituted decaborane been reported³; we chose to

(1) R. Schaeffer, *J. Am. Chem. Soc.*, **79**, 1006 (1957), as the original example.

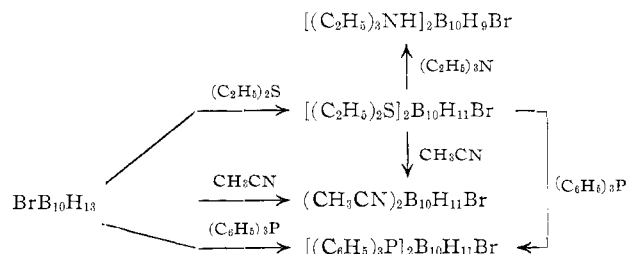
(2) B. M. Graybill and M. F. Hawthorne, *ibid.*, **83**, 2673 (1961), and others.

(3) C. Naar-Colin and T. L. Heying, *Inorg. Chem.*, **2**, 659 (1963).

prepare and study additional compounds of this type.

Acetonitrile reacted readily with 2-bromodecaborane⁴ in refluxing benzene or excess nitrile to give bis(acetonitrile)-2-bromodecaborane. Due to its limited solubility in the more useful solvents, it was not practical to study its further reactions but the more useful bis(diethyl sulfide)-2-bromodecaborane also formed easily in benzene and had better solubility and infrared characteristics as well as a definitive melting point. A detailed ^{11}B n.m.r. study of this compound has been reported⁵ and the same interpretation has been applied to all derivatives of this type herein described. Bis(triphenylphosphine)-2-bromodecaborane was also prepared by the spontaneous and rapid reaction of the phosphine with 2-bromodecaborane in ether.

The ligand displacement reaction in this series was demonstrated when bis(diethyl sulfide)-2-bromodecaborane was readily converted to the bis(triphenylphosphine) derivative on treatment with the phosphine at room temperature. On treatment with acetonitrile under the same conditions, bis(diethyl sulfide)-2-bromodecaborane was only slowly converted to the bis(acetonitrile) derivative. On the other hand, at room temperature in benzene, triethylamine reacted with bis(diethyl sulfide)-2-bromodecaborane to give bis(triethylammonium) bromononahydrodecaborate rather than the $B_{10}H_{11}Br(\text{ligand})_2$ derivative. This would indicate that the $BrB_{10}H_{11}$ unit is more prone to rearrangement to the decaborate structure than the $B_{10}H_{12}$ unit, which does so only slowly in boiling benzene.⁵ Other implications are discussed in more detail below.



Monoethyldecaborane⁶ containing 60% 2-ethyldecaborane and 40% 1-ethyldecaborane was also readily converted to the analogous ligand derivatives. Mixed bis(triphenylphosphine)-1- and -2-ethyldecaborane was readily isolated and well defined but mixed bis(diethyl sulfide)-1- and -2-ethyldecaborane was slow to form and was an oil which would not crystallize, probably because of the mixed isomers. The ^{11}B n.m.r. spectrum readily indicated the structure and the mixture was efficiently converted to the mixed bis(triphenylphosphine) derivative by ligand displacement. Isomer distribution in the ligand derivatives similar to that of the starting mixed ethyldecaboranes was apparent from their ^{11}B n.m.r.

(4) R. Schaeffer, J. N. Shoolery, and R. Jones, *J. Am. Chem. Soc.*, **80**, 2670 (1958).

(5) M. F. Hawthorne and A. R. Pitocheili, *ibid.*, **81**, 5519 (1959).

(6) R. L. Williams, I. Dunstan, and N. J. Blay, *J. Chem. Soc.*, 430 (1960); E. R. Altwicker, A. B. Garrett, and E. A. Weilmuenster, U. S. Patent 2,999,117.

spectra but the melting point of the triphenylphosphine compound was surprisingly sharp.

Although bis(diethyl sulfide)decaborane is converted to (diethyl sulfide)nonaborane⁷ on standing in absolute methanol for 30 min., bis(diethyl sulfide)-2-bromodecaborane was unaffected by this treatment. A (diethyl sulfide)bromononaborane was recovered, however, by refluxing in ethanol for several minutes. From consideration of the structure of (diethyl sulfide)nonaborane as assigned by Wang, Simpson, and Lipscomb,⁸ it is apparent that at least two isomers of the bromononaborane would be possible; the ¹¹B n.m.r. spectrum indicated that two isomers were present. We do not understand why the melting point (see Experimental section) of this mixture was so sharp but we point out that a similar situation exists with the mixed bis(triphenylphosphine)decaboranes described above.

Numerous attempts to replace the bromine atom from B₁₀H₁₁Br(ligand)₂ compounds were made without success. Particular emphasis was placed on reactions of organometallics with bis(diethyl sulfide)-2-bromodecaborane but neither displacement nor halogen metal interchange occurred.

Turning our attention to other chemistry of substituted decaboranes we noted that the report of the reaction which forms bis(triethylammonium) dodecahydrododecaborate from 2-iododecaborane and triethylamine,⁹ though interesting of itself, did not define the fate of the majority of the reacting boron hydride and prompted us to examine this reaction in more detail.

Under the conditions employed with 2-iododecaborane,⁹ 2-bromodecaborane was treated with excess triethylamine in refluxing benzene and toluene. In every instance some hydrogen was evolved and bis(triethylammonium) dodecahydrododecaborate was formed and in somewhat higher yields than had been obtained from 2-iododecaborane. Investigation of the remaining products established that the major boron-containing product was bis(triethylammonium) decahydrodecaborate and the bromine was recovered as triethylammonium bromide. The reaction was repeated several times in monoglyme and in these instances only bis(triethylammonium) decahydrodecaborate and triethylammonium bromide were formed. No evidence for a bromo-substituted boron product was found in any of these reactions. Incidental to this work five unreported phosphonium salts of the decahydrodecaborate ion were prepared and are reported in the Experimental section.

On the other hand, as noted above, when bis(diethyl sulfide)-2-bromodecaborane in benzene was treated with triethylamine at room temperature, rapid formation of bis(triethylammonium) bromononahydrodecaborate occurred.¹⁰ This strongly suggests that the bromine

atom of 2-bromodecaborane is extracted by the triethylamine in a reaction which precedes the formation of an intermediate such as bis(triethylamine)-2-bromodecaborane and it is this reaction which gives rise to the B₁₀H₁₀⁻² ions.

Trimethylamine reacted quite differently with 2-bromodecaborane in refluxing toluene. Only a trace quantity of trimethylammonium bromide was isolated, while the major product was bis(trimethylammonium) bromononahydrodecaborate (m.p. 259–260°).

The ¹¹B n.m.r. spectra of both bromononahydrodecaborate salts were identical. They were taken at 19.3 Mc./sec. in D₂O, dimethylformamide, and acetonitrile, and no variations in the spectra were observed. The spectrum at first glance seems to consist of two doublets; the first one at low field is completely resolved while a second one at high field is not so well resolved. Their intensity ratio is 1 to 4. This spectrum is obviously similar to the spectrum of a B₁₀H₁₀⁻² anion. The chemical shifts of the boron atom responsible for the first and second doublet were, respectively, 15 c.p.s. higher and 50 c.p.s. lower than the chemical shifts of the two "apical" borons and the eight "equatorial" borons of B₁₀H₁₀⁻². A more highly resolved spectrum, however, shows a broad peak of relative intensity 1/10 at 200 c.p.s. lower field than the center of the second doublet. This peak cannot be decoupled by exciting the proton at 60.0 Mc./sec. We therefore conclude that the resonance of an equatorial boron atom attached to a bromine nucleus gives rise to this line. The ¹¹B n.m.r. spectrum shows therefore that it is a B₁₀H₉Br⁻² derivative and that the substitution is at an equatorial boron atom, which provides additional evidence for the mechanism of the formation of the B₁₀H₁₀⁻² ion¹¹ since the bromine atom in each instance originated at the 2-position of decaborane.

To establish the fate of the remainder of the boron hydride in the reaction of trimethylamine with 2-bromodecaborane, two other products having solubility characteristics similar to bis(triethylammonium) bromononahydrodecaborate were also isolated. One compound, melting at 274–275°, gave an analysis which indicated the composition [(CH₃)₃NH]₃B₁₀H₉Br₂. Examination of its infrared, ¹¹B, and proton n.m.r. spectra gave no reason to differentiate it from the bromononahydrodecaborate, which suggests it to be a double salt of the type [(CH₃)₃NH]₂B₁₀H₉Br·(CH₃)₃NHBr. The second of these products did not melt below 350° and had an indicated composition of [(CH₃)₃NH]₃B₁₀H₉Br₃. Although its infrared spectrum differed slightly from that of the other two compounds, its ¹¹B and proton n.m.r. spectra were identical with theirs.

The monoethyldecaborane mixture reacted readily with triethylamine in either toluene or monoglyme to give a high yield of bis(triethylammonium) ethylonahydrodecaborate. Its ¹¹B n.m.r. spectrum showed the presence of a single, equatorially-substituted B₁₀H₁₀⁻²

(7) B. M. Graybill, A. R. Pitochelli, and M. F. Hawthorne, *Inorg. Chem.*, **1**, 626 (1962).

(8) F. E. Wang, P. G. Simpson, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **83**, 491 (1961).

(9) A. R. Pitochelli and M. F. Hawthorne, *ibid.*, **82**, 3228 (1960).

(10) Compounds of this type, prepared in another manner, were first reported by W. H. Knoth, H. C. Miller, D. C. England, G. W. Parshall, and E. L. Muettterties, *ibid.*, **84**, 1056 (1962).

(11) A. R. Pitochelli, R. Ettinger, J. A. Dupont, and M. F. Hawthorne, *ibid.*, **84**, 1057 (1962); M. F. Hawthorne, *Current Trends in Organometallic Chemistry Symposium*, Cincinnati, Ohio, June 12, 1963.

TABLE I
 PHOSPHONIUM DECAHYDRODECABORATE SALTS

Compound	M.p., °C*	Analysis				Recryst. from
		Calcd.		Found		
		C	H	C	H	
$[(C_6H_5)_3PC_2H_5]_2B_{10}H_{10}$	233 dec.	68.5	7.2	68.8	6.6	DMF-H ₂ O
$[(C_6H_5)_3P(n-C_3H_7)]_2B_{10}H_{10}$	226 dec.	69.2	7.5	69.4	7.9	DMF-H ₂ O
$[(C_6H_5)_3P(n-C_4H_9)]_2B_{10}H_{10}$	167 dec.	69.8	7.7	69.4	7.4	DMF-H ₂ O
$[(C_6H_5)_3PCH_2C_6H_5]_2B_{10}H_{10}$	235 dec.	72.9	6.6	72.8	6.3	...
$[(C_6H_5)_3PCH_2C_6H_5CH_3]_2B_{10}H_{10}$	210 dec.	73.2	6.9	73.00	6.9	DMF-ether

species. This suggests that not only the 2-boron atom of decaborane but also the 1-boron atom arrives at an equatorial position during the rearrangement to the $B_{10}H_{10}^{-2}$ species, further supporting the proposed mechanism of the formation of this ion. The evidence above which supports the proposed mode of formation of the decahydrodecaborate ion, however, does not exclude the possibility of the occurrence of a skeletal rearrangement which would produce an equatorially substituted ion *via* a combination of a 4 to 1 probability factor and thermodynamic preference.

Experimental

Bis(acetonitrile)-2-bromodecaborane. a.—A solution of 2.0 g. of 2-bromodecaborane and 2.0 g. of acetonitrile in 30 ml. of benzene was refluxed for 6 hr. After 1 hr., a crystalline solid had begun to separate. The solution was cooled and filtered, and the residue was recrystallized from acetonitrile-ethanol to give 2.4 g. (90%) of material which did not melt below 400° but turned orange at 220°.

Anal. Calcd. for $B_{10}C_4H_{17}N_2Br$: C, 17.1; H, 6.1; B, 38.6; N, 9.9. Found: C, 17.3; H, 6.2; B, 38.5; N, 9.9.

b.—2-Bromodecaborane (1.0 g.) was refluxed for 7 hr. in 15 ml. of acetonitrile. After cooling, 0.85 g. of product separated. This was removed and recrystallized from acetonitrile-ethanol (yield 61%).

Bis(diethyl sulfide)-2-bromodecaborane.—A solution of 10.0 g. of 2-bromodecaborane and 30 ml. of diethyl sulfide in 100 ml. of benzene was refluxed for 4 hr. The solution was concentrated to an orange oil to which was added about 250 ml. of ether with vigorous shaking to induce the oil to solidify. The solid was removed and recrystallized from acetone-petroleum ether (30–60°) to give 10.5 g. (55.4%) of bis(diethyl sulfide)2-bromodecaborane (m.p. 100–101.5°).

Anal. Calcd. for $B_{10}C_8H_{31}S_2Br$: C, 25.3; H, 8.2; B, 28.6. Found: C, 26.1, 26.2; H, 8.4, 8.5; B, 28.3, 28.2.

Bis(triphenylphosphine)-2-bromodecaborane. a.—To 1.0 g. of 2-bromodecaborane in 30 ml. of ether was added a solution of 5.25 g. of triphenylphosphine in ether. A yellow color formed immediately and in about 0.5 hr., 120 ml. of hydrogen had been evolved and a yellowish solid separated. This solid was recovered and treated with ethyl acetate to remove the yellow gummy material and the residual solid was recrystallized *carefully* from methylene chloride-pentane to give 2.2 g. of bis(triphenylphosphine)-2-bromodecaborane (m.p. 243–244°).

Anal. Calcd. for $B_{10}C_{30}H_{41}P_2Br$: C, 59.7; H, 5.8; B, 14.5; Br, 11.1. Found: C, 59.6, 60.0; H, 5.9, 5.8; B, 14.9, 14.9; Br, 11.1.

b.—A solution of 0.4 g. of bis(diethyl sulfide)-2-bromodecaborane and 0.6 g. of triphenylphosphine in 25 ml. of benzene was stirred at room temperature for 36 hr. The benzene was removed and the residue was recrystallized from ethyl acetate to give 0.5 g. (67%) of the phosphine derivative melting at 245°.

Bis(triethylammonium) bromononahydrodecaborate.—A solution of 4.0 g. of bis(diethyl sulfide)-2-bromodecaborane and 4.0 g. of triethylamine in 250 ml. of benzene was stirred for 40 hr. at room temperature. Cloudiness developed almost immediately and eventually fine crystals formed. These were removed and

recrystallized from acetone-ether to give 4.0 g. of bis(triethylammonium) bromononahydrodecaborate. Its solubility, infrared resemblance to other $B_{10}H_{10}^{-2}$ derivatives, and reaction with triphenylethylphosphonium iodide in water indicated it to be a $B_{10}H_9Br^{-2}$ compound. This was additionally confirmed by its ^{11}B n.m.r. spectrum.

Anal. Calcd. for $B_{10}C_{12}H_{41}N_2Br$: C, 35.9; H, 10.2; B, 27.0. Found: C, 35.6, 35.4; H, 9.8, 9.9; B, 26.7, 26.6.

Bis(triphenylphosphine)ethyldecaborane. a.—A solution of 1.0 g. of mixed 1- and 2-ethyldecaborane and 5.0 g. of triphenylphosphine in 25 ml. of benzene was stirred for 2 hr. whereupon suddenly a yellow color and then a white precipitate formed. After 3 hr. the mixture was filtered to recover 3.0 g. (67%) of a white solid which, due to its poor solubility, could not be recrystallized but, after thorough ether washing, melted at 212–213°.

Anal. Calcd. for $B_{10}C_{30}H_{46}P_2$: C, 67.9; H, 6.9; B, 16.2. Found: C, 67.9, 68.1; H, 7.2, 7.0; B, 15.8, 16.00.

b.—A solution of 4 g. of mixed 1- and 2-ethyldecaborane and 8 g. of diethyl sulfide in 75 ml. of benzene was refluxed for 20 hr. and cooled, and the benzene was removed to yield a yellow oil which was crude bis(diethyl sulfide)ethyldecaborane as indicated by its infrared and ^{11}B n.m.r. spectra. It could not be crystallized but was redissolved in 100 ml. of benzene to which was added 15 g. of triphenylphosphine. After 2 hr. a precipitate began to form and after stirring overnight, 12.8 g. of bis-(triphenylphosphine)ethyldecaborane was recovered by filtering and washing the residue with ether.

(Diethyl sulfide)bromononaborane.—Bis(diethyl sulfide)-2-bromodecaborane (0.5 g.) in 20 ml. of ethanol was warmed on a steam bath until all of the solid dissolved and then refluxed for 5 min. On cooling, about 0.1 g. of starting material precipitated and was removed. The alcoholic solution was evaporated to an orange oil which dissolved in ether to give a green solution. This was cooled in ice and petroleum ether (30–60°) was added to give an orange solid which was recovered and recrystallized from ether-petroleum ether to give a pale orange solid (0.2 g.) melting at 74.0–75.5°.

Anal. Calcd. for $B_9C_4H_{23}SBr$: C, 17.2; H, 7.9; B, 34.8. Found: C, 16.5, 16.4; H, 8.4, 8.5; B, 34.4, 34.3.

Reaction of 2-Bromodecaborane with Triethylamine in Toluene.—A solution of 4.0 g. of 2-bromodecaborane and 10 g. of triethylamine in 50 ml. of toluene was refluxed for 20 hr., during which time 145 ml. of hydrogen was evolved. The mixture was cooled and the toluene was decanted from the orange gummy material. When this residue was treated with 50 ml. of ethanol a white solid and a yellow-orange solution resulted. The white solid was removed by filtration. (The filtrate contained a small amount of pleasant smelling, yellow solid which has not been identified.) The solid was dissolved in a minimum of hot acetonitrile which, on cooling, deposited 0.93 g. (8.6%) of white crystals which were removed and recrystallized from acetonitrile (m.p. 273.5–274.5°).

Anal. Calcd. for $B_{12}C_{12}H_{44}N_2$: C, 41.6; H, 12.7; B, 37.5; N, 8.1. Found: C, 41.2; H, 12.8; B, 38.0; N, 8.5. The ^{11}B n.m.r. spectrum showed the strong doublet characteristic of the $B_{12}H_{12}^{-2}$ structure.

The acetonitrile filtrates above were combined and evaporated leaving a slightly yellow semisolid which was treated with 30 ml. of warm ethanol; the yellow portion dissolved. This was filtered and the white solid (3.5 g.) residue was washed with additional ethanol. It melted at 232–234°, showed no depres-

sion with authentic $[(C_2H_5)_3NH]_2B_{10}H_{10}$, and both infrared and B^{11} n.m.r. spectra were identical. Evaporation of the ethanolic filtrate deposited 2.0 g. of additional material which melted at 254° (lit. for triethylammonium bromide 253°) and its infrared spectrum was identical with Sadtler spectrum 9771 for $(C_2H_5)_3NHB_{10}H_{10}$.

Reaction of 2-Bromodecaborane with Triethylamine in Ethylene Glycol Dimethyl Ether (Monoglyme).—A solution of 2.0 g. of 2-bromodecaborane and 5.0 g. of triethylamine in 35 ml. of ethylene glycol dimethyl ether was refluxed for 6 hr. The white solid which had formed was separated from the yellow solution. This solid was dissolved in acetonitrile and on cooling 0.6 g. of triethylamine hydrobromide precipitated. The filtrate was evaporated to dryness and the residue was recrystallized from acetonitrile-acetone. The solid was removed and refluxed for a short time in ethanol and the remaining solid (2.25 g., 75%) was removed by filtration and melted at 235.5° . It was demonstrated to be $[(C_2H_5)_3NH]_2B_{10}H_{10}$. An additional small amount of $(C_2H_5)_3NHB_{10}H_{10}$ was recovered from the alcoholic filtrate. The original filtrate was examined, but nothing could be isolated which could be identified as a $B_{12}H_{12}^{2-}$, $B_{10}H_{10}^{2-}$, or $B_{10}H_{12}$ product.

Phosphonium Decahydrodecaborate Salts.—Five unreported phosphonium decahydrodecaborate salts were prepared. The preparation of bis(ethyltriphenylphosphonium) decahydrodecaborate is given. Others were prepared in an analogous manner and the results of these preparations are summarized in Table I.

One gram (3.1×10^{-3} mole) of bis(triethylammonium) decahydrodecaborate was dissolved in 5 ml. of warm dimethylformamide (DMF). To this was added a solution of 2.6 g. (6.2×10^{-3} mole) of ethyltriphenylphosphonium iodide dissolved in 5 ml. of warm DMF. The mixture was warmed on the steam bath for a few minutes, then 25 ml. of water was added. A white precipitate formed immediately. After cooling to room temperature, the precipitate was filtered, and the residue was recrystallized from DMF-water and dried.

Reaction of 2-Bromodecaborane with Trimethylamine in Toluene.—Trimethylamine was bubbled through a refluxing solution of 4.0 g. of 2-bromodecaborane in 35 ml. of toluene for 7 hr. The mixture was cooled and the toluene was decanted from the gummy residue. This residue was dissolved in acetonitrile and on cooling a solid separated which was collected and recrystallized from acetonitrile to give 1.0 g. of a white solid. Repeated recrystallization afforded two products (A and B) as yet unidentified. A, which is probably a double salt (see Discussion), melted at $274-275^\circ$. *Anal.* Found: C, 23.87, 23.60; H, 8.91, 8.95; B, 23.94, 24.19; N, 8.91, 8.70. B decomposed gradually on heating above 250° . *Anal.* Found: C, 21.10, 21.18; H, 7.12, 6.90; B, 19.64, 19.68; N, 7.40, 7.70; Br, 45.0.

The original acetonitrile filtrate was evaporated and treated with acetone to give a white solid which was recovered. This was recrystallized from a small amount of acetonitrile and then from a minimum of water to give 3.1 g. of white plates of bis(trimethylammonium) bromononahydrodecaborate melting at $259-260^\circ$.

Anal. Calcd. for $B_{10}C_6H_{26}N_2Br$: C, 22.7; H, 9.1; B, 34.1; N, 8.8; Br, 25.3. Found: C, 23.0, 23.2; H, 10.1, 9.8; B, 33.4, 33.7; N, 9.1, 8.9; Br, 24.1, 24.1.

Bis(trimethylammonium) Ethylnonahydrodecaborate.—A solution of 4.5 g. of monoethyldecaborane (60% 2- and 40% 1-substituted) and 15 g. of triethylamine in 60 ml. of benzene was refluxed for 24 hr. The mixture was cooled and the supernatant liquid was decanted from the yellow gum which had formed. This gum was treated with ethanol, whereupon it solidified. It was recrystallized several times from a large volume of ethanol to give 9.0 g. (85%) of a white solid melting at $193-194^\circ$. Its infrared spectrum was quite similar to that of bis(trimethylammonium) decahydrodecaborate.

Anal. Calcd. for $B_{10}C_{14}H_{48}N_2$: C, 47.7; H, 13.6; B, 30.8. Found: C, 48.3, 48.0; H, 14.2, 14.0; B, 30.9, 31.1.

Acknowledgment.—This research was supported by

the Office of Naval Research. We thank Mr. G. D. Vickers for obtaining the n.m.r. spectra and Dr. A. DiPippo for preparing the phosphonium salts.

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Synthesis of Molybdenum Tetrachloride

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Received July 13, 1963

Molybdenum tetrachloride has been difficult to prepare pure in appreciable quantities.¹ This is the result of the ease of its thermally-induced disproportionation and its oxidative instability.

It is then of interest that molybdenum tetrachloride can be prepared easily by the reaction of molybdenum pentachloride with refluxing benzene. Substantial quantities (300 to 400 g.) have been prepared routinely by this method to give products of 98 to 99% purity. No purification is required other than a simple benzene wash. This process, though developed independently in this laboratory, appears to be formally similar to the reduction of ferric chloride by chlorobenzene reported by Kovacic and Brace.²

The reaction of molybdenum pentachloride with refluxing benzene yields a small amount of black, polymeric, carbonaceous solid as impurity. This solid resembles the poly-*p*-phenylene which Kovacic and Lange have recently reported³ to result from the treatment of benzene with a cocatalytic system of molybdenum pentachloride and water. Therefore, it is important that the molybdenum pentachloride intermediate be freed of oxychloride hydrolysis products and that the reaction system be anhydrous. Under these conditions, variable benzene reflux periods extended beyond the time (8 to 10 hr.) required to achieve complete reduction to tetrachloride do not cause formation of substantial poly-*p*-phenylene. Furthermore, the rate of benzene reduction past the tetrachloride stage is very slow. Kovacic and Lange report³ that molybdenum trichloride was formed when a concentrated mixture of molybdenum pentachloride and benzene was refluxed for 1 hr. Their sole evidence for the formation of molybdenum trichloride was a potentiometric ceric titration of a 3 *N* hydrochloric acid extract of the reaction mixture. This conclusion can be discounted for two reasons: (1) molybdenum trichloride is insoluble in dilute hydrochloric acid^{1b};

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(2) P. Kovacic and N. O. Brace, *J. Am. Chem. Soc.*, **76**, 5491 (1954).

(3) P. Kovacic and R. M. Lange, *J. Org. Chem.*, **28**, 968 (1963).