of epichlorohydrin (0.6 mole) was dropped with stirring into 80 g. of 25% aqueous NaOH (0.5 mole) at 35–45°, and stirred 1 hour more at 70–80°. The mixture was poured into water and washed until neutral. Distillation of the organic layer gave 90 g. of product (60%), b.p. 145–148° (0.2 mm.), d^{25}_4 0.978, n^{25}_D 1.4805, visc. 17 cs., epoxy eq. wt. 357, calcd. 338.

Monoepoxysilicon compounds prepared by various methods are described in Table I. Diepoxysiloxanes prepared by addition of ≡SiH to olefinic epoxy compounds are described in Table II.

Reactions of Epoxysiloxanes. 1. Addition of Active Hydrogen Compounds.—The monoepoxydisiloxane $(CH_3)_3SiOSi(CH_3)_2CH_2CH_2CH_2OCH_2\overline{CHCH_2O}$ was used to study the reactions of various active hydrogen compounds with epoxysiloxanes. The resulting hydroxyalkyl substituted disiloxanes were stable to distillation temperatures over 170°. No indication was observed of hydroxyl groups "cutting into" the siloxane linkage to form cyclic silaethers and hexamethyldisiloxane. Difficulty was observed in getting reaction between water or ethylene glycol and the epoxysiloxane because of mutual insolubility.

One hundred g. (1.06 moles) of phenol and 1 g. of benzyltrimethylammonium hydroxide (40% solution in methanol) were refluxed with 50 g. of toluene while dropping in 78 g. of 3-(2,3-epoxypropoxy)-propylpentamethyldisiloxane. The mixture was refluxed 8 hours and then distilled through an 8″ packed column to recover 65 g. of a center cut (60% yield), b.p. 158–160° (0.5 mm.), d^{25}_4 0.986, n^{25}_D 1.4738, Si 15.93, 15.90% (calcd. for mono-adduct 15.72%), hydroxyl 5.08% (calcd. 4.78%). Infrared examination of recovered toluene detected only a trace of hexamethyldisiloxane (less than 0.5 g. total).

Various mono-adducts to 3-(2,3-epoxypropoxy)-propylpentamethyldisiloxane are described in Table III.

2. Hydrolysis.—3-(2,3-Epoxypropoxy)-propyltriethoxysilane (10 g., 0.036 mole) was initially insoluble in water, but after shaking with 90 g. of water for 4 hours at *p*H 3–5 (acetic acid) a clear solution resulted. The solution was stable indefinitely at this *p*H, but an oily precipitate settled out when the solution was made slightly alkaline. After 24 hours the oily layer was taken up in toluene, dried by azeotroping water with part of the toluene. Analysis of the residue indicated that 0.035 epoxy equivalent remained.

3. Alcoholysis.—3-(2,3-Epoxypropoxy)-propyltrimethoxysilane (47 g., 0.2 mole) was warmed with 2-methoxyethanol (50 g., 0.66 mole) while slowly removing distillate at 65–75° through a 12″ packed column. After no more low boiling distillate came over the residue was distilled to recover intermediate fractions and 30 g. of best product, b.p. 160–165° (0.1 mm.), d^{25}_4 1.077, n^{25}_D 1.4408, epoxy equiv. wt. 358 (calcd. for $(CH_3OCH_2CH_2O)_3SiCH_2CH_2CH_2OCH_2\overline{CHCH_2O}$, 368).

MIDLAND, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

The Chemistry of Borazene. II. The Synthesis of N-Trimethyl-B-trialkoxyborazenes and N-Trimethyl-B-triphenoxyborazene[1]

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N-Trimethyl-B-trichloroborazene reacts smoothly with the sodium salts of alkyl alcohols and of phenols to give the B-alkoxy- and B-phenoxyborazenes. By this method the following new compounds have been prepared: N-trimethyl-B-trimethoxyborazene, N-trimethyl-B-triethoxyborazene, N-trimethyl-B-tri-*n*-propoxyborazene, N-trimethyl-B-triisopropoxyborazene, N-trimethyl-B-tri-*n*-butoxyborazene, N-trimethyl-B-tri-*t*-butoxyborazene and N-trimethyl-B-triphenoxyborazene.

Most borazene derivatives have been prepared by starting with the appropriate substituent on nitrogen and boron and then synthesizing the ring. Very few reactions of borazenes in which other borazenes are produced without ring synthesis have been investigated. In general, water cleaves the borazene ring. However, under carefully controlled conditions N-triphenyl-B-trichloroborazene and N-tri-*p*-anisyl-B-trichloroborazene react with three equivalents of water to yield the B-trihydroxy derivatives[3,4]; N-tri-*p*-tolyl-B-trichloroborazene gives only ring cleavage in moist benzene.[5] The chlorine atoms of trichloroborazene may be replaced by cyanide, nitrite, nitrate, bromide and thiocyanate by metathesis with the appropriate silver or sodium salts.[6]

The work reported here gives a simple method for the synthesis of B-alkoxy- and B-phenoxyborazenes through the reaction of N-trimethyl-B-trichloroborazene with sodium alkoxides or phenoxide. Under similar conditions addition of alcohols and phenol to the chloroborazene results only in ring cleavage.

Experimental

N-Trimethyl-B-trichloroborazene.—N-Trimethyl-B-trichloroborazene was prepared by the reaction of boron trichloride with methylamine hydrochloride in refluxing chlorobenzene.[7,8]

Sodium Alkoxides.—Fisher dry, "purified" sodium methoxide was used without further purification. Commercial sodium phenoxide was washed with ether and heated under vacuum to 200° to remove the phenol. The other salts were prepared by the reaction of metallic sodium or sodium hydride with the anhydrous alcohols in a dry, nitrogen atmosphere and vacuum evaporation of the excess alcohols from the salts at 100°. Care must be exercised in removing the excess isopropyl and *t*-butyl alcohols from their gelatinous reaction products in order to remove as much alcohol as possible without forming large amounts of sodium oxide and the respective ether.

N-Trimethyl-B-trialkoxyborazene and N-Trimethyl-B-triphenoxyborazene.—In a typical experiment, 0.15 g. equiv. of N-trimethyl-B-trichloroborazene was placed in a two-necked, angle type, 250-ml. round bottom flask along

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[1] The most recently recommended names for these compounds are 1,3,5-trimethyl-2,4,6-trialkoxyborazine and 1,3,5-trimethyl-2,4,6-triphenoxyborazine.

[2] Abstracted from the Ph.D. Dissertation of Mildred J. Bradley submitted to the University of Florida, 1958, and available from University Microfilms, Ann Arbor, Michigan.

[3] R. G. Jones and C. R. Kinney, THIS JOURNAL, **61**, 1378 (1939).

[4] C. R. Kinney and C. L. Mahoney, *J. Org. Chem.*, **8**, 526 (1943).

[5] C. R. Kinney and M. J. Kolbezen, THIS JOURNAL, **64**, 1584 (1942).

[6] R. Schaeffer, G. Brennan and G. Dahl, Abstracts of Papers, 133rd Meeting, American Chemical Society, San Francisco, California, April, 1958, 37-L.

[7] C. A. Brown and A. W. Laubengayer, THIS JOURNAL, **77**, 3699 (1955).

[8] G. E. Ryschkewitsch, J. J. Harris and H. H. Sisler, *ibid.*, **80**, 4515 (1958).

TABLE I

N-TRIMETHYL-B-TRIALKOXYBORAZENES AND N-TRIMETHYL-B-TRIPHENOXYBORAZENE

Compound	Boiling range °C.	Mm.	Melting range, °C.	Refractive index	Yield, %	Analyses, % B Found Calcd.	N Found Calcd.	C Found Calcd.	H Found Calcd.
N-Trimethyl-B-trimethoxyborazene	62–65	0.07		1.4610^{23}	48	15.29	18.99	33.49	7.90
						15.26	19.76	33.88	8.53
N-Trimethyl-B-triethoxyborazene	79.5–80.5	.10		$1.4540^{22.5}$	46	12.70	16.18	42.38	9.49
						12.74	16.50	42.43	9.50
N-Trimethyl-B-tri-*n*-propoxyborazene	101–103	.15		1.4561^{22}	50	10.97	13.95	48.52	10.85
						10.93	14.16	48.55	10.19
N-Trimethyl-B-triisopropoxyborazene	85–87	.10		1.4460^{23}	20	10.97	13.72	48.43	9.78
						10.93	14.16	48.55	10.19
N-Trimethyl-B-tri-*n*-butoxyborazene	130–134	.30		1.4572^{23}	58	9.60	12.16	52.84	10.67
						9.58	12.40	53.17	10.71
N-Trimethyl-B-tri-*t*-butoxyborazene	120–125	.52	84–87		14	9.52	11.95	50.35	10.37
						9.58	12.40	53.17	10.71
N-Trimethyl-B-triphenoxyborazene	185–187	.07	81–84		43	8.09	10.13	60.87	6.43
						8.14	10.53	63.22	6.66

with 100 ml. of benzene, which previously had been dried over calcium hydride and filtered just before use. The flask was attached to a reflux condenser and protected from atmospheric moisture with a Drierite drying tube. During a 2 hr. period, 0.15 g. equiv. of the sodium alkoxide (or phenoxide) was added to the stirred mixture from a solid addition tube. The mixture usually was refluxed 8–12 hr. and then allowed to stand overnight with stirring. The solvent was removed under vacuum at room temperature, along with some of the lower boiling alkyl borates which formed if any alcohol impurity was present in the sodium alkoxide. The flask then was heated under vacuum until the bath temperature was 260–320° and the volatile materials collected in a trap cooled to Dry Ice temperature. The crude borazene derivative was purified by distillation at reduced pressure through a one-foot, heated column packed with glass helices and connected to a multiple take-off equipped with four receivers. All material transfers were made under nitrogen in a dry box since these borazenes are hydrolyzed readily by atmospheric moisture.

It was advantageous to use equivalent amounts of the sodium alkoxide and N-trimethyl-B-trichloroborazene. An excess of the alkoxide appeared to result in lower yields, whereas an excess of trichloroborazene complicated purification of the product since the trichloroborazene sublimes at about the temperature where the lower alkoxyborazenes distil. Rapid mixing of the alkoxide and N-trimethyl-B-trichloroborazene is not recommended. The reaction is exothermic, and, if the alkoxide is not added slowly, the benzene may vaporize so rapidly that the resulting pressure breaks the flask. From the manipulative stand-point, it would be more convenient to add a solution of N-trimethyl-B-trichloroborazene to the alkoxide; however, yields are better when dry salt is added to the chloroborazene solution so that the sodium alkoxide is never present in excess. Potassium salts may be substituted for sodium, although this change results in slightly lower yields. Optimum reflux time for salts of primary alkyl alcohols is 10–12 hr., whereas in the case of secondary and tertiary alcohols refluxing was omitted to diminish the extent of the side reaction forming sodium oxide and ether from the sodium alkoxide. In several experiments the solution was filtered (in the dry box) from the insoluble residue after the reaction was complete. The solvent was then evaporated *in vacuo* and the product distilled *in vacuo*. Yields were somewhat higher without the filtration step, indicating that the insoluble material does not cause the product to decompose at the distillation temperatures.

Physical and analytical data for the B-alkoxy- and B-phenoxyborazenes prepared in this investigation are listed in Table I.

Reaction of *n*-Propyl Alcohol with N-Trimethyl-B-trichloroborazene.—In a typical experiment, 0.133 g. equiv. of *n*-propyl alcohol was added dropwise to a chilled solution of 0.122 g. equiv. of N-trimethyl-B-trichloroborazene in 75 ml. of benzene. A white precipitate consisting of 0.037 g. equiv. of methylamine hydrochloride formed immediately. From the filtrate *n*-propyl borate and 0.078 g. equiv. of unreacted N-trimethyl-B-trichloroborazene were isolated. No N-trimethyl-B-tri-*n*-propoxyborazene was obtained.

Analysis.—Nitrogen was determined by titrating the methylamine obtained by distillation from an alkaline solution. Samples for boron and chlorine analysis were hydrolyzed by refluxing a solution made slightly acid with nitric acid (sulfuric acid for the phenoxy derivative) for 1 hr. Boron was titrated directly as boric acid complex in mannitol solution; chloride was determined by the Volhard method. Carbon and hydrogen analyses were done by Galbraith Microanalytical Laboratories, Knoxville, Tennessee.

Boiling Points.—Boiling points were determined by distillation at reduced pressures, which were measured to 0.01 mm. of mercury with a Stokes gauge.

Melting Points.—Melting point tubes were dried under vacuum and filled inside the dry box. They were sealed with Apiezon W immediately upon their removal from the dry box, and the melting points taken in the usual stirred bath.

Refractive Index.—In an air-conditioned room, samples were transferred quickly under a blanket of nitrogen to a Spencer 527 refractometer with a white light source. Under these conditions hydrolysis of the samples was negligible.

Infrared Spectra.—All infrared spectra were obtained with a Perkin–Elmer, Model 21, double beam, recording spectrophotometer with sodium chloride optics using a 0.206 mm. cell for the solution and a 0.209 mm. cell for the reference solvent. Table II gives the wave lengths in microns of the major absorption peaks of the N-trimethyl-B-trialkoxyborazenes and N-trimethyl-B-triphenoxyborazene in dry carbon tetrachloride.

Identification of the Alcohols from Hydrolyzed Alkoxyborazenes.—About 0.5 g. of the propoxy- and butoxyborazenes were hydrolyzed in 1 *N* hydrochloric acid and the alcohol–water azeotrope distilled. Under these conditions the other hydrolysis products—boric acid and methylamine hydrochloride—are non-volatile. The first few drops of distillate were extracted with carbon tetrachloride and the infrared spectra determined. The spectra of the alcohols obtained by thus hydrolyzing the alkoxyborazenes were identical with those of the original alcohols; therefore no rearrangement within the alkoxy group occurred during the reaction.

Discussion

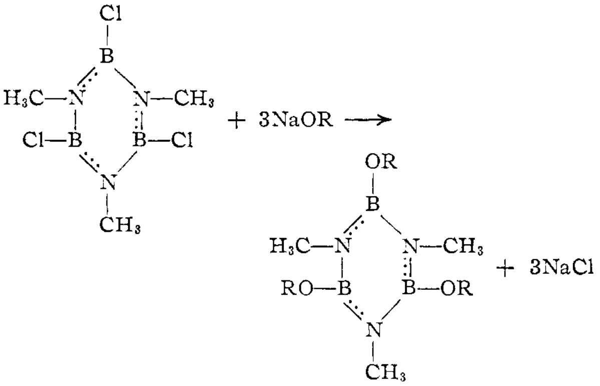
Synthesis.—N-Trimethyl-B-trichloroborazene reacts smoothly with the sodium salts of the aliphatic alcohols and of phenol to form B-alkoxy- and B-phenoxyborazenes by the reaction shown. No rearrangement within the alkoxy group occurs during the reaction. The purity of the sodium salts employed is quite critical. Under the conditions used in these experiments, reaction of the alcohols or phenol with N-trimethyl-β-trichloroborazene results only in ring cleavage to give methyl-

TABLE II

THE INFRARED SPECTRA OF N-TRIMETHYL-B-TRIALKOXYBORAZENES, N-TRIMETHYL-B-TRIPHENOXYBORAZENE AND N-TRIMETHYL-B-TRICHLOROBORAZENE; WAVE LENGTH IN μ

Methoxy-borazene	Ethoxy-borazene	*n*-Propoxy-borazene	*n*-Butoxy-borazene	Isopropoxy-borazene	*t*-Butoxy-borazene	Phenoxy-borazene	Chloro-borazene	Assignment
3.35w	3.37m	3.38m		3.33m	3.32m	3.34vw		C–H stretch
3.47w	3.43m		3.43m				3.40–3.44w	C–H stretch
						6.23w		Phenyl
6.74s	6.69s	6.72s	6.72m	6.72m	6.71m			$-CH_2-$ bend
						6.76m		Phenyl
				6.80sh	6.78m			
6.90m	6.91s	6.92s	6.92m	6.91m	6.92m	7.08vs	6.86s	Borazene ring
	7.04vs	7.04vs	7.04vs	7.07vs	7.12vs			$-CH_2-$ bend
7.16vs	7.24vs	7.24vs	7.28vs	7.24m	7.17vs		7.16vs	*sym*-CH_3 bend
				7.29w				
	7.33s			7.34m	7.32s			
7.53m	7.56s	7.56s	7.56m	7.59m	7.56m	7.52m		B–O bend
							7.78–7.80w	
						7.95vs		Phenyl C–O
7.82vvw			8.13w		8.04w			
						8.56w		
8.24s	8.44vs	8.46vs	8.49vs	8.49vs	8.42s	8.81m	9.21m	Borazene ring
8.70s	8.71s	8.77sh	8.75sh	8.80m	8.64vs			Alkyl C–O
				8.92m				
9.29vw	9.09vw		9.26w					
9.57w	9.46vw	9.47vw			9.41vw	9.34vw		
							10.25m	
9.97vw	9.82vw	10.24w		10.35w	10.59vw			
					10.83vw			
					11.02vw			
13.92m	13.94w	13.97w	13.96w	13.93vw		13.99vvw		
						14.50m	14.77m	
							14.90m	
							15.07m	

amine hydrochloride and trialkyl or triphenyl borate. Any alcohol or phenol present in the salt will cleave the ring. Sodium oxide also appears to lower yields considerably. With pure alkali metal salts of *n*-alkyl alcohols or phenol, using anhydrous conditions, 60–75% yields of crude B-alkoxy- or B-phenoxyborazenes and 45–60% yields of the purified products were obtained. Considerable difficulty is encountered in preparing the pure salts of secondary and tertiary alkyl alcohols, because of the low reactivity of the alcohol with the metal or metal hydride, pronounced gel formation of the salt with excess alcohol, and tendency of the salt to react with itself to form the ether and the metal oxide. Using the best secondary and tertiary salts, yields of only 30–37% of the crude borazene derivative could be obtained. Aside from the problems involved in preparing the salts, no significant steric effect of secondary and tertiary groups on the reaction itself was apparent, since the rather bulky phenyl group gave yields comparable to those of the *n*-alkoxy salts. Although the reaction of N-trimethyl-B-trichloroborazene with less than three moles of alkoxide did lead to products containing some halogen, no pure unsymmetrical B-alkoxy- (or B-phenoxy-) B-chloroborazenes were isolated.



The reaction of $(CH_3NBOR)_3$ with water and lower alcohols is instantaneous and exothermic. Accordingly all manipulations required the exclusion of atmospheric moisture. All the alkoxy borazenes prepared exhibited a high degree of thermal stability. During distillations the heating baths were kept at temperatures about 180° for several hours without causing noticeable decomposition.

Infrared Spectra.—Comparison of the infrared spectra of the alkoxyborazenes and phenoxyborazene with the spectra of the borate esters shows a number of similarities.[9–11] The absorption peaks at 3.3 and 3.4 μ correspond to the carbon–hydrogen stretching frequencies. Werner and O'Brien attribute the 6.74 μ peak to the $-CH_2-$ group, as well as the 7.06 μ peak in the alkyl borates.[11] The 7.24 μ peak corresponds to the symmetrical methyl bend-

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[9] J. V. Bell, J. Heisler, H. Tannenbaum and J. Goldenson, *Anal. Chem.*, **25**, 1720 (1953).

[10] P. D. George and J. R. Ladd, THIS JOURNAL, **77**, 1900 (1955).

[11] R. L. Werner and K. G. O'Brien, *Australian J. Chem.*, **8**, 355 (1955).

ing frequency. Werner and O'Brien and Bell have assigned the boron–oxygen valence vibration to the strong 7.5 μ band.[9,11] The alkyl carbon–oxygen band ranges from 8.64 to 8.92 μ which is well within the generally accepted range of 8.70 to 9.40 for alkyl ethers. The phenyl carbon–oxygen absorption appears at a shorter wave length being reported[12] generally as 7.87 to 8.14 μ and more specifically as 8.22 in phenyl borate.[11] These compare favorably with the strong peak at 7.95 μ in N-trimethyl-B-triphenoxyborazene.

The only major differences between the spectra of the borate esters and the alkoxy- and phenoxyborazenes are the strong peak at 6.91 μ and the very strong peak at 8.46 μ, which are present in the borazenes and absent in the borate esters. These probably correspond to borazene ring vibrations. Borazene itself has a ring vibration at 6.83 μ, while N-trimethylborazene has ring vibrations at 7.02, 7.45 and 7.73.[13]

Acknowledgment.—The support of this work by the Koppers Company through a research contract with the University of Florida is gratefully acknowledged.

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(12) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 100.

(13) W. C. Price, R. D. B. Fraser, T. S. Robinson and H. C. Longuet-Higgins, *Disc. Faraday Soc.*, **9**, 131 (1950).

GAINESVILLE, FLORIDA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTHERN CALIFORNIA]

The Sodium Salts of Tri-α-naphthylboron[1]

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Tri-α-naphthylboron reacts with an equivalent of sodium in tetrahydrofuran to form the paramagnetic tri-α-naphthylboron radical anion. Magnetic susceptibility measurements and molecular weight determinations indicate that the diamagnetic dimer forms in ethyl ether. The solid monosodium salt is also diamagnetic, as is the disodium salt in ether and tetrahydrofuran. The effect of solvent is discussed.

The reactions of the alkali metals with triarylboron compounds were first described by Krause[3] who showed by analyses that the one electron reduction product could be obtained

$$\mathrm{Na} + \mathrm{B(aryl)_3} \rightleftarrows \mathrm{NaB(aryl)_3} \tag{1}$$

The reversibility of reaction 1 and the conductance of the sodium salts in ether were investigated by Bent and Dorfman.[4] They found that the preparation of the salt of tri-α-naphthylboron, TNB, was complicated by the formation of the disodium salt

$$2\mathrm{Na} + \mathrm{TNB} \rightleftarrows \mathrm{Na_2TNB} \tag{2}$$

The compounds are colored, and they react rapidly, with loss of color, upon exposure to air.

If the monosodium salts of triarylboron compounds are monomeric or only partially associated, they should be paramagnetic and isoelectronic to the triarylmethyl radicals. The study of the extent of association of some of the triarylboron anions has been reported recently.[5] The results indicate that sodium triphenylboron is completely associated and diamagnetic,[6] while the sodium salts of trimesitylboron and tri-β-methylnaphthylboron are almost completely unassociated in tetrahydrofuran, THF, solutions. The investigation reported here shows that, while sodium tri-α-naphthylboron is dimeric in ethyl ether, it is paramagnetic and unassociated in THF.

Results

In THF solution tri-α-naphthylboron reacts with sodium to form a dark green solution of the monosodium salt and, with excess sodium, a black solution of the disodium salt. In ether solution the monosodium salt is orange and the disodium salt is black. In benzene the disodium salt does not form; the solution remains orange after prolonged shaking with excess sodium. The differences in color exhibited by NaTNB in the two solvents become understandable upon examination of the magnetic data in Table I. In THF solution the green NaTNB is paramagnetic, and a large fraction of the salt must exist as a monomer. By contrast, in the orange ether solution the monosodium salt is diamagnetic, indicating extensive association of the monomeric unit. The black solutions of $\mathrm{Na_2TNB}$ are diamagnetic, as anticipated.

A red solvated form of NaTNB is obtained by recrystallization from ether. Both this and the desolvated orange powder are diamagnetic. Either material forms a green paramagnetic solution in THF and an orange diamagnetic solid upon evaporation of the solvent. These latter results differ markedly from the behavior of sodium trimesitylboron, NaTMB, as reported by Chu and Weismann.[5b] In their studies NaTMB was found to be paramagnetic when prepared directly in THF, but recrystallization and thorough drying of the salt

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(1) Abstracted in part from the dissertation presented by C. W. Moeller to the Graduate School of the University of Southern California in partial fulfillment of the requirements for the Ph.D. degree, 1954. This work was supported in part by the Office of Naval Research.

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(3) E. Krause, *Ber.*, **57**, 216 (1924); E. Krause and H. Polack, *ibid.*, **59**, 777 (1926).

(4) H. Bent and M. Dorfman, THIS JOURNAL, **54**, 2133 (1932); **57**, 1259 (1935); **57**, 1924 (1935).

(5) (a) T. L. Chu, *ibid.*, **75**, 1730 (1953); (b) T. L. Chu and T. J. Weismann, *ibid.*, **78**, 23 (1956); (c) **78**, 3610 (1956).

(6) Our results confirm the diamagnetism of sodium triphenylboron and are in agreement with those reported in 5a except that only a single peak was found in the absorption spectrum rather than the two reported to Chu. In ether the peak is at 400 mμ and in tetrahydrofuran it is at 420 mμ. The second peak reported by Chu appears when mercury is in the system.