

ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE ROHM & HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION, HUNTSVILLE, ALA.]

Amine Boranes. IX. Dialkylamino Alkylboranes and Bis-(diethylamino) *n*-ButylboraneBY M. FREDERICK HAWTHORNE¹

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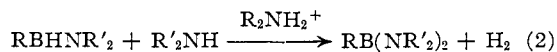
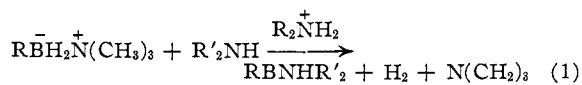
Dialkylamines and trimethylamine alkylboranes yielded either the corresponding bis-(dialkylamino)-alkylborane or the dialkylamino alkylborane at 100–150° in the presence of dialkylammonium ion catalyst. The nature of the reaction product was determined by the steric requirements of the alkyl group attached to boron. Methylamine and trimethylamine *t*-butylborane produced dimeric methylamino *t*-butylborane. The B¹¹ n.m.r. spectra of all products were determined and correlated with product structure and degree of association.

Among the various boron-nitrogen compounds described in the literature the B- and N-alkyl derivatives of aminoborane, H₂BNH₂, and diamino-borane, (H₂N)₂BH, appear to be exceedingly rare and available only by tedious procedures.² Thus, dialkylamino dialkylboranes and bis-(dialkylamino) alkylboranes have been reported. Boone and Burg³ have prepared dimethylamino methylborane. Alkylamino alkylboranes have not been reported.

As a portion of a research program aimed at the elucidation of the chemistry of trialkylamine alkylboranes,⁴ a relatively simple procedure has been developed for the preparation of certain dialkylamino and bis-(diethylamino) alkylboranes. That procedure and a description of the chemical properties of these materials is presented in this paper.

Results and Discussion

The recently described synthesis of B,B',B''-trialkylborazines⁵ by the ammonium ion-catalyzed reactions of ammonia with trimethylamine alkylboranes strongly suggested that dialkylamines would produce dialkylamino alkylborane and bis-(dialkylamino) alkylborane derivatives. Thus, a series of trimethylamine alkylboranes were treated



with diethylamine in the presence of catalytic amounts of diethylammonium ion. The results of these initial experiments prompted a detailed study of the reactions of a series of dialkylamines with the sterically encumbered derivative trimethylamine *t*-butylborane.

The reactions of diethylamine with trimethylamine *n*-butyl-, iso-butyl-, *s*-butyl- and *t*-butylboranes were examined in diglyme solution in the presence of small quantities of diethylammonium ion. Hydrogen and trimethylamine evolution proceeded smoothly between 100 and 150°. The reaction products were isolated by fractional distillation of the reaction mixtures at reduced pres-

ures. Diglyme was omitted from those reactions which gave products of boiling point near that of diglyme. Yields ranged from poor to moderately good.

The analysis of the product of the trimethylamine *n*-butylborane reaction agreed with that of bis-(diethylamino) *n*-butylborane. The infrared spectrum of this substance contained no B-H stretching band. Thus, the over-all reaction observed in this case proceeded through steps 1 and 2.

The products derived from isobutyl-, *sec*-butyl- and *t*-butylborane gave analyses in agreement with that of the corresponding diethylamino alkylborane. Additional evidence for these structural assignments was the presence of a B-H stretching band (2450 cm.⁻¹) in the infrared spectrum of each of these materials. From these results it is clear that α - or β -branching of the alkyl group attached to boron effectively inhibits reaction step 2. Table I presents the preparative data obtained.

Since dialkylamino alkylboranes were comparatively unknown,³ the reactions of a series of dialkylamines with trimethylamine *t*-butylborane were investigated. Dimethyl, diisobutyl-, diisopropyl and di-*n*-butylamines were employed with their corresponding dialkylammonium ions as catalysts. In each case well characterized products were obtained which proved to be the corresponding dialkylamino *t*-butylboranes on the basis of analyses and B-H stretching bands in their infrared spectra. Table I presents the preparative data obtained for these materials.

A further example of steric inhibition of reaction step 2 was the preparation of methylamino *t*-butylborane (see Table I) from methylamine and trimethylamine *t*-butylborane under the usual reaction conditions. A possible side reaction, the formation of N,N',N''-trimethyl-B,B',B''-tri-*t*-butylborazine, was not observed. The absence of this latter reaction might be attributed to the combined steric requirements of the *t*-butyl and the methyl groups in methylamino *t*-butylboranes. The corresponding reaction of trimethylamine *t*-butylborane with ammonia is known and was the basis of the preparation of B,B',B''-tri-*t*-butylborazine recently described.⁵

The data of Table I prove that the materials described in this study do not readily disproportionate to symmetrical products.

(1) Visiting Lecturer, Harvard University, Fall, 1960.

(2) The reader is referred to M. F. Lappert, *Chem. Revs.*, **56**, 959 (1956), for a recent survey of this area of boron chemistry.(3) A. B. Burg and J. L. Boone, *J. Am. Chem. Soc.*, **78**, 1521 (1956).(4) M. F. Hawthorne, *ibid.*, **83**, 831 (1961).(5) M. F. Hawthorne, *ibid.*, **83**, 833 (1961).

TABLE I
 CHARACTERIZATION OF ALKYLAMINO, DIALKYLAMINO AND BIS-(DIALKYLAMINO) ALKYLBORANES

R in R ₂ NH	R' in R'(BH ₂ N)(CH ₃) ₂	Product	Yield, %	B.p.		Analyses, %							
				°C.	Mm.	Calcd.				Found			
						C	H	B	N	C	H	B	N
Ethyl	<i>n</i> -Butyl	(R ₂ N) ₂ BR'	42	77	0.3	67.93	13.77	5.10	13.20	67.81	13.56	5.30	12.96
Ethyl	<i>i</i> -Butyl	(R ₂ N)BHR'	25	52	21 ^a	68.11	14.29	7.67	9.93	68.11	14.29	7.76	9.83
Ethyl	<i>s</i> -Butyl	(R ₂ N)BHR'	65	54	27 ^a	68.11	14.29	7.67	9.93	68.40	14.31	7.69	9.72
Ethyl	<i>t</i> -Butyl	(R ₂ N)BHR'	61	68	46	68.11	14.29	7.67	9.93	67.83	14.31	7.47	9.65
Methyl	<i>t</i> -Butyl	(R ₂ N)BHR'	46	48-40	80 ^{a,b}	63.76	14.27	9.58	12.39	63.55	14.45	9.75	12.45
<i>i</i> -Propyl	<i>t</i> -Butyl	(R ₂ N)BHR'	38	74	31	71.01	14.30	6.40	8.29	71.08	14.11	6.36	8.30
<i>i</i> -Butyl	<i>t</i> -Butyl	(R ₂ N)BHR'	43	54	3	73.09	14.32	5.49	7.10	72.93	14.52	5.52	6.89
<i>n</i> -Butyl	<i>t</i> -Butyl	(R ₂ N)BHR'	50	77	3.3	73.09	14.32	5.49	7.10	72.97	14.28	5.58	7.11
^c	<i>t</i> -Butyl	(MeHN)BHR'	68	42	110	60.66	14.25	10.93	14.16	60.97	14.10	10.82	14.20

^a Diglyme omitted in preparation. ^b Boiling point decreased as distillation proceeded. ^c Methylamine.

Bis-(diethylamino) *n*-butylborane was reasonably stable toward water at room temperature while all dialkylamino alkylborane derivatives reacted violently with cold water and dilute acids to produce hydrogen and uncharacterized hydrolysis products.

Table II presents the data obtained from an examination of the B¹¹ n.m.r. spectra of each of the compounds reported in Table I. Trimethyl borate was employed as a standard.

TABLE II

B¹¹ N.M.R. SPECTRA OF BIS-(DIALKYLAMINO) AND DIALKYLAMINO ALKYLBORANES

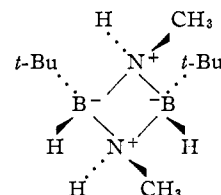
Compound	B ¹¹ resonance ($\delta \times 10^6$) ^a
Bis-(diethylamino) <i>n</i> -butylborane	Singlet (-21.2)
Diethylamino isobutylborane	Doublet -29.4 and -20.0)
Diethylamino <i>sec</i> -butylborane	Doublet (-29.6 and -20.5)
Diethylamino <i>t</i> -butylborane	Doublet (-28.5 and -20.0)
Dimethylamino <i>t</i> -butylborane	Doublet (-30.4 and -20.6)
	Weak doublet (+8.2 and +17.2)
Diisopropylamino <i>t</i> -butylborane	Doublet (-28.8 and -19.3)
Diisobutylamino <i>t</i> -butylborane	Doublet (-29.6 and -22.1)
Di- <i>n</i> -butylamino <i>t</i> -butylborane	Doublet (-29.4 and -20.0)
Methylamino <i>t</i> -butylborane	Doublet (+9.7 and +18.0)

^a Spectra determined as pure liquid.

As seen in Table II, the B¹¹ n.m.r. spectra of the compounds reported in this investigation are in agreement with their assigned structures. The positions of the observed resonances are in agreement with the data of Phillips, Miller and Muetterties⁶ who observed a single resonance at $\delta = -12.9 \times 10^6$ for tris-(diethylamino) borane. Substitution of hydrogen by dialkylamino groups results in a decreased chemical shift with respect to trimethyl borate.

Methylamino *t*-butylborane presents a doublet at higher field than trimethyl borate. This apparent anomaly was resolved by molecular weight measurements on diethylamino *t*-butylborane and methylamino *t*-butylborane. The former compound was purely monomeric in benzene solution at the freezing point while the latter material was dimeric. The high field doublet of methylamino *t*-butylborane is thus associated with nitrogen bridging in a cyclic dimer. Such dimers may exist in several stereoisomeric configurations. If, however, the steric interaction of near-neighbor groups is more important than transannular interactions, the preferred structure would be I. The B¹¹ n.m.r. spectrum of dimethylaminoborane dimer has been

reported⁶ as a triplet centered at $\delta = +14.5 \times 10^6$ and further supports this general conclusion. The infrared spectrum of methylamino *t*-butylborane contained a B-H stretching band at 2400 cm.⁻¹, a slightly lower frequency than that of the B-H stretching band of monomeric diethylamino *t*-butylborane (2450 cm.⁻¹).



The B¹¹ n.m.r. spectrum of dimethylamino *t*-butylborane contains two doublets: a strong low field doublet associated with monomer and a weak high field doublet which must represent small quantities of dimer or trimer. It is interesting to note that the slow distillation of this material resulted in a boiling point which slowly decreased as distillation proceeded (see Table I). Such behavior would be expected of dimeric material which slowly dissociated to a much more volatile monomer. The fact that this material is not strongly associated at room temperature may be explained on the basis of the greater steric requirements of two methyl groups on a nitrogen bridge.

The observed molecular weight of bis-(diethylamino) *n*-butylborane was correct for essentially pure monomer as was expected from its B¹¹ n.m.r. spectrum.

Experimental

Materials.—Trimethylamine alkylboranes were prepared as previously described⁴ and used without purification.

Diglyme was purified by distillation from lithium aluminum hydride at reduced pressure and stored in tightly sealed bottles, b.p. 62° at 17 mm.

Amines were of the highest purity commercially available.

General Procedure for the Preparation of Bis-(diethylamino) *n*-Butylborane and Dialkylamino Alkylboranes.—Concentrated sulfuric acid (0.2 ml.) and 0.5 g. of the desired dialkylamine was treated with 0.10 mole of the desired trimethylamine alkylborane in 20 ml. of diglyme. The diglyme was omitted in certain runs (see Table I). The system was flushed with dry nitrogen and heated to 100°. During the course of 3 hours the stoichiometric quantity of dialkylamine was added from the dropping funnel as the temperature was raised slowly to 150°. Hydrogen and trimethylamine were evolved smoothly through a bubble trap which functioned as a seal to the atmosphere. Stirring was carried out at all times. Following the reaction period, the mixture was cooled to room temperature and fractionated with a 30-plate spinning band column at reduced pressures. Table I records yields, boiling points and analytical data.

(6) W. D. Phillips, H. C. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959).

Dimethylamino *t*-butylborane and methylamino *t*-butylborane were prepared in an identical fashion except that the gaseous amines were passed through the reaction mixture with a gas inlet tube. In these cases excess amine was employed and the completion of the reaction was indicated by the cessation of hydrogen evolution.

B^{11} N.m.r. Spectra.—A Varian high resolution nuclear magnetic resonance spectrometer was employed at 12.8 mc. Spectra were obtained with pure liquids and measured relative to trimethyl borate contained in a capillary tube inserted in the sample tube.

Molecular Weight Determinations.—Solutions of bis-(diethylamino) *n*-butylborane, diethylamino *t*-butylborane and methylamino *t*-butylborane were prepared with pure benzene solvent in a glove-box. A completely sealed and

dried freezing point depression apparatus was employed with a Beckmann thermometer in the usual manner. Determinations were carried out in duplicate. The observed molecular weights were: bis-(diethylamino) *n*-butylborane, 202 and 198 (theor. 212); diethylamino *t*-butylborane, 143 and 151 (theor. 141); and methylamino *t*-butylborane, 198 and 195 (theor. 99).

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[CONTRIBUTION FROM THE ROHM & HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION, HUNTSVILLE, ALA.]

The Nature of the Colored 6,9-Bis-pyridine Decaborane Molecule, $B_{10}H_{12}Py_2$

BY BRUCE M. GRAYBILL AND M. FREDERICK HAWTHORNE¹

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Several highly colored 6,9-bis-pyridine decaborane derivatives have been prepared from substituted pyridines and their ultraviolet and visible absorption spectra determined. The absorption band found at longest wave length was successfully correlated with the Hammett σ -constant characteristic of each substituent. Electron-withdrawing substituents such as the *p*-cyano group markedly reduce the transition energy associated with this absorption band. Evidence is presented which indicates that the π -electron system of the pyridine nucleus is extended well into the $B_{10}H_{12}$ fragment.

The reaction of pyridines with decaborane has recently been examined by many workers.²⁻⁵ Due to the highly colored nature of these materials, other investigators^{6,7} have employed their quantitative formation as the basis of a colorimetric method for the determination of decaborane. The method of synthesis (*vide infra*), analyses and other data support the conclusion that these materials are actually members of the $B_{10}H_{12}X_2$ family.⁸ Reddy and Lipscomb⁹ have recently reported the structure of the bis-acetonitrile product, $B_{10}H_{12}(CH_3CN)_2$, and have discussed its bonding in terms of the three-center bond topology of Dickerson and Lipscomb.^{10,11} More recently, Sands and Zalkin¹² have determined the structure of the bis-dimethyl sulfide derivative, $B_{10}H_{12}[S(CH_3)_2]_2$. The structure of this compound was found to be in excellent agreement with that of the bis-acetonitrile product.⁹

Quite a large number of $B_{10}H_{12}X_2$ compounds have been prepared and characterized in the past. The ligand, X , has been varied widely and encom-

passes such species as phosphines,⁸ dialkylcyanamides,⁸ amines,¹³ nitrile,¹⁴ isonitriles,¹⁵ phosphite esters¹⁶ and tetrazoles.¹⁶ The pure $B_{10}H_{12}X_2$ compounds have been observed to be colorless when X does not have an extended π -electron system. The fact that the corresponding pyridine derivatives, $B_{10}H_{12}Py_2$, were highly colored and diamagnetic suggested an unusual electronic interaction of the $B_{10}H_{12}$ unit and the bonded pyridine molecule. In this paper we report the synthesis of several symmetrical 6,9-bis-pyridine decaboranes which bear substituents on the pyridine rings and a correlation of their spectroscopic properties with Hammett σ -constant characteristic of those substituent groups. Lastly, these results are combined in a rationale which makes use of the known structural features of $B_{10}H_{12}X_2$ molecules^{9,12} and the topological treatment of Lipscomb.^{10,11}

Results and Discussion

The synthesis of the required symmetrically substituted¹⁷ 6,9-bis-pyridine decaborane derivatives was accomplished in two steps. The 6,9-bis-diethyl sulfide intermediate was employed since the structure of the corresponding dimethyl sulfide derivative is known¹² and the displacement of diethyl sulfide by substituted pyridines occurs with great ease at room temperature and *without* hydrogen evolution.¹⁸ The preparation of 6,9-bis-diethyl sulfide decaborane from diethyl sulfide and decaborane may be accomplished in 83% yield and the subsequent step is always very effi-

(1) Visiting Lecturer, Harvard University, Fall, 1960.

(2) W. A. Mosher, H. C. Beachell, *et al.*, Univ. of Delaware, Newark, Del., Contract No. DA-36-034-ORD-2526-RD (unclassified), Quarterly Report Nos. 1-5, "Adducts of Boron Compounds."

(3) H. C. Beachell, D. E. Hoffman and B. F. Dietrich, *Angew. Chem.*, **72**, 40 (1960).

(4) L. A. Burkardt and N. R. Fetter, Abstracts of Papers, 135th Meeting, American Chemical Society, Boston, Mass., p. 45-M.

(5) L. A. Burkardt and N. R. Fetter, *Chemistry & Industry*, **38**, 1191 (1959).

(6) W. H. Hill and M. S. Johnston, *Anal. Chem.*, **27**, 1300 (1955).

(7) D. L. Hill, E. I. Gipson and J. F. Hancock, *ibid.*, **28**, 133 (1956).

(8) M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **80**, 6685 (1958), report several examples.

(9) J. Van der Maas Reddy and W. N. Lipscomb, *J. Chem. Phys.*, **31**, 610 (1959).

(10) R. E. Dickerson and W. N. Lipscomb, *ibid.*, **27**, 212 (1957).

(11) For a summary of this topological method see W. N. Lipscomb, "Advances in Inorganic and Radiochemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1959.

(12) D. E. Sand and A. Zalkin, Abstracts of Papers, International Congress of Crystallography, 1960.

(13) M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **81**, 5519 (1959).

(14) R. Schaefer, *ibid.*, **79**, 1006 (1957).

(15) B. M. Graybill and M. E. Hawthorne, unpublished results.

(16) N. R. Fetter, *Chemistry & Industry*, 1548 (1959).

(17) Unsymmetrical derivatives, $B_{10}H_{12}XX'$, have recently been prepared and will be reported in the near future.

(18) For previous examples of similar displacement reactions see M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **80**, 6685 (1958).