

ORGANIC AND BIOLOGICAL CHEMISTRY

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

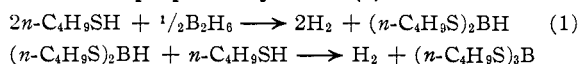
Amine Boranes. VII. The Preparation of Dialkyl Alkylthioboronate and Trialkylthioborate Esters¹

BY M. FREDERICK HAWTHORNE

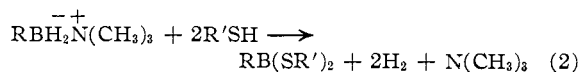
RECEIVED NOVEMBER 3, 1960

Dialkyl alkylthioboronate esters were conveniently prepared by the reaction of alkanethiols with a variety of trimethylamine alkylboranes at 60–100°. Treatment of these materials with mercuric chloride results in the formation of the corresponding alkylchloroboranes. Trialkylthioborate esters were prepared from alkane thiols and trimethylamine borane in an analogous manner.

Dialkylthioboronate and trialkylthioborate esters are virtually unknown materials. Indeed, a recent review of the literature of organoboron chemistry² reveals only one dialkyl alkylthioboronate ester.³ Trialkylthioborate esters fared little better with two entries regarding trimethylthioborate.⁴ More recently, Mikhailov and co-workers have reported the preparation of tri-*n*-butylthioborate⁵ which was prepared by route (1).



The ease with which trimethylamine alkylboranes enter into protolysis reactions with weakly acidic substrates⁶ suggested that similar reactions with alkanethiols would produce dialkyl alkylthioboronate esters (2).



Trimethylamine borane was expected to give analogous reactions and produce trialkylthioborate esters.

Results and Discussion

The preparation of dialkyl alkylthioboronates was simply accomplished by heating the appropriate trimethylamine alkylborane and two equivalents of alkanethiol to approximately 100°. No solvent or catalyst was required. Hydrogen and trimethylamine were evolved smoothly. This simple procedure allowed the preparation of products derived from alkanethiols of moderately high boiling point. 1,2-Ethanedithiol was employed in two examples and formed 1-bora-2,5-dithiocyclopentane derivatives. Methanethiol did not react under these conditions and ethanethiol gave only low yields of product. This experimental limitation could most likely be corrected by the use of a suitable autoclave. Products were isolated by fractional distillation of the reaction mixtures at

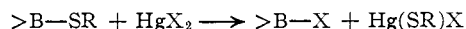
reduced pressures. Generally, such distillations proceeded smoothly and acceptable yields of product were obtained. No direct evidence of product disproportionation was observed although high-boiling residues of unknown composition were usually observed. Attempts to separate such residues by distillation were unsuccessful although a very efficient low-pressure column was employed. Further work is indicated in this area.

Tri-*n*-pentyl- and tri-*n*-butylthioborate were prepared from trimethylamine borane and the corresponding alkanethiols in 65 and 70% yields, respectively. The experimental procedure employed here was identical to that used in the preparation and purification of dialkyl alkylthioboronates.

Table I records preparative and characterization data for the dialkyl alkylthioboronates and trialkylthioborates obtained.

Properties of the Boron-Sulfur Bond.—The dialkyl alkylthioboronates and trialkylthioborates prepared in this study reacted rapidly and exothermically with water. The alkanethiol and the alkylboronic or boric acid were regenerated. In a qualitative sense such hydrolyses appear to be as rapid as those observed with simple trialkylborate esters.

The ability of mercuric chloride to form covalent bonds with alkanethiols and thioethers suggested the possible reaction of mercuric salts with compounds which contained the B-SR linkage. In agreement with this supposition, mercuric chloride



was found to react readily with di-*n*-pentyl-*n*-butylthioboronate and di-*n*-pentyl-*t*-butylthioboronate. Toluene was employed as the reaction solvent at 80°. In both cases a precipitate, assumed to be *n*-pentylthiomercureic chloride, was formed and the corresponding alkylchloroboranes were isolated in 60% yield. The *n*-butyl compound reacted much more readily than the *t*-butyl compound. The *n*-butyl- and *t*-butyldichloroboranes were shown to be pure by both infrared and H¹ n.m.r. spectra. These observations further confirm the fact that no alkyl group isomerization occurs during the preparation of dialkyl alkylthioboronates or their subsequent reaction with mercuric chloride.

The mercuric chloride reaction is interesting from a mechanistic standpoint since it might well involve a four-center transition state containing an

(1) Previously presented in part as a Communication to the Editor, *J. Am. Chem. Soc.*, **82**, 748 (1960).

(2) M. F. Lappert, *Chem. Revs.*, **56**, 959 (1956).

(3) W. A. Lazier and P. L. Solzberg, U. S. Patent 2,402,591; *C. A.*, **40**, 5769 (1946).

(4) A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **76**, 3307 (1954); also, J. Goubeau and H. W. Wittmeier, *Z. anorg. allgem. Chem.*, **270**, 16 (1952).

(5) B. M. Mikhailov and I. N. Bubnov, *Izvest. Akad. Nauk USSR, Otdel Khim. Nauk*, **10**, 1868 (1959).

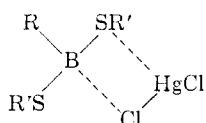
(6) For previously reported examples of this application of trialkylamine alkylboranes see M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 831 (1961), and **83**, 833 (1961).

TABLE I
 PREPARATION AND CHARACTERIZATION OF DIALKYL ALKYLTHIOBORONATE AND TRIALKYLTHIOBORATE ESTERS

	In RB(SR') ₂ R	R'	°C.	B.p. Mm.	Yield, %	Formula	Analyses, %					
							Calcd.			Found		
						C	H	B	C	H	B	
1	<i>n</i> -Propyl	<i>n</i> -Butyl	129	3.2	51	C ₁₁ B ₂₅ BS ₂	56.88	10.85	4.66	57.09	11.03	4.88
2	<i>i</i> -Propyl	<i>n</i> -Butyl	120	0.5	48	C ₁₃ H ₂₉ BS ₂	59.98	11.23	4.16	60.28	11.38	4.42
3	<i>n</i> -Butyl	Ethyl	100	6.5	21	C ₈ H ₁₉ BS ₂	50.52	10.07	5.68	50.28	10.06	5.69
4	<i>n</i> -Butyl	°	84	6	45	C ₆ H ₁₃ BS ₂	45.00	8.18	6.76	45.30	-8.32	6.49
5	<i>n</i> -Butyl	<i>n</i> -Propyl	131	9	35	C ₁₀ H ₂₃ BS ₂	55.03	10.62	4.96	55.24	10.75	5.20
6	<i>n</i> -Butyl	<i>n</i> -Butyl	116	0.6	33	C ₁₂ H ₂₇ BS ₂	58.52	11.05	4.39	58.83	11.35	4.48
7	<i>n</i> -Butyl	<i>n</i> -Pentyl	132	.5	29	C ₁₄ H ₃₁ BS ₂	61.29	11.39	3.94	61.07	11.39	4.19
8	<i>i</i> -Butyl	<i>n</i> -Butyl	104	.4	62	C ₁₂ H ₂₇ BS ₂	58.52	11.05	4.39	58.74	11.20	4.51
9	<i>i</i> -Butyl	°	83	6.5	38	C ₆ H ₁₃ BS ₂	45.00	8.18	6.76	45.14	8.38	6.67
10	<i>s</i> -Butyl	<i>n</i> -Butyl	105	0.8	63	C ₁₂ H ₂₇ BS ₂	58.52	11.05	4.39	48.45	11.01	4.67
11	<i>t</i> -Butyl	<i>n</i> -Pentyl	122	.5	72	C ₁₄ H ₃₁ BS ₂	61.29	11.39	3.94	61.42	11.49	4.09
12	<i>n</i> -Hexyl	<i>n</i> -Butyl	119	.3	58	C ₁₄ H ₃₁ BS ₂	61.29	11.39	3.94	61.39	11.57	4.23
13	<i>n</i> -Butylthio	<i>n</i> -Butyl	147	1.0 ^b	70	C ₁₂ H ₂₇ BS ₃	51.77	9.78	3.89	51.74	9.78	4.15
14	<i>n</i> -Pentylthio	<i>n</i> -Pentyl	164	0.4	65	C ₁₅ H ₃₃ BS ₃	56.22	10.38	3.38	56.09	10.20	3.54

° Ethanedithiol ester. ^b Ref. 5 reports b.p. 150–152° at 1 mm.

electrophilic mercury atom and a nucleophilic chlorine atom. That the formation of a strong



mercury-sulfur bond provides driving-force for these reactions is likely and this situation should allow extrapolation to other mercuric salts. Attempts to carry out similar reactions with diphenyl- and di-*n*-butylmercury were unsuccessful.

A recent survey of the B¹¹ nuclear magnetic resonance spectra of simple boron-containing compounds has appeared.⁷ It was observed that molecules which contained trigonal boron produced resonance lines at lower field strengths than trimethyl borate. In these simple derivatives the relative positions of the observed resonance lines were correlated roughly with the electron release afforded by the substituent groups and their electronegativities. Thus, trimethylborane is the compound observed at lowest field. The relative positions of the boron halides are also in accord with this general concept if the back coordination of fluorine and high polarizability of iodine is taken into account. Table II presents data obtained with compounds which contain the boron-sulfur bond and examples from Phillips, Miller and Muettterties.⁷

TABLE II

Compound	$\delta \times 10^6$
B(CH ₃) ₃ ^a	-68.2
<i>i</i> -BuB $\begin{cases} \text{SCH}_2 \\ \\ \text{SCH}_2 \end{cases}$	-51.9
<i>n</i> -BuB(S- <i>n</i> -Bu) ₂	-51.3
B(S- <i>n</i> -Bu) ₃	-47.9
<i>n</i> -C ₄ H ₉ B(OH) ₂ ^a	-14.3
B(OCH ₃) ₃ ^a	0

^a Data from ref. 7.

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

As seen in Table II the three thioborane derivatives have single resonance lines at extremely low field strengths relative to trimethylborate and *n*-butylboronic acid. In addition, the electronegativity⁸ of oxygen (3.5) is greater than that of sulfur (2.5) or carbon (2.5). Thus, on the basis of electronegativities alone the trimethylborate and *n*-butylboronic acid resonances are anomalously high. This result may be taken as evidence for back coordination of oxygen in borate esters which is nearly absent in the corresponding thioborane derivatives.

The compounds described in Table I were examined in the infrared region between 2 and 14 μ . A rather complicated spectrum was obtained in each case and no assignments were attempted. Trialkylthioborates absorbed strongly between 10–11 μ and moderately between 13.25–13.50 μ . Dialkyl alkylthioborates absorbed in these same regions and in addition gave strong bands between 9–10 μ . The fine structure associated with these bands varied considerably from compound to compound. The two cyclic derivatives 1-*n*-butyl-1-bora-2,5-dithiocyclopentane and 1-isobutyl-1-bora-2,5-dithiocyclopentane exhibited quite different infrared spectra from their non-cyclic counterparts. These materials gave sharp absorptions at 15.05 and 11.95 μ , weak absorption at 13.25 μ and strong bands at 9.0 and 9.25 μ .

Experimental

Materials.—Alkanethiols were commercially available materials of high purity and were employed without further purification. Trimethylamine alkylboranes were prepared as previously described and used without further purification.¹ Trimethylamine borane was prepared from sodium borohydride and trimethylammonium chloride in diglyme solution and purified by sublimation.

General Procedure for the Preparation of Dialkyl Alkylthioborates.—To 0.10 mole of trimethylamine alkylborane in a 100-ml. three-necked flask was added 0.20 mole of the desired alkanethiol (or 0.10 mole of 1,2-ethanedithiol). The solution was flushed with dry nitrogen, a reflux condenser attached and the reaction mixture gradually warmed to 100° with an oil-bath. Near 60° hydrogen evolution commenced and care was taken to prevent excessive frothing. When hydrogen evolution ceased at 100° the reaction

(8) L. Pauling, "The Nature of the Chemical Bond," 3rd Edition, The Cornell University Press, Ithaca, N. Y., 1960.

mixture was cooled and transferred to a 40 theoretical plate spinning-band distillation column. Distillation in a nitrogen atmosphere and at reduced pressures afforded a small forerun of starting materials followed by the desired product. In every case a distillation residue was obtained which could not be fractionated successfully at lower pressures. Table I reports the yields and characterization data obtained.

General Procedure for the Preparation of Trialkylthioborates.—This procedure was essentially that described above except that 0.10 mole of trimethylamine borane was employed with 0.30 mole of the desired alkanethiol. Table I records yields and characterization data.

Reaction of Mercuric Chloride with Di-*n*-pentyl-*n*-butylthioboronate.—To a well-stirred slurry of 27.3 g. (0.10 mole) of dry, powdered mercuric chloride in 30 ml. of dry toluene contained in a three-necked flask which carried a reflux condenser, stirrer and dropping funnel, was added 15.0 g. (0.05 mole) of di-*n*-pentyl-*n*-butylthioboronate. The addition was carried out in a dropwise fashion under nitrogen and over the course of 1 hour. The reaction mixture was maintained at 80° during the addition and for 1 hour thereafter. After the addition of the first few drops of thioester, a voluminous precipitate formed. The reaction mixture was cooled, filtered in the absence of air and the product separated by distillation in a nitrogen atmosphere. A small spinning-band distillation column was employed. The distillate weighed 4.2 g. (60%) and boiled at 104–106°.⁹ The infrared and H¹ n.m.r. spectra were

identical with an authentic sample of *n*-butyldichloroborane.

Reaction of Mercuric Chloride with Di-*n*-pentyl-*t*-butylthioboronate.—The same procedure described above for the similar reaction of di-*n*-pentyl-*n*-butylthioboronate was employed. This reaction proceeded much more slowly than that described above. Distillation of the reaction mixture afforded 4.2 g. (60%) of pure *t*-butyl dichloroborane boiling at 86–88°.¹⁰ The product was identical to an authentic specimen in its infrared and H¹ n.m.r. spectra.

Nuclear Magnetic Resonance Spectra.—All n.m.r. spectra were determined with neat samples and a 40 mc. H¹ probe or 12.8 m. B¹¹ probe. Boron spectra were measured with a trimethylborate reference contained in a capillary tube.

Infrared Spectra.—All infrared spectra were obtained with a model 21 Perkin-Elmer infrared spectrophotometer. Samples were examined as capillary layers prepared in an efficient dry-box.

Acknowledgment.—The author is indebted to Mrs. Carolyn P. Haney for the nuclear magnetic resonance measurements. This work was performed under U. S. Army Ordnance Contract No. DA-01-021-11878.

(9) P. A. McCusker, E. C. Ashby and H. S. Makowski, *J. Am. Chem. Soc.*, **79**, 5182 (1957), reported a boiling point of 106°.

(10) Ref. 9 reported a boiling point of 88°.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE, NEWARK, DEL.]

The Reaction of Decaborane with Aromatic Amines^{1,2}

BY HAROLD C. BEACHELL AND BRUCE F. DIETRICH

RECEIVED AUGUST 23, 1960

Decaborane reacts with *p*-anisidine, *p*-toluidine, *p*-chloroaniline, aniline, *N*-methylaniline and *N,N*-dimethylaniline to yield a product possessing the formula B₁₀H₁₂(amine)_{*n*}, where *n* = 2 or 3. The rates of reaction for these amines vary from 0.02 to 23.8 × 10⁻³ liter mole⁻¹ sec.⁻¹ at 25.0° in benzene solution. Rate constants have also been obtained for the reactions occurring at 20.0°, 30.3° and 35.9°. An activation energy of 11.9 ± 0.3 kcal. was calculated for aniline and the *p*-substituted anilines. Evidence is presented for the formation of a reaction intermediate.

Introduction

The reactions of decaborane with nitrogen-containing compounds have been known since the work of Stock.³ He noted that decaborane reacts with ammonia to form a diammonia compound. Since then investigations have been made involving other nitrogen compounds including the amines and nitrogen heterocycles.

The reactions involving amines were investigated mainly with the aliphatic series. Fitch⁴ reported obtaining amine adducts of decaborane from the reaction of the hydride with dimethylamine. He observed compounds with decaborane:dimethylamine ratios of 1:1, 1:2 and 1:3 with indications for 1:4 and 1:5 products. The formation of a salt was noted by Hawthorne⁵ when he added diethylamine to decaborane. The composition of the product was represented by the formula B₁₀H₁₂NH₂(C₂H₅)₂. Upon adding decaborane to ex-

cess amine this same investigator obtained a product which corresponded to B₁₀H₁₄(NH(C₂H₅)₂)₂.

An investigation of the reaction of decaborane with aniline and its *N*-methyl homologs was conducted recently by Terpko.⁶ His results indicated that the products formed were condensation type compounds and were represented by the formula B₁₀H_{14-x}(amine)_{*x*}.

Discussion

The addition of decaborane to a benzene solution of *p*-toluidine produces a white solid which precipitates from the reaction medium. Elemental analysis of the product indicates that it has a decaborane:amine ratio of 1:2. Stoichiometry studies show that the reaction is essentially quantitative and that one mole of hydrogen is evolved for each mole of decaborane reacted. Other amines which undergo the same type of reaction include *p*-anisidine, *p*-chloroaniline, *N*-methylaniline and *N,N*-dimethylaniline.

The product of the decaborane-aniline reaction has a decaborane:amine ratio of 1:3 as indicated by the results of an elemental analysis. Though three moles of amine are observed for each mole of decaborane, the reaction, nevertheless, releases only one mole of hydrogen. Since, as it will be shown

(1) Taken from the Ph.D. thesis of Bruce F. Dietrich submitted to the faculty of the University of Delaware, June, 1960.

(2) This research was carried out under Army Ordnance Contract No. DA-36-034-ORD-2526RD.

(3) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

(4) S. J. Fitch and A. W. Laubengayer, *J. Am. Chem. Soc.*, **80**, 5911 (1958).

(5) M. F. Hawthorne, A. R. Pitocheffi, R. D. Strahn and J. J. Miller, *ibid.*, **82**, 1825 (1960).

(6) S. P. Terpko, *Dissert. Abs.*, **20**, 1572 (1959).