on the basis of their infrared spectra appeared to be diphenyldiethoxysilane. There was insufficient material to distil so a few drops of the liquid were refluxed briefly with excess alcoholic alkali and were worked up to give 0.06 g. (4%) of diphenylsilanediol, m.p. 160–165°.

The isolation of traces of triphenylsilanol and diphenylsilanediol directly from the reaction suggests that traces of water were present.

Acknowledgment.—The authors are indebted to the Defence Research Board of Canada for grants in partial support of this work.

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

Amine Boranes. V. The Preparation of Trimethylamine Alkylboranes and 2-Alkylborobenzimidazolines[1]

BY M. FREDERICK HAWTHORNE

RECEIVED OCTOBER 15, 1960

A series of trialkylboroxines were reduced with lithium aluminum hydride in diethyl ether solution and in the presence of trimethylamine. Trimethylamine alkylboranes were obtained in up to 65% yield without alkyl group rearrangement. Trimethylamine alkylboranes were converted to the corresponding 2-alkylborobenzimidazolines by treatment with *o*-phenylenediamine in benzene solution at the reflux temperature. Primary, secondary and tertiary alkyl-, as well as cycloalkyl- and aralkylboroxines, were employed.

Recently, amine boranes have found some importance as intermediates in organoborane synthesis. A noteworthy example is the successful hydroboration of olefins with such materials as pyridine borane[2] and trimethylamine borane.[3,4] The presence of boron–hydrogen bonds in amine boranes suggests many interesting protolysis reactions from which new, or at least rare, families of substituted boranes could be derived. In the past such reactions usually employed the trialkylborane, the alkyl-substituted diboranes or diborane as starting materials. Organic substituents on boron generally were limited to the methyl and ethyl groups. It was therefore desirable to develop a convenient synthesis of trialkylamine alkylboranes and to determine their usefulness as synthetic intermediates.

A promising approach to the synthesis of trialkylamine alkylboranes was suggested by the facile reduction of arylboronic[5] and diarylborinic[6] esters to the corresponding trialkylamine and pyridine aryl- and diarylboranes. This was accomplished by the use of lithium aluminum hydride and the proper amine in diethyl ether solution and at low temperatures. In one instance,[5] triphenylboroxine was employed successfully as a starting material in such a reduction. This fact, coupled with the availability of a series of trialkylboroxines,[7] suggested this route to trialkylamine alkylboranes. As previously reported,[1] this is the method of choice and it may be applied to alkylboroxines which bear primary, secondary and tertiary alkyl groups or cycloalkyl groups. Equation 1 illustrates this reaction.

$$(RBO)_3 + 3NR'_3 \xrightarrow[Et_2O,\ 35°]{LiAlH_4} 3R\overset{-}{B}H_2\overset{+}{N}R'_3 \qquad (1)$$

R = primary, secondary and tertiary alkyl and cycloalkyl

All reductions of alkylboroxines with lithium aluminum hydride were carried out by the slow addition of the boroxine to a solution of lithium aluminum hydride in diethyl ether which contained a 70% excess of trimethylamine. A reaction temperature of 35° was chosen and the reductions were carried out under nitrogen to exclude water. The quantity of lithium aluminum hydride employed was critical with respect to the mechanics of product workup. The best results were obtained with a 3:1 mole ratio of lithium aluminum hydride to alkylboroxine. Although trimethylamine alkylboranes are quite stable toward hydrolysis, wet samples slowly evolve hydrogen and crystalline alkylboronic acid separates on standing. For this reason the quantity of water added during work-up was limited to four moles per mole of lithium aluminum hydride employed in the reduction. With these precautions, yields of 40–65% invariably were obtained. The crude products obtained by the evaporation of solvent were reasonably pure. Additional purification was achieved for characterization purposes by distillation in a molecular still at 30–50° or by rapid distillation with spinning-band column at reduced pressure. As will be seen in the following papers of this series, the crude products were employed as synthetic intermediates without additional purification.

With but few known exceptions, trimethylamine alkylboranes are liquids at room temperature and below. They exhibit two strong B–H stretching bands and two shoulders between 4.25–4.55 μ in the infrared. Trimethylamine alkylboranes also absorbed strongly at 11.90 μ in the infrared.

Silver ion and iodine reacted rapidly with trimethylamine alkylboranes and produced silver metal and iodide ion, respectively. Water and ethanol were essentially inert toward the B–H hydrogen present. Strong proton donors such as hydrochloric and trifluoroacetic acid gave rapid hydrogen evolution in accordance with eq. 2. This latter reaction was utilized as a criterion of product purity.

$$R\overset{-}{B}H_2\overset{+}{N}R'_3 + H_2O + H_3\overset{+}{O} \longrightarrow RB(OH)_2 + \overset{+}{N}HR'_3 + 2H_2 \qquad (2)$$

---

[1] Presented previously as a Communication to the Editor, M. F. Hawthorne, *J. Am. Chem. Soc.*, **81**, 5836 (1959).

[2] M. F. Hawthorne, *J. Org. Chem.*, **23**, 1788 (1958).

[3] R. Köster, *Angew. Chem.*, **69**, 684 (1957).

[4] E. C. Ashby, *J. Am. Chem. Soc.*, **81**, 4791 (1959).

[5] M. F. Hawthorne, *ibid.*, **80**, 4291 (1958).

[6] M. F. Hawthorne, *ibid.*, **80**, 4294 (1958).

[7] P. A. McCusker, E. C. Ashby and H. S. Makowski, *ibid.*, **79**, 5179 (1957).

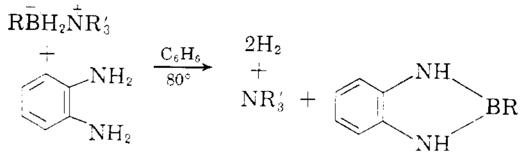
TABLE I

CHARACTERIZATION OF TRIMETHYLAMINE ALKYLBORANES (TMAB) AND 2-ALKYLBOROBENZIMIDAZOLINES (BBI)

Alkyl group	Derivative	Yield, %	M.p. (b.p. (mm.)) °C.	Moles H_2/mole compd.	Analyses, %							
					Calcd.				Found			
					C	H	B	N	C	H	B	N
1-Propyl	TMAB	65	*a*	2.01	62.64	15.77	9.41	12.18	62.45	15.60	9.50	12.06
	BBI	95	102–103^c		67.54	8.19	6.76	17.51	67.48	8.17	6.66	17.64
2-Propyl	TMAB	65	*a*	1.97	62.64	15.77	9.41	12.18	62.54	15.79	9.39	12.23
	BBI	91	124–126		67.54	8.19	6.76	17.51	67.50	8.19	6.95	17.80
1-Butyl	TMAB	64	(72 (3.0))^b	1.97	65.14	15.62	8.38	10.86	64.88	15.38	8.23	10.83
	BBI	85	66–67		69.00	8.69	6.21	16.10	69.05	8.62	6.00	16.28
2-Butyl	TMAB	66	(60 (2.5))^b	2.00	65.14	15.62	8.38	10.86	65.02	15.29	8.41	10.80
	BBI	92	61–62		69.00	8.69	6.21	16.10	69.10	8.45	6.43	15.96
Isobutyl	TMAB	61	*a*	2.02	65.14	15.62	8.38	10.86	65.31	15.68	8.18	10.61
	BBI	95	90–92^a		69.00	8.69	6.21	16.10	68.85	8.55	5.97	15.82
t-Butyl	TMAB	64	(60 (3.5))^b	1.99	65.14	15.62	8.38	10.86	65.14	15.45	8.36	10.61
	BBI	72	93–95		69.00	8.69	6.21	16.10	69.01	8.73	6.05	16.40
1-Pentyl	TMAB	58	*a*	1.95	67.15	15.50	7.56	9.79	66.97	15.60	7.42	10.00
	BBI	51	69–71		70.24	9.11	5.76	14.89	70.46	8.85	5.78	15.02
1-Hexyl	TMAB	52	*a*	1.98	68.80	15.40	6.89	8.91	68.74	15.30	6.85	8.67
	BBI	79	96–97		71.31	9.48	5.35	13.86	71.05	9.35	5.38	13.56
Cyclohexyl	TMAB	44	40–41	1.95	69.69	14.30	6.98	9.03	69.64	14.34	6.74	8.84
	BBI	89	78–80		72.03	8.56	5.41	14.00	72.00	8.29	5.48	13.89
Benzyl	TMAB	65	58–60	1.99	73.65	11.13	6.63	8.59	73.54	10.91	6.53	8.36
	BBI	92	54–56		75.04	6.30	5.20	13.46	75.30	6.60	5.06	13.58

^{a} Molecular distillation. ^{b} Fractionation with spinning-band distillation column. ^{c} Ref. 9 reports m.p. 92–94°.

Letsinger and Hamilton[8] and Nyilas and Soloway[9] described the preparation of 2-substituted borobenzimidazolines (I, R = alkyl and aryl). These authors prepared these materials from the corresponding alkylboronic acid and *o*-phenylenediamine by azeotropic removal of water from the reaction mixture. In order to prove that the B-alkyl groups of trimethylamine alkylboranes had not undergone rearrangement during the reduction step, the direct synthesis of 2-alkylborobenzimidazolines from trimethylamine alkylboranes was accomplished. The method employed (eq. 3) consisted of merely treating the trimethylamine



(3)

alkylborane with an equivalent quantity of *o*-phenylenediamine in benzene solution at the reflux temperature until hydrogen and trimethylamine ceased to be evolved. The 2-alkylboroimidazolines were obtained in high yield by removal of solvent. In each case the product was identical with that prepared by the method of Letsinger and Hamilton.[3] Table I presents data pertinent to the preparation of several trialkylamine boranes and their corresponding 2-alkylboroimidazolines.

As seen in Table I, the yields of trimethylamine alkylboranes obtained did not exceed 65%. This may be no more than a fortuitous circumstance and the author hesitates to attach real significance to it. However, Povlock and Lippincott[10] have obtained similar results in their study of the reaction of aryl Grignard reagents with trimethoxyboroxine. They observed a maximum yield of borinic acid which approached 66%. Both their work and our own indicate that one-third of the available boron atoms are not utilized.

The subsequent papers of this series will report the utility of trimethylamine alkylboranes as synthetic intermediates.

Experimental

Alkylboroxines were prepared as described by McCusker, Ashby and Makowski[7] and purified by distillation at reduced pressures with a 40-plate spinning-band distillation column.

General Procedure for the Preparation of Trimethylamine Alkylboranes.—A solution of 3.8 g. (0.10 mole) of lithium aluminum hydride in 100 ml. of dry diethyl ether was prepared by stirring the hydride with the ether at the reflux temperature until solution was effected. To this solution, after cooling to room temperature, was added 15 ml. (10 g. or 0.17 mole) of trimethylamine by distillation from a condensation trap calibrated to deliver 15 ml. of liquid. The reaction flask carried a Dry Ice and acetone condenser which effectively retained the trimethylamine. The solution was then heated to the reflux temperature in a slow stream of nitrogen and 0.033 mole of the desired alkylboroxine in 25 ml. of dry diethyl ether was added in a dropwise fashion during the course of 1 hour. Vigorous stirring and a slow stream of nitrogen were maintained during this addition. The reaction mixture then was maintained at the reflux temperature for 1 additional hour and then cooled in an ice-bath. Exactly 6.5 ml. of water was added slowly in a nitrogen atmosphere and with vigorous stirring, from the dropping funnel. During this addition excess hydride was decomposed with the evolution of hydrogen. The cold slurry of inorganic hydrous salts was clarified by filtration through filter-aid and the filtrate evaporated under reduced pressure. The residual oil (or crystalline solid) was either subjected to a molecular distillation at 30–50° and 10^{-3} mm. pressure or rapidly distilled with a 40-plate spinning band distillation column at reduced pressure (see Table I). Trimethylamine benzylborane (m.p. 58–60°) and trimethylamine cyclohexylborane (m.p. 40–41°) were further purified by recrystallization from pentane at −80°. Table I presents the yield data obtained. Preparations of 0.40-mole scale have been successfully carried out with this procedure.

Hydridic Hydrogen Analyses of Trimethylamine Alkylboranes.—In order to substantiate further the purity of the trimethylamine alkylboranes obtained in this study, hy-

---

(8) R. L. Letsinger and S. B. Hamilton, *J. Am. Chem. Soc.*, **80**, 5411 (1958).

(9) E. Nyilas and A. H. Soloway, *ibid.*, **81**, 2681 (1959).

(10) T. P. Povlock and W. T. Lippincott, *ibid.*, **80**, 5409 (1958).

dridic hydrogen analyses were obtained. A conventional vacuum line equipped with a gas measuring apparatus was used. Approximately 2.0 mmoles of sample was accurately weighed and introduced into a dry flask attached to the vacuum line. About 10 ml. of approximately 1 *N* aqueous trifluoroacetic acid was added through a side arm and the evolved hydrogen collected. Table I records the results obtained.

General Procedure for the Preparation of 2-Alkylborobenzimidazolines.—The 2-alkylborobenzimidazolines reported in Table I were prepared by the method of Nyilas and Soloway.[9] These same materials were prepared by the reaction of 0.02 mole each of trimethylamine alkylborane and *o*-phenylenediamine in 10 ml. of dry benzene at the reflux temperature. After the cessation of hydrogen and trimethylamine evolution, the reaction mixture was cooled, the solvent reduced in volume to about 3–4 ml. and 10 ml. of dry pentane was added. The crystalline product was separated by filtration and recrystallized to constant melting point from benzene–pentane. Table I reports the analytical data and melting points obtained. Yields reported in Table I are yields of crude, although essentially pure, product.

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

Amine Boranes. VI. The Preparation of B,B,B-Trialkylborazines from Trimethylamine Alkylboranes and Ammonia[1]

BY M. FREDERICK HAWTHORNE

RECEIVED OCTOBER 15, 1960

The reaction of trimethylamine alkylboranes with excess ammonia in diglyme solution at 100–150° yields the corresponding B,B,B-trialkylborazines, hydrogen and trimethylamine. The reaction apparently is catalyzed by ammonium chloride. Yields of borazine ranged from 65 to 91%.

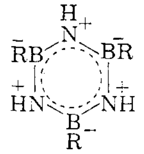
The previous paper of this series[2] described a convenient synthesis of a variety of trimethylamine alkylboranes. In addition, the conversion of these materials to the corresponding 2-alkyl borobenzimidazolines was demonstrated. The latter series of reactions consisted of the elimination of a hydrogen molecule from a hydridic B–H group and an acidic hydrogen of a primary amino function. The similar reaction of a series of trimethylamine alkylboranes and ammonia was subsequently employed as a general route to the relatively rare B,B,B-trialkylborazines. That study is reported here.

Although borazine has been known for some years and many varieties of substituted borazines have been prepared by convenient procedures, relatively few B,B,B-trialkylborazines have been reported. Procedures employed in the past for the preparation of these compounds have been of three general types: treatment of trimethylborane with borazine[3] at high temperature, the condensation of methyldiboranes with ammonia,[4] and more recently the direct reaction of alkyldichloroboranes with ammonia.[5] In view of the fact that no convenient method existed for the preparation of borazines of this type, it was desirable to develop a simple and reliable synthetic method.

Trimethylamine alkylboranes were logical starting materials since they could be prepared conveniently in good yield.[2,3] Furthermore, the ease with which these materials could be handled in the laboratory would allow the use of conventional laboratory equipment and avoid tedious vacuum line manipulations. Formally, the displacement of trimethylamine from a trimethylamine alkylborane with ammonia would produce an intermediate which is capable of conversion to the corresponding B,B,B-trialkylborazine by the elimination of hydrogen.

$$R\overset{-}{B}H_2\overset{+}{N}(CH_3)_3 + NH_3 \longrightarrow R\overset{-}{B}H_2\overset{+}{N}H_3 + N(CH_3)_3$$

$$3R\overset{-}{B}H_2\overset{+}{N}H_3 \longrightarrow 6H_2 +$$



Accordingly, trimethylamine alkylboranes were found to react rapidly with excess ammonia at atmospheric pressure and in the presence of ammonium chloride catalyst. Diglyme was employed as the reaction medium and a reaction temperature of 100–150° was required. In each case studied, hydrogen was eliminated smoothly along with trimethylamine. The precise role of the ammonium chloride catalyst is presently unknown. However, it is apparent that the ammonium ion may function as proton source under the reaction conditions and thus catalyze the removal of hydridic hydrogen from an intermediate amine borane.[6] An example of such a reaction sequence is

$$RB\overset{-}{H}_2\overset{+}{N}H_3 + NH_4{}^+ \longrightarrow H_2 + NH_3 + RBH\overset{+}{N}H_3$$

$$RBH\overset{+}{N}H_3 + NH_3 \longrightarrow R\overset{-}{B}H\overset{+}{N}H_2 + NH_4{}^+$$

$$R\overset{-}{B}H\overset{+}{N}H_2 + NH_4{}^+ \longrightarrow RB{=}\overset{+}{N}H_2 + NH_3 + H_2$$

$$RB{=}\overset{+}{N}H_2 + NH_3 \longrightarrow RB{=}NH + NH_4{}^+$$

$$3RB{=}NH \longrightarrow \text{borazine}$$

The B,B,B-trialkylborazine products were isolated from the reaction mixtures by fractional distil-

---

[1] Presented in preliminary form as a Communication to the Editor, *J. Am. Chem. Soc.*, **81**, 5836 (1959).

[2] M. F. Hawthorne, *ibid.*, **83**, 831 (1961).

[3] H. I. Schlesinger, D. M. Ritter and A. B. Burg, *ibid.*, **60**, 1296 (1938).

[4] H. I. Schlesinger, L. Horvitz and A. B. Burg, *ibid.*, **58**, 409 (1936).

[5] W. Ruigh, 16th International Congress of Pure and Applied Chemistry, Paris, 1957; "Papers Presented to the Section on Mineral Chemistry," Butterworth's Scientific Publications, London, 1958, p. 545.

[6] It is recognized that the reaction of trialkylamine alkylborane with ammonium ion could initiate the reaction sequence which leads to the borazine. Trimethylamine must then be displaced from an intermediate. Such a wide variety of possible mechanisms exist as to make further discussion unprofitable.