TABLE I

R	M.P.	$RSO\cdot SR$, % S Calcd.	$RSO\cdot SR$, % S Found	M.P.	$RSO_2\cdot SR$, % S Calcd.	$RSO_2\cdot SR$, % S Found
n-C_{11}	52–53	16.41	16.04[a]	39–39.5	15.77	16.08
n-C_{12}	53	15.31	15.52[b]	(43.5–44)		
		(Calcd. C, 68.90; H, 12.03. Found C, 68.91; H, 12.11)[b]				
n-C_{14}	62–62.5	13.50	13.53	53–53.5	13.06	13.05[a]
n-C_{16}	69–70	12.08	12.08	59–60	11.72	11.71

[a] Microanalysis by Alfred Bernhardt, Max-Planck Institute, Mülheim (Ruhr), Germany. [b] Microanalysis by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

disulfone were obtained, 0.005 g., m.p. 218–220° and 0.004 g. of lower melting solid, approximately 7–8% yield.

1-Dodecyl disulfone. A. With 0.156 g. (0.36 mmole) of dodecyl dodecanethiolsulfonate and the same quantities of reagents as used with p-tolyl thiolsulfonate, solid formed in a few minutes. More acetic acid was added; after two days the solid was filtered off, and recrystallized from ethanol; yield 0.037 g. (22%) of disulfone.

B. A solution of 0.3 g. of dodecyl thiolsulfonate in 20 ml. of acetic acid and 500% excess 34.5% hydrogen peroxide was kept at 50–55° for 2.5 hr. After standing about a day, the mixture had crystals of disulfone, m.p. 100°, yield 0.083 g. (26%). Replacing the peroxide by peracetic acid raised the yield to 37%.

C. Direct oxidation of dodecyl disulfide by 500% excess hydrogen peroxide for 2.5 hr. at 50–55° gave 10–13% of disulfone; 0.3 g. of disulfide in 30 ml. of acetic acid and 500% excess peracetic acid warmed at 50–55° for 2.5 hr. yielded 0.055 g. (16%) of disulfone.

Stability of thiolsulfinates. Undecyl, tetradecyl and hexadecyl thiolsulfinates were kept at a pressure of 10^{-4} mm. for 48 hr. at room temperature; dodecyl thiolsulfinate was kept at 10^{-6} mm. for 36 hr. There was no change in melting point or appearance of any of the samples. Dodecyl thiolsulfinate did not change in melting point on standing 18 months in the laboratory in a stoppered vial.

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[CONTRIBUTION FROM THE REDSTONE ARSENAL RESEARCH DIVISION, ROHM and HAAS CO.]

A New Preparation of Some Dimethylamino Derivatives of Boron

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The reaction of $Al[N(CH_3)_2]_3$ with the following types of boron compounds, R_3B, $(RBO)_3$, $(RO)_3B$ and $RBH_2\cdot N(CH_3)_3$ was found to produce the dimethylamino derivatives; $R_2BN(CH_3)_2$ $RB[N(CH_3)_2]_2$, $B[N(CH_3)_2]_3$, and $RBNH(CH_3)_2$, respectively.

The dialkylaminoboranes have recently been the subject of several investigations. Niedenzu and Dawson[1,2] synthesized numerous derivatives of the type R_2BNR_2 by the reaction of a dialkylaminodichloroborane or a dialkylaminochlorophenylborane derivative with a suitable Grignard reagent. The dialkylaminodialkylboranes were also recently studied by Coates and Livingstone.[3]

Only a few examples of another class of aminoboranes, the bis-dialkylaminoalkylboranes, are known.[4] Hawthorne obtained bis-diethylamino-n-butylborane from the reaction of diethylamine with trimethylamine-n-butylborane. However, it was not possible to prepare the corresponding s-butyl- and t-butyl derivatives by this method. Instead, derivatives of the type $RBHN(C_2H_5)_2$ were obtained.

The observation that dimethylaminoboron dichloride was produced in the reaction between boron trichloride and trisdimethylaminoalane[5] suggested that other boron compounds might undergo a similar exchange reaction. It was found that by reaction of the appropriate boron compound with trisdimethylaminoalane, dimethylaminoalkylborane derivatives of the following types $R_2BN(CH_3)_2$, $RBHN(CH_3)_2$, $RB[N(CH_3)_2]_2$, and $B[N(CH_3)_2]_3$ could be prepared.

RESULTS

The reaction between trisdimethylaminoalane and boron trichloride[5] was extended to other simple boron compounds in order to determine the scope of the reaction. The compounds investigated may be divided into three general classes: the trialkylboranes or triarylboranes, boron compounds containing an oxygen-boron linkage and trimethyl-

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(1) K. Niedenzu and J. W. Dawson, *J. Am. Chem. Soc.*, **81**, 5553 (1959).

(2) K. Niedenzu and J. W. Dawson, *J. Am. Chem. Soc.*, **82**, 4225 (1960).

(3) G. E. Coates and J. G. Livingstone, *J. Chem. Soc.*, 1000 (1961).

(4) M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 2671 (1961).

(5) J. K. Ruff, *J. Am. Chem. Soc.*, **83**, 2835 (1961).

aminealkylboranes [$RBH_2 \cdot N(CH_3)_3$]. An exchange reaction was observed in most cases studied and several new dimethylamino borane derivatives were obtained.

The primary trialkylboranes or triphenylborane were found to react with trisdimethylaminoalane readily to produce dimethylaminodialkyl or (diphenyl)boranes in excellent yields.

$$2\ R_3B + Al[N(CH_3)_2]_3 \longrightarrow 2\ R_2BN(CH_3)_2 + R_2AlN(CH_3)_2$$

$$R = n\text{-}C_4H_9,\ n\text{-}C_3H_7 \text{ or } C_6H_5$$

Only one of the alkyl or phenyl groups could be replaced. In fact no reaction was observed between dimethylaminodi-*n*-butylborane and trisdimethylaminoalane. Furthermore, tri-*s*-butylborane was unreactive toward the alane under similar conditions.

The boron-oxygen bond was found to be very reactive towards trisdimethylaminoalane. Ethyl diphenyl borinite and diethyl phenyl boronate produced dimethylaminodiphenylborane and bisdimethylaminophenylborane, respectively, when allowed to react with the alane.

$$2(C_6H_5)_2BOC_2H_5 + Al[N(CH_3)_2]_3 \longrightarrow 2(C_6H_5)_2BN(CH_3)_2 + (C_2H_5O)_2AlN(CH_3)_2$$

$$C_6H_5B(OC_2H_5)_2 + Al[N(CH_3)_2]_3 \longrightarrow C_6H_5B[N(CH_3)_2]_2 + (C_2H_5O)_2AlN(CH_3)_2$$

No disproportionation of bisdimethylaminophenylborane was observed in contrast to the behavior of the corresponding methyl derivative.[6]

Cleavage of the boroxine ring also occurred easily and the trialkylboroxine was converted to the corresponding bisdimethylaminoalkylborane by the action of trisdimethylaminoalane.

$$2(RBO)_3 + 3\ Al[N(CH_3)_2]_3 \longrightarrow (RB[N(CH_3)_2]_2 + \frac{3}{x}[(CH_3)_2NAlO^-]_x$$

$$R = n\text{-}C_4H_9,\ s\text{-}C_4H_9, \text{ and } t\text{-}C_4H_9$$

Disproportionation of bisdimethylamino-*n*-butylborane occurred during distillation producing dimethylaminodi-*n*-butylborane and trisdimethylaminoborane.

$$2\ C_4H_9B[N(CH_3)_2]_2 \longrightarrow (C_4H_9)_2BN(CH_3)_2 + B[N(CH_3)_2]_3$$

The corresponding *s*-butyl and *t*-butyl derivatives showed less tendency to undergo this reaction.

Trisdimethylaminoborane was obtained in good yield when trialkyl borates were allowed to react with trisdimethylaminoalane:

$$(RO)_3B + Al[N(CH_3)_2]_3 \longrightarrow B[N(CH_3)_2]_3 + Al(OR)_3$$

$$R = CH_3,\ C_2H_5,\ C_2H_5, \text{ and } n\text{-}C_4H_9$$

No dimethylaminoborane derivatives of the types $[(CH_3)_2N]_2BOR$ or $(CH_3)_2NB(OR)_2$ could be isolated regardless of the ratio of borate to alane employed. Disproportionation of such derivatives is expected to be more facile than for the corresponding alkyl compounds so that only the symmetrically substituted compounds would be obtained. The yield was generally better when *n*-butyl borate was used. Lithium tetrakisdimethylaminoaluminate could be employed in the reaction instead of the alane although the yields were lower.

Trisdimethylaminoalane was allowed to react with a series of trimethylaminealkylboranes. Under the conditions employed only the hydride atom was replaced. When the *s*-butyl and *t*-butyl derivatives were employed, it was found that only one of the hydride atoms was exchanged, and the dimethylaminoalkylboranes were isolated in moderate yield.

$$2\ RBN_2 \cdot N(CH_3)_3 + Al[N(CH_3)_2]_3 \longrightarrow RBHN(CH_3)_2 + N(CH_3)_3 + H_2AlN(CH_3)_2$$

Complete exchange of hydride occurred when the *n*-butyl derivative was used.

$$n\text{-}C_4H_9BH_2 \cdot N(CH_3)_3 + Al[N(CH_3)_2]_3 \longrightarrow n\text{-}C_4H_9B[N(CH_3)_2]_2 + N(CH_3)_3 + H_2AlN(CH_3)_2$$

The major product of this reaction was bisdimethylamino-*n*-butylborane. Some trisdimethylaminoborane and dimethylaminodi-*n*-butylborane were present. The latter two materials probably arise from the disproportionation of bisdimethylamino-*n*-butylborane, although the dimethylaminodi-*n*-butylborane could have resulted from the disproportionation of the hydride derivative.[7] A small yield of dimethylamino-*n*-butylborane was obtained when an excess of the trimethylamineborane derivative was used.

No attempt was made to isolate and characterize any of the aluminum containing species formed in the above reactions. The composition of the aluminum products written in the equations above is based upon the stoichiometric ratio of the reactants employed and the nature of the borane that was obtained.

DISCUSSION

The facile exchange of dimethylamino groups on aluminum with a variety of groups which are bonded to boron results in a general method of preparation of dimethylaminoalkylboranes and trisdimethylaminoborane. The method is probably most useful in the preparation of derivatives of the type $RB[N(CH_3)_2]_2$ and $B[N(CH_3)_2]_3$, as the dialkylaminodialkylboranes are easily obtained from the dialkylaminoboron dichloride and a suitable Grignard reagent.[1,2]

Dimethylaminoboranes are found both in monomeric and polymeric states depending upon the type of derivative. All of the dimethylaminoalkylboranes containing only alkyl and dimethylamino

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(6) G. E. Coates, *J. Chem. Soc.*, 3481 (1950).

(7) A. B. Burg and J. L. Boone, *J. Am. Chem. Soc.*, 78, 1321 (1956).

TABLE I

Compound	B.P.	Yield	Calcd.		Found	
			B	N	B	N
$B[N(CH_3)_2]_3$	146–147	82%	7.56	29.4	7.50	29.3
$(n\text{-}C_3H_7)_2BN(CH_3)_2$	42°/9 mm.	85%	7.67	9.93	7.65	10.2
$(n\text{-}C_4H_9)_2BN(CH_3)_2$	77/9 mm.	93%	6.40	8.28	6.62	8.25
$(C_6H_5)_2BN(CH_3)_2$	96–98/10^{-3} mm.	82%	5.17	6.70	5.25	6.85
$C_6H_5B[N(CH_3)_2]_2$	61/2.5 mm.	92%	6.14	15.9	6.02	15.8
$n\text{-}C_4H_9B[N(CH_3)_2]_2$	50–51/5 mm.	28%	6.93	18.0	7.05	17.8
$s\text{-}C_4H_9B[N(CH_3)_2]_2$	51°/7 mm.	52%	6.93	18.0	6.87	18.2
$t\text{-}C_4H_9B[N(CH_3)_2]_2$	66°/20 mm.	35%	6.93	18.0	7.14	17.9
$t\text{-}C_4H_9BHN(CH_3)_2$	40°/81 mm.	70%	10.31	0.842[a]	9.94	0.831[a]
$s\text{-}C_4H_9BHN(CH_3)_2$	49°/91 mm.	67%	10.31	0.842[a]	9.79	0.828[a]
$n\text{-}C_4H_9BHN(CH_3)_2$	114°	5%	10.31	0.842[a]	10.46	0.886[a]

[a] Active hydrogen analyses.

TABLE II

PHYSICAL PROPERTIES OF SOME DIMETHYLAMINOBORANE DERIVATIVES

Compound	B^{11}NMR Resonance ($\delta \times 10^6$)[a]	Infrared, (B—N)μ	Mol. Wt. (obs.)	$\bar{n}$
$(n\text{-}C_4H_9)_2BN(CH_3)_2$	Singlet (−27.2)	6.65	177	1.05
$(C_6H_5)_2BN(CH_3)_2$		6.58	216	1.03
$n\text{-}C_4H_9B[N(CH_3)_2]_2$	Singlet (−16.0)	6.67	150	0.96
$s\text{-}C_4H_9B[N(CH_3)_2]_2$	Singlet (−17.3)	6.67	—	—
$t\text{-}C_4H_9B[N(CH_3)_2]_2$	Singlet (−17.7)	6.68	—	—
$C_6H_5B[N(CH_3)_2]_2$	Singlet (−14.3)	6.64	187	1.06
$B[N(CH_3)_2]_3$	Singlet (−9.0)	6.66	155	1.08
$n\text{-}C_4H_9BHN(CH_3)_2$	Doublet (+12.1)	V. wk. 6.60	—	—
$s\text{-}C_4H_9BHN(CH_3)_2$	Doublet (−25.5) Doublet (+12.3)	6.60	146	1.29
$t\text{-}C_4H_9BHN(CH_3)_2$	Doublet (−25.5) (5) Wk doublet (+13.7)	6.55	127	1.13

[a] Relative to trimethylborate.

groups are monomeric as evidenced by their B^{11} NMR spectra (see Table II) and a molecular weight determination. The dimethylaminoalkylboranes are intermediate between the monomeric $R_2BN(CH_3)_2$ boranes and the associated dimethylaminoborane. The aggregation of the dimethylaminobutylborane derivatives was demonstrated by two methods; cryoscopic molecular weight measurement and by determining the chemical shift of the B^{11} NMR resonance.[4,8] The *t*-butyl derivative is predominantly monomeric although association does occur to a small extent as indicated by its B^{11} NMR spectrum.[4] Dimethylamino-*s*-butylborane consists of a mixture of monomer and polymer and the *n*-butyl derivative exists primarily in an associated form as indicated by the single high field doublet (relative to methyl borate) in its B^{11} NMR spectrum. Furthermore, all of the monomeric dialkylaminoboranes exhibit a sharp absorption band in the infrared at 6.5 μ to 6.7 μ which was assigned to a B—N double bond.[1,2] A strong band in this region was found in the infrared spectra (see Table II) of all of the derivatives prepared except dimethylamino-*n*-butylborane which exhibited only a very weak band. This could be due to an impurity or to a small degree of depolymerization of the dimeric species. The trend in the degree of association is just that which would be predicated if steric factors were important. However, the variation in the inductive effect is in the same direction so that it is not possible to determine to what extent the steric factors are important.

EXPERIMENTAL

Materials. Trisdimethylaminoalane was prepared as described previously.[5] The tributylboroxines and the phenyl borinic and boronic esters were prepared by literature methods.[9,10] The trimethylamine complexes of the butylboranes were prepared by the method of Hawthorne.[11] The trialkylboranes and triphenylborane were prepared from boron trifluoride etherate and the appropriate Grignard. The alkyl borates were commercially available.

Analyses. Nitrogen was determined by either the Dumas method or by a modified Kjeldahl.[5] The boron content was determined by standard techniques. The active hydrogen content of the $RBHN(CH_3)_2$ compounds was determined by hydrolysis with trifluoroacetic acid. The gas was collected in a calibrated bulb by means of a Toepler pump.

Preparation of the $R_2BN(CH_3)_2$ compounds. The trialkylborane (0.1 mole) was placed in a flask with trisdimethylaminoalane (0.06 mole). The mixture was heated under nitrogen at 100° to 120° with an oil bath for 1 hr. The mixture was distilled under high vacuum and the crude distil-

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

[9] R. L. Letsinger and I. S. Koug, *J. Am. Chem. Soc.*, **77**, 2491 (1955).

[10] P. A. McCusker, E. C. Ashby, and H. S. Makouski, *J. Am. Chem. Soc.*, **79**, 5179 (1957).

[11] M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 831 (1961).

late was redistilled on a 20-plate spinning band column. When triphenylborane was employed, *n*-heptane was used as a solvent.

Preparation of $RB[N(CH_3)_2]_2$ compounds. The butylboroxines, (0.033 mole) were allowed to react with 0.1 mole of trisdimethylaminoalane at 75° for 1 hr. The reaction mixture was distilled under high vacuum keeping the pot temperature below 70°. The crude product was purified as above. When *n*-butylboroxine was employed, the reactants were placed in the pot of the spinning band column and heated to 50° for 15 min. The product was then distilled directly from the reaction mixture under vacuum. The pot temperature was maintained at 50–55° in an effort to minimize the disproportionation of the product.

Preparation of $\phi B[N(CH_3)_2]_2$. Diethyl phenyl boronate (0.1 mole) was allowed to react with trisdimethylaminoalane (0.05 mole) for 1 hr. at 85–90°. Distillation under high vacuum separated the crude product from the reaction mixture. Purification was accomplished by distillation on a 20-plate spinning band column. The reaction of ethyl diphenyl borinite (0.2 mole) with the alane (0.1 mole) was performed in the same manner.

Preparation of $B[N(CH_3)_2]_3$. Lithium aluminum hydride (0.22 mole) was dissolved in 400 ml. of ether in a 3-neck flask equipped with a stirrer, condenser, and a nitrogen purge. Solid trimethylammonium chloride (0.2 mole) was slowly added. After reaction was complete, gaseous dimethylamine was passed into the mixture for approximately 2 hr. Then 0.15 mole of tri-*n*-butylborate in 200 ml. of ether was added. The mixture was refluxed 1 hr. and filtered. The ether was distilled from the filtrate until a pot temperature of 50–55° was obtained. The system was evacuated and the product distilled under high vacuum into a −80° trap. It was necessary to heat the residue at 100° for several hours to obtain good yields. The crude product was purified by distillation on a 20 plate spinning band column.

Preparation of $RBHN(CH_3)_2$ compounds. Trimethylamine-*s*-butylborane or trimethylamine-*t*-butylborane, 8 g., was added slowly to 5 g. of trisdimethylaminoalane. After the addition was complete, the mixture was warmed slowly to 70° and heated for 0.5 hr. The products were distilled directly out of the reaction mixture under vacuum. Under these conditions trimethylamine-*n*-butylborane produced bisdimethylamine-*n*-butylborane and other products expected from the disproportionation of the bisaminoborane.

The reaction employing an excess of the borane did produce a low yield of the desired material. A 0.12-mole sample of the borane was allowed to react with 0.04 mole of trisdimethylaminoalane in 10 ml. of hexane. The mixture was refluxed for 15 min. and the volatile components were removed under high vacuum at ambient temperature. They were then distilled at atmosphere pressure on a Holtzmann column.

NMR spectra. The B^{11} NMR spectra of the compounds prepared were obtained on the neat liquids with a Varian Model V4300 B spectrometer operating at 12.8 megacycles.

Molecular weight determinations. The apparent molecular weights of some of the compounds were determined cryoscopically in benzene. The apparatus and the method of preparation of the solutions were described previously.[5]

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY AT IOWA STATE UNIVERSITY]

The Synthesis of Some Organosilicon Compounds, Particularly Those Containing Halophenyl Groups

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A series of organosilicon compounds containing halophenyl groups has been obtained by treating the appropriately substituted chlorosilanes with *m*-fluorophenyl-, *m*-chlorophenyl-, and *p*-chlorophenyllithium. Several new compounds having either the $R_3Si(CH_2)_nSiR_3$, $R_3SiC_6H_4SiR_3$, or $R_3SiC_6H_4C_6H_4SiR_3$ structure have been prepared.

We are reporting the synthesis and physical constants for a number of organosilicon compounds and one organogermanium compound. The tetrasubstituted silanes listed in Tables I and II were prepared by treating either *m*-fluorophenyl-, *m*-chlorophenyl-, or *p*-chlorophenyllithium with the appropriate chlorosilane or silicon tetrachloride. The halophenyllithium compounds were obtained *via* the halogen-metal interconversion reaction[1] employing *n*-butyllithium and the proper bromochloro- or bromofluorobenzene in diethyl ether. The equations depicting the synthesis of di(*m*-fluorophenyl)diphenylsilane illustrate the general procedure used:

$$n\text{-}C_4H_9Li + m\text{-}FC_6H_4Br \xrightarrow{-40^\circ} n\text{-}C_4H_9Br + m\text{-}FC_6H_4Li$$

$$2\ m\text{-}FC_6H_4Li + Cl_2Si(C_6H_5)_2 \longrightarrow (m\text{-}FC_6H_4)_2Si(C_6H_5)_2 + 2LiCl$$

In Table III are listed eight new compounds having either the $R_3Si(CH_2)_nSiR_3$, $R_3SiC_6H_4SiR_3$, or $R_3SiC_6H_4C_6H_4SiR_3$ structure. The first six were prepared by the reaction of 1,2-ethylenebis-, *m*-phenylenebis-, and *p*-phenylenebis(trichlorosilane) with an organometallic compound; benzylmagnesium chloride was employed in the synthesis of the tribenzylsilyl derivatives, and alkyllithium compounds were used for the trialkylsilyl types.

$$6\ RLi + Cl_3SiCH_2CH_2SiCl_3 \longrightarrow R_3SiCH_2CH_2SiR_3 + 6LiCl$$

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(1) For a general discussion and bibliography on the halogen-metal interconversion reaction, see R. G. Jones and H. Gilman in *Organic Reactions*, **Vol. VI**, R. Adams, ed., John Wiley and Sons, Inc., New York, 1951, pp. 339–366.