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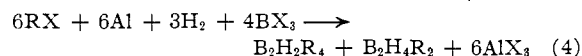
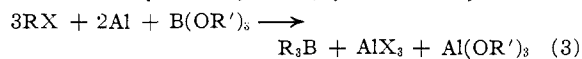
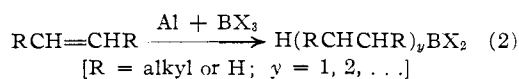
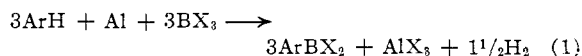
Synthesis of Organoboranes

By E. L. MUETTERTIES

RECEIVED JANUARY 16, 1960

Several new syntheses of organoboranes are described. These are preparation of aryl- and alkylidihaloboranes from aromatic and olefinic hydrocarbons, trialkylboranes from alkyl halides and alkylidiboranes from alkyl halides and hydrogen. In all cases aluminum metal and BCl_3 or $\text{B}(\text{OR})_3$ are the other reagents.

Synthetic routes to organoboranes have largely involved use of organometallic compounds¹ and of olefin-hydride additions.²⁻⁶ It is the purpose of this article to describe a new and general approach to several classes of organoboranes. This approach is based on aluminum metal as a reactant. In summation, these class reactions are



Aryldihaloborane Synthesis.^{7,8}—Arylhaloboranes have been prepared by simply passing boron trichloride into a slurry of aluminum metal in an aromatic hydrocarbon. The reaction is mildly exothermic and the completion of the reaction is signaled by a temperature drop. The only necessary condition is that an inert atmosphere be maintained to prevent deactivation of the aluminum surface by oxygen. Initial activation of the surface can be effected with a trace of methyl iodide, iodine or aluminum chloride. Boron tribromide and triiodide also form arylidihaloboranes in this reaction system but boron trifluoride⁹ is completely unreactive. These reactions are summarized in Table I.

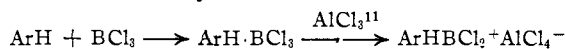
When boron trichloride was passed into a mixture of toluene and aluminum trichloride, absorption took place with the formation of two immiscible liquids. The light layer consisted largely of toluene and the lower, viscous, slightly electrically conducting layer contained Al, B, Cl and toluene. The latter liquid reacted with aluminum metal to form tolyldichloroborane. These steps suggest a mechanism for the arylidihaloborane synthesis. The first

TABLE I
ARYLDIHALOBORANE SYNTHESSES

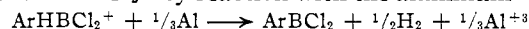
Hydrocarbon	Temp., °C.	Product
Benzene	20-150	$\text{C}_6\text{H}_5\text{BX}_2$ (X = Cl, Br, I)
Toluene	140	$\text{CH}_3\text{C}_6\text{H}_4\text{BCl}$ (3:2, <i>p:m</i>)
Toluene	35	$\text{CH}_3\text{C}_6\text{H}_4\text{BCl}_2$ (4.6:1, <i>p:m</i>)
Ethylbenzene	35	$\text{C}_2\text{H}_5\text{C}_6\text{H}_4\text{BCl}_2$ (5:1, <i>p:m</i>)
<i>p</i> -Xylene	35 or 140	2,5-(CH_3) ₂ $\text{C}_6\text{H}_3\text{BCl}_2$
<i>m</i> -Xylene	35 or 140	3,5-(CH_3) ₂ $\text{C}_6\text{H}_3\text{BCl}_2$
<i>o</i> -Xylene	35 or 140	3,4-(CH_3) ₂ $\text{C}_6\text{H}_3\text{BCl}_2$
Mesitylene	35	No reaction
Mesitylene	140	2,5-(CH_3) ₂ $\text{C}_6\text{H}_3\text{BCl}_2$
Durene	140	No reaction
Biphenyl	35	$\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{BCl}_2$, $\text{Cl}_2\text{BC}_6\text{H}_4\text{C}_6\text{H}_4\text{BCl}_2^a$
Phenyl ether	140	$\text{C}_6\text{H}_5\text{OC}_6\text{H}_4\text{BCl}_2$
Naphthalene	35	$\beta\text{-C}_{10}\text{H}_7\text{BCl}_2^a$

^a Tentatively identified.

step would be an interaction analogous to the known $\text{AlCl}_3\text{-HCl-ArH}$ system¹⁰



The first step in the above sequence, complex formation, is supported by the appearance of a new maximum in the ultraviolet spectrum of the toluene-BBr₃ system. This complex is much weaker than the BCl_3 -olefin complex described below. The second sequence is simply loss of a proton from ArHBCl_2^+ by reaction with the aluminum



Hydrogen was identified definitely as a product of this reaction. Further support for this reaction scheme is found in the distribution of isomers from toluene and the isomeric xylenes (Table I). These distributions are typical of a classical Friedel-Crafts system run in the presence of aluminum trichloride. It is notable that the BCl_2 group never goes in a position *ortho* to a CH_3 group unless, as in the *p*-xylene case, there is no other possibility. Also notable is the lack of reaction in the case of mesitylene (except at elevated temperatures where it is isomerized) and durene. If it is assumed that in the complexes the BCl_2 group preferentially approaches *two* ring¹² carbon atoms, models show

(10) Solvation of the BCl_3^+ ion is a necessity. In the absence of a donor molecule, *i.e.*, an aromatic hydrocarbon, there was no evidence of interaction between BCl_3 and AlCl_3 . The latter had no significant solubility in liquid BCl_3 , and molten aluminum chloride did not absorb significant amounts of boron trichloride.

(11) Aluminum halide is used as an activator in the arylidihaloborane synthesis and is, of course, a product of the main reaction.

(12) The greater steric problem for an $\text{ArH} \cdot \text{BCl}(\text{C}_6\text{H}_5)^+$ intermediate might explain the absence of $(\text{C}_6\text{H}_5)_2\text{BCl}$ in the $\text{ArH} \cdot \text{BCl}_3\text{-Al}$ reaction. However, this is not probable in view of the findings of Buijwid, Gerrard and Lappert⁸ that both $\text{C}_6\text{H}_5\text{BBr}_2$ and $(\text{C}_6\text{H}_5)_2\text{BBr}$ are formed from C_6H_5 , BBr_3 and AlX_3 .

(1) For a review of this subject, see M. F. Lappert, *Chem. Revs.*, **56**, 959 (1956).

(2) D. T. Hurd, *THIS JOURNAL*, **71**, 20 (1949).

(3) H. C. Brown and B. C. Subba Rao, *ibid.*, **78**, 5694 (1956); **81**, 6423, 6428, 6434 (1959).

(4) R. Koster, *Angew. Chem.*, **70**, 371 (1958).

(5) E. C. Ashby, *THIS JOURNAL*, **81**, 4791 (1958).

(6) M. F. Hawthorne and J. A. Dupont, *ibid.*, **80**, 5830 (1958).

(7) For an initial communication see: E. L. Muetterties, *ibid.*, **81**, 2597 (1959).

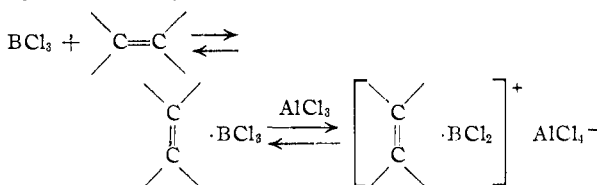
(8) More recently, a synthesis of arylidibromoboranes and diaryl-bromoboranes from the aromatic hydrocarbons, boron tribromide and aluminum halide was described by Z. J. Buijwid, W. Gerrard and M. F. Lappert, *Chem. and Ind. (London)*, 1091 (1959).

(9) Aluminum fluoride, a reaction product in this case, is non-volatile and gives a coating similar to an oxide coating that leads to deactivation of the aluminum surface.

significant steric problems in durene·BCl₂⁺ and mesitylene·BCl₂⁺ intermediates, since neither durene nor mesitylene has a C-C sequence with only hydrogen substitution at the carbon atoms. In contrast to durene, 1,2,3,4-tetramethylbenzene reacted smoothly at 35°.

Alkyldihaloborane Synthesis.¹³—Boron trichloride and aluminum when heated to 90–150° exothermally absorbed such olefins as ethylene, propylene, butenes and cyclohexene. The olefin addition when carried to completion yielded viscous and non-volatile organoborane derivatives that contained organoaluminum groups; the molar ratio of olefin to boron halide in such a product was about 6:1 in the case of ethylene. However, when the addition was terminated at about a 1:1 molar ratio of olefin:BCl₃, volatile organoborane products were obtained. In the case of ethylene, distillation of the crude mixture gave materials that boiled in the range from ~50° (760 mm.) to 109° (30 mm.) and ranged in analysis from C₂H₅BCl₂ to C₁₄H₂₉·BCl₂. Propylene and butenes also gave similar series of volatile RBCl₂ compounds. Cyclohexene gave only cyclohexyldichloroborane.

Boron trichloride is exothermally absorbed by such olefins as tetramethylethylene and cyclohexene, and the stoichiometry (crudely measured) is about 1:1. Spectra of these complexes show only the sum of the infrared bands and the H¹ and B¹¹ magnetic resonances of the pure components as do many other such olefin complexes, e.g., Ag⁺·olefin, but there are new maxima in the ultraviolet spectra. This complex could ionize in the presence of aluminum chloride as postulated for the aromatic hydrocarbon synthesis



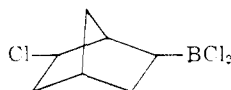
Such a cation species could react further with more olefin in a telomerization sequence and this could account for the formation of high boiling alkyldichloroboranes in the case of ethylene. At 50°, telomerization was found to be fast with respect to the termination step because little or no ethyldichloroborane and largely high boiling boranes form from ethylene. As the synthesis temperature is increased, the yield of ethyldichloroborane increases at the expense of the higher boranes.

The termination step, if analogous to the aromatic hydrocarbon reaction, would produce vinyl-dichloroborane (or alkenyldihaloborane) and hydrogen

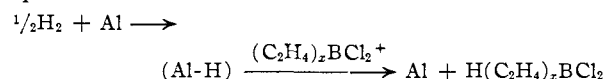


The hydrogen produced could then directly reduce

(13) Recently, M. F. Lappert (*Angew. Chem.*, **72**, 36 (1960)) reported the addition of BCl₃ to norbornadiene to give



the alkenylboranes to alkylboranes or could react as an hydridic hydrogen with a (C₂H₄)_xBCl₂⁺ species



The stoichiometry demands that equal amounts of alkylboranes and alkenylboranes be produced. The alkenylboranes probably polymerized and represented the nonvolatile fraction of the products.

Synthesis of Alkylboranes and Alkyldiboranes.—Borate esters were found to react with alkyl halides in the presence of aluminum to form trialkylboranes. The rate of reaction decreased markedly in going from alkyl iodides to alkyl chlorides. Trimethylborane was obtained in 97% conversion from trimethylborate and excess methyl iodide at ~45°, whereas only a 30% conversion was obtained from trimethyl borate and excess methyl chloride at 130°. Since aluminum and alkyl halides form trialkylaluminum or alkylaluminum halides with rates increasing from RCl to RI, it is presumed that an alkylaluminum is the intermediate in the reaction.

Boron trichloride reacts in a fashion similar to the esters, and when hydrogen was added to the system, the products were alkyldiboranes. The principal products from CH₃I, H₂, Al and BCl₃ at 160° were tetramethyldiborane and unsymmetrical dimethyldiborane.

Experimental

Phenyldihaloboranes.—A stainless steel-lined pressure vessel, charged with 120 g. of C₆H₆, 60 g. of BCl₃, 30 g. of Al powder, 0.1 g. of I₂ and 0.1 g. of CH₃I, was heated to 150° with agitation for 45 minutes or to 30–50° for 24 hours. The reaction product, a slurry (210 g.), was filtered and distilled to give 59 g. of C₆H₅BCl₂ boiling at 95° (48 mm.).

Anal. Calcd. for C₆H₅BCl₂: C, 45.37; H, 3.17; B, 6.81; Cl, 44.65. Found: C, 45.87; H, 3.54; B, 7.39; Cl, 44.31.

The yields of purified C₆H₅BCl₂ in this reaction varied from 60–79%. Gross variations in the molar ratios of BCl₃:C₆H₆ did not detectably affect the nature of the product; there was no evidence for the formation of either C₆H₄(BCl₂)₂ or (C₆H₅)₂BCl. In some cases, there was evidence for the formation (either in the reaction or in the distillation of the crude product) of (C₆H₅)₃B.

Boron tribromide (50 g.), benzene (80 g.), aluminum powder (2 g.) and methyl iodide (0.1 g.) were placed in a flask fitted with a reflux condenser which was blanketed with a nitrogen atmosphere and then heated to mild reflux for 6 hours. Distillation of the product yielded 38 g. of C₆H₅BBr₂ boiling at 71° (5 mm.).

Anal. Calcd. for C₆H₅BBr₂: C, 29.09; H, 2.03; B, 4.37; Br, 64.51. Found: C, 29.11; H, 2.33; B, 4.27; Br, 64.74.

This procedure was repeated with boron triiodide (20 g.). The product was not distilled but was hydrolyzed to C₆H₅B(OH)₂ which was identified by its infrared spectrum.

All attempts to substitute BF₃ for BCl₃ in this synthesis were unsuccessful (temperature range, 20–250°).

C₂H₅C₆H₄BCl₂ and C₂H₅C₆H₄BCl₂.—A round-bottomed flask fitted with thermometer, gas entry tube, magnetic stirrer and reflux condenser (maintained at –78° to minimize loss of unreacted BCl₃) was thoroughly purged with argon and then charged with 150 g. of toluene, 20 g. of aluminum powder, 0.5 g. of AlCl₃ and 0.5 g. of CH₃I. A very slow stream of argon through the reaction slurry was maintained and then BCl₃ was passed into the slurry at as rapid a rate as was possible without noticeable fuming at the exit of the reflux condenser (capped with a CaCl₂ column). A total of 64 g. of BCl₃ was introduced in a period of 65 minutes and reaction temperature rose to a maximum of 59° and

then dropped. The product was filtered and the filtrate distilled to give 40 g. of $C_7H_7BCl_2$ (b.p. 64° , 5 mm.).

Anal. Calcd. for $C_7H_7BCl_2$: C, 48.64; H, 4.08; B, 6.25; Cl, 41.03. Found: C, 48.15; H, 4.09; B, 6.18; Cl, 40.92.

A pressure vessel, charged with 125 g. of toluene, 60 g. of BCl_3 , 35 g. of aluminum powder and 0.1 g. of CH_3I was heated to 150° for 30 minutes. The product, after filtration, was distilled and 53 g. of $CH_3C_6H_5BCl_2$ boiling at 42° (0.8 mm.) was obtained. Hydrolysis of the chloride to the acid and H_2O_2 oxidation to the phenol gave a 3:2 molar mixture of *para* and *meta* cresol. Proportions of isomers were determined by infrared comparison with known mixtures. No *ortho* cresol was detected. A preparation of $CH_3C_6H_5BCl_2$ carried out at 35° (24 hours) gave 4.6:1 molar ratio of *para* to *meta* isomers. With the above procedure (24 hours at 30°), ethylbenzene gave $C_2H_5C_6H_4BCl_2$ (41 g.) boiling at 90° , 4 mm.

Anal. Calcd. for $C_8H_9BCl_2$: C, 51.41; H, 4.86; B, 5.79; Cl, 37.95. Found: C, 51.50; H, 4.94; B, 5.66; Cl, 36.82.

Hydrolysis and oxidation of the product yielded a mixture of *para* and *meta* ($\sim 5:1$ molar ratio) ethylphenols. Again, no *ortho* isomer was detected.

Xylyldichloroboranes.—The three isomeric xylenes were treated at 35° for 24 hours in a pressure vessel and molar quantities identical to those used in the phenyldichloroborane synthesis were employed. *p*-Xylene gave a product that distilled at $\sim 71^\circ$ (5 mm.) (32 g.).

Anal. Calcd. for $C_8H_8BCl_2$: C, 51.41; H, 4.86; B, 5.79; Cl, 37.95. Found: C, 52.46; H, 5.11; B, 5.59; Cl, 37.18.

Hydrolysis and oxidation of the product gave needles that melted at 76° . A mixed melting point with authentic 2,5-dimethylphenol showed no significant depression. Infrared analysis was also in agreement with the 2,5-dimethylphenol identification; there was no evidence for other isomers. *o*-Xylene gave 42 g. of xylyldichloroborane boiling at $\sim 80^\circ$, 4 mm.

Anal. Found: C, 52.05; H, 4.95; B, 5.61; Cl, 37.52.

The chloride was converted to the boronic anhydride (m.p. $244\text{--}245^\circ$).

Anal. Calcd. for $(C_8H_8BO)_3$: C, 72.80; H, 6.87; B, 8.20. Found: C, 73.06; H, 6.84; B, 8.47.

Infrared analysis indicated 3,4-xylylboronic acid. This was confirmed by conversion of the acid to the phenol (m.p. found, 64° ; reported, 62.5°) and comparison of the infrared spectrum of this phenol and authentic 3,4-dimethylphenol. No other isomers were detected.

m-Xylene gave xylyldichloroborane boiling at $\sim 83^\circ$, 4 mm.

Anal. Found: C, 51.65; H, 5.09; B, 5.50; Cl, 38.06.

Hydrolysis and oxidation of the product gave a phenol melting at $60\text{--}63^\circ$ [reported for 3,5-dimethylphenol, $65\text{--}68^\circ$]. Infrared analysis of the product indicated 3,5-dimethylphenol with a possible trace of 2,5-dimethylphenol.

The three isomeric xylenes were also treated at 150° (0.5 to 1.0 hour); the products were the same as obtained at 35° and the yields ranged from 20–60% higher than those for the 35° runs.

Miscellaneous Arylborane Syntheses.—Although nitrobenzene reacted extensively with the BCl_3 –Al reagents, no nitroarylboranes were isolated. Chlorobenzene did not react at temperatures up to 60° . Anisole and methyl benzoate suffered cleavage at the CH_3 –O bond (CH_3Cl evolved) at room temperature. Thiophene underwent extensive secondary reactions at room temperature. Naphthalene (dissolved in *n*-heptane) tended to give tarry products. No pure naphthyldichloroborane was isolated but hydrolysis of the boron-containing product gave an impure boronic acid that appeared to be largely β -naphthylylboronic acid on the basis of infrared analysis.

Phenyl ether (100 g.), aluminum (20 g.), boron trichloride (60 g.) and methyl iodide (0.1 g.) reacted at 140° for 30 minutes. Distillation of the product did not give clean fractions. One fraction (4 g.) boiling at 135° (2 mm.) gave a poor analysis for $C_6H_5OC_6H_4BCl_2$; phenyl ether also was present. Conversion of this chloride to the acid by hydrolysis gave a white solid.

Anal. Calcd. for $C_6H_5OC_6H_4B(OH)_2$: C, 73.53; H, 4.63; B, 5.52. Found: C, 73.85; H, 5.34; B, 4.62.

Biphenyl (100 g.), reagents as above, and 50 ml. of petroleum ether reacted at 35° . Distillation of the product gave about 5 g. of material boiling at 107° (2 mm.) that contained $C_6H_5C_6H_4BCl_2$ contaminated with biphenyl. From this mixture the boronic anhydride (m.p. $338\text{--}340^\circ$) was obtained by hydrolysis [infrared spectrum consistent with $(C_6H_5C_6H_4BO)_3$].

Anal. Calcd. for $(C_{12}H_9BO)_3$: C, 79.62; H, 5.57; B, 5.98. Found: C, 79.86; H, 5.28; B, 5.80.

The high boiling ($135\text{--}150^\circ$, 2 mm.) fraction (3 g.) was hydrolyzed and fractional crystallization of the hydrolyzate yielded fractions that contained up to 8% boron, indicative of the presence of $(OBC_6H_4C_6H_4BO)$; infrared analysis showed the presence of the $(C_6H_5C_6H_4BO)_3$ compound and a second, similar structure.

Olefin Additions to BCl_3 .—A stainless steel-lined pressure vessel which contained 90 g. of BCl_3 , 20 g. of Al powder, 0.5 g. of CH_3I and 0.5 g. of $AlCl_3$ was heated to 120° . Ethylene was added in ~ 4 g. portions until a total of 32 g. was added. The reaction then was maintained at 120° for 3 hours and finally cooled to 50° . Materials volatile at 50° and ~ 5 mm. were distilled into a cylinder. The remaining product, a slurry which was recovered after the vessel cooled to 25° , was filtered and added to the volatile (50°) fraction. Distillation gave only one relatively clean cut (~ 14 g.) at 52.5° (760 mm.) which was characterized as $C_2H_5BCl_2$.

Anal. Calcd. for $C_2H_5BCl_2$: mol. wt., 110.8; reported b.p. 50.8° (747 mm.). Found: mol. wt., 108, 112 (by freezing point depression in C_6H_6); b.p. 52.5° , 760 mm.).

The infrared spectrum showed only the bands expected for this borane; no vinyl function was present in detectable amounts. The chloride also was characterized by hydrolysis to the boronic acid.

Anal. Calcd. for $C_2H_5B(OH)_2$: C, 32.47; H, 9.55. Found: C, 33.17; H, 9.54.

The remaining distillation fractions (30 g.) ranged in analysis from $C_4H_9BCl_2$ (b.p. 100° , 760 mm.) to $C_{14}H_{29}BCl_2$ (b.p. 109° , 30 mm.) but these were contaminated with a hydrocarbon.

Propylene (55 g.) was reacted, as above, with BCl_3 . After collection of volatiles and filtration of the liquid slurry, about 140 g. of organoborane crude product was distilled. Distillation gave fractions that boiled in the range of 65° , (760 mm.) to 180° (4 mm.). About 6 g. of a product boiling at 78° (760 mm.) was indicated to be *n*-propyldichloroborane by physical properties (reported b.p. 78.2° (739 mm.)) and by its infrared spectrum. No other clean fractions were obtained. Analysis of one fraction that boiled at 120° (760 mm.) corresponded to $H(C_3H_7)_3BCl_2$, but it boiled too low for this compound and was probably a mixture of $H(C_3H_7)_2BCl_2$ and hydrocarbon. Mass spectrographic analysis confirmed that these fractions were contaminated with hydrocarbons. A similar behavior was found for 1-butene and 2-butene; butylboranes along with higher boiling organoboranes and hydrocarbons were produced.

Cyclohexene (100 g.) was treated, as above, with BCl_3 . The liquid slurry was filtered and the filtrate was distilled. Fractions were obtained that boiled from 80° (760 mm.) to 147° (6 mm.). Only a small amount of material (6 g.) boiling in the range 160° to 198° (760 mm.) contained a BCl_2 function. This is close to the boiling point of $C_6H_{11}BCl_2$ (167° (748 mm.)). This fraction gave analysis for a BCl_2 compound, *i.e.*, 1:2 boron to chlorine ratio but carbon values were high (58% found *versus* 44% theor. for $C_6H_{11}BCl_2$, which indicated contamination by a hydrocarbon. This fraction inflamed in air. Hydrolysis and oxidation (H_2O_2) yielded cyclohexanol. Mass spectrographic analysis indicated that the hydrocarbon contaminant had a bicyclic structure similar to bicyclo[0]nonanes. This could have been derived from cyclohexadiene which in turn could have formed by thermal decomposition of cyclohexenyldichloroborane.

Synthesis of Trialkylboranes.—A glass reactor fitted with a nitrogen inlet and a reflux condenser using cooled (5°) water was charged with 34 g. of trimethyl borate and 30 g. of 20-mesh aluminum. The exit end of the condenser was connected through a nitrogen tee to a glass trap cooled to -78° . The system was thoroughly purged with nitrogen and, while a slight positive pressure of nitrogen was maintained therein, 127 g. of methyl iodide was added dropwise over a period of 3 hours. At the end of the addition, the reaction mixture was heated to mild reflux for 4 hours. There

was thus obtained in the cold trap 60.2 g. of low boiling material which by mass spectrometer analysis was shown to contain mostly methyl iodide and small amounts of trimethylborane plus a trace of trimethyl borate. Upon precision distillation of the liquid product, there was obtained 16 g. (97% yield and conversion) of trimethylborane boiling at -20° at atmospheric pressure.¹⁴

In the same manner as above, except that the -78° cold trap was omitted, 120 g. of ethyl iodide was added dropwise over a period of 1.5 hours to 36 g. of trimethyl borate and 30 g. of 8- to 20-mesh aluminum. At the end of the addition, the reaction mixture was heated at reflux for 1.5 hours. The reactor then was cooled to about -70° and the system evacuated. An evacuated stainless steel cylinder then was connected to the system and the reactor warmed slowly to about 50° . The volatile reaction products distilled over into the cylinder. There was thus obtained 24 g. of volatile reaction products which by mass spectrometer analysis were shown to contain mainly triethylborane and ethyl iodide.

A stainless steel-lined pressure vessel was charged with 21

(14) E. L. Muettterties, U. S. Patent 2,840,590 (1958).

g. of trimethyl borate, 40 g. of 8- to 20-mesh aluminum, 5 g. of aluminum powder and 0.5 g. of iodine. The reactor was closed, evacuated, charged with 41 g. of methyl chloride and then heated under autogenous pressure for 3 hours at 130° . After cooling to room temperature, there was obtained by distillation into a stainless steel cylinder, cooled in a liquid nitrogen bath, 35 g. of volatile products which by mass spectrometry were shown to contain 85–88% of methyl chloride, 10–11% of trimethylborane and 1.8–2.0% of trimethyl borate. The amount of trimethylborane obtained corresponds to a 30% conversion based on the ester.

Hydrogenation of Alkylboranes.—A stainless steel-lined pressure vessel was charged with 20 g. of Al powder, 30 g. of BCl_2 , 50 g. of CH_3I and 1 g. of AlCl_3 , heated to 80° and then pressured with hydrogen to about 800 atm. After 2 hours at 80° and 3 hours at 160° , the vessel was cooled and bled through a trap cooled to collect condensables. The condensables were methane and methylated diboranes. This mixture was distilled. Two high boiling fractions, -1 to 1° ($\sim 70\%$) and 58 – 64° ($\sim 30\%$) were obtained and mass spectrographic analysis indicated they were $\text{B}_2\text{H}_2(\text{CH}_3)_4$ (reported b.p., -2.6°) and unsymmetrical $\text{B}_2\text{H}_4(\text{CH}_3)_2$ (reported b.p., 68.6°), respectively.

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY, CAMBRIDGE, MASS.]

Dimethylgermanium Oxide and Dimethylgermanium Sulfide

BY M. P. BROWN¹ AND E. G. ROCHOW

RECEIVED NOVEMBER 2, 1959

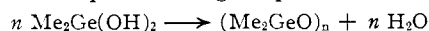
Trimeric, tetrameric and high-polymeric forms of dimethylgermanium oxide have been prepared and characterized. At room temperature the high-polymeric form is the most stable and the trimeric form the least stable. At elevated temperatures the vapors of dimethylgermanium oxide and dimethylgermanium sulfide are trimeric.

Although the polysiloxanes $(\text{Me}_2\text{SiO})_n$ (where n is three or more²) have been well characterized and studied, the corresponding dialkylgermanium oxides R_2GeO (where R is methyl,³ ethyl,^{4,5} n -propyl,⁶ isopropyl⁷ or phenyl⁸) have not received as much attention. The present paper examines more closely dimethylgermanium oxide and dimethylgermanium sulfide.³

We find that dimethylgermanium oxide is most conveniently prepared and purified as the tetramer, which is easily obtained in 67% yield by hydrolysis of dimethyldichlorogermane with aqueous sodium hydroxide, followed by extraction with petroleum ether and subsequent crystallization. The well-defined colorless crystals (m.p. 92°) were identified as tetrameric $(\text{Me}_2\text{GeO})_4$ by cryoscopic measurements in benzene, in which they are readily soluble. By analogy with octamethylcyclotetrasiloxane, an eight-membered ring structure is assumed for this tetramer.

Unlike its silicon analog, the tetramer is very soluble in water, although the rate of solution is somewhat slow. Cryoscopic measurements on a dilute aqueous solution give a molecular weight corresponding to one Me_2GeO unit. We assume

hydration to form the diol $\text{Me}_2\text{Ge}(\text{OH})_2$, already postulated as a hydrolysis product of dimethyldichlorogermane.⁹ On allowing an aqueous solution of dimethylgermanium oxide to evaporate, a white fibrous material, $(\text{Me}_2\text{GeO})_n$, is obtained, with the same melting point (132 – 133°) as the material previously obtained by distillation.³ This material does not sublime in a high vacuum until its melting point is reached and then gives a sublimate which melts over a large range; the tetramer readily sublimates unchanged at about 45° . This behavior suggests a high-polymeric structure which breaks down on melting. The insolubility in organic solvents such as cyclohexane, benzene and carbon tetrachloride and the fibrous nature of the material are also in accordance with a high-polymeric structure. It may be assumed that a condensation reaction takes place during evaporation of the water



The reaction is reversible, since the polymer can be dissolved in water (although the rate of solubility is very slow). A dilute solution again contains only monomeric units. Only a trace of water is necessary to catalyze this over-all change of tetramer to high-polymer, but in the absence of moisture the tetramer is stable for months at room temperature.

Tensimetric experiments (described below) show that, at temperatures of about 160 to 250° and in the vapor phase at pressures of about 100 mm., dimethylgermanium oxide exists as the trimer $(\text{Me}_2\text{GeO})_3$. However, as the tensimeter cools to room temperature a heterogeneous solid with a large melting range is obtained, probably a mixture of

(1) Research Fellow in Chemistry at Harvard University 1958–1959.

(2) M. J. Hunter, J. F. Hyde, E. L. Warrick and H. J. Fletcher, *THIS JOURNAL*, **68**, 667 (1946).

(3) E. G. Rochow, *ibid.*, **70**, 1801 (1948).

(4) E. A. Flood, *ibid.*, **64**, 1663 (1932).

(5) H. H. Anderson, *ibid.*, **72**, 194 (1950).

(6) H. H. Anderson, *ibid.*, **74**, 2370 (1952).

(7) H. H. Anderson, *ibid.*, **75**, 814 (1953).

(8) (a) G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, **127**, 1760 (1925); (b) C. A. Kraus and C. L. Brown, *THIS JOURNAL*, **52**, 2690 (1930).

(9) E. G. Rochow and A. L. Allred, *ibid.*, **77**, 4489 (1955).