[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Organoboron Compounds. III. Preparation and Properties of Alkyldichloroboranes[1-3]

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The reaction of boron chloride with trialkylboroxines has been found to provide a new general method for the preparation of alkyldichloroboranes. The normal alkyl compounds, ethyl- through hexyl-, isopropyl-, isobutyl-, *sec*-butyl-, *t*-butyl- and cyclohexyl- have been prepared, purified and characterized. Fractional distillation at their normal boiling points causes no disproportionation of these compounds. The alkyldichloroboranes are more pyrophoric in character than the corresponding fluoro- compounds and the pyrophoric character increases with branching of the alkyl groups. The oxygen–boron bond in complexes of ether with alkyldichloroboranes is stronger than in complexes of ether with alkyldifluoroboranes. Cleavage products in which the oxygen to boron bond is retained are formed on heating alkyldichloroborane–ether complexes.

A preliminary report on the use of the reaction of boron chloride with trialkylboroxines for the preparation of alkyldichloroboranes has been given previously.[4] In this report it was shown that *n*-butyldichloroborane could be prepared in good yield by the reaction of boron chloride with tri-*n*-butylboroxine. The reaction has now been applied to a large number of trialkylboroxines and has been found to provide a convenient method for the preparation of all types of alkyldichloroboranes. The preparation of a number of new alkyldichloroboranes by this method and their characterization are described herein.

Experimental

Trialkylboroxines were prepared and purified as previously described.[1]

Alkyldichloroboranes.—The apparatus and procedure, used for the preparation of *n*-butyldichloroborane and those of lower molecular weight, differed somewhat from those used for the higher molecular weight compounds. The lower molecular weight compounds are spontaneously inflammable in air and require handling in a system completely protected from air and moisture. The higher molecular weight compounds can be exposed to the air momentarily, without danger of fire, and can be handled in ordinary distillation systems. The detailed procedure for the preparation of ethyldichloroborane will be described as typical of that used for the lower molecular weight compounds. The procedure described for the preparation of *n*-hexyldichloroborane is typical of that used for the higher molecular weight compounds.

Ethyldichloroborane.—A 200-ml., round-bottom flask was fitted with a simple distilling head, an inlet tube extending to the bottom of the flask, a condenser, fraction cutter and a 500-ml., round-bottom, 2-necked flask as receiver. The receiver was attached to the base of a 1.3 × 60-cm., glass-helix packed column of the total reflux, partial take-off type. The distilling column was equipped with a rotating type receiver which permitted distillate to be collected in several tubes with constricted necks. By the use of T-tube connections and sulfuric acid bubbling bottles, dry nitrogen was available to all parts of the apparatus. The entire system was thoroughly flushed out with dry nitrogen and the glass parts flamed. Eighty four grams (0.5 mole) of triethylboroxine was placed in the reaction flask and boron chloride passed in rapidly under the surface of the boroxine. The boron chloride was absorbed rapidly by the trialkylboroxine at room temperature with liberation of heat. After about 15 minutes the mixture was heated, with continued passage of boron chloride, and the product was distilled into the receiver. When absorption of boron chloride ceased, a stopcock separating the reaction section from the distillation section was closed and the product fractionated through the packed column. Excess dissolved boron chloride was collected in a cold trap and ethyldichloroborane collected in the receivers. A one-tenth degree fraction was collected at 50.8° at 745 mm.; yield 108 g., 65%. The receiver tubes were sealed off with a flame for storage of the product. Hydrolysis of ethyldichloroborane was accomplished by opening the sealed receiver tube in an oxygen-free dry-box, adding the alkyldichloroborane cautiously to an excess of water and filtering off the ethylboronic acid formed.

Hexyldichloroborane.—Tri-*n*-hexylboroxine (103 g., 0.33 mole) was placed in a 300-ml., round-bottom flask, fitted with a distilling head, condenser, vacuum adapter and receiver. The adapter was connected to a 100-ml., round-bottom flask, cooled in a solid carbon dioxide-bath and connected with bubbling bottles containing toluene. Boron chloride was passed at a moderately rapid rate through mercury bubbling bottles and into an inlet tube extending below the surface of the boroxine. The reaction mixture became hot and after 15 minutes the formation of a gel was observed. After about 1.5 hr. absorption of boron chloride and distillation ceased and a dark colored, puffy solid remained. The distillate was redistilled through a 60-cm., glass-helix packed column connected with a cold trap to catch excess boron chloride. Eighty-four grams of product (50% yield) boiling at 150–157° was collected. Redistillation gave a pure fraction boiling at 157.2° at 747 mm.

In a number of preparations the residues from the reaction flask and the distillation were combined and dissolved in warm water. The alkylboronic acid was extracted with ether and recovered by evaporation of the ether.

Reaction of Boron Chloride with Alkylboronic Acids.—Moist, unpurified *n*-hexylboronic acid (100 g.) was placed in a 300-ml. flask and boron chloride passed into the flask. Reaction was slow but after a period of 5 to 10 minutes the solid partly liquefied. From the reaction mixture a small amount of *n*-hexyldichloroborane was isolated, but the procedure in general was less satisfactory than that using the direct reaction between trialkylboroxines and boron chloride and was not further investigated.

Attempted Reaction of Titanium Tetrachloride with Tri-*n*-butylboroxine.—Tri-*n*-butylboroxine (0.12 mole) and titanium tetrachloride (0.22 mole) were mixed and refluxed for 8 hr. During this time a small amount of purple solid formed. On fractionation of the liquid, however, the starting materials were recovered unchanged.

Reaction of *n*-Butyldichloroborane with Ether.—To 100 ml. of ether, cooled to solid carbon dioxide temperature, in a 500-ml. flask fitted with stirrer and condenser, was added dropwise 30 ml. of *n*-butyldichloroborane. An exothermic reaction occurred and a white crystalline solid formed in the reaction mixture. On warming to room temperature the solid dissolved in the excess ether. The ether was removed by distillation through a packed column. Continued heating after removal of the ether resulted in rapid evolution of a gas which condensed in a solid carbon dioxide trap. The gas was identified as ethyl chloride. The residual liquid distilled from 95 to 139°. Redistillation gave a main fraction boiling at 138 to 139°, which had a chlorine content of 23.1%; calcd. for $(C_2H_5O)(C_4H_9)BCl$, Cl 23.9. Attempts to further purify this fraction by repeated fractional distilla-

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[1] Paper II, THIS JOURNAL, **79**, 5179 (1957).

[2] The authors acknowledge with thanks helpful discussions with Professor G. F. Hennion.

[3] Presented in part at the Minneapolis Meeting of the American Chemical Society, September, 1955.

[4] P. A. McCusker and L. J. Glunz, *ibid.*, **77**, 4253 (1955).

tions led to a number of fractions of wide boiling range, apparently as a result of disproportionation.

Physical Properties and Analyses.—The pyrophoric character of the lower boiling and branched chain alkyldichloroboranes and the reactivity of all the alkyldichloroboranes with the moisture in the air made measurement of physical properties, other than the boiling point, experimentally difficult. In a few cases densities and refractive indexes were measured as previously described.[1] The compounds were analyzed for chlorine by breaking small ampoules, filled in an oxygen-free dry-box, under the surface of water in a stoppered flask and titrating the liberated hydrochloric acid with standard base.

Results and Discussion

The reaction of organometallic reagents with boron halides cannot in general[5] be used for the preparation of alkyldichloroboranes. The reaction of dimethylzinc with boron chloride was found by Wiberg and Ruschmann[6] and by Becher[7] to yield trimethylborane but no isolable methyldichloroborane. Organomercury compounds, which have been used for the preparation of aryldichloroboranes, have not been used for the preparation of alkyldichloroboranes. Grignard reagents, which can be made to react with boron chloride to yield alkylboronic acids, cannot be used for the preparation of alkyldichloroboranes.

The high temperature reaction of boron chloride with trimethylborane has been used by Wiberg and Bolz[8] and by Becher[9] to prepare methyldichloroborane and presumably would be applicable to higher molecular weight compounds, but the experimental conditions and yields have not been established.

The reaction of hydrogen chloride with tri-*n*-butylborane in the presence of aluminum chloride has been used for the preparation of *n*-butyldichloroborane.[10] While the percentage yield in this reaction may be high, two-thirds of the alkyl groups are lost as hydrocarbon and maximum conversion to alkyldichloroborane is only one-third.

The reaction of boron chloride with trialkylboroxines appears to be applicable to the preparation of any alkyldichloroborane and, as a laboratory procedure, it is convenient and easily carried out. It is not limited to very small quantities and requires only commonly available apparatus. Although the actual yields obtained are only 50 to 60%, no by-products are observed and the reaction appears to stop for mechanical reasons, due to precipitation of boric oxide (or mixed boron-alkylboron oxide). Unreacted trialkylboroxine can be recovered from the reaction mixture by hydrolysis to the acid and subsequent dehydration.[1] In several instances the reaction and distillation residues were hydrolyzed and the alkylboronic acids recovered. In these cases the yields calculated on the basis of trialkylboroxine used exceeded 90%. It is not certain whether the solid product is boric oxide or a mixed polymer of boric and alkylboronic oxide. Hydrolysis would result in the formation of boric oxide and alkylboronic acid in either case.

While the stoichiometry of the reaction of boron chloride with trialkylboroxines appears to be quite straightforward, the mechanism of the reaction has not been established clearly. It has been shown previously[4] that aluminum chloride reacts with trialkylboroxines to give, among other products, some alkyldichloroborane. Other halogenating agents such as hydrogen chloride, silicon tetrachloride, etc.,[4] which do not form strong coördinate bonds with ethereal oxygen gave no reaction. Since aluminum chloride, like boron chloride, acts as a strong acceptor toward oxygen compounds, it was considered of interest to check whether other acceptor halides would react with trialkylboroxines to form alkyldichloroboranes. Titanium tetrachloride forms a strong coördinate covalent bond with ethers. It was refluxed, therefore, with tri-*n*-butylboroxine to see whether reaction could be effected. On long refluxing, however, no appreciable reaction occurred between titanium tetrachloride and tri-*n*-butylboroxine. This is evidence that mere acceptor character in the halide is not sufficient to cause reaction with the boroxine. So far it appears that the reaction is limited to boron chloride and aluminum chloride.

There is an advantage in the use of alkylboronic acids rather than the anhydrides for the laboratory preparation of alkyldifluoroboranes,[4] due to the solution of boric acid in the boron fluoride hydrate formed. There is no such advantage in the use of alkylboronic acids for the preparation of the alkyldichloroboranes. Boron chloride does not form a hydrate, no solution of the boric oxide occurs and large quantities of boric oxide, which interferes mechanically, are formed. The preferred procedure for the preparation of the chloro- compounds involves the use of the anhydride rather than the acid.

The properties of the alkyldichloroboranes prepared in this work are listed in Table I. These compounds have not been reported previously, although the ethyl- compound has been mentioned.[8]

TABLE I

PROPERTIES OF ALKYLDICHLOROBORANES

	B.p.				Chlorine, %	
Compound	°C.	Mm.	d^{25}	$n^{25}D$	Calcd.	Obsd.
$C_2H_5BCl_2$	50.8	745	....	....	..	[a]
i-$C_3H_7BCl_2$	72.0	749	....	....	56.8	57.0
n-$C_3H_7BCl_2$	78.2	739	....	....	56.8	56.8
t-$C_4H_9BCl_2$	88.0	744	....	....	51.1	51.5
i-$C_4H_9BCl_2$	96.8	754	....	....	51.1	51.6
s-$C_4H_9BCl_2$	99.0	748	....	....	51.1	51.4
n-$C_5H_{11}BCl_2$	133.0	747	0.9804	1.4204	46.4	45.2
n-$C_6H_{13}BCl_2$	157.2	747	0.9705	1.4261	42.5	41.2
Cyclo-$C_6H_{11}BCl_2$	167.0	748	1.0810	1.4627	43.0	42.5

[a] Ethyldichloroborane was identified by hydrolyzing to the alkylboronic acid and taking a mixed melting point with an authentic sample of ethylboronic acid.

The variation in boiling points of the alkyldichloroboranes follows the normal pattern of increase with molecular weight and decrease with degree of branching of the alkyl group. This is strong evidence that no isomerization of the alkyl groups occurs during the reaction of boron chloride with trialkylboroxines. Various isomeric alkyldichloro-

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(5) M. F. Lappert, *Chem. Revs.*, **56**, 1049 (1956).

(6) E. Wiberg and W. Ruschmann, *Ber.*, **70B**, 1583 (1937).

(7) H. J. Becher, *Z. physik. Chem., Frankfurt*, **2**, 276 (1954).

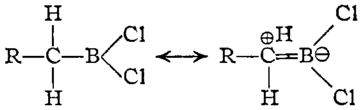
(8) E. Wiberg and A. Bolz, *Fiat Review, Inorganic Chem.*, **I**, 238 (1948).

(9) H. J. Becher, *Z. anorg. allgem. Chem.*, **271**, 243 (1953).

(10) R. B. Booth and C. A. Kraus, THIS JOURNAL, **74**, 1415 (1952).

boranes can be identified by their boiling points when they are obtained pure.

The alkyldichloroboranes are strongly fuming liquids whose vapors undergo rapid hydrolysis in moist air. The straight chain compounds, boiling below about 100°, react sufficiently rapidly on exposure to air to ignite spontaneously. *n*-Butyldichloroborane (b.p. 106°) does not ignite on very short exposure to air, but at slightly elevated temperatures or on longer exposure does inflame spontaneously. As has been observed previously[4] for the alkyldifluoroboranes, the tendency toward pyrophoric character increases markedly with branching of the alkyl groups. Cyclohexyldichloroborane (b.p. 167°) is especially susceptible to self ignition in air. This increase in pyrophoric character with branching of the alkyl group is not readily explained. The steric and inductive factors would lead one to expect that attack by oxygen would be slower in the case of the branched alkyl compounds than in the case of the straight chain compounds. It is possible that the electrophilic character of the boron in the straight chain compounds may be reduced by contributions of structures resulting from hyperconjugation.



The resistance of these compounds to disproportionation, at least below about 170°, is established by the fact that repeated fractional distillation at atmospheric pressure results in boiling point ranges of less than one-tenth degree. Under conditions of fractionation in a packed column, any tendency to disproportionate into boron chloride and trialkylborane would cause ready separation of boron chloride during distillation and produce a residue of trialkylborane. Disproportionation, even to a slight extent, into any other products would cause noticeable variation in the distillation temperatures. It has been assumed in some cases[6] that failure to isolate alkyldichloroborane may have been due to disproportionation into boron chloride and trialkylborane. It is evident that at temperatures below 160° no such disproportionation occurs. The possibility remains that disproportionation may occur at temperatures much above those used in this work.

The acceptor character toward oxygen is evidently stronger in the alkyldichloroboranes than in the alkyldifluoroboranes. While complete separation of the complex of ether with *n*-amyldifluoroborane into its components can be effected by fractional distillation,[4] attempts to effect a similar separation of the ether complex of *n*-butyldichloroborane result in cleavage of the ether according to the equation: $C_2H_5O\text{-}RBCl_2 \rightarrow C_2H_5Cl + (C_2H_5O)(C_4H_9)BCl$. The comparative behavior of alkyldifluoroboranes and alkyldichloroboranes with ether is the same as that of boron fluoride and boron chloride. A partial dissociation of ether–boron fluoride has been observed,[11] while cleavage of ether results from heating the ether–boron chloride complex.[12] The reduced electrophilic character of the boron in alkyldifluoroboranes compared to boron fluoride, due to the inductive effect, is sufficient to permit complete dissociation of the ether–alkyldifluoroborane complex. The greater electrophilic character of boron in boron chloride[13] is not sufficiently reduced by replacement of one chlorine by an alkyl group to weaken the oxygen–boron bond enough to permit separation. In this connection it is possible to explain why alkyldichloroboranes cannot be prepared by the action of boron chloride even with an excess of Grignard reagent, although alkylboronic acids may be so prepared. It would appear that monoalkylation of boron chloride can be effected and the alkyldichloroborane formed can be hydrolyzed to alkylboronic acid. Without hydrolysis, however, the alkyldichloroborane formed is not separable from the ether used as solvent.

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[11] H. C. Brown and R. M. Adams, THIS JOURNAL, **64**, 2557 (1942).

[12] H. Ramser and E. Wiberg, *Ber.*, **63**, 1136 (1930).

[13] H. C. Brown and R. B. Holmes, THIS JOURNAL, **78**, 2173 (1956).