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

Organoboron Compounds. I. Preparation and Properties of Some Alkyldifluoroboranes[1,2]

BY PATRICK A. MCCUSKER AND LOUIS J. GLUNZ

RECEIVED MARCH 9, 1955

The reaction of boron fluoride with alkylboronic acids or alkyl boron oxides has been found to provide a general method for the preparation of alkyldifluoroboranes. The following new compounds have been prepared: *n*-butyl-, *n*-amyl-, *n*-hexyl-, cyclohexyl-, 2-*sec*-, amyl- and *t*-amyldifluoroborane. These compounds have been found to be completely stable in the absence of air and moisture and show no tendency to disproportionate. The secondary and tertiary compounds are spontaneously inflammable in air. Separation of alkyldifluoroboranes from ether occurs on fractional distillation. Reaction of Grignard reagents with excess boron fluoride-etherate yields trialkylborane but no alkyldifluoroborane. The action of other halogenating agents on alkylboron oxides has been surveyed as an aid in establishing some points in the mechanism of the reaction.

A number of organodichloro- and organodibromoboranes, both alkyl[3,4] and aryl,[5] are reported in the literature but only one alkyldifluoroborane, the gaseous methyl compound prepared by Burg[6] by the reaction of boron fluoride with methyl boron oxide. Since we were interested in a general study of organohalogenoboranes, methods for the preparation of these compounds were investigated. The reaction of boron fluoride with alkylboronic acids or alkyl boron oxides has been found to yield alkyldifluoroboranes in yields of 50% or higher. The preparation of a number of these compounds and some of their properties are reported in the present paper.

Experimental

Alkylboronic Acids.—The normal and secondary alkylboronic acids were prepared, in yields of 70%, by the method of Snyder, Kuck and Johnson[7] using a 10–20% excess of methanol-free methyl borate. For the preparation of *t*-amylboronic acid, the chloride Grignard was used and the reaction was carried out at ice-bath temperature. It was observed that the secondary and tertiary alkylboronic acids air-oxidized more rapidly than the normal alkyl boronic acids.

Alkyldifluoroboranes.—The procedure for preparation of *n*-hexyldifluoroborane, adaptable with minor variations to other alkyl-difluoroboranes, is described. One-half mole of crude, moist hexylboronic acid was placed in a 200-ml., round-bottom flask fitted with a distilling head, a condenser, a vacuum adapter and a 50-ml. receiver, which was cooled in an acetone–Dry Ice bath. The adapter was connected to an acetone–Dry Ice-cooled trap and then to a Gilman bridge containing sulfuric acid. Boron fluoride from a cylinder was passed at a fairly rapid rate through a Gilman bridge containing sulfuric acid, and a mercury safety release, through a 7 mm. tube extending through the distilling head to the bottom of the reaction flask. Immediately on contact with the gas, the solid began to liquefy and the mixture became warm. Separation into two layers then occurred. Complete absorption of boron fluoride continued without external heating. When absorption of the gas slowed down, the reaction flask was heated with an oil-bath from 100 to 200°. At the higher temperature all the upper layer distilled over and a viscous liquid remained as a residue. The contents of the receiver and cold trap were combined by transfer under nitrogen pressure and fractionally distilled through a 1.9 × 56 cm. glass-helix packed, total-reflux, partial take off column in an atmosphere of nitrogen. The fraction boiling at 91.9–92.0° (744 mm.) was collected and stored under nitrogen in a glass-stoppered flask. The yield of purified product was 28.5 g. (0.21 mole, (47.5%)).

The lower boiling alkyldifluoroboranes require correspondingly lower oil-bath temperatures. The secondary and tertiary compounds require complete protection from air since they ignite spontaneously in air.

When the alkyl boron oxides, prepared from the alkylboronic acids by the method of Snyder, Kuck and Johnson,[7] were used instead of the alkylboronic acids, reaction with boron fluoride occurred readily to give the alkyldifluoroboranes and a residue of boric oxide.

Physical Properties and Analyses.—Densities of these compounds were obtained using a 5-ml. Lipkin pycnometer flushed out with dry nitrogen and filled under nitrogen pressure. The refractive index of *n*-amyldifluoroborane was obtained with an Abbe refractometer in a nitrogen atmosphere. The compounds were analyzed for fluorine by the method of Booth and Martin[8] for boron fluoride-etherate. Analytical data and physical properties for the compounds prepared are listed in Table I.

TABLE I

DATA ON ALKYLDIFLUOROBORANES

Compound	B.p. °C.	Mm.	d^{25}	n^{25}_D	Fluorine, % Calcd.	Obsd.
$n\text{-}C_4H_9BF_2$	36.3–36.5	742	0.8510	....	35.83	35.74
$n\text{-}C_5H_{11}BF_2$	64.5–64.6	743	.8550	1.3409	31.68	31.55
$n\text{-}C_6H_{13}BF_2$	91.9–92.0	744	.8591	....	28.36	28.10
cyclo-$C_6H_{11}BF_2$	95.7–96.0	743	.9734	....	27.58	27.71
2-*sec*-$C_5H_{11}BF_2$	57.9–58.0	742	.8409	....	31.68	30.94
t-$C_5H_{11}BF_2$	47.7–47.9	748	.8448	....	31.68	31.68

Identification of Lower Layer.—The lower layer formed during the reaction of boron fluoride and *n*-hexylboronic acid was distilled through a 15-in. Vigreux column. A large volume of boron fluoride was evolved during the distillation and a viscous distillate came over at 162°. This is a characteristic distillation behavior of boron fluoride-dihydrate containing excess boron fluoride and dissolved boric oxide.[9]

Formation and Dissociation of the Etherate of *n*-Amyldifluoroborane.—*n*-Amyldifluoroborane (18.3 g., 0.05 mole) was added dropwise to ethyl ether (11.8 g., 0.15 mole) in a 50-ml. round-bottom flask with the evolution of some heat, to give a slightly fuming solution. This solution was fractionally distilled through a 56 cm., glass-helix packed column and yielded two fractions, one at the ether boiling point and one at the boiling point of *n*-amyldifluoroborane. No other products were obtained.

Stability of *n*-Amyldifluoroborane.—A sample of *n*-amyldifluoroborane (20.6 g.) was distilled under a nitrogen atmosphere directly into a tubular receiver constricted near the mouth to facilitate sealing. Without removing from the distillation set-up, the receiver was cooled in Dry Ice,

---

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

[2] From the dissertation submitted by Louis J. Glunz in partial fulfillment of the requirement for the degree of Doctor of Philosophy, University of Notre Dame, 1954. Presented at the Kansas City Meeting of the American Chemical Society, March 1954.

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

[4] H. J. Becher, *Z. anorg. allgem. Chem.*, **271**, 243 (1953).

[5] A. Michaelis and E. Richter, *Ann.*, **315**, 29 (1901).

[6] A. Burg, THIS JOURNAL, **62**, 2228 (1940).

[7] H. R. Snyder, J. A. Kuck and J. R. Johnson, *ibid.*, **60**, 105 (1938).

[8] H. S. Booth and D. R. Martin, "Boron Trifluoride and its Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 245.

[9] J. S. McGrath, G. N. Stack and P. A. McCusker, THIS JOURNAL, **66**, 1263 (1944).

sealed off with a flame and stored in the dark for a period of one month. The liquid remained perfectly colorless and on opening of the tube there was no indication of pressure. Redistillation of the liquid occurred without change in boiling point. There was no fore-run or residue and 18.2 g. of product was recovered.

Reaction of Excess Boron Fluoride-Etherate with *n*-Hexylmagnesium Bromide.—Boron fluoride (196 g., 2.9 moles) was added to 300 ml. of ether. To the ether solution, cooled to Dry Ice temperature, was added with vigorous stirring over a period of four hours, 0.5 mole of *n*-hexylmagnesium bromide in 300 ml. of ether. After addition was complete, stirring was continued for an additional four hours. A white solid settled to the bottom of the flask and on warming to room temperature two liquid layers were formed. The upper layer was fractionally distilled to give 20 g. of a product boiling at 97° at 0.02 mm. This was identified as trihexylborane. The lower layer was identified as boron fluoride-etherate. There was no indication of the presence of *n*-hexyldifluoroborane.

Reaction of Aluminum Chloride with *n*-Butyl Boron Oxide.—A 300-ml., 3-necked flask was fitted with a stirrer and condenser. *n*-Butylboron oxide (35.0 g., 0.139 mole of trimer) was placed in the flask and 34.3 g. (0.258 mole) of anhydrous aluminum chloride was added in small portions over a period of 1.5 hours. Heat was liberated during the addition and the solution fumed and became dark brown and viscous. The reaction mixture was distilled under a slight vacuum to give 20 ml. of distillate and 2–3 ml. of low boiling liquid caught in a Dry Ice cold trap. The low boiling liquid was identified as boron chloride and the residue was shown to contain aluminum oxide. The 20 ml. of original distillate on redistillation boiled over a range of 50 to 140°, and fumed in air. On hydrolysis of a small portion butylboronic acid was formed. Analysis of the distillate indicated a chlorine content midway between that calculated for *n*-butyldichloroborane and di-*n*-butylchloroborane.

Discussion

The stoichiometry of the reaction of boron fluoride with alkyl boron oxides appears to be that first proposed by Burg[6] and represented by the equation

$$(RBO)_3 + 2BF_3 \longrightarrow 3RBF_2 + B_2O_3$$

In our work the formation of a glassy residue of boric oxide was always observed and no other reaction products were found. Failure to obtain quantitative yields of alkyldifluoroboranes appears to be due to the retention of unreacted alkyl boron oxide in the viscous boric oxide, and thermal decomposition as evidenced by a certain amount of charring of the reaction mixture. In practice the yield of the lower boiling alkyldifluoroboranes was generally a little higher than the yield of higher boiling compounds.

The use of a boronic acid, rather than a boronic acid anhydride, as starting material for the preparation of alkyldifluoroboranes has the advantage of eliminating the dehydration step in the synthesis. Crude moist alkylboronic acids may be used directly and reaction of the acid with boron fluoride proceeds smoothly. The boric oxide formed in the reaction dissolves in the lower layer of boron fluoride hydrate while the alkylboron oxide remains as the upper layer. This has the effect of removing boric oxide from the liquid in which reaction is occurring, and permits more complete reaction between boron fluoride and the alkyl boron oxide.

All the alkyldifluoroboranes prepared in this work are water-white liquids which fume profusely in air. The *n*-alkyl compounds are not spontaneously inflammable in air, but the secondary and tertiary compounds ignite on exposure to air. If kept in an atmosphere of dry nitrogen these compounds show no change on standing for as long as one month. Under no conditions was any disproportionation into boron fluoride and trialkylborane observed. The boiling points of the three *n*-alkyldifluoroboranes increase, as would be expected, by about 30° for each additional carbon atom. Branching in the chain causes a lowering of the boiling point.

The fact that the secondary and tertiary alkyldifluoroboranes are spontaneously inflammable at room temperature, while the normal alkyl compounds are not, is paralleled by the fact that more rapid air oxidation occurs with the secondary and tertiary alkylboronic acids, than with the normal alkylboronic acids. The spontaneous inflammability of the secondary and tertiary alkyldifluoroborines is not dependent on volatility since the lower boiling *n*-butyldifluoroborane can be poured repeatedly through the air without catching fire.

The acceptor tendency of the boron in alkyldifluoroboranes is apparently less than in boron fluoride. While only a slight dissociation of ether–boron fluoride[10] occurs on vaporization complete dissociation of ether–amyldifluoroborane occurs. The decreased strength of the donor–acceptor bond in this complex probably results from a reduced residual positive charge on the boron. Further quantitative studies of donor–acceptor bonding between ethers and the alkyldifluoroboranes are in progress.

The reaction of an alkyl Grignard even with a sixfold excess of ether–boron fluoride at Dry Ice temperature does not produce alkyldifluoroborane but yields instead trialkylborane. It appears from our experimental results that the replacement of one fluorine in boron fluoride by an alkyl group increases the reactivity of the remaining fluorines to the Grignard reagent. The second and third fluorines react more readily than the first. The isolation of trialkylborane only from the reaction of Grignard reagent with excess boron fluoride–etherate might possibly be considered as resulting from the disproportionation of the alkyldifluoroborane after its formation. It has been shown, however, that no disproportionation of the alkyldifluoroboranes occurs, even in the presence of ether.

The following halogenating agents were found not to react with the alkyl boron oxides: hydrogen chloride, thionyl chloride, phosphorus trichloride, silicon tetrachloride and silicon tetrabromide. Aluminum chloride, however, reacts quite readily with the alkyl boron oxides in a manner similar to the boron halides, but with the production of a number of by-products. In the reaction of *n*-butyl boron oxides with aluminum chloride, spontaneously inflammable mixtures were formed which were quite difficult to separate. The presence of boron trichloride and some mixed alkylchloroborines in the mixture, was established, however. The nature of the halogenating agents which react with the alkyl boron oxides to form alkyldihalogenoboranes give some indication as to the mechanism of the reaction. Boron fluoride and aluminum chloride both act as acceptors toward oxygen while the other halogenating agents, even the silicon halides, do not.

---

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

This suggests that the mechanism of the reaction involves, as a first step, coördinate bond formation between the oxygen of the alkyl boron oxide and the boron or aluminum halide. Whether the subsequent reaction involves internal displacement (SNi reaction) or some other mechanism cannot be decided with the data so far available.

The applicability of this general reaction to the preparation of alkyldichloroboranes has been demonstrated in some of our preliminary studies. *n*-Butyldichloroborane[3] has been prepared in good yield by the reaction of boron chloride with butylboronic acid or butyl boron oxide. Further work on the preparation of alkyldichloroboranes is in progress.

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT STANDARD OIL COMPANY (INDIANA)]

Synthesis of 4-Aryl-1,2-dithiole-3-thiones by Reaction of Cumenes with Sulfur

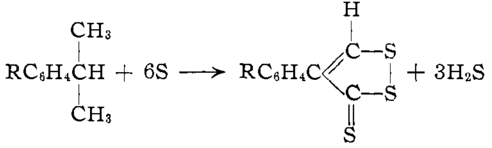
BY ELLIS K. FIELDS

RECEIVED SEPTEMBER 29, 1954

Cumenes react with sulfur at atmospheric pressure in the presence of bases to give good yields of 4-aryl-1,2-dithiole-3-thiones. The scope of the reaction has been studied and four new dithiolethiones have been prepared. Bases of greatly different strength give about the same results. The cumenes probably are converted to α-methylstyrenes, which in turn rapidly react with sulfur to give dithiolethiones. Many aryldithiolethiones can be made easily from readily available saturated hydrocarbons by means of this new reaction.

Aryldithiolethiones can be prepared by the reaction of arylalkenes with sulfur.[1] This method of preparation suffers from four disadvantages: (a) the yields are low, (b) the high reaction temperatures of 190–250° often make pressure equipment necessary, (c) tedious purification is required because of the excess sulfur that must be used, and (d) few arylalkenes are readily available.

In the presence of catalytic amounts of bases, cumenes have been found to react with sulfur and give good yields of aryldithiolethiones according to the equation



The reaction proceeds at atmospheric pressure. Excess hydrocarbon is used rather than excess sulfur; almost pure dithiolethiones crystallize directly from the reaction mixture.

Five cumenes have been converted to dithiolethiones, of which four are new. Properties of the cumenes are listed in Table I. The effect of different *para*-substituting radicals on the rate of reaction with sulfur has been studied.

TABLE I

CUMENES USED FOR PREPARING DITHIOLETHIONES

Cumene	Boiling point °C.	Boiling point Mm.	n^{20}_D	Yield, %
Cumene	152	745	1.4912	..
Cymene	175	745	1.4889	..
p-Ethylcumene[a]	73	10	1.4935	27
p-*t*-Butylcumene[b]	74–76	2.5	1.4930	67
p-*t*-Amylcumene[b,c]	81.5–83	2.3	1.4934	41

[a] Prepared according to Klages and Keil, *Ber.*, **36**, 1632 (1903). [b] Prepared according to Barbier, *Helv. Chim. Acta*, 19, 1345, 1349 (1936). [c] d^{20}_4 0.684. *Anal.* Calcd. for $C_{14}H_{22}$: C, 88.42; H, 11.58; mol. wt., 190. Found: C, 88.55; H, 11.58; mol. wt., 194.

Preparations

The dithiolethiones listed in Table II were prepared by heating a mixture of 1 mole of hydrocarbon, 1.5 gram atoms of sulfur and 0.00165 mole of di-*o*-tolylguanidine at reflux (cumene, *p*-cymene) or at 185–200° until no free sulfur remained.[2] After the mixture was chilled at 0–10° for several hours, the crystals were filtered and recrystallized from benzene alone or diluted with hexane. Analyses of the materials prepared are given in Table III. The methiodide derivatives were made in nearly quantitative yields from the dithiolethiones and excess methyl iodide in *n*-butyl acetate at reflux for 2 hours.

TABLE II

PREPARATION OF 4-ARYL-1,2-DITHIOLE-3-THIONES

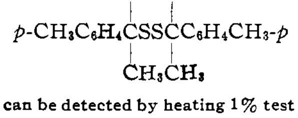
Catalyst: 0.00165 mole of di-*o*-tolylguanidine

Hydrocarbon	Temp., °C.	Time, hours	Yield,[a] %
Cumene	156	174	78
p-Cumene	185	21	76
p-Ethylcumene	199	4.5	40
p-*t*-Butylcumene	193	24	61
p-*t*-Amylcumene	190	15.5	36

[a] Based on sulfur.

In a typical preparation a mixture of 1108 g. (8.25 moles) of *p*-cymene, 400 g. (12.5 gram-atoms) of sulfur and 8.2 g. of ditolylguanidine was refluxed at 185° for 21 hours. Hydrogen sulfide was evolved steadily. The mixture then was kept at 5° for 2 hours to allow the dithiolethione to crystallize. The red crystals were collected on a filter, washed with 400 ml. of 1:3 benzene:hexane, and sucked dry. There was obtained 355 g. (1.58 moles, 77% based on sulfur) of 4-*p*-tolyl-1,2-dithiole-3-thione, m.p. 119–120°. After one recrystallization from benzene, it melted at 122.5–123°.

Vacuum distillation of the filtrate from the dithiolethione crystals gave 575 g. of *p*-cymene (b.p. 34–39° at 10 mm.) and 330 g. (1 mole) of a deep-red viscous residue which may be



$$p\text{-}CH_3C_6H_4\overset{CH_3}{\underset{CH_3}{C}}SS\overset{CH_3}{\underset{CH_3}{C}}C_6H_4CH_3\text{-}p$$

---

[1] B. Böttcher and A. Lüttringhaus, *Ann.*, **557**, 89 (1947); A. Lüttringhaus, H. B. König and B. Böttcher, *ibid.*, **560**, 201 (1947); J. Schmitt and A. Lespagnol, *Compt. rend.*, **230**, 551 (1940); M. G. Voronkov, A. S. Braun and G. B. Karpenko, *J. Gen. Chem.* (*U.S.S.R.*), **19**, 1927 (1949); N. Lozac'h, *Bull. soc. chim. France*, 840 (1949).

[2] Free sulfur can be detected by heating 1% test sample in an inert hydrocarbon (high-boiling ligroin or refined oil) with a polished copper strip at 100° for 1 hour. Free sulfur will blacken the strip.