bromide. The distillate was dissolved in 10 ml. of carbon tetrachloride and washed with a 5% aqueous solution of sodium carbonate and with water. The solution was treated with an excess of 5% potassium permanganate in acetone–water and heated on a steam-plate until the violet color remained. The solution was filtered, washed with water until the solution was colorless, dried by passing it through a column of calcium chloride, and rectified to give 4.9 g. (53%) of (1-heptafluoropropyl)-benzene, b.p. 127–128°, $n^{20}\text{D}$ 1.3875, d^{20}_4 1.384.

Anal. Calcd. for $C_9H_5F_7$: C, 43.92; H, 2.04; MR_D, 41.09. Found: C, 43.57; H, 2.01; MR_D, 41.91.

The Preparation of Pentafluoroethyl Grignard Reagent: Reaction with Acetone.—A 500-ml., round-bottomed flask was equipped with a stirrer and two closed-circuit addition funnels. The system was flamed out in a stream of dry nitrogen and cooled in a Dry Ice-bath prior to the addition of 75 ml. of anhydrous ether and 49 g. (0.2 mole) of pentafluoroethyl iodide.[11] In one funnel was placed 200 ml. (0.21 mole) of 1.07 molar phenylmagnesium bromide in ether and in the other 12 g. (0.2 mole) of acetone in 100 ml. of anhydrous ether. The contents of the funnels were simultaneously added to the flask during 3 hours while the reaction mixture was held at Dry Ice temperature. The reaction mixture was allowed to come to room temperature and cooled in ice-water and hydrolyzed with 150 ml. of a 10% aqueous solution of hydrochloric acid. Very little evolution of gas was observed throughout the experiment. The ether solution was separated, the acid layer was washed three times with ether and the combined ether portions were dried over Drierite. The ether was distilled through a glass-helices packed column and the residue rectified to give 13.1 g. (38%) of 3,3,4,4,4-pentafluoro-2-methyl-2-butanol, b.p. 94–97°, $n^{20}\text{D}$ 1.3325–1.3335.[16]

The Treatment of Heptafluoropropane with Methylmagnesium Iodide.—Methylmagnesium iodide was prepared from 2.4 g. (0.1 g.-atom) of magnesium shavings and 14.2 g. (0.1 mole) of methyl iodide in 75 ml. of anhydrous ether. The reagent was transferred to a Carius tube and the tube was cooled in Dry Ice (a nitrogen atmosphere was maintained.) Heptafluoropropane (12 g., 0.07 mole, b.p. −14 to −15°) was distilled into the tube and the tube was sealed. The tube was allowed to warm to room temperature and to stand, with occasional shaking, for 24 hours. It was then cooled in a liquid nitrogen bath, opened and quickly connected to a system consisting of a Dry Ice trap and an inverted bottle filled with water which could be filled with gas by displacement of the water. The tube was removed from the liquid nitrogen bath, allowed to warm slightly and placed in a Dry Ice-bath. There was a 100-ml. evolution of a non-flammable gas within a few minutes that would correspond to no more than that caused by thermal expansion. On removing the tube from the Dry Ice-bath and warming to 30° no further gas evolution was observed, but 7 g. (58%) of heptafluoropropane was recovered. Since no methane was formed, it was concluded that heptafluoropropane does not react at room temperature with methylmagnesium iodide.

Acknowledgment.—The authors are indebted to Westinghouse Electric Corporation for financial support of this work.

WEST LAFAYETTE, INDIANA

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(16) E. T. McBee, J. F. Higgins and O. R. Pierce, THIS JOURNAL **74**, 1387 (1952).

[CONTRIBUTION FROM THE SHELL DEVELOPMENT CO.]

The Synthesis of Alkylhaloboranes[1,2]

BY V. W. BULS, O. L. DAVIS AND R. I. THOMAS

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Alkylchloroboranes and alkylfluoroboranes have been prepared by a high temperature reaction of a trialkylborane with the appropriate trihaloborane. Attempts to isolate compounds containing both chlorine and fluorine attached to boron were not successful. However, an equimolar mixture of butyldichloroborane and butyldifluoroborane reacts with alcohols in a manner that would be expected of the compound $C_4H_9B(F)Cl$.

The alkylhaloboranes are versatile intermediates which can be utilized for the preparation of many organic boron compounds containing one or two boron–carbon bonds. The halides, except the fluorides, are very reactive. They readily undergo reactions in which the halogen is replaced without affecting the boron–carbon bonds. Alkylhaloboranes have been prepared by a number of different reactions. These include the dealkylation of trialkylboranes with hydrogen chloride or chlorine or bromine,[3–5] the addition of acetylene to trichloroborane[6] and the reaction of alkylboryl oxides with trifluoroborane.[7] The reaction of aliphatic Grignard reagents with trihaloboranes gives excellent yields of trialkylboranes, but attempts to prepare alkylhaloboranes in this manner have not been successful. Only trialkylboranes are recovered despite low temperatures and an excess of trihalide. Arylhaloboranes have, however, been prepared using aryl Grignard reagents[8] or diaryl mercury.[9] A mixture of trimethylborane, dichloromethylborane and chlorodimethylborane has been reported from the reaction of trichloroborane with zinc dimethyl.[10]

The present investigation has developed a synthesis of alkylhaloboranes which consists of heating a trialkylborane with a trihaloborane under pressure, thus effecting a redistribution of alkyl and halogen groups

$$R_3B + BX_3 \rightleftarrows R_2BX + RBX_2$$

The reaction is reversible, the rate depending upon the nature of the substituent groups. Thus dichloromethylborane and chlorodimethylborane are said to undergo complete disproportionation to trichloroborane and methylborane on attempted distillation.[10] Analogous reactions are known in other fields of organometallic chemistry. Kocheshkov[11] prepared the three butyltin chlorides by heating tetrabutyltin with the appropriate amounts of an-

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(1) This paper reports work done under contract with the Chemical Corps. U. S. Army, Washington 25, D. C.

(2) Recommendations of an American Chemical Society Nomenclature Committee have been followed in naming these compounds; see *Chem. Eng. News*, **34**, 560 (1956).

(3) E. Frankland, *Ann.*, **124**, 137 (1862).

(4) J. R. Johnson, H. R. Snyder and M. G. Van Campen, Jr., THIS JOURNAL, **60**, 115 (1938).

(5) R. B. Booth and C. A. Kraus, *ibid.*, **74**, 1415 (1952).

(6) H. R. Arnold, U. S. Patent 2,402,589, June 25, 1946.

(7) A. B. Burg, THIS JOURNAL, **62**, 2228 (1940).

(8) E. Krause and R. Nitsche, *Ber.*, **55B**, 1261 (1922).

(9) A. Michaelis and P. Becker, *ibid.*, **13**, 58 (1880).

(10) E. Wiberg and W. Ruschmann, *ibid.*, **70B**, 1583 (1937).

(11) K. A. Kocheshkov, *J. Gen. Chem. USSR*, **5**, 211 (1935).

TABLE I

BORANE–HALOBORANE REDISTRIBUTION EXPERIMENTS

Temperature 200°, heating time, experiment 1, 4 hours, experiments 2–5, 20 hours

Reactants				Mole ratio		Products recovered						
Borane	Mole	Halo-borane	Moles	Halo-borane Borane	R_3B Mole	BX_3 Mole	R_2BX Mole	R_2BX Yield, %[a]	RBX_2 Moles	RBX_2 Yield, %[a]	Total yield, %[a]	Recovery of boron, mole %
$(C_2H_5)_3B$	0.64	BCl_3	1.28	2/1	0.041	0.78	0.56	61.4	0.54	30.0	91.4	99.0
$(C_4H_9)_3B$	.33	BCl_3	0.67	2/1	.066	0.27[b]	.009	2.4	.65	74.4	76.8	100[b]
$(C_4H_9)_3B$	.60	BCl_3	.65	1/1	.083	None	.59	69.2	.51	30.2	99.4	94.8
$(C_4H_9)_3B$	.41	BF_3	.81	2/1	.11	0.22	None	..	.84	90.6	90.6	93.1
$(C_4H_9)_3B$	.18	BF_3	.088	1/2	.085	None	0.042	30.9	.090	29.6	60.5	73.5

[a] Yield is based on alkyl groups consumed. [b] BCl_3 contains C_4H_{10}, quantity not determined.

TABLE II

ANALYSES AND BOILING POINTS OF ALKYLHALOBORANES

Compound	B.p., °C.	B.p., Mm.	Boron, % Calcd.	Boron, % Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Fluorine, % Calcd.	Fluorine, % Found	Chlorine, % Calcd.	Chlorine, % Found
$C_2H_5BCl_2$	+1	100	9.77	9.7	21.7	..	4.55	..	..	..	64.1	64.5
$(C_2H_5)_2BCl$	25	100	10.4	10.2	46.0	..	9.65	..	..	..	34.0	35.3
$C_4H_9BCl_2$	+4	10	7.79	8.1	34.6	..	6.53	..	..	..	51.1	51.2
$(C_4H_9)_2BCl$	31	10	6.74	6.5	59.9	61.6	11.3	11.7	..	..	22.1	22.3
$C_4H_9BF_2$	35	760	10.2	10.8	45.4	..	8.56	..	35.9	34.4	..	..
$(C_4H_9)_2BF$	−5	100	7.5	7.1	66.7	67.0	12.6	12.7	13.2	9.1	..	..

hydrous stannic chloride. The redistribution of trialkyl- and triarylarsines with arsenic trichloride has long been known as a method for preparing the corresponding dichloroarsines.[12]

This investigation was limited to the preparation of the chloroethylboranes, the butylchloroboranes and the butylfluoroboranes. A temperature of 200° and a reaction time of approximately 4 hr. was found to be satisfactory for the chloroethylboranes. With the butylchloroboranes and butylfluoroboranes 20 hr. was allowed. The choice of temperature and reaction time is necessarily a compromise. Short reaction times and low temperatures give incomplete reaction; excessively long reaction times or excessive temperatures lead to pyrolysis of the alkyl groups.[13] At 200° degradation does not appear to be serious. The reactions were performed in a stainless steel hydrogenation vessel which was evacuated before charging the reactants. Oxygen and moisture must be rigorously excluded since all the components oxidize and hydrolyze readily. All of the materials prepared proved to be pyrophoric with the exception of butyldifluoroborane.

Distillation of the products usually was performed at reduced pressure. The products from the redistribution of tributylborane and trichloroborane when distilled at atmospheric pressure gave a distillation curve that would indicate a complex mixture. On the other hand, distillation at 10 mm. gave clean separations with no evidence of disproportionation. Refrigerated storage at −20° was used to prolong the shelf life of purified samples.

Several attempts were made to isolate compounds containing both chlorine and fluorine attached to boron. These were not successful. Experiments were performed heating trichloroborane and trifluoroborane alone and in the presence of several per cent. of butyldichloroborane. No products boiling between −101° and +13° were recovered. The redistribution of equal molar quantities of tri-*n*-butylborane, trichloroborane and trifluoroborane gave approximately equivalent quantities of butyldichloroborane and butyldifluoroborane. Distillation at 10 mm. gave no indication of the presence of the mixed dihalide, $C_4H_9B(F)Cl$ which was expected to boil at about −20°. However, the following evidence suggests that an equilibrium exists in which the interchange of halogen atoms is extremely rapid.

$$C_4H_9BCl_2 + C_4H_9BF_2 \rightleftarrows 2C_4H_9B(F)Cl$$

Butyldichloroborane reacts rapidly with alcohols to give dialkoxy derivatives and hydrogen chloride. Butyldifluoroborane under similar conditions gives no apparent reaction. However, it was found that the reaction of an alcohol with an equimolar mixture of the two halides at −40° gave a fair yield of an alkoxybutylfluoroborane along with the expected dialkoxybutylborane

$$C_4H_9BCl_2 + C_4H_9BF_2 + 2ROH \longrightarrow 2ROB(F)C_4H_9 + 2HCl$$

$$C_4H_9BCl_2 + 2ROH \longrightarrow (RO)_2BC_4H_9 + 2HCl$$

In this way butylfluoroisopropoxyborane and butylcyclohexyloxyfluoroborane were prepared in 34 and 21% yield, respectively.

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Experimental

Alkylhaloboranes.—Triethylborane and tri-*n*-butylborane were prepared by the method of Johnson, *et al.*,[4] using the appropriate Grignard reagent with ethyl ether trifluoroborane. Gaseous trichloroborane and trifluoroborane were obtained commercially. The alkylhaloboranes listed in Table I were prepared under similar experimental conditions. The following experiment on the preparation of the butylchloroboranes will serve to illustrate the techniques used: Tri-*n*-butylborane (0.65 mole, 118 g.) was charged to an evacuated 300-cc. stainless steel hydrogenation vessel. The vessel was cooled to 0° and 0.60 mole (70 g.) of gaseous trichloroborane was weighed from a commercial cylinder using a flexible connecting loop of 22 gage hypodermic tubing. The vessel was then sealed and heated to 200° for

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(12) A. Michaelis and R. Reese, *J. Gen. Chem. USSR*, **15**, 2876 (1882).

(13) L. Rosenblum, THIS JOURNAL, **77**, 5016 (1955).

20 hr.; maximum pressure attained was 90 p.s.i.g. The vessel was cooled and pressured to 200 p.s.i.g. with purified, dry nitrogen to facilitate removal of the products. The contents of the vessel were then charged to a distillation flask held at Dry Ice temperature. Distillation of the product under purified nitrogen at 10 mm. gave 0.51 mole (71 g.) of butyldichloroborane, b. +4° (10 mm.), and 0.59 mole (94.5 g.) of dibutylchloroborane, b. 54° (10 mm.). Both products are colorless when first distilled and are pyrophoric in air. Both products hydrolyze violently in water.

Butylfluoroisopropoxyborane.—Butyldifluoroborane (0.25 mole, 24.6 g.) and 0.25 mole (34.7 g.) of dichlorobutylborane were charged to a stirred flask at −40°. Isopropyl alcohol (0.50 mole, 35 g.) was added dropwise in 30 minutes. Hydrogen chloride was evolved. Distillation gave two major fractions: butylfluoroisopropoxyborane, b. 60° (100 mm.), 0.17 mole (24.6 g.), 34%, and butyldiisopropoxyborane, b. 105° (100 mm.), 0.13 mole (24.8 g.), 27%. The entire preparation was performed under an atmosphere of purified, dry nitrogen.

Anal. Calcd. for $C_7H_{16}OBF$: C, 57.5; H, 11.0; B, 7.41; F, 13.2. Found: C, 58.9; H, 11.7; B, 7.6; F, 12.5; Cl, 0.0. Calcd. for $C_{10}H_{23}O_2B$: C, 64.5; H, 12.4; B, 5.82. Found: C, 64.2; H, 12.4; B, 6.7; F, 0.9.

Butylcyclohexyloxyfluoroborane.—Butyldichloroborane (0.14 mole, 20 g.), and 0.15 mole (16 g.) of difluorobutylborane were charged to a flask equipped with a stirrer. Cyclohexanol (0.35 mole, 33.5 g.) was added dropwise in 30 minutes at about −80° and the solution was allowed to come to room temperature. During this time hydrogen chloride was removed with a nitrogen sweep. Calcium carbonate, 2 g., was then added and stirring was continued an additional 2 hr. Distillation gave 0.049 mole (9 g.) of butylcyclohexyloxyfluoroborane, b.p. 60–65° (10 mm.), 21%, and 0.12 mole (30.5 g.) of butyldicyclohexyloxyborane, b.p. 156–160° (1 mm.), 50%. Butylcyclohexyloxyfluoroborane tends to disproportionate to butyldicyclohexyloxyborane and butyldifluoroborane during distillation. Traces of acid catalyze this disproportionation. The entire preparation was performed under an atmosphere of purified, dry nitrogen.

Anal. Calcd. for $C_{10}H_{20}OBF$: C, 64.5; H, 10.8; F, 10.2; B, 5.81. Found: C, 65.1; H, 11.4; F, 12.1; B, 4.3; Cl, <0.2. Calcd. for $C_{16}H_{31}O_2B$: C, 73.7; H, 11.7; B, 4.06. Found: C, 74.8; H, 12.1; B, 4.1; Cl, <0.2; F, <0.5.

EMERYVILLE, CALIF.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Preparation of Some Derivatives of Phenoxasilin, a Silicon Analog of Xanthene

BY KATASHI OITA AND HENRY GILMAN

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The dimetalation of diphenyl ether with *n*-butyllithium yielded 2,2′-dilithiodiphenyl ether. From the reaction of 2,2′-dilithiodiphenyl ether with diphenyldichlorosilane, dimethyldichlorosilane and silicon tetrachloride there were obtained 10,10-diphenylphenoxasilin, 10,10-dimethylphenoxasilin and 10,10′-spirobiphenoxasilin, respectively. 10,10-Diphenylphenoxasilin and 10,10′-spirobiphenoxasilin were cleaved by lithium in dioxane to yield *o*-hydroxyphenyltriphenylsilane and bis-(*o*-hydroxyphenyl)-diphenylsilane, respectively.

In a Fisher–Hirschfelder–Taylor model of 5,5-diphenyldibenzosilole[1] the silicon–carbon bonds which are part of the 5-membered cyclic system are under a considerable strain. We are reporting the synthesis of a new heterocyclic system in which the strain is alleviated by the presence of an oxygen atom in the central, 6-membered, cyclic system. The compounds prepared were 10,10-diphenylphenoxasilin (I), 10,10-dimethylphenoxasilin (II) and 10,10′-spirobiphenoxasilin (III),[2] silicon analogs of 9,9-diphenylxanthene, 9,9-dimethylxanthene and 9,9′-spirobixanthene, respectively.

In both the dibenzosilole and phenoxasilin syntheses the key reaction was that of an 2,2′-dilithium compound and an appropriate dichlorosilane (silicon tetrachloride for the spiro compound). In the preparation of 5,5-diphenyldibenzosilole the intermediate, 2,2′-dilithiobiphenyl, was prepared by a halogen–metal interconversion reaction of *n*-butyllithium and 2,2′-dibromobiphenyl. For phenoxasilin derivatives the corresponding dilithium intermediate, 2,2′-dilithiodiphenyl ether, was prepared by the dimetalation of a more accessible reagent, diphenyl ether, with *n*-butyllithium. 2,2′-Dilithiodiphenyl ether may prove to be the reagent of choice for preparing other diphenyl ether derivatives with substituents in the 2,2′-positions.

In order to prove that dimetalation of diphenyl ether occurred in the 2,2′-positions, the dilithium compound was carbonated and the product so formed was acidified to yield 2,2′-dicarboxydiphenyl ether, confirmed by a mixed melting point with an authentic specimen.[3] The infrared spectra of the phenoxasilin derivatives synthesized, also supported, the 2,2′-positions of dimetalation. 10,10-Diphenylphenoxasilin had strong absorption bands at 13.2 and 13.5 μ, characteristic of an *ortho* disubstituted benzene and a monosubstituted benzene, respectively, but the only aromatic-substitution band present in 10,10-dimethylphenoxasilin and 10,10′-spirobiphenoxasilin was that of *ortho* disubstituted benzene at 13.2 μ.

The cleavage of compounds I and III with metallic lithium in dioxane[4] to yield *o*-hydroxyphenyltriphenylsilane and bis-(*o*-hydroxyphenyl)-diphenylsilane, respectively, is not a rigorous proof for the assigned structures I and III, but it supports them. The identity of *o*-hydroxyphenyltriphenylsilane from the cleavage reaction was established by a mixed melting point determination with the compound prepared from the reaction of *o*-hydroxyphenyllithium and triphenylchlorosilane[5] and by a comparison of their infrared spectra.

Bis-(*o*-hydroxyphenyl)-diphenylsilane could not be isolated from the reaction of *o*-hydroxyphenyllithium and diphenyldichlorosilane. However, this is not too surprising since forcing conditions were used even in the direct preparation of *o*-hydroxy-

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[1] H. Gilman and R. D. Gorsich, THIS JOURNAL, **77**, 6380 (1955).

[2] The names and the numbering system used herein were recommended by the editorial staff of *Chemical Abstracts*.

[3] Kindly provided by Mr. S. H. Eidt of this Laboratory.

[4] H. Gilman and D. L. Esmay, THIS JOURNAL, **75**, 2947 (1953).

[5] H. W. Melvin, unpublished studies.