

AN ABSTRACT OF THE THESIS OF

James Elroy William Walsh for the degree of Master of Science

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Title: Decomposition of Perfluoroalkyl Groups Bonded to Boron

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Theran D. Parsons

All attempted synthesis of perfluoroalkyl boron bonded groups have resulted in the formation of boron-fluorine bonds from the probable decomposition by α -fluorine transfer. The substance alkali metal di-n-butylborate (I) has been identified as the potassium derivative by its reaction with di-n-butylboron chloride and isolation of potassium chloride. The reaction of potassium di-n-butylborate (I) with trifluoriodomethane in aprotic solvents was studied by ^{19}F NMR resulting in the identification of a transient intermediate tri-fluoromethyldi-n-butylboron which decomposed upon warming.

Decomposition of Perfluoroalkyl Groups
Bonded to Boron

by

James Elroy William Walsh

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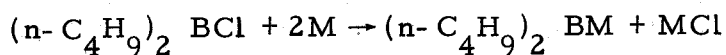
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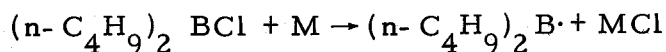
DECOMPOSITION OF PERFLUOROALKYL GROUPS BONDED TO BORON

INTRODUCTION

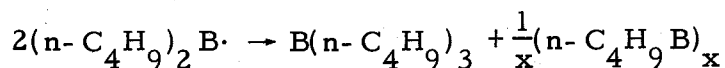
The diverse chemistry of the reagent, di-n-butylborate (I) anion, can be realized by examination of the various substrates with which it has been reported to react. Auten and Krauss (1) first studied the preparation of this reagent by treating di-n-butylboron chloride with sodium potassium alloy (1:2 atom ratio) in diethyl ether. With excess alloy, complete reduction occurred to give alkali metal di-n-butylborate (I) in 60% yield. The composition of the alkali metal was not established.



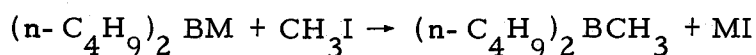
With one equivalent of alloy present, incomplete reduction to the di-n-butylborate (II) species was obtained.



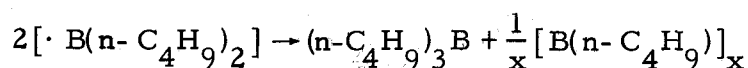
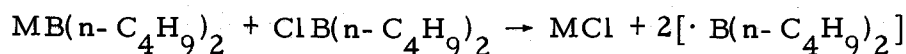
The nature of this di-n-butylboron (II) species was not examined, but upon heating in vacuo disproportionation occurred to give n-butylboron polymer and tri-n-butylborane which was recovered.



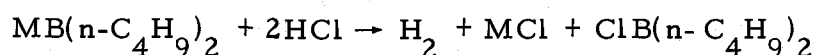
Methyl iodide reacted with alkali metal di-n-butylborate (I) in 45% reported yield based upon the original amount of di-n-butylboron chloride.



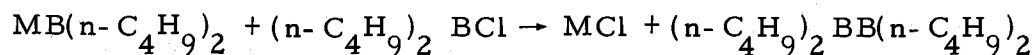
Addition of di-n-butylboron chloride to alkali metal di-n-butylboron (I) produced, upon distillation, tri-n-butylborane and polymer. The intermediate di-n-butylboron (II) species was thought to have disproportionated during distillation as described above.



Treatment of alkali metal di-n-butylborate (I) with anhydrous hydrogen chloride produced di-n-butylboron chloride, hydrogen gas and alkali halide in 67% reported yield and this reaction can be used to ascertain the yield of alkali metal di-n-butylborate (I) by measuring the evolved hydrogen.



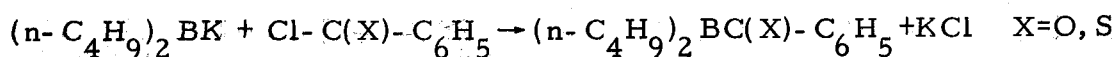
It was Schaad (33) who established the existence of a boron-boron bond in the di-n-butylboron (II) species and gave evidence for the probable existence of tetra-n-butyldiboron from the reaction of alkali metal di-n-butylborate (I) and di-n-butylboron chloride.



The tetra-n-butyldiboron was not isolated but consumed ethylene and evolved hydrogen gas upon basic hydrolysis, in a manner typical of compounds containing a boron-boron bond. Tetraalkyldiboron

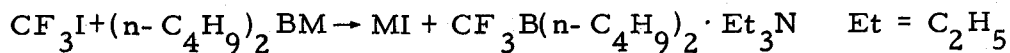
compounds (6) are known to be unstable to disproportionation upon attempted isolation. In addition, Schaad developed triethylamine as an aprotic solvent for the preparation of alkali metal di-*n*-butylborate (I).

Schmid and Nöth (34) studied the action of benzoyl chloride and thiobenzoyl chloride on alkali metal di-*n*-butylborate (I) in ether obtaining boron ketones in 55% and 30% reported yield respectively.

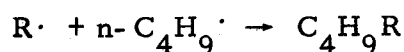
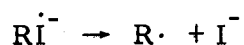
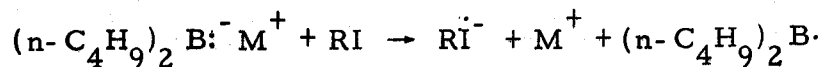


The exothermic reaction was carried out at room temperature and the authors reported a B:K ratio of 4:3 for alkali metal di-*n*-butylborate (I) although no details were given for this analysis. The product compounds were characterized by elemental analysis, cryoscopic molecular weight, infrared analysis and ^{11}B NMR. It should be noted that the ^{11}B NMR signal for the product compounds was observed to be in the same region -53 ppm (external $BF_3O(C_2H_5)_2$), as for R_2BOR and R_2BSR (-74 ppm) type compounds. Tri-*n*-butylborane was also obtained as a side product upon distillation of the product mixture from the potassium chloride residue.

In a doctoral dissertation, Self (35) prepared trifluoromethyldi-*n*-butylborane from the reaction of gaseous trifluoromethyliodide with the di-*n*-butylborate (I) anion in triethylamine in 30% reported yield.



To account for these observations, a mechanism involving a one-electron transfer from the di-n-butylborate (I) anion to the substrate was proposed followed by decomposition of the radical anion.



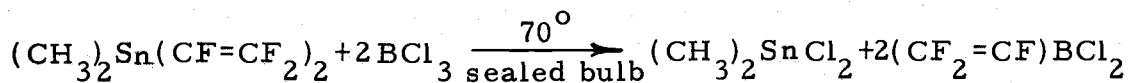
The fate of the di-n-butylboryl radical was not determined but it was thought to have reacted with the solvent to form a di-n-butylborinate derivative, $ROB(n-C_4H_9)_2$, since the ^{11}B spectra of the product mixture produced a signal at -52 ppm in the region typical of dialkylborinates.

Following the work of Self, it was originally thought that the di-n-butylborate (I) anion would serve as a useful reagent for the preparation of trifluoromethyl di-n-butylborane. Interest in perfluoromethyl and perfluoroalkyl derivatives of boron stems in part from the interesting chemistry of these and related types of perfluoroboron compounds characterized to date.

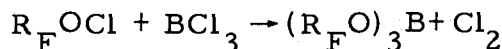
Perfluorovinylboranes, $B(CF=CF_2)_n X_{3-n}$ $X = Cl, F$; perfluoroalkylborate esters $(R_FO)_3B$; bis(dimethylamino)perfluoropropylborane,

$B[N(CH_3)_2]_2C_3F_7$ and salts of trifluoromethylfluoroboric acid, $CF_3BF_3^- X^+$ $X=K^+, Ba^{+2}, NH_4^+$ have been prepared (41, 44, 11, 12).

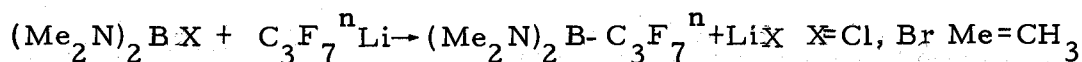
Dimethyl-bis-(perfluorovinyl)tin was used to prepare perfluorovinyl dichloroborane (41).



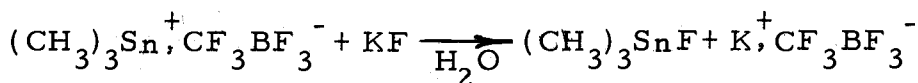
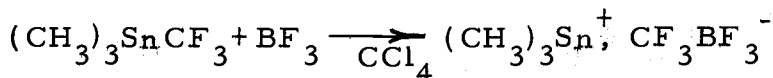
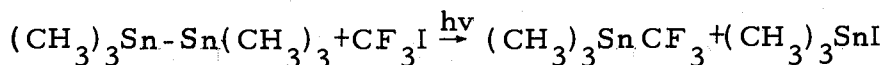
Treatment of boron trichloride with perfluoroalkyl hypochlorites gave perfluoroalkyl borate esters (44).



Bis(dimethylamino)haloboranes reacted with perfluoro-n-propyl-lithium at low temperature to produce bis(dimethylamino)perfluoropropylborane (11).

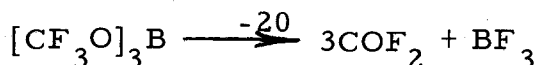
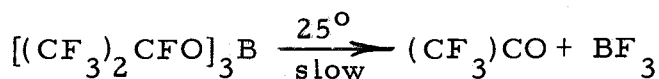


Salts of trifluoromethylfluoroborate (12) anion were synthesized starting from trifluoromethyl iodide and hexamethyldistannane

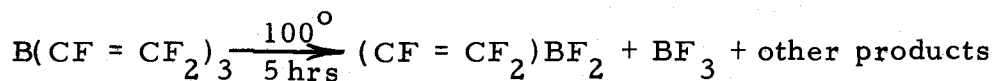


All of the above perfluoroboron compounds show varying degrees of thermal stability. Of the three known perfluoroalkyl borate esters, only one, $[(CF_3)_3CO]_3B$, is stable indefinitely at room temperature while the other two undergo an internal beta fluorine atom transfer

and formation of boron trifluoride.



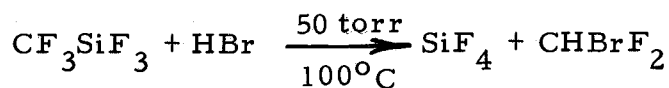
Most of the perfluorovinylboranes are unstable towards loss of boron trifluoride on storage for extended periods of time and trisperfluorovinylborane decomposes at 100° to perfluorovinylborane and boron trifluoride by an unknown mechanism.



Bis(dimethylamino)perfluoro-n-propylborane was reported to be stable to distillation at 35°C . Apparently, back π -bonding from the nitrogen atom to the empty P_z orbital on boron imparts stability to the molecule by hindering a probable internal fluorine atom transfer and hexafluoropropene elimination. Pyrolysis of the compound at 172°C produced 1H-heptafluoropropane.

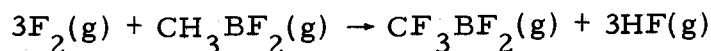
When the vacant P_z orbital on boron is satisfied by coordination, as in the tetravalent trifluoromethyl-fluoroborate anion, good thermal stability is exhibited. The potassium salt was stable in vacuo to 300°C . Above this temperature tetrafluoroethylene, perfluorocyclopropane and potassium fluoroborate are produced by difluorocarbene elimination. Depending upon the condition of the pyrolysis, the ratio of perfluorocyclopropane to perfluoroethylene could be changed. Higher pyrolysis pressure increased the amount of perfluorocyclopropane.

In contrast to the thermal stability of the trifluoromethyl-fluoroborate anion, the isoelectronic trifluoromethyl-trifluorosilane (36) eliminates difluorocarbene upon heating above 80°C. The carbene was trapped with anhydrous hydrogen bromide.



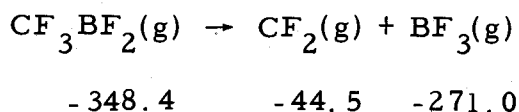
Trifluoromethyltrifluorosilane, under these conditions, has a reported half life of seven minutes. Pyrolysis of the compound, in the absence of a carbene trap, produced perfluorocyclopropane and silicon tetrafluoride by way of α -fluorine transfer from the trifluoromethyl-group and carbene elimination. Carbene expulsion is typical (29,2) of the thermal behavior of trifluoromethyl derivatives of the main group elements.

Loss of difluorocarbene is a kinetically favorable decomposition route for trifluoromethyldifluoroborane, CF_3BF_2 , and likely to occur in a manner similar to the behavior of other trifluoromethyl derivatives. However, the calculated thermodynamic stability for CF_3BF_2 is quite high. From the known bond dissociation energies (13) and heats of formation (42) for the fluorination reaction of methyldifluoroborane, the enthalpy of formation of trifluoromethyldifluoroborane is calculated to be -348 kcal/mole.

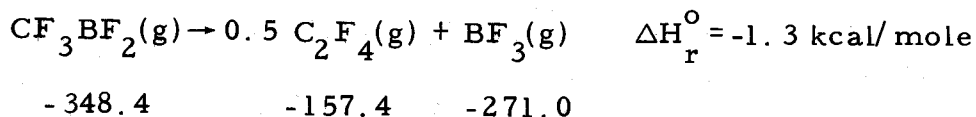
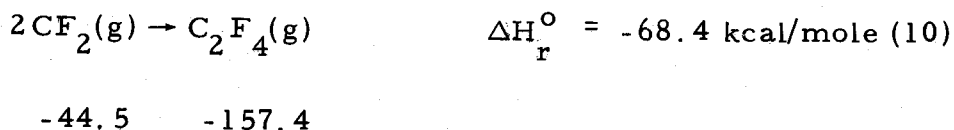


Using the known enthalpies of formation for difluorocarbene (10) and

boron trifluoride (16), the enthalpy of reaction for the elimination of difluorocarbene from trifluoromethyldifluoroborane is 32.9 kcal.

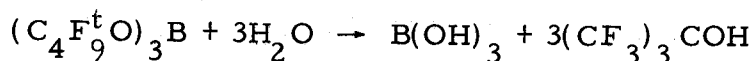


If the difluorocarbene dimerizes to tetrafluoroethylene, then the decomposition reaction becomes thermodynamically favorable.



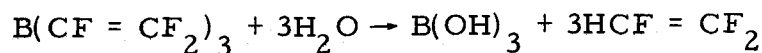
The splitting out of the very stable boron trifluoride molecule and the favorable dimerization of difluorocarbene provide the driving force for this latter reaction.

Hydrolytic stability of perfluoroboron compounds is apparently similar to the thermal stability in that when the empty p_z orbital on boron is occupied by coordination or back π -bonding from bonded groups, then the substance is stable to hydrolysis. Nonafluoro-tertbutylborate is stated to be readily hydrolyzed to nonafluoro-tertbutyl alcohol.



Tris(perfluorovinyl)borane is stable to hydrolysis at room temperature,

but quantitatively gives trifluoroethylene at elevated temperature in a sealed tube.

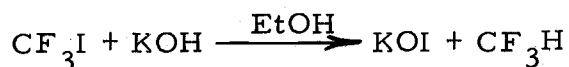


Perfluoropropylbis(dimethylamino)borane requires base for quantitative conversion to 1H-heptafluoropropane. The trifluoromethylfluoroborate anion is freely soluble in water and stable to boiling hydroxide. Only in 50% sulfuric does it decompose to yield six fluorides per original anion instead of the expected fluoroform.

Trifluoriodomethane, synthesized from silver trifluoroacetate and elemental iodine, exhibits some properties of a pseudohalogen in that heating to 250°C or exposing a sample to ultraviolet light homolytically cleaves the carbon-iodine bond producing the trifluoromethyl radical. The estimated carbon-iodine bond dissociation energy amounts to 54 kcal/mole (5). The production of trifluoromethyl radicals has been advantageously used to prepare trifluoromethyl-containing organometallic derivatives. For example, trifluoromethylmercury iodide, tris(trifluoromethyl)phosphine and trifluoromethyltrimethylstannane have been prepared from heating or photolysis of trifluoriodomethane. Trifluoromethyl radicals have been used to initiate the polymerization of olefins (22).

In contrast to the chemical behavior of methyl iodide, trifluoromethyliodomethane does not undergo heterolytic cleavage readily by

nucleophilic reagents (20). Hydroxide, amide, cyanide, ethoxide and nitrite ions fail to react with CF_3I in solvents of high dielectric strength favorable to nucleophilic substitution reactions. Alcoholic potassium hydroxide is reactive toward CF_3I , producing fluoroform, suggesting that a chemical reaction occurred at a positive iodine atom.



This reaction was explained by Emeleus (19) on the basis of a carbon-iodine bond polarity, $\delta^- \text{C}-\text{I}^{\delta+}$, which is opposite to that found in methyl iodide. Trifluoriodomethane and trimethylamine react (30) to form a donor-acceptor complex with a nitrogen iodine bond observed in the infrared spectrum of a gaseous mixture of CF_3I and $(\text{CH}_3)_3\text{N}$.

As stated previously, the original goal of this work was to prepare a trifluoromethylfluoroborane by the method of Self using alkali-metal di-n-butylborate (I) and trifluoriodomethane. Unfortunately, this method appears not to produce the desired product stable to the conditions of the experiment. In an attempt to understand the reaction of trifluoriodomethane and alkali metal di-n-butylborate (I), a fluorine 19 NMR study was undertaken. In addition to this study and many repeated attempts to reproduce Self's work, the nature of the alkali metal di-n-butylborate (I) was investigated to ascertain the element associated with the di-n-butylborate anion in alkali metal di-n-butylborate (I).

EXPERIMENTAL

Starting Materials

$(C_2H_5)_2O$: Mallinckrodt anhydrous diethyl ether was dried and stored over sodium ribbon. Prior to use, it was treated with calcium hydride and degassed followed by a final drying with the sodium ketyl of benzophenone.

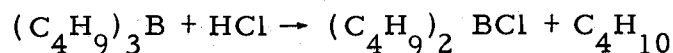
$(C_2H_5)_3N$: Eastmann triethylamine was distilled from powdered phosphorous pentoxide under dry nitrogen atmosphere. Prior to use it was dried again with calcium hydride, degassed and finally dried with sodium potassium alloy or the sodium ketyl of benzophenone. Triethylamine was shown to be pure by 1H NMR, melting point and glc on a 8 ft column of Dow-Corning QF-1(FS-1265) on 100/120 mesh Varaport 30. Separation of amines was indicated by separation of a mixture of $(i-C_3H_7)_2NH$ and $(C_2H_5)_3N$. Varaport 30 (26) is a sized chromosorb W support treated with DMDS, dimethyldichlorosilane. DC QF-1 is a siloxane polymer oil containing the 3, 3, 3 trifluoropropyl group.

NaK: Sodium potassium alloy was obtained from Mine Safety Appliances in sealed ampoules or was prepared directly by adding potassium metal to melted sodium under mineral oil (3). It was stored under nitrogen and dry n-hexane.

CF₃I: Trifluoroiodomethane was prepared by the method of Henne & Finnegan (24). It was subsequently passed through an ascarite tube prior to introduction into the vacuum line where further fractionation, to remove traces of CF₃H, produced spectroscopically pure trifluoroiodomethane.

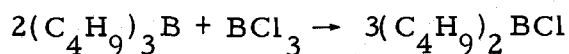
(CH₃)₃N: Matheson trimethylamine was transferred to the lower manifold on the vacuum line containing a U-tube packed with phosphorous pentoxide on glass beads. By repeated passes through the U-tube, primary and secondary amine impurities are removed (23) as shown by vapor pressure measurements at two different temperatures.

(n-C₄H₉)₂B Cl: Di-n-butylboron chloride was prepared by the method of Booth and Krauss (4). Anhydrous hydrogen chloride was bubbled through tri-n-butylborane at 110°C in an inert atmosphere of dry nitrogen until butane evolution ceased. The resulting di-n-butylboron chloride was distilled at reduced pressure through a short Vigreux column or where very pure samples were required, through a spinning band column. The material in 88% yield was stored in a tube with a J. T. Young greaseless teflon and glass stopcock.



By an alternate improved synthesis, di-n-butylboron chloride could be prepared by the method of Hennion & McCusker (25). This method involved bubbling boron trichloride through mercury into a reaction

flask containing tri-*n*-butylborane. The di-*n*-butylboron chloride was distilled out under N_2 and redistilled as before.



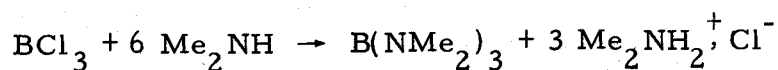
The second method gave a higher yield of product based upon tri-*n*-butylborane than the first method where butane is evolved. All boron-carbon bonds are conserved when boron trichloride and tri-*n*-butylborane undergo a redistribution reaction.

$(n-C_4H_9)_2BF$: Di-*n*-butylboron fluoride was prepared by a method similar to DeWitt (15). Di-*n*-butylboron chloride was distilled in vacuo onto freshly sublimed antimony trifluoride in a dry 100 ml round bottom flask. This operation was repeated with a fresh batch of antimony trifluoride to insure complete conversion to the fluoride compound.

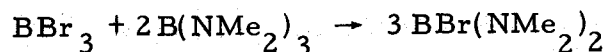
BF_3 : Boron trifluoride from a Matheson lecture bottle was purified from its benzonitrile adduct according to the procedure of Brown and Johannesen (8).

$B[N(CH_3)_2]_3$: Tris(dimethylamino)borane was prepared by a method following Skinner and Smith (38). Matheson dimethylamine was dried with potassium hydroxide, barium oxide and finally metallic potassium. 0.904 moles dry dimethylamine was transferred in vacuo to a dry 300 ml 3-neck flask containing 125 ml dry *n*-pentane. The flask was then equipped with an oil-sealed stirrer and dry nitrogen atmosphere. 138 mmoles boron trichloride, purified by fractional

distillation condensation, was added to 50 ml dry pentane in an addition funnel. The boron trichloride solution was added slowly with stirring to the dimethylamine solution at -80. The resulting mixture was allowed to warm to room temperature and the product solution was filtered from dimethylamine hydrochloride in the glove box. Removal of pentane and distillation of product through a spinning band column yielded 74 mmoles tris(dimethylamino)borane. Total yield amounted to 53% based upon boron trichloride.



B(NMe₂)₂Br: Bis(dimethylamino)bromoborane was prepared by the method of Brotherton and Steinberg et al. (7).



Boron tribromide, 36.9 mmoles, in 50 ml dry pentane was added slowly to 73.8 mmoles tris(dimethylamino)borane in 75 ml dry pentane at -50 forming a white solid which dissolved upon warming the mixture with rapid stirring to ambient temperature. Excess pentane was removed and the product distilled through a spinning band column yielding 15.1 g of material for a yield of 76.5%. The product was characterized by mass spectrometry.

Methyl Lithium: 2.5 M methyl lithium-lithium bromide complex in diethyl ether was obtained from Aldrich Chemical Company.

Experimental Results

Analysis of $(n\text{-C}_4\text{H}_9)_2\text{BCl}$: B & Cl analysis

Small samples (.6 to 1.1g) of di-n-butylboron chloride in fragile glass bulbs were crushed under aqueous sodium hydroxide containing dilute hydrogen peroxide in a semiclosed 250 ml erlenmeyer flask. After quantitative dilution, aliquots were taken for gravimetric chloride and boron analysis using the standard mannitol titration (31). The results are shown in Table I.

Table 1. Analysis of $(n\text{-C}_4\text{H}_9)_2\text{BCl}$

	1	2	3
m moles $(\text{C}_4\text{H}_9)_2\text{BCl}$	4.12	1.91	2.31
m moles boron	3.99	1.88	2.26
m moles chloride	4.18	1.93	2.32

Small samples of di-n-butylboron chloride were weighed in vacuo and quantitatively transferred to an apparatus similar to one described by Brown (9). Using this apparatus, which consisted of a 500 ml bulb and self-contained mercury monometer, the vapor pressure and molecular weight of di-n-butylboron chloride could be obtained. Excellent agreement with the reported (39) vapor pressure was obtained. The calculated molecular weight was 160.5 in good

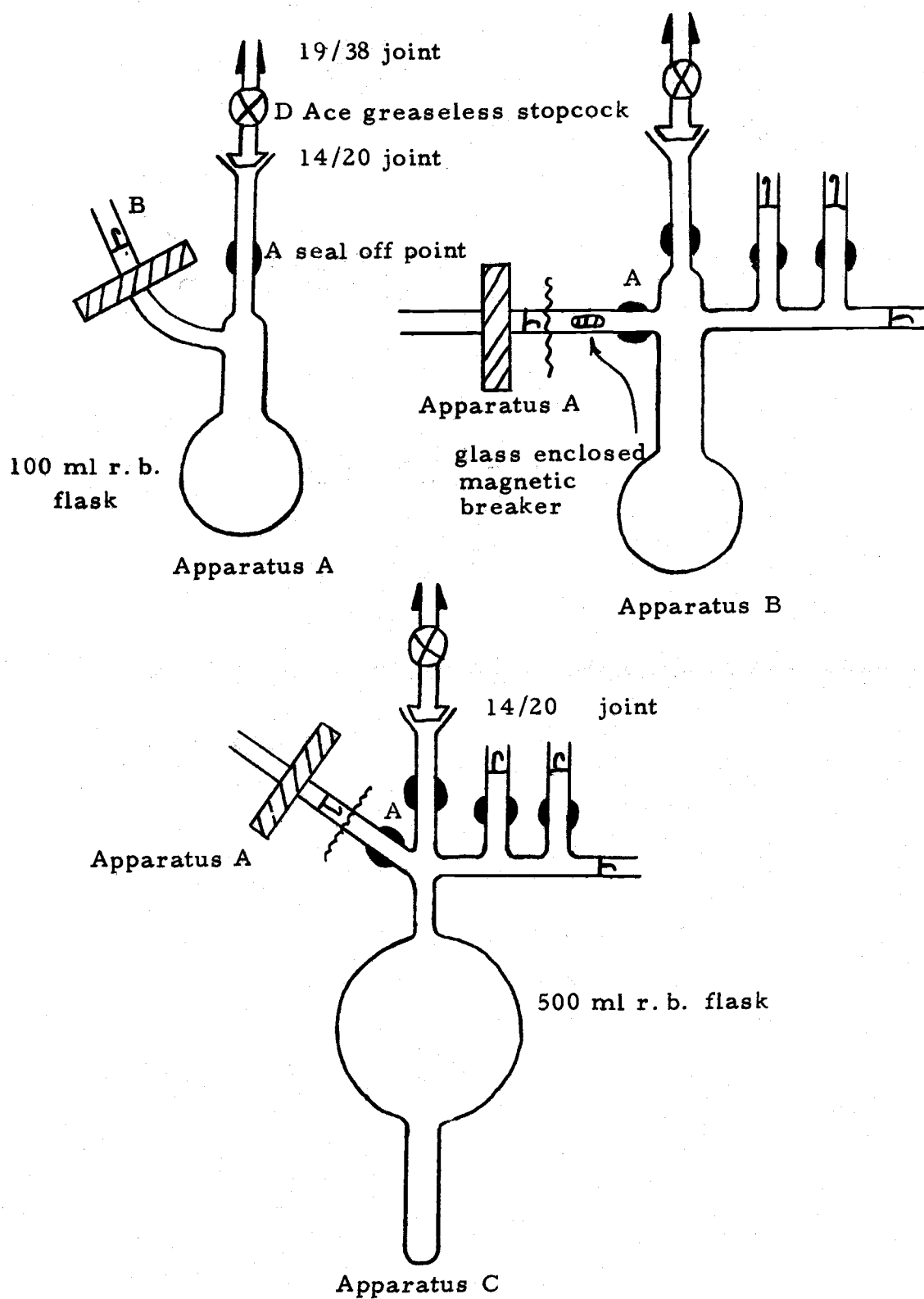
agreement with theory, 160.495.

Preparation of $\text{KB}(\text{n-C}_4\text{H}_9)_2$ in Aprotic Solvents

A typical small scale reaction in triethylamine or diethyl ether will be described (see Figure 1). Apparatus A was attached to the vacuum line by stopcock D and evacuated and dried by flaming with a torch while pumping. Then it was taken off the vacuum line and introduced into the glove box whereupon stopcock D was opened to the dry N_2 atmosphere. At this time, 3 to 5 ml of 70% NaK alloy was syringed in. Apparatus A was reattached to the vacuum line, evacuated and 10 to 20 mmoles of $(\text{n-C}_4\text{H}_9)_2\text{BCl}$ was distilled in followed by 50 ml of solvent while apparatus A was held at -196 . The apparatus was sealed off the vacuum line at point A.

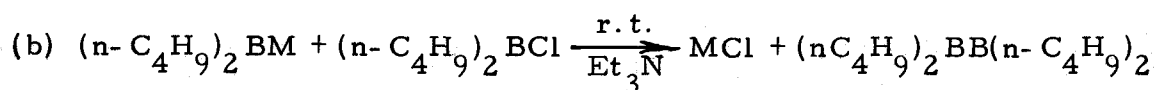
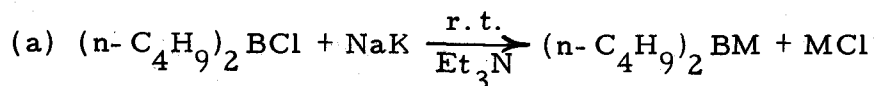
Upon warming to -80 , the $(\text{C}_4\text{H}_9)_2\text{BCl}$ dissolved in the solvent and the apparatus warmed to 0°C . If the alloy was a liquid at this temperature, the mixture immediately took on a dark blue color with the concomittant disappearance of alloy. After several hours, shiny droplets of alloy began to appear and the mixture became darker with the liquid layer becoming brown. After several days standing, the liquid layer was dark brown whereupon it was filtered into apparatus B or C for further reaction studies. Apparatus B or C was sealed off at points A after completion of filtration.

Figure 1. Experimental Apparatus



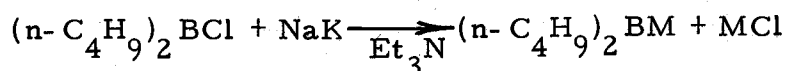
Analysis and Reaction of Alkali Metal Di-n-butylboron (I)

A study was undertaken to determine the alkali metal content of alkali metal di-n-butylborate (I) and yield of this material by OH^- , K^+ and Cl^- analysis. The following reaction scheme was carried out in apparatus similar to Figure 1.



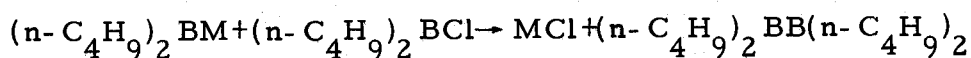
Mixture (a) was filtered and the apparatus opened for analysis of alkali halide residue and excess NaK alloy. Mixture (b) was likewise filtered and apparatus B opened for analysis of alkali halide. In the case where excess alloy was present, the mixture was treated with excess n-butanol and quantitatively extracted with water followed by titration with acid and analysis for potassium with sodium tetraphenylboron (21) on aliquot samples. Gravimetric chloride was also used. Sodium content was inferred by the difference between total alkali (OH^-), determined acidimetrically, and potassium (K^+), determined gravimetrically. The results are summarized in Tables 2, 3 and 4 (quantities stated in mmoles).

Table 2A. Reaction Sequence (a) Part 1



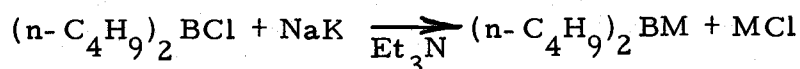
	OH ⁻	K ⁺	Na ⁺	Cl ⁻	(C ₂ H ₅) ₃ N
Original (C ₄ H ₉) ₂ BCl				12.5	143
Original alloy used	67.3	37.2	30.1		
Residue after filtration	49.3	33.1	16.2	10.6	
Filtrate (inferred by difference)	18.0	4.1	13.9		

Table 2B. Reaction Sequence (b)



	K ⁺	Cl ⁻
Added (n-C ₄ H ₉) ₂ BCl		10.3
Alkali halide ppt.	4.40	3.88
		4.14 average

Table 3. Reaction Sequence (a) Part 2



	OH ⁻	K ⁺	Na ⁺	Cl ⁻	(C ₂ H ₅) ₃ N
Original (n-C ₄ H ₉) ₂ BCl				13.5	104
Original alloy used	60.1	43.0	17.1		
Residue after filtration	38.9	35.9	3.0	11.4	
Filtrate inferred by difference	21.2	7.1	14.1		

Table 4. Summary of Results from Tables 2A, 2B and 3

	2A	2B	3
Wgt % K in alloy	55.3		71.5
%K in filtrate, (n-C ₄ H ₉) ₂ BCl basis	32.8	33.1	52.6
%Cl ⁻ in residue, (n-C ₄ H ₉) ₂ BCl basis	84.8	33.1	84.4
(C ₂ H ₅) ₃ N	143		104
%(n-C ₄ H ₉) ₂ BK, (n-C ₄ H ₉) ₂ BCl basis	32.8		52.6

Reaction of Potassium Di-n-butylborate (I) with
Trifluoroiodomethane and Boron Trifluoride,
Isolation and Identification of Products.

An attempt to reproduce the preparation of $\text{CF}_3\text{B}(\text{n-C}_4\text{H}_9)_2$ and CF_3BF_2 using Self's method (5) was made.

Potassium di-n-butylborate (I) was prepared as described earlier from 19.2 mmoles of di-n-butylboron chloride and 3.13 g NaK (70%) alloy in 24.7 g anhydrous triethylamine. The brown product solution was isolated, after several days of reaction, in a closed bulb equipped with break seals.

The bulb containing the filtered potassium di-n-butylborate (I) was attached to the vacuum line and 2.14 mmoles CF_3I was introduced at -80°C . The solution became straw yellow. Excess amine and other volatiles were removed. Trifluoroiodomethane and CF_3H were identified by I. R. analysis of the amine mixture. Trifluoromethane, 0.261 mmole, was isolated from the amine solution.

The remaining light amber material was transferred in vacuo to a 500 ml bulb equipped with break seals and 36.4 mmoles boron trifluoride was added and allowed to stand over the liquid for a few days. White solid was produced characteristic of $(\text{C}_2\text{H}_5)_3\text{NBF}_3$. The volatile materials were passed through a mercury float valve to a fractionation train on a standard stock (32) vacuum line. At this time, excess BF_3 , an unknown compound, n-butylboron difluoride and

di-n-butylboron fluoride, in order of decreasing volatility, were isolated by fractional condensation and identified by vapor pressure. The amber liquid was again treated with boron trifluoride for 18 hours and the volatile materials subsequently separated on the fractionation train. Fractions of the same volatility from the two separations were combined.

n-Butylboron difluoride gave a vapor pressure within 3% of the reported value (33) and a few ml of less volatile di-n-butylboron fluoride were obtained. The unknown compound, less than one mmole, had a vapor pressure similar to that reported by Self for CF_3BF_2 (35). However, the molecular weight by vapor density was found to be 79.0 and 81.3 in two experiments. Trifluoromethyldifluoroborane has a molecular weight of 117.8. The I. R. spectrum of the unknown compound is shown in Figure 2. Boron 10 and 11 doublets, seen in the spectrum of boron trifluoride, are absent. Instead, carbon-hydrogen bands in the 3000 cm^{-1} region and carbon-fluorine bands in the 1200 cm^{-1} region can be seen. Based upon its I. R. spectrum and molecular weight, the compound was identified as 1,1 difluorocyclopropane. The theoretical molecular weight for 1,1 difluorocyclopropane is 78.3. An additional band at 1000 cm^{-1} is characteristic of the cyclopropyl derivatives show a strong absorption between 95 and 10.0μ and this region is characterized as the most suitable region for the identification of the ring.

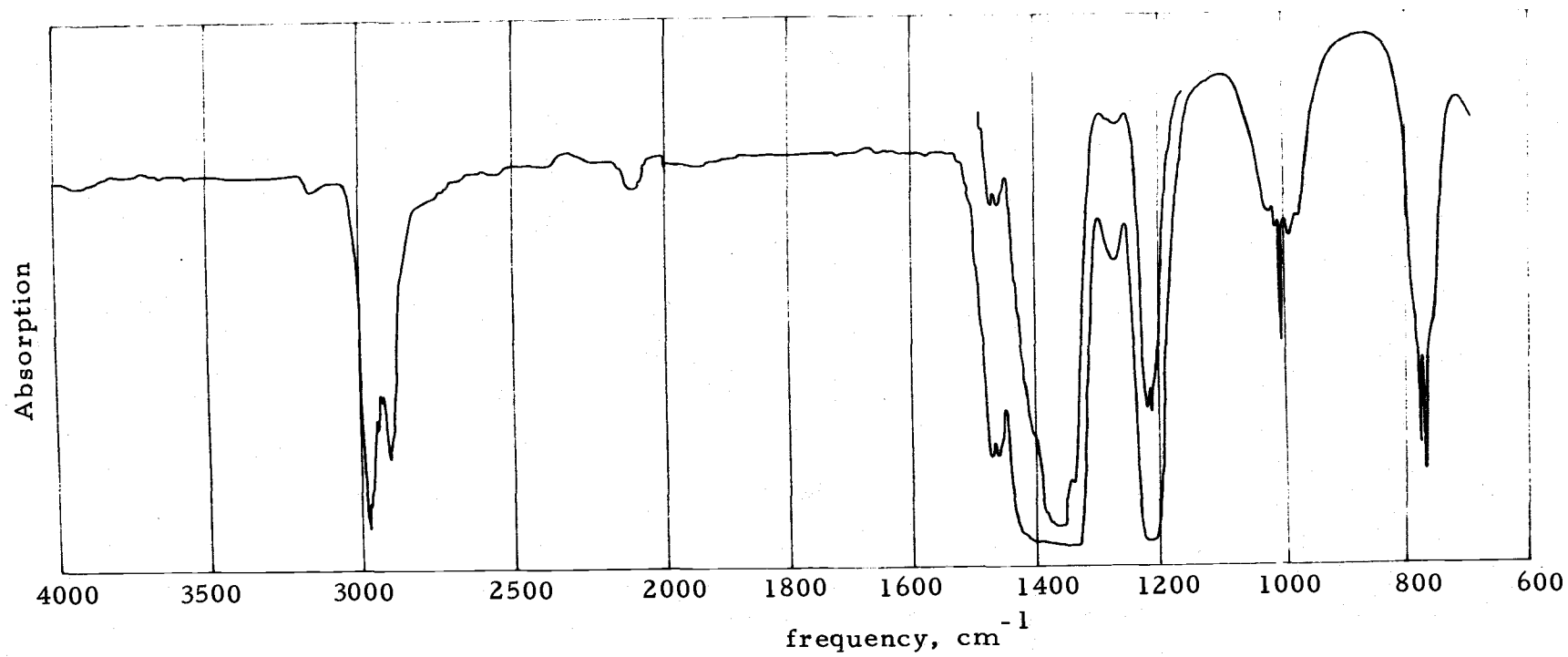
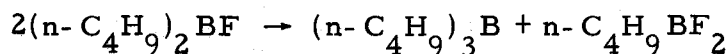


Figure 2. I.R. Spectrum of an Unknown Reaction Product.

A third addition of boron trifluoride was made to the original liquid and the volatile materials were passed through a low temperature distillation column. This column is similar in construction to one described by Shriver (37) and is sketched in Figure 3. Bands of material moved up the central column and were collected. Boron trifluoride, 1,1-difluorocyclopropane and $n\text{-C}_4\text{H}_9\text{BF}_2$ were obtained.

It was noted that the vapor pressure of the di-*n*-butylboron fluoride fraction increased with time in addition to producing a few drops of difficult to transfer non-volatile material. It is thought that di-*n*-butylboron fluoride disproportionated as follows:

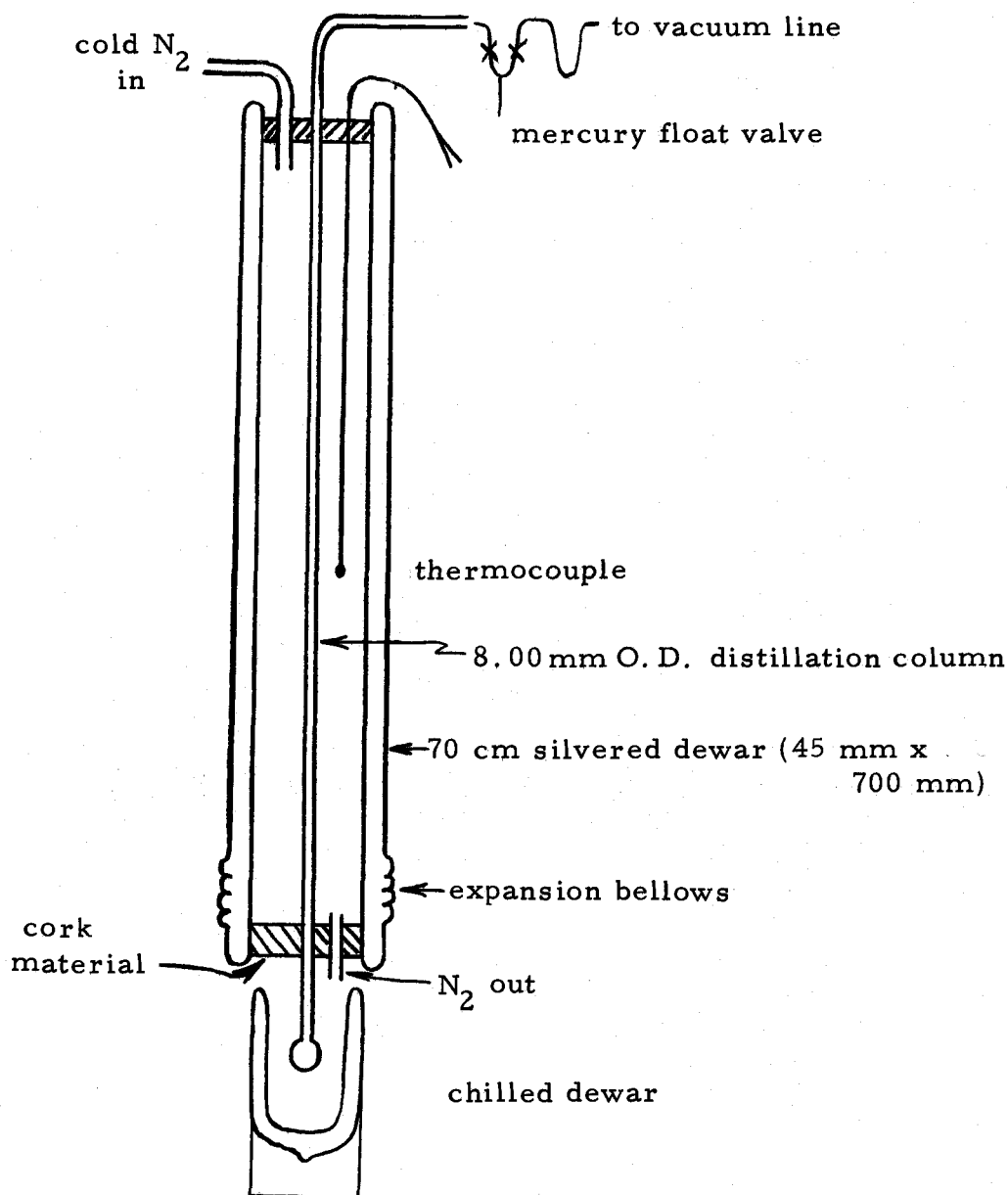


n-Butylboron difluoride has a higher vapor pressure than di-*n*-butylboron fluoride and the vapor pressure of tri-*n*-butylboron is 0.16 torr at room temperature.

Studies of the Products from the Reaction of Potassium
Di-*n*-butylborate (I) with Trifluoroiodomethane and
Subsequent Treatment with Anhydrous Hydrogen Chloride

Potassium di-*n*-butylborate (I) was prepared on a large scale under nitrogen atmosphere in a glove box. The apparatus consisted of a 250 ml 3-neck flash equipped with a by-pass dropping funnel, magnetic stirrer and condenser. Ninety-five mmoles of di-*n*-butylboron chloride, 15 ml NaK (80% K) alloy, and 125 ml anhydrous

Figure 3. Low Temperature Distillation Column



Operation: cold N_2 gas was generated by passing dry nitrogen through a copper coil immersed in liquid nitrogen. By varying the flow rate of N_2 gas using capillary tubes of different lengths, varying degrees of coldness could be produced ranging in temperature from about -30 to -130°C . A cylinder of tank nitrogen supplied gaseous N_2 .

triethylamine were held in contact with stirring for ten days. The resulting mixture was filtered in vacuo into a 15 cm long tube (4.5 cm diam.) equipped with break seals.

Thirty-three mmoles CF_3I was added to a layer of triethylamine which had been condensed on top of the solution of $(n\text{-C}_4\text{H}_9)_2\text{BK}$. The flask was held at -123 to -114 for three hours with stirring and warmed to -80 . A yellow liquid was produced plus a white semisolid which later was found to pass a medium frit. Non-condensable gas was produced also along with 5.4 mmoles CF_3H . Excess amine and CF_3I were removed. The remaining contents of the tube were transferred in the glove box to a round-bottom flask equipped with a stopcock. Periodically, anhydrous triethylamine was added to the flask with shaking and then distilled away. Excess unreacted CF_3I was removed by this treatment as indicated by the absence of CF_3I bands in the I. R. spectrum of the last triethylamine removal. The final mixture was the reaction mixture upon which further experiments were conducted.

Caprylic acid is known to cleave boron-carbon bonds (14) with the formation of borate esters and hydrocarbons. To a few ml of the reaction mixture in 40 ml of triglyme in a dry 100 ml evacuated flask was added 5 ml caprylic acid in 10 ml triglyme. The mixture was heated to $+160^\circ\text{C}$ for several hours and the volatile fractions isolated by fractional distillation condensation. Volatile fractions

all showed the absence of I. R. bands attributable to CF_3H . n-Butane was identified by I. R. spectrum and vapor pressure. Triethylamine was also identified by ^1H NMR, I. R. spectrum and vapor pressure.

Seventy-five ml of dry n-hexane was added to most of the reaction mixture producing a gelatinous precipitate containing iodide ion and a yellow solution which was filtered in the glove box into a flask equipped with break seals. Excess hexane was distilled away and anhydrous hydrogen chloride subsequently added. The hydrogen chloride treatment produced an amber liquid and n-butylboron difluoride, identified by its molecular weight by vapor density and I. R. spectrum. The resulting amber liquid was distilled in vacuo into a U-tube held at -45° . Before sealing off the U-tube, it was warmed to 0°C and the volatiles collected on the vacuum line. This produced n-butylboron difluoride, a trace amount of n-hexane as well as a fraction thought to contain di-n-butylboron chloride and fluoride.

A sample of the neat liquid distillate from the U-tube was transferred to a NMR tube in the glove box. The ^{11}B NMR probe was employed to identify four peaks. Boron trifluoride diethyletherate was used as an external reference in a sealed capillary. The peaks were identified as follows (in ppm):

- (1) -29.7 , $\text{n-C}_4\text{H}_9\text{BF}_2$ by comparison with known sample previously made and literature values: $\text{C}_2\text{H}_5\text{BF}_2$ - 28.6 by literature (18) and $(\text{n-C}_4\text{H}_9)\text{BF}_2$ - 29.0 (43).

(2) -60.2 $(n-C_4H_9)_2BF$ by comparison to the literature for

$(C_2H_5)_2BF - 59.6$ (18) and $(n-C_4H_9)_2BF - 60.0$ (43).

(3) -78.0 , $(n-C_4H_9)_2BCl$ by comparison with known neat sample previously made.

(4) -86.1 , $(n-C_4H_9)_3$ by comparison with literature values for

$B(CH_3)_3 - 86.0$, $B(C_2H_5)_3 - 86.5$, $B(C_3H_7-n)_3 - 85.0$ and

$B(n-C_4H_9)_3$ in $(C_2H_5)_2O - 86.5$ (18).

The Reaction of $(n-C_4H_9)_2BCl$ with NaK Alloy in
 $(C_2H_5)_3N$; Subsequent Treatment with CF_3I and
Glc Analysis of the Product Mixture

Potassium di-n-butyborate (I) in triethylamine was prepared, as previously described, and stored, after filtering, in a sealed bulb equipped with break seals. This preparation was made by treating 13.5 mmoles di-n-butylboron chloride with 2.09 g NaK alloy (71.5% K) in 10.5 g anhydrous triethylamine for a period of several weeks.

Gaseous CF_3I (45.2 mmoles) was then distilled into the brown filtrate contained in a 100 ml bulb equipped with break seals and a glass enclosed magnetic stir bar. Excess amine and CF_3I were removed. Non-condensable gas, presumed to be H_2 , and 2.24 mmoles CF_3H were obtained with the CF_3I treatment. The resulting viscous amber liquid was treated with excess anhydrous hydrogen chloride producing a yellow liquid and solid Et_3NHCl which was filtered off

in vacuo. The yellow product liquid was analyzed by glc and found to be a three component mixture of di-n-butylboron fluoride, di-n-butylboron chloride and tri-n-butylborane by comparison of retention times of known samples of these substances. The volatile components of the yellow liquid filtrate was also introduced into the vacuum line and separated by several repeated fractional distillations condensations, producing equal volumes of di-n-butylboron chloride and di-n-butylboron fluoride, both identified by vapor pressure.

For glc analysis, a 4 ft column of 6% DC710 silicone polymer fluid on 100 mesh Chromosorb W was used. Special provisions for obtaining dry nitrogen carrier gas stream were used. This consisted of drying the nitrogen gas with a copper column of molecular sieve 13X and employing a copper tube containing BASF catalyst-oxygen scavenger, essentially a supported copper catalyst. The gas chromatograph used was a Barber-Colman Series 5000 instrument equipped with a standard flame ionization detector and Hamilton liquid injection port. Column temperature was 122°C. Samples, both neat and in hexane solution, were stored in glass vials equipped with rubber septum for needle penetration under inert atmosphere. Samples were loaded into the septum vials from reaction containers in the glove box.

The Reaction of $(n\text{-C}_4\text{H}_9)_2\text{BK}$ with $(n\text{-C}_4\text{H}_9)_2\text{BCl}$
as Studied by Glc Analysis

Ten mmoles di-n-butylboron chloride was added to potassium di-n-butylborate (I) in triethylamine and the resulting yellow liquid was filtered in vacuo from white potassium chloride. Fifty-nine mmoles CF_3I was added and then excess amine and CF_3I removed. The resulting liquid was treated with anhydrous hydrogen chloride and filtered to remove $(\text{C}_2\text{H}_5)_3\text{NH}^+, \text{Cl}^-$. Non-condensable gas was pumped off. The product liquid was analyzed by glc techniques, as previously described, and found to contain only di-n-butylboron chloride and tri-n-butylborane.

By comparison of retention times with known samples of di-n-butylboron chloride and tri-n-butylboron, no di-n-butylboron fluoride was observed. Both neat and n-hexane solutions of boron compounds were used for glc analysis.

The Reaction of $(n\text{-C}_4\text{H}_9)_2\text{BK}$ with CF_3I in $(\text{C}_2\text{H}_5)_2\text{O}$
and $(\text{C}_2\text{H}_5)_3\text{N}$ as Studied by ^{19}F NMR

Potassium di-n-butylborate (I) in triethylamine was prepared, as described earlier, from 2.25g $(n\text{-C}_4\text{H}_9)_2\text{BCl}$ and 4 ml NaK alloy (50% K) in 50 ml anhydrous triethylamine. The boron filtrate was stored in a 100 ml bulb equipped with a J. T. Young greaseless stop-cock. This bulb was attached to a NMR tube with provisions for

evacuation and sealing off the NMR tube (see Figure 4).

After evacuation of the apparatus and flaming out to dry the equipment, the brown filtrate was poured into the NMR tube. The apparatus was then reattached to the vacuum line and triethylamine was distilled away. This series of operations was repeated to obtain a concentrated solution of $(n\text{-C}_4\text{H}_9)_2\text{BK}$ as judged by its dark color. Gaseous CF_3I was distilled into the concentrated $(n\text{-C}_4\text{H}_9)_2\text{BK}$ solution at -196 and the NMR tube was sealed off.

Upon warming to -130 , liquid CF_3I was seen to immediately decolorize the brown filtrate. The NMR tube could be tipped to further mix the reactants. Periodically, the ^{19}F NMR spectrum of the mixture was monitored and the NMR tube removed from the spectrometer and turned upside down to mix, keeping the temperature of the NMR tube at the NMR probe temperature with an appropriate slush bath. The final mixture in the NMR tube consisted of two phases, one light in color and semiviscous, the other a pale yellow liquid. These two phases made mixing difficult.

A similar experiment in diethyl ether was accomplished using 2.82 g $(\text{C}_4\text{H}_9)_2\text{BCl}$, 2.9 g 50% NaK alloy and 43.7 g anhydrous diethyl ether to prepare a solution of potassium dibutylborate (I).

The results of these experiments are summarized in Tables 5, and 6 and Figures 5 and 6.

Table 5. ^{19}F NMR of $(n\text{-C}_4\text{H}_9)_2\text{BK} - \text{CF}_3\text{I}$ Reaction Products in $(\text{C}_2\text{H}_5)_3\text{N}$ at -60°C

Time (min.)	Φ (ppm vs external CCl_3F)			
9	55.2 S	78.0 D		
21	55.2 S	78.0 D	109.7 S, B	
40	52.2 S	78.0 D	109.7 S, B	
43		78.0 D	109.7 S, B	195.9 S, B
145		78.0 D	109.7 S, B	195.9 S, B
overnight		78.0 D		

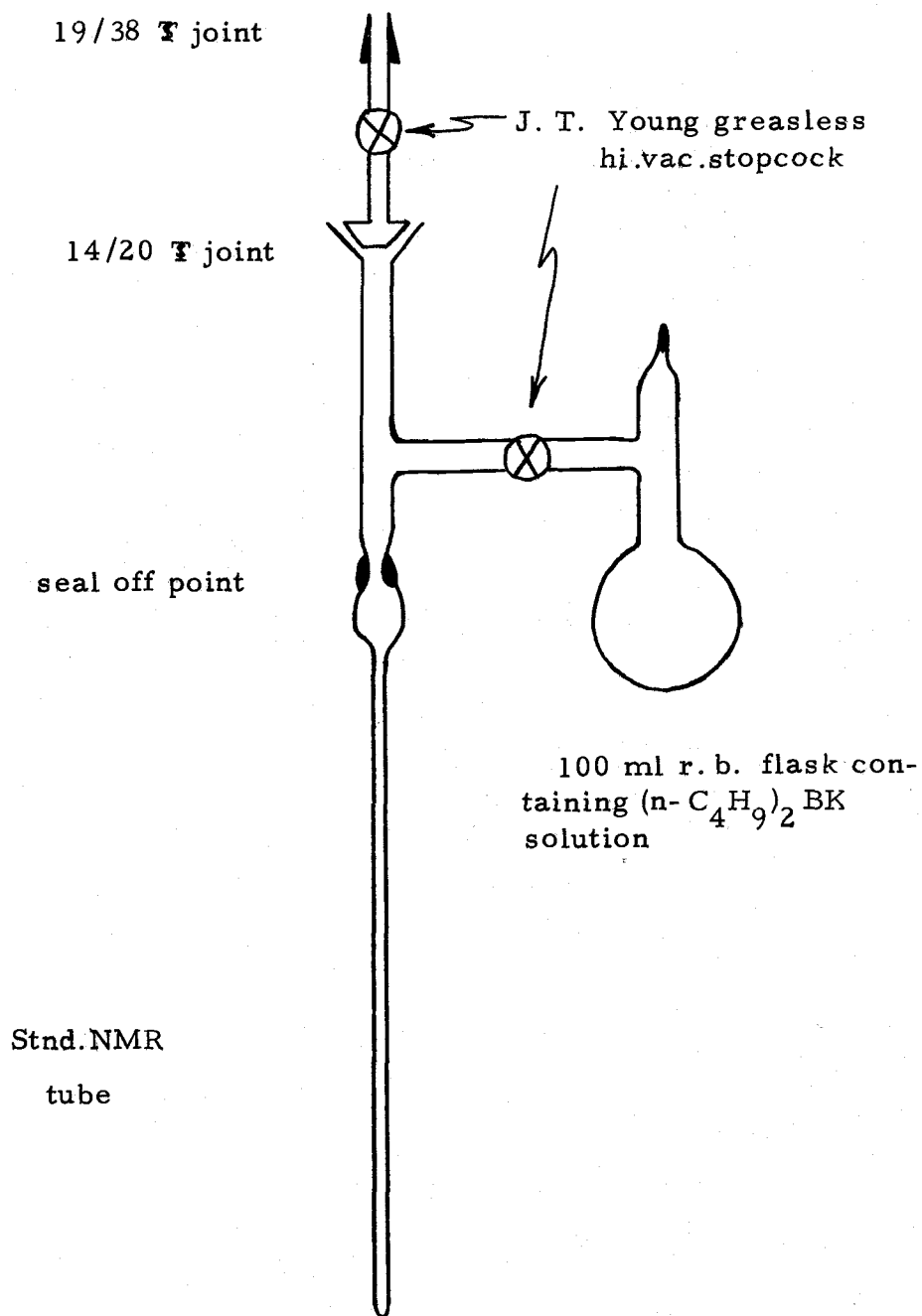
S = Singlet D = Doublet B = Broad resonance

Table 6. ^{19}F NMR of $(n\text{-C}_4\text{H}_9)_2\text{BK} - \text{CF}_3\text{I}$ Reaction Products in $(\text{C}_2\text{H}_5)_3\text{N}$ at -30°C .

Time (min)	Φ (ppm vs. external CCl_3F)			
5	53.9 S	77.9 D		
15	53.9 S	77.9 D	109.5 S, B	
75	54.0 S	77.8 D	109.5 S, B	195 S, B
101		78.0 D	110.1 S, B	195 S, B
140		78.0 D	110.1 S, B	195 S, B

S = Singlet D = Doublet B = Broad resonance

Figure 4. Apparatus for ^{19}F NMR



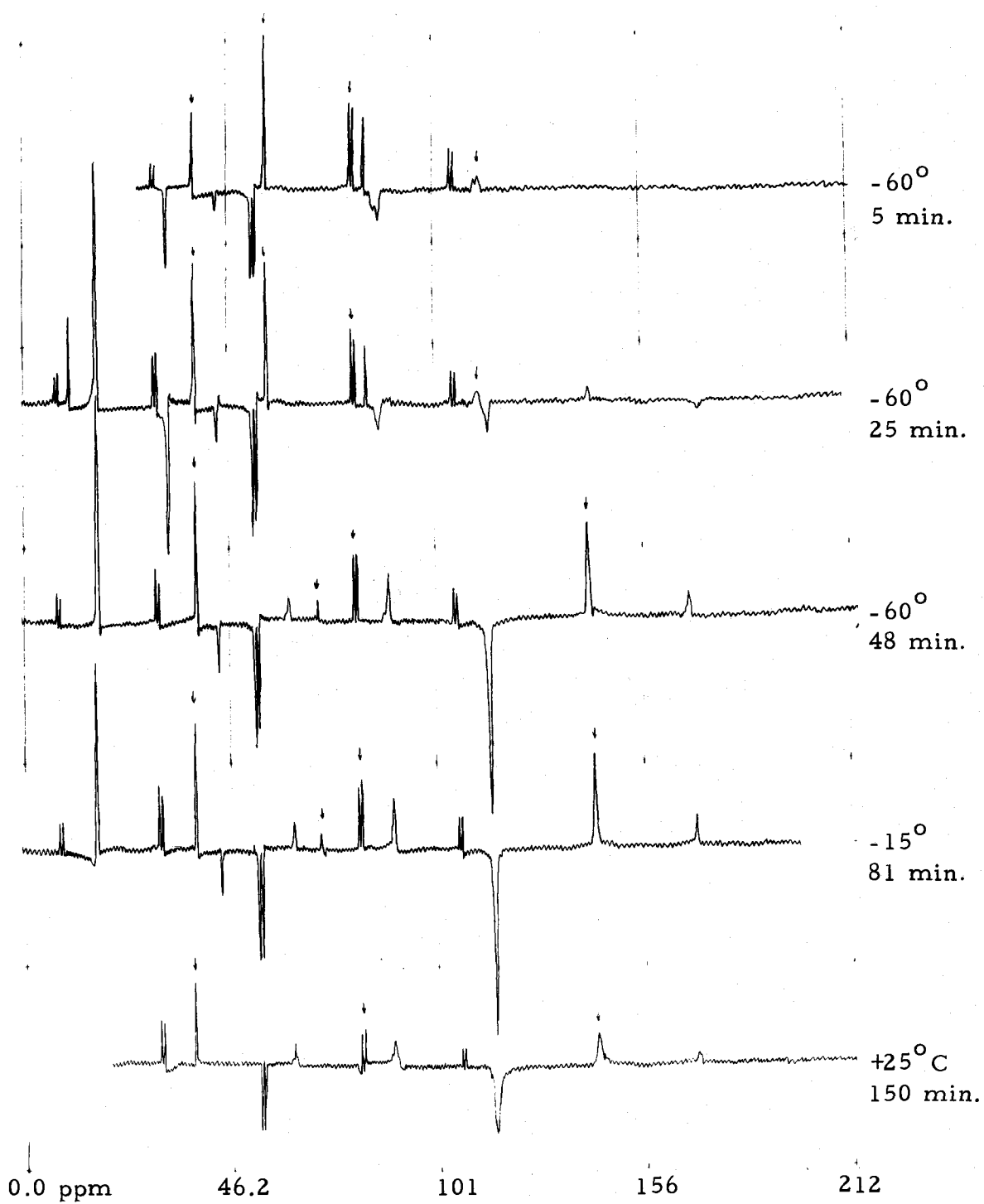


Figure 5. ^{19}F NMR of $\text{CF}_3\text{I} - \text{KB}(\text{n-C}_4\text{H}_9)_2$ in $(\text{C}_2\text{H}_5)_2\text{O}$ at -60°C.

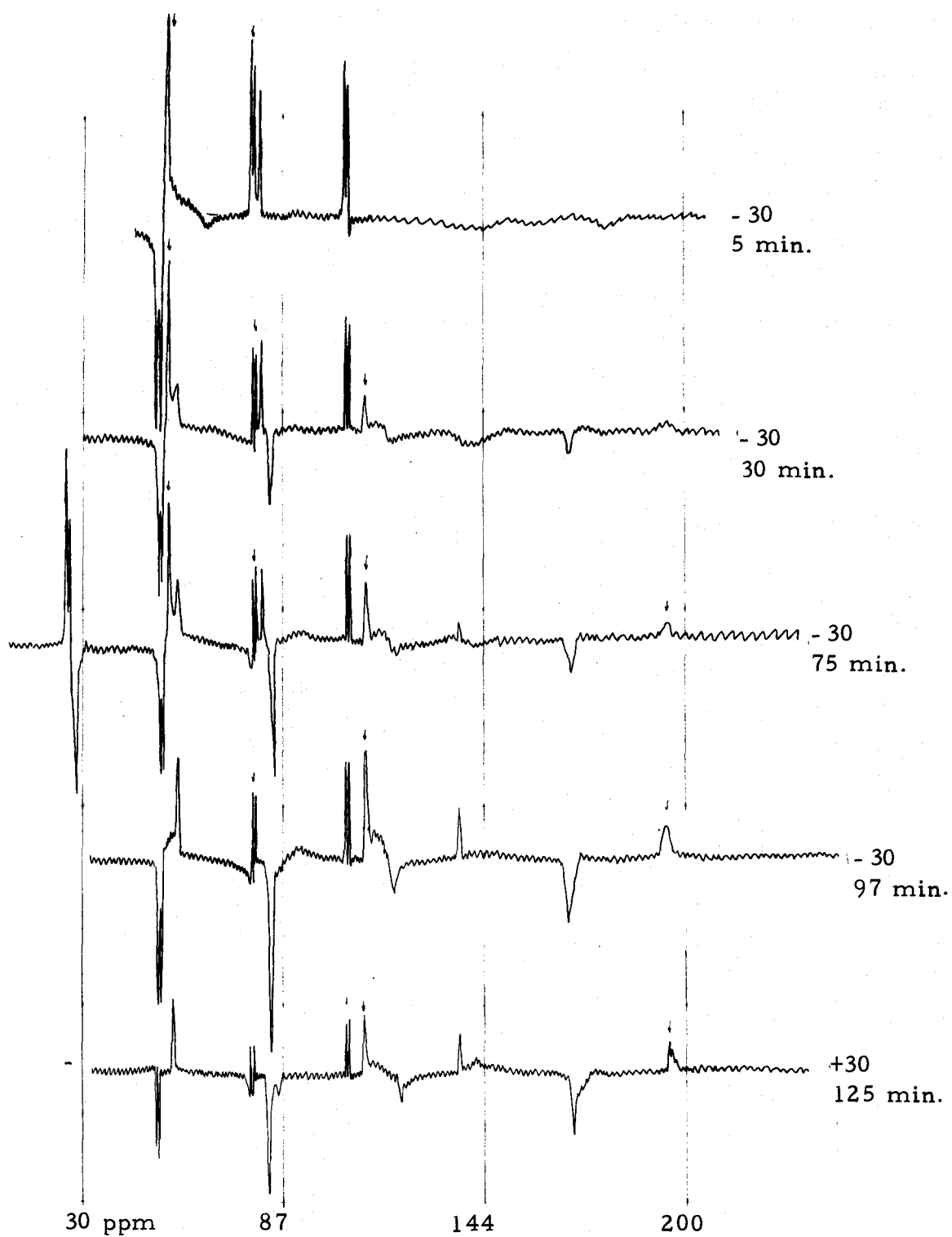


Figure 6. ^{19}F NMR of $\text{CF}_3\text{I-KB}(\text{n-C}_4\text{H}_9)_2$ in $(\text{C}_2\text{H}_5)_3\text{N}$ at -30°C .

Reaction of $[(CH_3)_2N]_2BBr$ with Perfluoro-n-propyl-lithium

In a typical experiment following the work of Chivers (11), 10.0 ml 2.5 M methyllithium-lithium bromide complex in ether was added slowly to 18.9 mmoles perfluoro-n-propyl iodide in 40 ml anhydrous diethylether at $-80^{\circ}C$. After allowing the reactants to equilibrate for 30 minutes at -80 , the mixture was allowed to warm slowly to $-50^{\circ}C$ when 18.4 mmoles bis(dimethylamino)bromoborane in 15 ml anhydrous diethyl ether was added slowly to the perfluoro-n-propyl-lithium in ether. The additions were carried out in a 3-neck r. b. 250 ml flask under a dry nitrogen atmosphere. Very little precipitate was observed when the final mixture was allowed to warm to ambient temperature. A by-pass dropping funnel was replaced by a high vacuum stopcock and the contents of the flask were transferred in small portions to the vacuum fractionation train. Careful repeated fractional distillations condensations of this ethereal mixture gave a few ml of product liquid collecting in a -45 bath. The mass spectrum of the more volatile ethereal fraction showed a parent peak 142 for methyl iodide, indicating that perfluoro-n-propyl-lithium had formed by the exchange of methyl lithium with perfluoro-n-propyl iodide. In addition, a peak in the mass spectrum at 150 indicated the presence of perfluoropropene from the probable decomposition of perfluoro-n-propyl-lithium.

The product liquid collecting in the -45 bath was hydrolyzed using 25 ml of 6N sodium hydroxide. Hydrolysis products were distilled through a -45°C trap to remove water and the material which passed this trap was subjected to mass spectroscopic examination. The mass spectrum of the material gave a peak at 45 indicative of $(\text{CH}_3)_2\text{NH}$. No peak at 170 was observed for perfluoropropane. This experiment was repeated with similar results.

A portion of the original product material collecting in the -45 bath gave a molecular weight by vapor density of 142. The mass spectrum suggested the presence of tris(dimethylamino)borane with major peaks at 99 and 143. The tris(dimethylamino)borane probably was present in the original sample of bis(dimethylamino)bromoborane.

The Reaction of Boron Trifluoride with Perfluoro-n-propyl-lithium in Diethyl Ether

Fourteen ml of 2.5 M methyllithium-lithium bromide complex was added to perfluoro-n-propyl iodide in 75 ml triethylamine at -80. Simultaneously, 26.2 mmoles of boron trifluoride triethylamine adduct was added. Upon warming a large amount of white precipitate formed. The solution was filtered and excess diethyl ether was removed by vaporization. The resulting liquid was treated with boron trifluoride for several hours. Fractionation of volatile products gave only BF_3 . The liquid was nonvolatile and probably

polymeric in composition.

The Reaction of Di-n-butylboron Chloride with
Perfluoro-n-propyl-lithium in Diethyl Ether

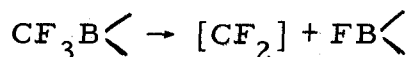
The trimethylamine adduct of di-n-butylboron chloride (23.8 mmoles) was formed directly at -80. Diethyl ether was then added as a diluent. In a three neck round bottom flask under a dry nitrogen atmosphere was placed 19.6 mmole $n\text{-C}_3\text{F}_7\text{I}$ in 50 ml anhydrous diethyl ether at -80. Ten ml of methyl lithium-lithium bromide complex was slowly added over twenty minutes. After equilibration for 30 minutes at -80, the amine adduct of di-n-butylboron chloride was added from a by-pass dropping funnel. The mixture was maintained at -25 for 4 hrs. and allowed to warm to ambient temperature over 4 additional hours. The mixture was then filtered and excess diethyl ether and volatiles were removed. Fourteen mmoles of CH_3I was shown to be present by ^1H NMR. Excess anhydrous hydrogen chloride was then added, the mixture taking up 14.9 mmoles. The resulting volatile materials were fractionated and di-n-butylboron fluoride was identified by its I. R. spectrum (3) and mass spectrum.

In another experiment, perfluoropropene, C_3F_6 was seen in the mass spectrum of the ethereal volatiles before adding anhydrous hydrogen chloride.

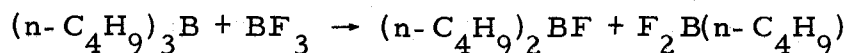
DISCUSSION

Concerning the analysis and reaction of alkali metal di-n-butylborate (I), several observations arise from Tables 2, 3 and 4. The production of $(n-C_4H_9)_2BM$ depends upon the percent potassium in the original alloy used for the reduction (compare %K in the filtrate and wgt %K in the alloy in Table 4). A higher %K in the original alloy results in a higher %K in the filtrate. Potassium di-n-butylborate (I) is active in reacting with additional di-n-butylboron chloride as the average amount of potassium chloride obtained agrees numerically with the yield of potassium in the filtrate before adding $(n-C_4H_9)_2BCl$ (compare average alkali halide in Table 2B with the potassium in the filtrate, Table 2A). Thus, the alkali metal di-n-butylborate (I) is predominately the potassium derivative. Both reductions (Table 2A and 3) appear to be incomplete by 15% with respect to the original amount of $(n-C_4H_9)_2BCl$ added and chloride produced (Table 4). This 15% is independent of the amount of triethylamine used as the solvent and is probably not due to an impurity in the solvent. The yield of potassium di-n-butylborate (I) is not quantitative, depends upon the %K in the alloy and amounts to 52.6% [$(n-C_4H_9)_2BCl$ basis] for 71.5% K alloy. The reduction of di-n-butylboron chloride to tetra-di-n-butylidiboron may occur and this latter compound may not be reduced by NaK alloy to potassium di-n-butylborate (I).

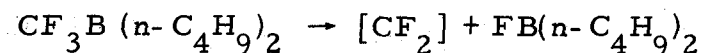
The treatment of potassium di-n-butylborate (I) with trifluoriodomethane and subsequent boron trifluoride additions resulted in the separation and identification of n-butylboron difluoride, di-n-butylboron fluoride and 1,1 difluorocyclopropane, that latter in trace amounts, with each boron trifluoride addition. One, 1 difluorocyclopropane could have resulted from a carbene elimination of a trifluoromethylboron compound. The source of ethylene to which the difluorocarbene added is unknown and presumably comes from the solvent, the only apparent source of ethyl groups.



n-Butylboron difluoride may have been the product of the reaction of boron trifluoride and tri-n-butylborane, present from the original solution of potassium dibutylborate (I). The



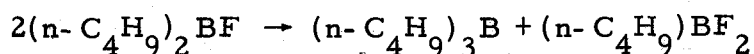
source of di-n-butylboron fluoride could have been from the reaction of boron trifluoride with tri-n-butylborane or from the decomposition by α -fluorine transfer of a trifluoromethylboron compound.



It should be noted that $(\text{n-C}_4\text{H}_9)_3\text{B}$ and BF_3 as pure compounds do not react with each other at room temperature. Thus, the more probable modes of formation of B-F compounds is from the decomposition of trifluoromethylboron compound or by group exchanges

involving a boron atom bonded to the electronegative trifluoromethyl group.

The reaction of potassium di-n-butylborate (I) with trifluoriodomethane followed by treatment with anhydrous hydrogen chloride to free boron-containing compounds from their amine adducts produced, by ^{10}B NMR and glc analysis, n-butylboron difluoride, di-n-butylboron fluoride, tri-n-butylborane and di-n-butylboron chloride, n-Butylboron difluoride may have resulted from the disproportionation of di-n-butylboron fluoride to tri-n-butylborane and n-butylboron difluoride.



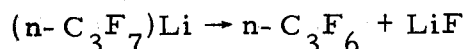
Tri-n-butylborane and di-n-butylboron chloride may have been present during the course of reaction of trifluoriodomethane and potassium di-n-butylborate (I). Since the only source of fluorine in this latter system was trifluoriodomethane, the formation of di-n-butylboron fluoride suggests that the trifluoromethyl group was not transferred intact to boron or that it subsequently decomposed to produce di-n-butylboron fluoride.

To attempt to answer this question, examination should be made of Tables 5 and 6 and Figures 5 and 6 dealing with a ^{19}F NMR study of the reaction of trifluoriodomethane with potassium dibutylboron (I) in aprotic solvents. Trifluoriodomethane in either solvent, if present in excess during the course of reaction, absorbs in the region

of 10 ppm with respect to external CFCl_3 in TMS. Trifluoromethane is identified as the peak at 79.0 ppm in either solvent occurring as a doublet with a coupling constant, J_{HCF} , equal to 80.1 Hz. This compares with the literature value of 79.0 Hz (27). Ten trifluoromethyl derivatives of the main group elements absorb in the region of 30 to 80 ppm (17). As examples, perfluorodimethylsulfide absorbs at 38.64, perfluorodimethylether at 62.0, perfluorodimethylmercury at 36.0 and tristrifluoromethylphosphine at 50.8. In Figure 5 or 6, the peak at 55 ppm in either solvent has been identified as a trifluoromethylboron derivative on the basis of chemical shift. It would appear that a trifluoromethyl-group transfer to boron has taken place but since this peak disappears with warming, decomposition occurred with the probable formation of di-n-butylboronfluoride by α -fluorine transfer. The peak at 196 ppm in triethylamine, which grows in with the concomittant disappearance of the peak at 55 ppm, has been identified as the amine adduct of di-n-butylboron fluoride. A sample of authentic di-n-butylboron fluoride in trimethylamine absorbs at 187 ppm. Similar results were obtained in diethyl ether.

The reaction of perfluoro-n-propyl iodide with methyl lithium in diethyl ether resulted in the formation of methyl iodide identified by ^1H NMR and mass spectroscopically. The appearance of perfluoropropene in the mass spectrum of the ether soluble fraction suggests that decomposition of the preformed perfluoro-n-propyl-lithium

obtained to give lithium fluoride and perfluoropropene rather than reaction with the substrate, bis(dimethylamino)bromoborane. Alternately, perfluoro-n-propylbis(dimethylamino)borane could have

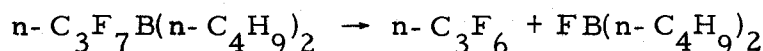


decomposed by α -fluorine transfer to produce perfluoro-n-propene and dis(dimethylamino)fluoroborane.

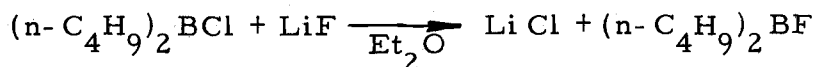
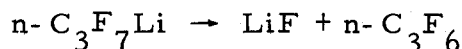


The absence of perfluoro-n-propane upon alkaline hydrolysis of the product mixture assures the absence of bis(dimethylamino)perfluoro-n-propylborane.

The reaction of preformed perfluoro-n-propyl-lithium with the amine adduct of di-n-butylboron chloride gave, upon treatment with anhydrous hydrogen chloride, di-n-butylboron fluoride. This could arise from the decomposition of perfluoro-n-propyl-di-n-butylborane to di-n-butylboron fluoride and perfluoropropene. Alternately, the preformed perfluoro-n-propyl-lithium could have decomposed upon



warming to perfluoropropene and lithium fluoride which subsequently reacted with di-n-butylboron chloride to produce the isolated product, di-n-butylboron fluoride.



Perfluoropropene was observed in the ether soluble fraction before adding anhydrous hydrogen chloride, so it would seem that decomposition of the preformed perfluoro-n-propyl-lithium has taken place in preference to the reaction of it with the substrate presented.

As studied by glc analysis of the product mixture, the reaction of tetra-n-butyldiboron with CF_3I failed to produce any fluorine containing boron compounds. The tetra-n-butyldiboron was formed from the reaction of di-n-butylboron chloride with potassium di-n-butylborate (I). Analysis of the mixture after removal of excess CF_3I gave only tri-n-butylborane and di-n-butylboron chloride. It would appear that CF_3I does not add across a boron-boron bond in the manner of the reaction of CF_3I with a tin-tin bond in hexamethyldistannane. The mixture was not photolyzed.

In conclusion, this work has demonstrated the absence of perfluoroalkyl groups bonded to boron in contrast to the work of previous authors (11, 35). While evidence was presented for the transient existence of perfluoroalkyl groups bonded to boron, they were not stable to isolation or separation from reaction mixtures. All possible precautions were taken to avoid the introduction of impurities into the various systems, such as oxygen and moisture, so one may conclude that either the presence of an unknown substance catalyzed the decomposition of perfluoroalkyl boron-bonded groups or that these groups are inherently unstable under the reaction conditions studied.

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