Title: SYNTHESIS AND PROPERTIES OF TRIFLUOROMETHYL SUBSTITUTED DIBORANES

Abstract approved: Redacted for privacy

Dr. Theran D. Parsons

The reaction of CF₃Hgl or (CF₃)₂Hg and diborane in dimethyl sulfide has been shown to give dimethylsulfide-trifluoromethylborane as a product. This is the first report of successful CF₃ exchange in which a trifluoromethyl-mercury compound is the starting material. Dimethylsulfide-trifluoromethylborane is a stable, highly polar, white solid melting at 212-214°C.

The complex is unaffected by hot concentrated acid or base and is not oxidized by hot chromic acid. Treatment of the complex with antimony pentachloride at elevated temperature failed to replace trifluoromethylborane. The high stability of the complex is attributed to the enhanced electrophilicity of the boron when bonded to a trifluoromethyl group.

The transition state for the CF₃-hydride exchange is postulated to be a bridged adduct of BH₃ and (CH₃)₃Hg or CF₃Hgl. The reactions leading to the formation of (CH₃)₃SBH₂CF₃ may be summarized...
as follows:

\[
\text{(CH}_3\text{)}_2\text{SBH}_3 \rightleftharpoons \text{(CH}_3\text{)}_2\text{S} + \text{BH}_3
\]

\[
\text{BH}_3 + (\text{CF}_3)_2\text{Hg} \rightarrow \text{H}_2\text{BCF}_3 + \text{H}_2\text{BCF}_3 + [\text{HHgCF}_3]
\]

\[
[\text{HHgCF}_3] \rightarrow \text{CF}_3\text{H} + \text{Hg}
\]

\[
\text{BH}_3 \rightarrow \text{H}_2\text{BCF}_3 + \text{H}_2 + \text{Hg}
\]

\[
\text{CF}_3\text{BH}_2 + (\text{CH}_3\text{)}_2\text{S} \rightarrow (\text{CH}_3\text{)}_2\text{SBH}_2\text{CF}_3
\]

The reaction of either CF$_3$I or CF$_3$HgI with NaBH$_4$ in diglyme has been shown to give only CF$_3$H, B$_2$H$_6$, and NaI.

Amines or ethers did not prove to be useful solvents for the reaction of CF$_3$HgI or (CF$_3$)$_2$Hg with B$_2$H$_6$. Diborane and CF$_3$HgI in diethyl ether gave predominantly (C$_2$H$_5$)$_2$OBF$_3$. 
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in charge of major

Redacted for privacy

Chairman of Department of Chemistry

Redacted for privacy

Dean of Graduate School

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The electrophilic character of trivalent boron compounds is the single most significant aspect of their chemical behavior. This electrophilic character is best understood in terms of simple valence theory. In a typical trivalent compound, BX$_3$, the B-X $\sigma$-bonding electrons are regarded as occupying three $sp^2$ hybrid orbitals, resulting in a trigonal-planar configuration of the molecule. The remaining boron orbital of principle quantum number two is substantially vacant and lies perpendicular to the plane of the molecule. The study of the properties of trivalent boron compounds is then a study of the various mechanisms by which electron density is fed into the fourth orbital of the boron, thereby imparting some extra degree of stability to the molecule.

The consequence of imparting this stability by increasing the electron density in the fourth orbital of the trivalent boron is a modification of the bonding of the boron. The basic bonding modifications are donor-acceptor dative bonding, back $\pi$-bonding, and three-center bridge bonding.

Donor-acceptor dative bonding is the result of the incorporation
of a pair of electrons from a Lewis base into the fourth boron orbital to form a coordinate covalent bond. The compounds arising from dative bond formation are the coordination compounds of boron. For a complete review of this subject see Coyle and Stone (15). The formation of coordination complexes is by far the most general method of stabilization of trivalent boron compounds. That is, this mechanism is available to almost all trivalent boron species, and it tends to override back $\pi$-bonding and three-center bond formation as alternate means of stabilization. Compounds of the type $(RO)_3B$ and $(R_2N)_3B$ are highly stabilized by the back $\pi$-bonding mode and show no tendency whatsoever to coordinate even with the strongest of Lewis bases.

The second bonding situation which can provide stability to trivalent boron compounds is the participation of non-bonding electrons of an atom bound directly to boron, in a partial $\pi$-bond incorporating the vacant $p$ orbital of the boron and a $p$ orbital of the donating atom. Compounds in which boron is $\sigma$-bonded to oxygen, nitrogen, sulfur, phosphorus, and the halogens are all stabilized to some degree by this means of charge redistribution which results from partial $\pi$-overlap of adjacent filled $p$ orbitals with the vacant $p$ orbital on the boron. The structural manifestation of partial $\pi$-character of the bonds is a shorter than normal bond length (46, p. 317).
The third category arises in the case of the compounds for which there is no intramolecular stabilization by the mechanism of back π-bonding. In this category are the hydrides and alkyls of boron. The mechanism of stabilization of the boron hydrides is the formation of the well-known three-center, or bridge bond. The structure of the bridge bonded diborane was first proposed in 1921 by Dilthey (16) and was later confirmed by the infrared studies of Price (48).

The hydrogen bridge bond is a characteristic structural unit of all the known boron hydrides. Three theoretical approaches have been advanced to explain the structures, the nature of the bonding and the bonding forces in the boron hydrides. The three approaches which have provided some measure of understanding of these compounds are: the half-bond approach of Rundle (50, 51, 52), the resonating bond approach of Pauling (46), and the three-center bond approach of Eberhardt, Crawford, and Lipscomb (18).

The half-bond theory of Rundle is essentially a valence bond approach to the structure of electron-deficient molecules. Two significant principles developed from this treatment: that (1) the underlying principle of electron-deficient bonding is the tendency to use all low lying orbitals, and (2) an element may use one orbital to bond to more than one other atom.

The application of these principles led to the proposal that
the molecule $B_2H_6$ existed as a dimer due to the formation of four boron-hydrogen half bonds.

![Diagram of B2H6 dimer](image)

The energy of the half-bonds was assumed to be somewhat more than half the bond energy of a single bond.

The conditions established for the formation of half-bonds were (50):

1. That there be two sets of atoms, one having fewer valence electrons than stable bond orbitals and the other having a deficiency of stable orbitals.
2. The bonds formed between the two different atoms must be strong covalent bonds.
3. The electronegativities of the two elements must be nearly the same.

Although the half-bond approach provided a reasonable description of diborane, no basis was established for predicting the structures of the higher boron hydrides. The theory also neglected to account for any direct boron-boron bonding even though the boron-boron distance corresponds to a bond order of about one-half.

The Pauling (46) resonating bond approach treats diborane by considering all of the valence-bond structures that can be written,
for the known geometry of diborane, using six electron pairs and the stable valence orbitals of boron and hydrogen. The twenty contributing structures are of five basic types:

This theory was well able to account for the molecular dimensions of diborane, but was rather tedious when applied to the known higher hydrides. The approach is further restricted in that it has not been developed to the point where it can be used to make predictions regarding the geometries or stabilities of new or unknown borane molecules.

The three-center bond model of the boron hydrides proposed by Eberhardt, Crawford, and Lipscomb (18) is the most generally accepted of the three models. The theory proposes the concept of a "three-center bond," which is the result of three atoms supplying three orbitals, one centered on each atom. These orbitals interact to form one bonding and two antibonding orbitals. If two electrons
are available, they will just fill the bonding orbital to form a three-center bond.

The basic assumptions of the approach are given as:

1. Only the 1s orbital of hydrogen and the four sp$^3$ orbitals of the boron are used.
2. Each external boron-hydrogen bond is regarded as a "normal," localized single bond.
3. Each boron-hydrogen-boron bridge bond is regarded as a filled three-center, localized bonding orbital.
4. The orbitals and electrons of any boron are allotted so as to satisfy first the requirements of the external boron-hydrogen single bonds and the bridge boron-hydrogen-boron bonds. The remaining orbitals and electrons are assigned to framework molecular orbitals.
5. The framework molecular orbitals are constructed from hybridized boron orbitals directed by the immediate environment of each atom. Only bonding orbitals are used, and they are completely filled with the available framework electrons.

The application of this approach provides adequate structural descriptions of the lower hydrides. The higher hydrides require a degree of electron delocalization comparable to the delocalization in benzene. Using the concepts of resonance, it is possible to
successfully extend the approach to the higher more complex hydrides. For a more comprehensive discussion of this approach, see Lipscomb (33, ch. 2).

The diborane molecule may be considered as the stabilized result of the formation of two three-center bonds from two normal boron-hydrogen bonds and two vacant orbitals contributed from two trivalent borane units. This amount of stabilization, 35.1 kcal/mole, has been determined as the gaseous dissociation energy of diborane (6).

The boron alkyls do not have available any intramolecular back \( \pi \)-bonding mechanism for stabilization nor are they observed to form stable bridge bonded dimers. Since the trimethyl-metal compounds of other group III metals form stable bridge-bonded dimers, much controversy has arisen concerning the reasons that trimethylborane does not.

In their discussion of the bridge bonded alkyls of group III, Lewis and Rundle (32) predict that the stability of the dimer will decrease as the size of the metal atom increases, due to the increase in repulsion between bridged metal atoms caused by the inner shell electrons. Their calculations show that aluminum-aluminum bonding makes a significant contribution to the stability of the dimer of trimethylaluminum. The structure of trimethylaluminum (32) shows an aluminum-aluminum distance of 2.55 Å.
which is approximately the single bond distance (46, p. 246). The reduction in the stability of the bridged dimers, as larger alkyl groups are bonded to aluminum, is explained as being caused by steric repulsions. Nowhere in their calculations did they find it necessary to invoke hyperconjugation in order to account for the observed properties or dimensions of trimethylaluminum dimer.

The stable monomeric state of trimethylborane was reasoned to be caused by trigonal hyperconjugation, according to Mulliken (41). His calculations indicate that trimethylborane could be stabilized by as much as 34 to 46 kcal/mole by hyperconjugation. This energy is much larger than that which one would expect to result from a resonance effect, particularly where the canonical structures require a high degree of charge separation.

It is more reasonable to conclude that the stability of the trimethylborane monomer results more from an even greater lack of stability of the dimer than from its own inherent stability. If one assumes, as a model for the trimethylborane dimer, the structure of the trimethylaluminum dimer with the aluminum atoms replaced by boron atoms, then it becomes apparent that the inter-boron distance necessary for accommodation of the methyl groups into the bridge will not allow the effective orbital overlap necessary for strong three-center bond formation. The long distance between the borons would eliminate any boron-boron bonding interaction.
which would favor dimer formation. In similar fashion the substitution of methyl groups for hydrogens in a diborane model also points to steric effects as being responsible for a stable monomer. It is worthy to note here that in the half-bond approach to bridge formation, Rundle (50) reasoned that if a bridging group in a borane dimer were to contribute a unidirectional orbital, such as a tetrahedral \textit{sp}^3 orbital, that steric problems and consequently poor overlap of orbitals would result.

In view of this argument it is interesting to note that alkyl groups, particularly methyl groups, do form transiently stable bridges between boron atoms (44). It becomes interesting to speculate that if bridge bond formation is a manifestation of the basic tendency of trivalent boron compounds to incorporate some electron density into the fourth predominantly vacant orbital, then the inherent acidity of the boron in its molecular environment should be reflected in its tendency to form bridge bonds.

The study, therefore, of the structure and properties of a series of trivalent boron compounds with one or more trifluoromethyl groups bonded to the boron atom would aid in the elucidation of some of the theoretical aspects of electron-deficient bonding. The highly electrophilic trifluoromethyl group would be expected to withdraw electron density from the boron atom through the boron-carbon \textit{o}-bond and at the same time contribute no means of intramolecular
stabilization via back \( \pi \) -bonding.

The first aspect of such a study would be to characterize the enhancement of the Lewis acidity of the boron resulting from the presence of a trifluoromethyl group on the boron. The relative stability of trifluoromethylborane complexes and information concerning the acid-base replacement reactions of these complexes would lead to a qualitative description of the enhancement of the Lewis acidity. This knowledge would serve as a foundation upon which one could later correlate observations concerning the relative abilities of the trifluoromethylboranes to undergo dimerization via bridge-bond formation. Also, a correlation of the information concerning the trifluoromethylborane complexes with the body of knowledge already known about boron complexes would serve to further broaden this field.

The second aspect of this study would be to observe the relative tendencies of trifluoromethylboranes to undergo dimerization via bridge-bond formation. This aspect could be expected to evaluate the effects of successively replacing the hydrides of diborane with trifluoromethyl groups. One very important observation would be whether the tendency of \( (\text{CF}_3)_3 \text{B} \) to dimerize would be great enough to counteract the steric effects which would tend to destabilize the dimer.

The third aspect of the study would be the exchange reactions
of unsymmetrically substituted trifluoromethylboranes. If one were not able to synthesize \((\text{CF}_3)_3\text{B}\) or to observe its dimer formation with trifluoromethyl groups in the bridge positions, then observations as to the ability of trifluoromethylboranes to undergo rearrangements in which a trifluoromethyl group could transiently occupy a bridge site would be of value.

**Chemistry of Trifluoromethyl-Metal Compounds**

The chemistry of trifluoromethyl compounds has been the subject of several reviews (1, 8, 29, 65). In terms of its size, a trifluoromethyl group is just slightly larger than a methyl group (8). In terms of its inductive effects within a molecule, however, it more nearly resembles a halogen. Determinations of the electronegativity of the trifluoromethyl group place it between chlorine and fluorine. Lagowski has given it the value of 3.3 on the Pauling scale (29, p. 237).

An examination of the electronegativities of the elements (46, p. 93) shows that those which form stable trifluoromethyl compounds all have electronegativities greater than 1.7. A correlation of the electronegativity difference and percent ionic character of a bond (46, p. 98) shows that the ionic character of the C-X bond in various trifluoromethyl compounds does not exceed approximately 50 percent. In the cases where the
trifluoromethyl group becomes appreciably anionic, a rearrangement to fluoride and difluorocarbene appears to be favored.

Non-metallic elements form an abundance of trifluoromethyl-substituted derivatives. As the metallic character of the elements increases, the occurrence of trifluoromethyl derivatives shows a marked decrease. The lower elements of group IV all form a single trifluoromethyl derivative. Germanium(II) iodide reacts with CF$_3$I at elevated temperatures forming CF$_3$GeI$_3$ (10). Trifluoromethyl derivatives of tin (9, 28) and lead (28) have been synthesized by subjecting a mixture of CF$_3$I and (CH$_3$)$_6$Sn$_2$ or (CH$_3$)$_6$Pb$_2$ to heat or irradiation with ultraviolet light. The only metal to display a multiple substitution of trifluoromethyl groups is mercury. Trifluoromethyl-mercury iodide has been prepared by the reaction of CF$_3$I with mercury vapor under the influence of ultraviolet light (19). Bis(trifluoromethyl)mercury has been synthesized by the reaction of CF$_3$I with cadmium amalgam (20).

Trifluoromethyl-metal compounds analogous to the alkyls of lithium, cadmium, and zinc, which are so useful in the field of organometallic synthesis, do not exist. A Grignard reagent, CF$_3$MgI, has been reported (19), but it is formed in such small amount that it is of no use synthetically (23).

Although numerous attempts have been made to prepare trifluoromethyl compounds of boron, only three actual compounds have
been reported. The attempts to react diborane and fluoroethylenes (2) resulted only in the formation of boron trifluoride and ethylboron fluorides. The reactions of bis(trifluoromethyl)mercury and boron halides (30) in each case resulted in the formation of boron trifluoride. Nuclear magnetic resonance and infrared data from the work indicated that CF$_3$-B bonds had formed, but they immediately decomposed to give BF$_3$. Mahler, in a novel approach, attempted to react BF$_3$ at 120°C with (CF$_3$)$_3$PF$_2$, a known source of difluorocarbene (35). The BF$_3$ was recovered from the reaction mixture unchanged. In view of the known stability of CF$_3$BF$_2$ (45), which one would predict as a possible reaction product, it is not surprising that at 120°C no CF$_3$-boron compound was formed. In fact, considering the reversibility of difluorocarbene formation by (CF$_3$)$_3$PF$_2$ (35),

\[
\text{(CF}_3\text{)}_3\text{PF}_2 \rightleftharpoons \text{(CF}_3\text{)}_2\text{PF}_3 + \text{CF}_2
\]

it is quite probable that at room temperature, a mixture of CF$_3$BF$_2$ and (CF$_3$)$_2$PF$_3$ would give BF$_3$ and (CF$_3$)$_3$PF$_2$.

Self (59) reported that the reaction of CF$_3$Hgl and BBr$_3$ leads to BF$_3$ with almost 100 percent conversion of the fluorine. His studies of the systems, CF$_3$Hgl/B$_2$F$_4$, (CF$_3$)$_2$Hgl/B$_2$F$_4$, and CF$_3$Hgl/Bu$_2$BCl, showed that in these cases also, BF$_3$ was the predominant product. The separation of the products of the B$_2$F$_4$ reactions gave substances which decomposed to BF$_3$ before an
identification could be made. Massey, et al. (38) reported that B$_2$Cl$_4$ and CF$_3$N=NCF$_3$ failed to give any CF$_3$-boron compound. Gritton (23), in his study of the (CF$_3$)$_2$Hg/(CH$_3$)$_2$BCl system, reported the formation of an unstable product which had a molecular weight corresponding to (CH$_3$)$_2$BCF$_3$ but decomposed to (CH$_3$)$_2$BF below room temperature.

The first synthesis of a trifluoromethyl-boron compound was reported by Parsons, et al. (45). Trifluoromethylboron difluoride, an "enduringly metastable compound," was prepared in two reactions. In the first, a compound, Bu$_2$BCF$_3$ (eventually characterized by Self (59)) produced in the reaction of Bu$_2$BK and CF$_3$I, when treated with successive portions of BF$_3$, repeatedly gave low yields of CF$_3$BF$_2$. Trifluoromethylboron difluoride is also one of the products of the reaction of CF$_3$SCI and diborane (45). Trifluoromethylboron difluoride is stable for long periods in vacuum, but exposure to air or glyptal resin and probably other catalysts causes its quantitative decomposition to BF$_3$ and (CF$_2$)$_n$. A trifluoromethylboron compound, KCF$_3$BF$_3$, prepared by Chambers, et al. (7) in the reaction of (CH$_3$)$_3$SnCF$_3$ and BF$_3$ followed by treatment with aqueous KF, shows remarkable stability, apparently due to complete utilization of all four boron orbitals.

The lack of success of several attempts to synthesize trifluoromethylboron compounds has led to the hypothesis that these compounds
are inherently unstable due to the lack of appreciable π-bonding from
the trifluoromethyl group to the fourth orbital of the boron (45). The
manifestation of this instability is the facile rearrangement of a
CF$_3$-B by means of a fluoride shift to give B-F and CF$_2$. The thesis
that the trifluoromethylboranes are unstable due to a lack of back
π-bonding is substantiated by the existence of tris(perfluorovinyl)-
borane (61) and tris(perfluorophenyl)borane (36, 37). The stability
of both compounds is attributed to π-bonding contributions from the
unsaturated system of the substituent to the fourth orbital of the boron.
The degree of π-bonding stabilization is seen in the observation that
tris(perfluorovinyl)borane is much more stable with respect to BF$_3$
formation than is perfluorovinylboron difluoride. The tris(perfluoro-
phenyl)borane is exceedingly stable. It survives heating to 270° for
several days in a vacuum. The ease of synthesis of these compounds
points to the advantages of having the lithium and magnesium com-
pounds as starting materials.

With respect to the lack of π-bonding stabilization, it is evident
that the trifluoromethyl group behaves neither as an alkyl nor as a
halogen, but more as an amplification of the "hydridic" nature of
hydrogen in the boranes. Indeed, should the synthetic problems
everually be overcome, the field of trifluoromethylboranes could
become as broad and as complex as the boranes themselves.

From this survey it is apparent that the synthesis of
trifluoromethyl-metal compounds has been accomplished only by
direct methods using CF$_3$I and the corresponding metal or a com-
 pound of that metal in a reduced state. The formation of the CF$_3$BF$_3$
anion may be a result of the transfer of a trifluoromethyl group from
tin to boron in a one-step process, or a two-step transfer of first
difluorocarbene followed by a fluoride. In the formation of CF$_3$BF$_2$
there may be CF$_3$ exchange between boron atoms or exchange of
butyl groups for fluorines. Excluding these two possibilities, there
has been no reported mutual exchange of a trifluoromethyl group and
some other group. It is a matter of conjecture as to whether this is
due to the fact that this method has been applied only to the synthesis
of proposed compounds of questionable stability, or to whether the
trifluoromethyl group is in some way forbidden to conform to the
requirements of the transition state necessary to accomplish this
exchange.

Synthesis of Organoboranes

The synthesis of organo-boron compounds is usually accom-
plished by one of two methods (4, 12, 22, 31). The first is the
reaction of a boron halide or a borate ester with an organo-metal
compound. Lithium, zinc, magnesium, mercury, cadmium, tin,
and aluminum organometallics have all been used in the synthesis
of organo-boranes. These methods of synthesis can usually be
modified to allow mono-, di-, or trisubstitution of organic groups on the boron substrate. The second, the hydroboration reaction (4), has opened up a route of synthesis which has made possible the existence of more complex alkylboranes.

The synthesis of alkyldiboranes is accomplished by several means (42). The most frequently used is the exchange reaction of trialkylboranes with diborane. Four of the five possible methyl-diboranes can be prepared by the room temperature equilibration of diborane and trimethylborane (58). The heating, under pressure, of a mixture of HCl or BF$_3$, a trialkylborane and a metal borohydride or lithium aluminum hydride gives a mixture of alkyldiboranes (34). The extent of diborane alkylation is controlled by the ratio of reactants. A mixture of tetraalkyldiboranes and 1,1-dialkyldiboranes results from the room temperature reaction of diborane and the esters of dialkyborinic acids (39). Alkyldiboranes are also reported to be the products of the alkylation of diborane using lithium (55) and gallium alkyls (57).

**Research Objectives**

Excluding the methods which have already been tried, a correlation of possible trifluoromethyl-metal starting materials with the various means of synthesizing boron-carbon bonds leaves very
few hints as the means of accomplishing the synthesis of trifluoromethyldiboranes. Reactions analogous to the hydroboration reaction and to all reactions using boron alkyls as starting materials are, of course, not possible approaches for the synthesis of trifluoromethyldiboranes.

The use of the trifluoromethyl-mercury compounds would be desirable due to the relative ease of their preparation. The reaction of $\text{CF}_3\text{HgI}$ or $(\text{CF}_3)_2\text{Hg}$ with $\text{B}_2\text{H}_6$ appears to be a route which may have some success. Diborane would probably be much less reactive than the boron halides in a reaction such as this. A factor which may definitely favor the reaction of $(\text{CF}_3)_2\text{Hg}$ and $\text{B}_2\text{H}_6$ is that the necessary product of the exchange of trifluoromethyl groups on the mercury for hydrogens would be $\text{HgH}_2$, which is unstable and decomposes to mercury and hydrogen.

Two other types of reactions also appear to have some probability of success. Haupshein et al. (24) have reported the reaction of $\text{CF}_3\text{I}$ and $\text{LiAlH}_4$ to give $\text{H}_2$ and probably $\text{LiAl(CF}_3\text{H}_2\text{I)}$. The reaction of $\text{LiBH}_4$ and $\text{CF}_3\text{I}$ should prove to be quite illuminating since the basicity of iodide is so small that a compound such as $\text{LiB(CF}_3\text{H}_2\text{I)}$ would probably break down to $\text{LiI}$ and $\text{CF}_3\text{BH}_2$. Traylor (64) has reported the reaction of mercury alkyls with $\text{LiAlH}_4$ to give alkylated lithium aluminohydrides. A reaction analogous to this using $\text{CF}_3\text{HgI}$ and $\text{LiBH}_4$ could go to yield $\text{LiI}$, $\text{Hg}$, $\text{H}_2$ and $\text{CF}_3\text{BH}_2$. 
The basic goals of this research project will be the attempted synthesis of a trifluoromethyl substituted diborane and the study of its properties. The systems to be studied will be: (1) the reaction of \((\text{CF}_3)_2\text{Hg}\) or \(\text{CF}_3\text{Hgl}\) and \(\text{B}_2\text{H}_6\), either alone or in some solvent favorable for the formation of \(\text{BH}_3\) as a reactive intermediate or for the stabilization of a possible highly unstable product; (2) the study of the reaction of \(\text{CF}_3\text{I}\) or \(\text{CF}_3\text{Hgl}\) with \(\text{LiBH}_4\) or other borohydrides.
II. EXPERIMENTAL

Apparatus and Technique

Vacuum Manipulation

A universal vacuum apparatus similar to those described by Stock (62) and Sanderson (53) was constructed and used for the manipulation of the volatile components of reaction mixtures and products. Using this vacuum apparatus, the separation of components of a volatile mixture is accomplished by a combination of fractional distillation and fractional condensation through a series of "U" tube traps (53, p. 90). This process hereafter will be referred to as a fractionation.

A fractionation relies on there being sufficient difference in the vapor pressures of the individual components in a mixture such that each component will have an appreciable volatility (nominally, five to ten mm vapor pressure is sufficient for an efficient separation) when the component of next lowest volatility is cooled to a temperature where its vapor pressure is negligible. A pressure of one-tenth mm or less is considered negligible.

In practice, a multi-component mixture is separated by allowing the condensed mixture to vaporize slowly and pass through a trap which is cooled by an appropriate low temperature bath. The passage
of the mixture through that trap achieves the isolation of one component. The remainder of the mixture is treated in a like manner until all components are isolated. This method of separation is approximately equivalent in efficiency to a simple distillation separation using a column of one theoretical plate. The constant temperature baths used for fractionations are given in Table I.

Table 1. Constant temperature baths.

<table>
<thead>
<tr>
<th>Bath</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon tetrachloride slush</td>
<td>-23</td>
</tr>
<tr>
<td>Bromobenzene slush</td>
<td>-30.7</td>
</tr>
<tr>
<td>Chlorobenzene slush</td>
<td>-45.2</td>
</tr>
<tr>
<td>Chloroform slush</td>
<td>-63.5</td>
</tr>
<tr>
<td>Carbon dioxide-acetone slush</td>
<td>-80±5</td>
</tr>
<tr>
<td>Toluene slush</td>
<td>-95</td>
</tr>
<tr>
<td>Carbon disulfide slush</td>
<td>-111.8</td>
</tr>
<tr>
<td>Ethyl bromide slush</td>
<td>-119</td>
</tr>
<tr>
<td>Methylcyclohexane slush</td>
<td>-126.4</td>
</tr>
<tr>
<td>Petroleum ether slush</td>
<td>-145±5</td>
</tr>
<tr>
<td>Isopentane slush</td>
<td>-160</td>
</tr>
<tr>
<td>Liquid oxygen</td>
<td>-183</td>
</tr>
<tr>
<td>Liquid nitrogen</td>
<td>-196</td>
</tr>
</tbody>
</table>

Reaction Apparatus

The reaction vessels used in this study were assembled from standard tapered lab-ware or, when the absence of stopcock greases was necessary, integral units were constructed utilizing breakseal-constriction combinations to allow access to and from the vacuum system. Figure 1 shows the three types of integral reaction units used.
Figure 1. Reaction apparatus.
Of the three vessels in Figure 1, Type A was most often used. The general procedure was to introduce solid reactants and a magnetic stirring bar through the open side-arm. The side-arm was then sealed off and the apparatus sealed to the line at one of the break-seal tubes. The break-seal was then broken with a glass-incased iron weight, the tube evacuated, the volatile components condensed in, and the vessel sealed off at the constriction. After completion of the reaction, the vessel was sealed back to the line, the break-seal broken, and the volatile products removed for separation and identification. For reactions utilizing large volumes of gases, the modification shown as Type B was used.

The reaction tube was modified by the addition of a filter and receiver tube (Type C) to allow the separation of an insoluble product. The reaction was set up as described previously. After completion of the reaction, all products more volatile than the solvent were removed, and the apparatus was sealed from the line at a constriction. The solution was then filtered through the sintered glass filter, and the solvent was condensed from the receiver back into the reaction tube to be used again as a wash solvent. The reaction tube and filter were separated from the receiver by sealing the constriction below the filter. The precipitate and solution were then treated separately.

The reaction apparatus assembled from standard tapered
lab-ware will be described in connection with the specific experiment where used.

**Safety Precautions**

Some of the reaction mixtures described in the following section exploded. It is recommended that the reaction vessels containing mixtures such as these be isolated behind proper shielding and handled with the proper protective equipment.

**Purity of Materials**

Generally, the vapor pressure of a substance was used as a criterion of its state of purity. A compound was considered to be pure when it exhibited a vapor pressure which coincided with the value reported in the literature for that same temperature. The agreement of vapor pressures of a given sample measured in two widely different volumes at constant temperature, or the agreement of vapor pressures of two different fractions of the same material measured at the same temperature was also used as evidence for purity. Occasionally, the purity of a material was determined by the agreement of the infrared spectrum of that material and the spectrum of a known pure sample.
Preparation of Materials

Triethylamine

Reagent triethylamine was dried over CaH$_2$ and then treated with P$_2$O$_5$, to remove primary and secondary amines. Prior to use, the triethylamine was distilled through a 24-inch long, 12 mm diameter distilling column packed with pyrex glass helices.

Diethylether

Reagent diethylether was dried over CaH$_2$ and distilled prior to use.

Tetrahydrofuran

Reagent tetrahydrofuran was dried over CaH$_2$ and then distilled from LiAlH$_4$.

Methylcyclohexane

Reagent grade methylcyclohexane was dried over CaH$_2$ and distilled as described for triethylamine.

Diglyme (Diethylene Glycol Dimethyl Ether)

Reagent diglyme was dried over CaH$_2$ and distilled from LiAlH$_4$ as described for triethylamine.
Dimethyl Sulfide

Dimethyl sulfide, supplied by Chemical Products Division, Crown Zellerback Corp., Camas, Washington, was dried over CaH$_2$ and distilled through a Nestor-Faust spinning band fractionation column. The fraction taken distilled at 38$^\circ$.

Lithium Borohydride

Lithium Borohydride supplied by Metal Hydrides Inc. was used without further purification.

Diborane

Diborane was prepared by the action of iodine on sodium borohydride as described by Freeguard and Long (21). The diborane, containing only traces of the solvent diglyme, was purified by vacuum fractionation through -127$^\circ$ into -196$^\circ$.

Triethylamine-Borane

Triethylamine-borane was prepared by the method of Schaeffer and Anderson (54). The crude material was purified by low pressure distillation through a spinning band distillation column. The fraction taken distilled at 41-42$^\circ$ under the vacuum produced by a mechanical pump.
Trifluoriodomethane

Trifluoriodomethane was prepared by the method of Henne and Finnegan (25).

Trifluoromethylmercury Iodide

Trifluoromethylmercury iodide was prepared by the method of Emeleus and Haszeldine (19) with modifications in the apparatus as described by Parsons (43). Final purification was accomplished by recrystallization from a mixture of ten percent ether in methylcyclohexane.

Bis(trifluoromethyl)mercury

Bis(trifluoromethyl)mercury was prepared by the method of Emeleus and Haszeldine (20). The procedure followed was that given by Gritton (23) with one modification. For larger quantities of materials it was found to be easier to isolate the crude product by vacuum rotary evaporation of the solvent.

Aluminum Borohydride

Aluminum borohydride was prepared by the reaction of LiBH$_4$ with AlCl$_3$ as described by Schlesinger, Brown, and Hyde (56). The product was purified by fractionation from -45$^\circ$ through -95$^\circ$ into -196$^\circ$. 
The -95° fraction, having a vapor pressure of 119 mm at 0°, was used.

Other Reagents

Boron trifluoride, hydrogen chloride, and trimethylamine were compressed cylinder gases supplied by the Matheson Company and purified by vacuum fractionation.

Common Reaction Products

Diborane

Diborane was purified by fractionation through -127° into -196°. Boron trifluoride in the sample was removed by treatment with diethylether. The purified material gave agreement with the literature citations for vapor pressure (11) and infrared spectrum (48).

Trifluoromethane

Trifluoromethane was purified by fractionation through -127° into -196°. When necessary, B$_2$H$_6$ and/or BF$_3$ were removed by treatment with triethylamine. The infrared spectrum of the material was in agreement with that given by Plyler and Benedict (47).
Hydrogen

Hydrogen was pumped into a calibrated volume from the reaction vessel through a -196\(^\circ\) trap by means of an automatic Toepler pump. In some cases recycling through a -196\(^\circ\) trap was necessary to remove entrained condensible gases. Confirmation of the purity of the hydrogen gas was accomplished by oxidation to \(H_2O\) over hot CuO.

Mercury

Mercury, when formed as a reaction product, was washed with acetone, filtered, dried quickly, and weighed in a tared container.

Reactions

Reaction of CF\(_3\)I and Borohydrides

Into a 50 ml round bottom reaction flask fitted with a 19/38 standard tapered inner joint were placed 4 ml diglyme and 0.30 g (13.7 mmoles) LiBH\(_4\). The flask was quickly attached to the line and evacuated. The flask was cooled to -196\(^\circ\) and 12.0 mmoles CF\(_3\)I condensed in. The flask was allowed to warm to -80\(^\circ\) and held there for one-half hour. The flask was then allowed to warm to room temperature. The following volatile products were separated
and identified: $\text{H}_2$, 3.0 mmoles; $\text{CF}_3\text{H}$, 4.1 mmoles; $\text{CF}_3\text{I}$, 4.9 mmoles; and $\text{B}_2\text{H}_6$, trace.

In a similar reaction, 10.0 mmoles sodium trimethoxyborohydride in 4 ml diglyme were treated with 9.7 mmoles $\text{CF}_3\text{I}$. The volatile products separated and identified were: 2.2 mmoles $\text{CF}_3\text{I}$, 4.5 mmoles $\text{CF}_3\text{H}$, and a large amount of a liquid which condensed at -80°. Vapor pressures of the material corresponded to that of pure methylborate (66). The residual diglyme solution gave a positive test for iodide.

Again, in a similar fashion, 12.0 mmoles $\text{CF}_3\text{I}$ were treated with excess aluminum borohydride in diglyme. The entire amount of $\text{CF}_3\text{I}$ was recovered unreacted.

**Reaction of $\text{CF}_3\text{HgI}$ and Borohydrides**

A reaction assembly consisting of a 30 mm diameter tube ending in a 19/38 standard tapered outer joint and a stopcock adaptor from a 19/38 inner to a 14/35 inner was charged with 6.0 g (15 mmoles) $\text{CF}_3\text{HgI}$, 0.33 g (15 mmoles) $\text{LiBH}_4$, and a few large glass beads. The assembly was attached to the line and evacuated. The apparatus was removed and the contents, under vacuum, were shaken to insure complete mixing. The tube was reattached to the line and the contents heated in an oil bath to 105° with no evidence of any reaction. At approximately the melting point of the $\text{CF}_3\text{HgI}$, the
solid turned a yellowish-grey and exploded. The solid material left coating the glass fragments was greenish grey in color.

A Type B reaction tube (Figure 1) was charged with 4.0 g (10.0 mmoles) CF$_3$HgI and evacuated on the line. Into the tube were condensed 1.2 mmoles aluminum borohydride. The contents were allowed to warm to -64°. After a few minutes the tube exploded, leaving a greenish grey solid as before.

An apparatus was assembled consisting of a 100 ml three-neck standard tapered flask fitted with a 25 ml by-pass dropping funnel and a dewar trap exit connected to the vacuum line. Into the flask were placed: 0.15 g (3.75 mmoles) NaBH$_4$, 20 ml diglyme, and a teflon-covered magnetic stirring bar. One and a half grams (3.75 mmoles) CF$_3$HgI dissolved in 15 mls diglyme were placed in the dropping funnel. The third arm of the flask was sealed with a plug and the entire apparatus evacuated. The dewar trap was maintained at -80° to prevent large amounts of solvent from distilling into the line.

The CF$_3$HgI solution was added to the stirred contents of the flask over a period of one-half hour. The reaction mixture was stirred at room temperature for 16 hours. At the end of that time, 2.88 mmoles H$_2$, 1.80 mmoles CF$_3$H, 1.76 mmoles B$_2$H$_6$, and 3.05 mmoles Hg were separated and identified.
Reaction of $\text{CF}_3\text{HgI}$ and Diborane in Ethers

A reaction apparatus (Type C, Figure 1) was assembled. Four grams (10.0 mmoles) $\text{CF}_3\text{HgI}$ were placed into the tube through the open side-arm, the side-arm was sealed off, and the apparatus was sealed to the line. The break-seal was broken and the apparatus evacuated. Approximately 5 mls THF were distilled into the tube followed by 9.8 mmoles $\text{B}_2\text{H}_6$. The tube was sealed from the line at the constriction and the contents allowed to warm to room temperature. After reacting for three days the apparatus was sealed back to the line. The volatile products were separated and identified as: 1.73 mmoles $\text{H}_2$, 4.0 mmoles $\text{CF}_3\text{H}$, 4.6 mmoles $\text{B}_2\text{H}_6$, and 8.77 mmoles $\text{Hg}$. The formation of a low temperature eutectic (49) prevented the complete separation of diborane from THF.

Evaporation of the THF left a liquid of low volatility which could be separated into two components by vacuum distillation through a 5 cm-long micro-vigreux column. The more volatile component gave negative tests for boron and iodine while the less volatile gave positive tests for both. No further examination of the system was made.

In a similar apparatus and using a procedure as described above, 10.0 mmoles $\text{CF}_3\text{HgI}$ and 14.4 mmoles $\text{B}_2\text{H}_6$ were allowed to react in 6 mls diethyl ether. Initially, on warming to room
temperature, a white gel formed. A few freezing and warming cycles were necessary to break the gel. Warming to 40° C in a water bath initiated a vigorous reaction which, on occasion, had to be moderated by cooling with liquid nitrogen. When the fizzing had stopped, an hour and a half later, there was a clear liquid containing a greenish-grey precipitate. Separation and identification of the volatile products gave 8.80 mmoles H₂, 7.5 mmoles B₂H₆, but no CF₃H.

The solvent and any less volatile materials were separated from the precipitate by filtration followed by washings with recondensed solvent. The solid was treated with several small portions of dimethyl sulfide. Filtration of the mixture gave a yellow solution and a grey powder. Evaporation of the dimethyl sulfide gave red crystals of HgI₂. The grey solid gave negative tests for boron and iodine but did react vigorously with concentrated nitric acid.

The solvent fraction was vacuum fractionated through -45° into -80°. The -80° fraction was diethyl ether contaminated by traces of a boron-containing compound. The -45° fraction was identified as a mixture of ether and boron trifluoride etherate. Attempted vacuum distillation of the remaining nonvolatile liquid resulted in its decomposition to white and yellow solids.

A scale-up of this reaction using 54.5 mmoles CF₃HgI, 16.3 mmoles B₂H₆, and several ml's diethyl ether gave the following
products: 23.2 mmoles H₂, 1.06 mmoles CF₃H, 24.4 mmoles boron trifluoride etherate, but no nonvolatile liquids. The green solid was much darker in color.

Reaction of CF₃HgI and Diborane in Triethylamine

Ten mmoles B₂H₆, 10.0 mmoles CF₃HgI, and 30 mmoles triethylamine were combined in an evacuated 100 ml round bottom flask. The mixture, with stirring, turned dark and droplets of mercury soon formed. After standing for nearly six hours, the mixture exploded. Another reaction involving the direct combination of CF₃HgI and triethylamine borane was quite vigorous giving a greenish-grey solid, but no volatile products.

Reaction of CF₃HgI and Diborane in Dimethyl Sulfide

The reaction of CF₃HgI and dimethylsulfide-borane was run several times, the results of which are given in Table 2. In a typical reaction, a Type C reaction apparatus (Figure 1) was charged with CF₃HgI and a teflon-covered stirring bar. After sealing to the line and evacuating, approximately 7-8 mls dimethyl sulfide were condensed in, followed by B₂H₆. The apparatus was sealed from the line and the contents allowed to react, with stirring, at room temperature. After a short time, droplets of mercury were visible
Table 2. CH$_3$HgI and B$_2$H$_6$ in dimethyl sulfide.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>CF$_3$HgI, mmoles</th>
<th>B$_2$H$_6$, mmoles</th>
<th>H$_2$, mmoles</th>
<th>CF$_3$H, mmoles</th>
<th>Hg, mmoles</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.0</td>
<td>10.0</td>
<td>2.2</td>
<td>0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>5.0</td>
<td>5.9</td>
<td>1.12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>5.0</td>
<td>5.7</td>
<td>3.26</td>
<td></td>
<td></td>
<td>4.72</td>
</tr>
<tr>
<td>4</td>
<td>5.0</td>
<td>5.5</td>
<td>2.36</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>10.0</td>
<td>excess</td>
<td>6.0</td>
<td>trace</td>
<td></td>
<td>BF$_3$</td>
</tr>
<tr>
<td>6</td>
<td>16.6</td>
<td>18.3</td>
<td>5.68</td>
<td>1.35</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

in the bottom of the tube along with a fluffy grey sediment. Two days to a week were usually allowed for the reaction to go to completion.

The apparatus was again sealed to the line, the CF$_3$H and H$_2$ removed, and the vessel sealed off. Repeated extraction of the solid material gave a yellow dense liquid which was very slightly soluble in the mixture of dimethyl sulfide and excess dimethylsulfide-borane.

The receiver tube was separated from the reactor by sealing the constriction. Volatile materials adhering to the solid in the reactor were removed by pumping overnight at room temperature and then for four hours at 50-60°C. The tube was removed from the line, broken open and the solids extracted with hot water. The solution fizzed vigorously for a few minutes. The slurry was filtered hot and the filtrate evaporated giving a white solid. The residue from the
water treatment was extracted with hot ethanol. Filtration, followed by evaporation of the filtrate, gave a yellow solid.

The white solid was purified by recrystallization from acetone. Several washings of the solid with ethanol and ether gave a material, melting at 199-206°. By means of this procedure, reaction number six gave 0.374 g of crude product. It was later determined by comparison of the infrared spectra that this material was identical to that produced by the reaction of \((\text{CF}_3)_2\text{Hg}\) and dimethylsulfide-borane. A more detailed description of the product will be given later.

Recrystallization of the yellow solid from ethanol gave a material melting at 154-158°. It was soluble in dimethyl formamide, acetonitrile, dimethyl sulfoxide, and KI solution. The addition of silver nitrate to the solution in DMF gave a yellow precipitate. Elemental analysis gave 46 percent iodine and 23 percent mercury. The mole ratio I/Hg was 3.2. The compound gave a negative test for boron. The compound may be a sulfonium triiodomercurate(II) such as \([\text{(CH}_3\text{)}_2\text{CF}_3\text{S}]\text{HgI}_3\). Compounds of the type \(\text{R}_3\text{SHgI}_3\) have been reported by Hoffman and Rabe (26, 27). No further characterization was made.

Reaction of \((\text{CF}_3)_2\text{Hg}\) and Diborane

A Type B reaction bulb (Figure 1) was constructed, into which were placed 2.72 g (8.0 mmoles) \((\text{CF}_3)_2\text{Hg}\). The bulb was attached
to the line, evacuated, and 19 mmoles $B_2H_6$ condensed in. The bulb was sealed at the constriction. No noticeable reaction occurred after standing 15 months at room temperature.

The reaction above was repeated utilizing 10.0 mmoles $(CF_3)_2Hg$, 20.7 mmoles $B_2H_6$, and 25 ml methylcyclohexane. After standing ten days at room temperature without any indication of a reaction having taken place, the flask was immersed in a water bath heated to 95°. After 20 hours the flask was removed and cooled to room temperature. A greenish-grey solid coated the inner surfaces of the bulb and also was suspended in the solvent. Separation and identification of the volatile products gave 12.3 mmoles $H_2$, 11.4 mmoles $B_2H_6$, and 7.8 mmoles $BF_3$.

Attempts were made to use both diethyl ether and tetrahydrofuran as reaction media, but $B_2H_6$ and $(CF_3)_2Hg$ failed to react in either.

A 100 ml round bottom reaction flask containing 5 mmoles $(CF_3)_2Hg$ and a teflon-covered magnetic stirring bar was attached to the line through a standard tapered joint and stopcock. The flask was evacuated and 30 mls triethylamine condensed in, followed by 10.0 mmoles $B_2H_6$ in small portions. The mixture was stirred for 24 hours at room temperature. The solution had turned a light rose color and a black residue containing droplets of free mercury had formed. No hydrogen was detected as a reaction product.
The excess solvent was distilled off and the nonvolatile liquid remaining was treated with excess anhydrous HCl. The rose color of the liquid vanished, and 18.6 mmoles of H$_2$ were formed. The reaction consumed 39.0 mmoles of HCl. Fractionation of the products gave 2.3 mmoles CF$_3$H and 2.93 mmoles of a compound condensing at -127$^\circ$. The vapor pressure curve and infrared spectrum of the compound agreed with the references cited for HCCIF$_2$ (3, 47). The molecular weight, determined by vapor density, was 83.4. The calculated value for HCCIF$_2$ is 86.5. The mercury formed in the reaction was 0.603 g (3.00 mmoles).

The preparation was repeated in an apparatus similar to that described for the reaction of CF$_3$HgI and NaBH$_4$ and using 20.0 mmoles triethylamine-borane and 5 ml triethylamine as a solvent. The flask was evacuated and a solution of 10.0 mmoles (CF$_3$)$_2$Hg in 15 ml triethylamine was added dropwise to the stirred solution from the by-pass dropping funnel. There was no observable evidence of a reaction. Following the removal of the excess solvent, treatment with excess BF$_3$ gave a reaction producing 4.50 mmoles H$_2$, 8.30 mmoles B$_2$H$_6$, and consuming 20.3 mmoles BF$_3$. Treatment of the residue with excess HCl produced 2.0 mmoles BF$_3$ and consumed 23.5 mmoles HCl. No information could be gained concerning the solid residue. The mercury formed by the reaction was 6.05 mmoles.
Preparation of Dimethylsulfide-Trifluoromethylborane

In a typical reaction, the \((\text{CF}_3)_2\text{Hg}\) and a magnetic stirring bar were sealed into a type A reaction vessel (Figure 1). Following evacuation, approximately 6-7 ml of dimethyl sulfide were condensed into the tube followed by \(\text{B}_2\text{H}_6\). The tube was sealed from the line and allowed to warm to room temperature. After stirring for a day, drops of mercury were visible. On the second day a heavy opaque liquid settled on top of the mercury. The reaction was stirred for three to ten days longer to insure that it had gone to completion. The tube was sealed to the line and the volatile products analyzed. A tabulation of the reactants and products is given in Table 3.

Evaporation of the solvent and excess dimethylsulfide-borane gave a heavy oily liquid, sometimes white. It was sometimes dark gray, apparently due to suspended mercury. A solid material was obtained by heating the liquid to 50-60° for approximately six hours while evacuating the tube. More dimethylsulfide-borane was distilled off in this process. The tube was removed from the line and broken open to the air. The solid was not reactive toward air. A crude white solid was obtained by dissolving the material in acetone, filtering to remove mercury, and vacuum-evaporating the solvent. A pure material, melting at 212-214° C, was obtained by recrystallization from acetone and subsequent washing with anhydrous ether.
<table>
<thead>
<tr>
<th>Experiment</th>
<th>Reactants</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(CF$_3$)$_2$Hg, mmoles</td>
<td>B$_2$H$_6$, mmoles</td>
</tr>
<tr>
<td>1</td>
<td>6.4</td>
<td>9.2</td>
</tr>
<tr>
<td>2</td>
<td>5.0</td>
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<tr>
<td>3</td>
<td>10.4</td>
<td>excess</td>
</tr>
<tr>
<td>4</td>
<td>12.5</td>
<td>15.1</td>
</tr>
<tr>
<td>5</td>
<td>6.16</td>
<td>11.3</td>
</tr>
<tr>
<td>6</td>
<td>7.88</td>
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<td>9</td>
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</tr>
<tr>
<td>10</td>
<td>8.58</td>
<td>9.3</td>
</tr>
</tbody>
</table>
The reaction using 12.5 mmoles \((\text{CF}_3)_2\text{Hg}\) and 15.1 mmoles \(\text{B}_2\text{H}_6\) was run in a very limited amount of solvent (30.2 mmoles).

The mixture fizzed gently for 24 hours and then exploded.

**Characterization of Dimethylsulfide-Trifluoromethylborane**

The determination of the molecular weight for the compound in acetone solution using a Mechrolab Vapor Pressure Osmometer Model 301 gave 155 and 157. The calculated value for \((\text{CH}_3)_2\text{SBH}_2\text{CF}_3\) is 144. Elemental analyses of the compound are given in Table 4.

<table>
<thead>
<tr>
<th>Element</th>
<th>Found</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a)</td>
<td>(b)</td>
</tr>
<tr>
<td>Carbon</td>
<td>22.22</td>
<td>21.98</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.48</td>
<td>5.32</td>
</tr>
<tr>
<td>Sulfur</td>
<td>20.33</td>
<td>19.58</td>
</tr>
<tr>
<td>Boron</td>
<td>9.27</td>
<td>7.14</td>
</tr>
<tr>
<td>Fluorine</td>
<td>39.85</td>
<td></td>
</tr>
</tbody>
</table>

\(a\) Galbraith Laboratories, Inc., Knoxville, Tennessee  
\(b\) Schwarzkopf Microanalytical Labs, Woodside, New York  
\(c\) Chemistry Department, Oregon State University, Corvallis, Oregon

The infrared spectrum from 650 to 4000 cm\(^{-1}\), using 300 mg. KBr pellets, was run on a Beckman IR-7. The sample size per pellet varied from 12 mg to approximately 0.2 mg. The major absorptions and some tentative assignments are given in Table 5. The complete spectrum is shown in Figure II.
Table 5. Major infrared absorptions of \((\text{CH}_3)_2\text{SBH}_2\text{CF}_3\).

<table>
<thead>
<tr>
<th>Frequency, cm(^{-1})</th>
<th>Intensity</th>
<th>Assignment (13)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2997</td>
<td>s</td>
<td>C-H asym. str. ((\text{CH}_3\text{-S}))</td>
</tr>
<tr>
<td>2917</td>
<td>m</td>
<td>C-H sym. str. ((\text{CH}_3\text{-S}))</td>
</tr>
<tr>
<td>2370</td>
<td>w</td>
<td>B-H str. ((\text{BH}_4\text{ or NBH}_3))</td>
</tr>
<tr>
<td>1435</td>
<td>s</td>
<td>C-H asym. def. ((\text{CH}_3\text{-S}))</td>
</tr>
<tr>
<td>1331</td>
<td>m</td>
<td>sym. def. ((\text{CH}_3\text{-S}))</td>
</tr>
<tr>
<td>1305</td>
<td>m</td>
<td>sym. def. ((\text{CH}_3\text{-S}))</td>
</tr>
<tr>
<td>1125</td>
<td>s</td>
<td>unassigned</td>
</tr>
<tr>
<td>1085</td>
<td>vs</td>
<td>&quot;</td>
</tr>
<tr>
<td>1067</td>
<td>vs</td>
<td>&quot;</td>
</tr>
<tr>
<td>1040</td>
<td>vs</td>
<td>&quot;</td>
</tr>
<tr>
<td>943</td>
<td>s</td>
<td>&quot;</td>
</tr>
<tr>
<td>768</td>
<td>m</td>
<td>&quot;</td>
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<tr>
<td>734</td>
<td>m</td>
<td>&quot;</td>
</tr>
<tr>
<td>669</td>
<td>m</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

The NMR spectrum (Figure III) for a solution of the \((\text{CH}_3)_2\text{SBH}_2\text{CF}_3\) in acetonitrile was run using a Varian A-60.

The compound was soluble in water, acetone, acetonitrile, methyl formate, dimethyl formamide, and dimethyl sulfoxide. It dissolved without reaction in 85 percent phosphoric acid, but was insoluble in 30 percent sodium hydroxide. Treatment with 100 percent sulfuric acid gave only a small amount of \(\text{SO}_2\). It failed to decolorize acidic potassium permanganate solution. Treatment with hot chromic oxide in concentrated sulfuric acid failed to give any volatile oxidation products.

Attempts to replace dimethyl sulfide with triethylamine or trimethylamine were not highly successful. Heating the compound
Figure II. The infrared spectrum of \((\text{CH}_3)_2\text{SBH}_2\text{CF}_3\).

- a) 4 mg/pellet
- b) 0.2 mg/pellet
- c) 12 mg/pellet
Figure III. The proton NMR spectrum of $\left(\text{CH}_3\right)_2\text{SBH}_2\text{CF}_3$. 
to 210° in the presence of dimethylamine gave only a trace of di-
methyl sulfide. Refluxing triethylamine in DMF at 60° for one hour
failed to replace any dimethyl sulfide from the compound. The
treatment of the compound with antimony pentachloride in vacuo
failed to give any volatile boron compounds or any evidence of de-
composition even when heated.

The compound showed no signs of decomposition when heated
to 300° in air. Heating of 0.091 g (0.63 mmoles) of the compound
in vacuo by a Bunsen burner flame produced a rapid boiling, but
only 0.16 mmoles (CH₃)₂S were observed as the only decomposition
product.
III. DISCUSSION OF RESULTS

Dimethylsulfide-trifluoromethylborane has been prepared in two reactions. It is the product of the reaction of diborane, in dimethyl sulfide solvent, with either $(\text{CF}_3)_2\text{Hg}$ or $\text{CF}_3\text{Hgl}$. The compound is a stable, highly polar white solid melting at 212-214$^\circ$. The experimental molecular weight, 155-157, compared with that calculated for $(\text{CH}_3)_2\text{SBH}_2\text{CF}_3$, 144, indicates a slight association in acetone.

The formulation of $(\text{CH}_3)_2\text{SBH}_2\text{CF}_3$ is based upon its elemental analysis and information from the IR and NMR spectra. The $\text{CH}_3$-$\text{S}$ absorption frequencies all point to preservation of the $(\text{CH}_3)_2\text{S}$ structure in the compound. The B-H stretch at 2370 cm$^{-1}$ is characteristic of $\text{R}_3\text{N-BH}_3$ or $\text{BH}^+$. The complexity of the spectrum below 1200 cm$^{-1}$ did not allow an assignment of those frequencies; however, the very strong absorptions between 1150 and 1000 cm$^{-1}$ most certainly are due in part to C-F absorptions.

The strong absorption at 2.56 ppm in the NMR is due to protons of dimethyl sulfide shifted down field from a normal 2.2-2.1 ppm. This shift is apparently caused by the deshielding arising from complex formation with the trifluoromethylborane. The pattern of the protons bonded to boron could not be identified with certainty. Possibly, the large B-H coupling constant resulted in only part of the
pattern showing in the A-60 range.

From the information obtained from the experiments it is not possible to formulate with certainty the mechanism for the formation of \((\text{CH}_3)_2\text{SBH}_2\text{CF}_3\). However, these conclusions are consistent with the experimental observations:

1. BH\(_3\) is the reacting form of the borane in equilibrium with \((\text{CH}_3)_2\text{SBH}_3\).

2. There is no reason to believe that the CF\(_3\)-hydride exchange occurs via any other transition state than a bridged dimer involving BH\(_3\) and the trifluoromethyl mercury species.
   \[
   \text{BH}_3 + \text{CF}_3\text{HgX} \rightarrow \begin{array}{c}
   \text{H}_2\text{B} \\
   \text{CF}_3
   \end{array} \begin{array}{c}
   \text{H} \\
   \text{HgX}
   \end{array}
   \]
   (where X = CF\(_3\) or I)

3. This exchange produces an unstable intermediate.
   \[
   \begin{array}{c}
   \text{H}_2\text{B} \\
   \text{CF}_3
   \end{array} \begin{array}{c}
   \text{H} \\
   \text{HgX}
   \end{array} \rightarrow \text{H}_2\text{B CF}_3 + [\text{H Hg X}]
   \]

4. The intermediate may decompose, disproportionate, or may react further with BH\(_3\).
   \[
   \text{HX} + \text{Hg} \quad \text{[H Hg X]} \quad \rightarrow \quad \text{Hg} + \text{H}_2 + \text{HgX}_2
   \]
   \[
   \text{BH}_3 \rightarrow \text{H}_2\text{BX} + \text{H}_2 + \text{Hg}
   \]
The variation in behavior of the reaction in different solvents supports the supposition that BH\textsubscript{3} is the reacting species. The equilibrium concentration of BH\textsubscript{3} in either B\textsubscript{2}H\textsubscript{6} or (C\textsubscript{2}H\textsubscript{5})\textsubscript{3}N (cases where substantially no reaction occurred) is very small. In ethers, B\textsubscript{2}H\textsubscript{6} may be in a molecular state, or dissociated into ions (5). This may be the reason for the incongruent behavior of these solvents.

The high degree of dissociation of (CH\textsubscript{3})\textsubscript{2}SBH\textsubscript{3} (14), particularly in the gas phase, establishes a significant equilibrium concentration of BH\textsubscript{3}.

The highly specific nature of the formation of (CH\textsubscript{3})\textsubscript{2}SBH\textsubscript{2}CF\textsubscript{3} is indicative of the formation of a bridged transition state rather than the initial formation of a free radical or ionic intermediate. No reaction products were observed which would indicate the more indiscriminate reactions of BH\textsubscript{2} or CF\textsubscript{3} radicals or ions.

The contrasting behavior of CF\textsubscript{3}HgI and (CF\textsubscript{3})\textsubscript{2}Hg with respect to the formation of CF\textsubscript{3}H as a by-product indicates the importance of the HHgX species as an intermediate. For the reaction of (CF\textsubscript{3})\textsubscript{3}Hg, the intermediate HHgCF\textsubscript{3} could give either CF\textsubscript{3}H and Hg or react further to produce H\textsubscript{2}BCF\textsubscript{3}, Hg, and H\textsubscript{2}. The amounts of CF\textsubscript{3}H produced in this reaction varied greatly, but in no case did the formation amount to as much as 50 percent of the initial amount of the (CF\textsubscript{3})\textsubscript{2}Hg used. This large variation may be due to subtle differences in the reaction conditions which could stabilize the
HHgCF$_3$ intermediate. In the case of the reactions of CF$_3$HgI, HHgI could not give CF$_3$H. The majority of the reactions studied, using CF$_3$HgI as a reactant, show that CF$_3$H formation is negligible. The alternate modes of reaction of HHgI are not well substantiated experimentally. Mercuric iodide or boron triiodide could be reaction products, although neither was observed. Undoubtedly, the HHgI is in some way involved in the formation of the possible dimethyltrifluoromethylsulfonium triiodomercurate(II).

The reactions involved in the formation of (CH$_3$)$_2$SBH$_2$CF$_3$

may be summarized as follows:

$$(\text{CH}_3)_2\text{SBH}_3 \rightleftharpoons (\text{CH}_3)_2\text{S} + \text{BH}_3$$

BH$_3$ + (CF$_3$)$_2$Hg $\rightarrow$ [H$_2$BCF$_3$ $\text{HgCF}_3$] $\rightarrow$ H$_2$BCF$_3$ + [HHgCF$_3$]

[H$_2$BCF$_3$ + HHgCF$_3$] $\rightarrow$ CF$_3$H + Hg

BH$_3$ $\rightarrow$ H$_2$BCF$_3$ + Hg + H$_2$

H$_2$BCF$_3$ + (CH$_3$)$_2$S $\rightarrow$ (CH$_3$)$_2$SBH$_2$CF$_3$

There is evidence to indicate that solvent stabilization of the intermediate HHgCF$_3$ is a necessary requirement of the reaction. In the reaction which resulted in an explosion, there was a solvent deficiency to such an extent that after the formation of the borane complex the excess solvent/(CF$_3$)$_2$Hg ratio was near unity. The long
induction period was required for the build-up of an appreciable concentration of the unstable intermediate which then decomposed explosively. The possibility also exists that a small localized violent decomposition of HHgCF$_3$ could initiate the decomposition of (CF$_3$)$_2$Hg in a free-radical chain explosion.

The unusually high stability of (CH$_3$)$_2$SBH$_2$CF$_3$ is manifest in several ways. It is hydrolytically and oxidatively stable. No hydrolysis products were detected when it was treated with hot concentrated acid or base, and it is recovered unreacted from boiling water. The complex did not decolorize aqueous, acid permanganate, and when treated with hot chromic acid, failed to give any volatile oxidation products.

Attempts to replace either the trifluoromethylborane with stronger Lewis acids or the dimethyl sulfide with stronger Lewis bases were largely unsuccessful. Dimethylsulfide-trifluoromethylborane was unreactive toward antimony pentachloride even when warmed, and toward amines at slightly above room temperature. Some displacement of (CH$_3$)$_2$S was observed when (CH$_3$)$_2$SBH$_2$CF$_3$ was heated to 200° with (CH$_3$)$_3$N in a sealed tube.

The reluctance of (CH$_3$)$_2$SBH$_2$CF$_3$ to undergo acid-base displacement and its hydrolytic stability indicate that there is no significant equilibrium dissociation of the complex into its acid-base components. Normally, acid-base replacement reactions take place
predominantly by an equilibrium competition (17) of two acids for one base or two bases for one acid. In a closed system the end result will be an equilibrium mixture favoring the more stable adduct. Shifting the equilibrium by removing a component can cause the complete displacement of one unit by a stronger one. At higher temperatures, which would favor the dissociation of the complex, some displacement of \((\text{CH}_3)_2S\) is accomplished.

Thermal decomposition of the complex was achieved only at a temperature higher than \(300^\circ\) and was accompanied only by the formation of a small amount of \((\text{CH}_3)_2S\). The \((\text{CH}_3)_2S\) could be either some occluded solvent or the result of the slight disproportionation of the complex to \((\text{CH}_3)_2S\) and possibly an adduct of two molecules of trifluoromethylborane and one molecule of \((\text{CH}_3)_2S\).

The high stability of \((\text{CH}_3)_2SB\text{H}_2\text{CF}_3\) is considered to be the result of the enhanced electrophilic character of the boron when it is bonded to the trifluoromethyl group. Not only does the presence of a trifluoromethyl group on the boron increase the strength of the boron-sulfur bond, but also it withdraws negative charge from the hydrogens attached to boron, reducing their hydridic character. The high resistance to electrophilic or nucleophilic attack can be caused by a mixture of steric shielding due particularly to the CF3 group and electrostatic repulsion of the incoming group by the presence of a like formal charge at its normal point of attack.
The reactions of CF$_3$Hgl and B$_2$H$_6$ in ethers show contrasting behavior. In tetrahydrofuran, the reduction product was mercury and in diethyl ether it was predominantly Hg$_2$I$_2$. In tetrahydrofuran 40 percent of the CF$_3$Hgl was converted to CF$_3$H, whereas in diethyl ether there was only two percent conversion. In tetrahydrofuran it is likely that the final state of the iodine is BI$_3$ complexed to THF. There is also the possibility that CF$_3$ or CF$_2$ in some way reacted with the THF to give the other slightly volatile product which did not contain boron. The reaction in diethyl ether in one case shows the strong tendency for CF$_3$Hgl to act as a fluorinating agent. In the situation where fluorinations do take place, BF$_3$ is the most thermodynamically stable product which can result.

Several aspects of the reaction in diethyl ether indicate that it merits further study. The fact that the production of CF$_3$H is very low and that in one reaction, only a small amount of fluorination did take place indicates that under the proper set of conditions the reaction can possibly go to give the diethyl ether complex of
trifluoromethylborane. However, in order to be able to isolate a
pure sample of the material, improved methods for the efficient
purification of small amounts of reactive, slightly volatile, liquids
must be developed.

The lack of success of the CF$_3$I-borohydride reactions is best
explained by the ease of removal of a hydride from the borohydride
anion by CF$_3$I giving BH$_3$, CF$_3$H and iodide.

NaBH$_4$ + CF$_3$I $\rightarrow$ \[ \begin{array}{c}
\text{Na}^+ \\
\text{H}^- \\
\text{BH}_3 \\
\text{I}^- \\
\text{CF}_3
\end{array} \]

\[ \rightarrow \text{NaI} + \text{CF}_3\text{H} + \frac{1}{2} \text{B}_2\text{H}_6 \]

This indicates the potential existence of a different mechanism for
the formation of LiAlH$_2$(CF$_3$I). Possibly, the use of the d orbitals
of the aluminum facilitates the replacement of two hydrogens by
CF$_3$I by means of a mechanism in which the coordination sphere of
aluminum is increased to six. Boron is incapable of increasing its
coordination sphere beyond four and, consequently, is not permitted
to undergo a similar substitution of hydrides by CF$_3$I.

The reactions of CF$_3$HgI with borohydrides were uncontrollable
except in the reaction of CF$_3$HgI and NaBH$_4$ in diglyme. This reac-
tion followed the general behavior of the CF$_3$I reaction.

The reactions of (CF$_3$)$_2$Hg and CF$_3$HgI with B$_2$H$_6$ in triethyl-
amine displayed unusual behavior. The reaction of CF$_3$HgI and
B$_2$H$_6$ in triethylamine was run in a minimum of solvent and it
exploded. This situation is similar to the explosion described previously and may have been initiated in a similar fashion.

The reaction of \((\text{CF}_3)_2\text{Hg}\) and triethylamine-borane in excess amine in one case gave a pink-colored solution and some free mercury. In another similar mixture there was no reaction whatsoever. After removing excess solvent from the pink solution, HCl was added in excess in an attempt to replace any complexed borane species. Instead of any borane displacement, the treatment produced a large amount of hydrogen, some CF\(_3\)H, and some HCCIF\(_2\). The HCCIF\(_2\) must arise from the addition of difluorocarbene to the HCl. However, it is not known whether the difluorocarbene precursor is a CF\(_3\)-boron compound, or unreacted \((\text{CF}_3)_2\text{Hg}\). The reaction of BrCCl\(_2\text{HgC}_6\text{H}_5\) with HCl is known to give HCCl\(_3\) by a dichlorocarbene addition mechanism (60). In a second reaction, BF\(_3\) was added to see if it would trap a CF\(_2\) to form CF\(_3\)BF\(_2\). In this case, the BF\(_3\) displaced the diborane from the excess triethylamine-borane.

No definite conclusions can be drawn from this study concerning the ability of the trifluoromethyl group to participate in the formation of a three-center bridge bond. The high stability of the trifluoromethylborane complex which was synthesized precluded the formation of the uncomplexed trifluoromethylborane. The prospect of the success of further studies designed to directly observe bridge-bond formation by a trifluoromethyl group is encouraging.
This is true in view of the proposal that the transition state for the formation of $\text{CH}_3_2\text{SBH}_2\text{CF}_3$ is a bridged adduct in which a trifluoromethyl group and a hydride occupy the bridge positions. Since it has been shown that a trifluoromethyl group, when bonded to a boron, does markedly increase the electrophilic nature of the boron, this study should stimulate the further search for a means of preparing trifluoromethylboranes in an uncomplexed state.

In view of the high stability of $\text{CH}_3_2\text{SBH}_2\text{CF}_3$ more work should be done in the area of producing and characterizing other complexes of trifluoromethylborane. The trimethylphosphine complex would definitely be of interest since it can be predicted that it would be even more stable than the dimethyl sulfide complex.

A far-reaching aspect of this work would be the study of trifluoromethylborane complexes in connection with the current studies of highly stable polymer systems. A polymer consisting of

\[
\begin{array}{c}
\text{CH}_3 \\
\text{S} \\
\text{H} \\
\text{n}
\end{array}
\quad \begin{array}{c}
\text{CF}_3 \\
\text{B} \\
\text{H}
\end{array}
\]

as a basic unit may prove to have a stability comparable to that of teflon. One could use not only boron-sulfur, but also boron-nitrogen or boron-phosphorus repeating units as the backbone in similar polymeric structures. One possible route to these polymers would be
the formation of trifluoromethylborane complexes of $\text{CH}_3\text{SH}$, $(\text{CH}_3)_2\text{PH}$, or $(\text{CH}_3)_2\text{NH}$. These complexes would be expected to readily undergo elimination of hydrogen to give the polymeric structures.
IV. SUMMARY

The reaction of CF$_3$HgI or (CF$_3$)$_2$Hg and diborane in dimethyl sulfide has been shown to give dimethylsulfide-trifluoromethylborane as a product. This is the first report of successful CF$_3$ exchange in which a trifluoromethyl-mercury compound is the starting material. Dimethylsulfide-trifluoromethylborane is a stable, highly polar, white solid melting at 212-214$^\circ$.

The complex is unaffected by hot concentrated acid or base and is not oxidized by hot chromic acid. Treatment of the complex with antimony pentachloride at elevated temperature failed to replace trifluoromethylborane. The high stability of the complex is attributed to the enhanced electrophilicity of the boron when bonded to a tri- fluoromethyl group.

The transition state for the CF$_3$-hydride exchange is postulated to be a bridged adduct of BH$_3$ and (CH$_3$)$_2$Hg or CF$_3$HgI. The reactions leading to the formation of (CH$_3$)$_2$SBH$_2$CF$_3$ may be summarized as follows:

\[
(CH_3)_2SBH_3 \leftrightarrow (CH_3)_2S + BH_3
\]

\[
BH_3 + (CF_3)_2Hg \rightarrow H_2B\overset{H}{\cdot}HgCF_3 \rightarrow H_2BCF_3 + [HHgCF_3]
\]
The reaction of either CF$_3$I or CF$_3$HgI with NaBH$_4$ in diglyme has been shown to give only CF$_3$H, B$_2$H$_6$, and NaI.

Amines or ethers did not prove to be useful solvents for the reaction of CF$_3$HgI or (CF$_3$)$_2$Hg with B$_2$H$_6$. Diborane and CF$_3$HgI in diethyl ether gave predominantly (C$_2$H$_5$)$_2$C:B$_3$F$_3$. 
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