the proton nmr spectrum, (a) is assigned to methyl protons which are split into a doublet of intensity six by ^{31}P; (b) arises from the BH_3 protons which are split by ^{11}B into a 1:1:1:1 quartet, each member of which is further split into a doublet by ^{31}P. The fine structure (c) is due to ^{10}B. The ^{11}B nmr spectrum of I consists of two overlapping quartets created by a similarity in the B–P and B–H coupling constants. The infrared spectrum of I compares favorably to the structurally related compounds $Na(CH_3)_2N(BH_3)_2$[7] and $KH_2P(BH_3)_2$.[8]

The thermal and hydrolytic stabilities of I are similar to those reported for $KH_2P(BH_3)_2$.[8,9] Attempts to prepare μ-dimethylphosphinodiborane from I and either polyphosphoric acid or hydrogen chloride failed. The compound $Na(CH_3)_2N(BH_3)_2$ has been shown to react with diborane in monoglyme to form μ-dimethylaminodiborane and sodium heptahydrodiborate (eq 4).[10] Treatment of I with diborane results only in recovery of the starting materials. The deuterium exchange of I

$$Na(CH_3)_2N(BH_3)_2 + B_2H_6 \longrightarrow \mu\text{-}(CH_3)_2NB_2H_5 + NaB_2H_7 \quad (4)$$

with B_2D_6 may possibly be explained by a process similar to eq 4. In this case (eq 5) the equilibrium may lie well to the left, while in the case of the nitrogen compounds, product formation is favored, perhaps owing to

$$Li(CH_3)_2P(BH_3)_2 + B_2H_6 \rightleftharpoons \mu\text{-}(CH_3)_2PB_2H_5 + LiB_2H_7 \quad (5)$$

steric effects. The possibility that deuterium exchange results from interchange of borane groups (eq 6) is unlikely in the light of the stability of I in aqueous solution for extended periods of time.

$$Li(CH_3)_2P(BH_3)_2 \rightleftharpoons Li(CH_3)_2PBH_3 + 0.5B_2H_6 \quad (6)$$

Acknowledgment.—Support for this work was provided by the National Aeronautics and Space Administration in the form of a traineeship held by L. D. S. and by a grant from the National Science Foundation. The authors gratefully acknowledge this support.

[7] P. C. Keller, data to be submitted for publication.

[8] J. W. Gilje, K. W. Morse, and R. W. Parry, *Inorg. Chem.*, **6**, 1761 (1967).

[9] N. R. Thompson, *J. Chem. Soc.*, 6290 (1965).

[10] P. C. Keller, *Chem. Commun.*, 1465 (1969).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CENTRAL WASHINGTON STATE COLLEGE,
ELLENSBURG, WASHINGTON 98926

Trifluoromethylsulfur Trifluoride Adducts. Adducts with Phosphorus Pentafluoride, Boron Trifluoride, Arsenic Pentafluoride, and Antimony Pentafluoride

BY M. KRAMAR AND L. C. DUNCAN*

Received August 13, 1970

Trifluoromethylsulfur trifluoride was first reported by Tyczkowski and Bigelow in 1953.[1] More recently Sheppard has reported a convenient general preparative route to the monosubstituted derivatives of SF_4 through fluorination of the respective disulfides.[2] He suggested, in that report, that the chemistry of the monosubstituted derivatives is similar to that of SF_4.

In the present work the reactions of CF_3SF_3 with PF_5, BF_3,[3] AsF_5, and SbF_5 were investigated and in each case the 1:1 adduct was prepared and isolated. The Infrared spectra of the solids $CF_3SF_3\cdot BF_3$, $CF_3SF_3\cdot AsF_5$, and $CF_3SF_3\cdot SbF_5$ are interpreted to indicate that they are ionic of the type $CF_3SF_2^+MF_{n+1}^-$ where MF_n represents the acceptor used. This fluoronium[4] type structure has been reported for a number of adducts involving SF_4[5] or other fluoride donors[6,7] with acceptors such as BF_3, AsF_5, and SbF_5.

Experimental Section

Materials.—Phosphorus pentafluoride (Matheson), boron trifluoride (J. T. Baker), and arsenic pentafluoride (Ozark Mahoning) were used directly from the cylinders. Antimony pentafluoride (Ozark Mahoning) was transferred to a glass container from the stock received, pumped down until rapid gas evolution ceased, distilled at atmospheric pressure, and then vacuum transferred to the reaction vessel. Trifluoromethylsulfur trifluoride was prepared and isolated using the procedure given in a previous communication.[3] All CF_3SF_3 samples were checked for the presence of SF_4 before use.

Apparatus.—The volatile materials were manipulated in a glass–metal vacuum system. All joints and stopcocks were lubricated with Halocarbon 25-5S grease. The $CF_3SF_3\cdot BF_3$ preparation and dissociation pressure measurements were carried out in a 110-ml Monel–steel system equipped with a Heise Monel Bourdon tube absolute vacuum gauge. Pressure measurements were reproducible to ±1 Torr. The metal system was connected to the glass vacuum line through a Monel needle valve.

Infrared Spectra.—Infrared spectra were studied using a Perkin-Elmer Model 521 spectrometer. Gaseous samples were investigated in a 10-cm glass cell fitted with sodium chloride windows. Spectra of the solid $CF_3SF_3\cdot BF_3$ and $CF_3SF_3\cdot AsF_5$ adducts were obtained by examination of films deposited on a liquid nitrogen-cooled KBr support. This support window was positioned within a glass cell capped with KBr windows. The films were prepared by subliming the adducts directly onto the cold support. The $CF_3SF_3\cdot SbF_5$ spectra were obtained at ambient temperature by studying a layer of powdered adduct between KBr plates. Sample plates were prepared in a drybox and the window edges were liberally coated with Halocarbon grease before exposure to the atmosphere. The samples remained colorless during the studies.

Preparation.—The $CF_3SF_3\cdot PF_5$, $CF_3SF_3\cdot BF_3$, and $CF_3SF_3\cdot AsF_5$ adducts were prepared by direct combination of the reagents. Trifluoromethylsulfur trifluoride and an excess of the respective acceptor were transferred to a reactor held at −195°, and the reactor was warmed to −20° to promote contact and reaction; then the system temperature was lowered to a point at which the respective adduct showed a dissociation pressure less than 1 Torr [$CF_3SF_3\cdot PF_5$ (−80°), $CF_3SF_3\cdot BF_3$ (−65°), $CF_3SF_3\cdot AsF_5$ (25°)], where the volatiles remaining in the system were removed, leaving the white solid adduct.

The $CF_3SF_3\cdot SbF_5$ was obtained by warming a mixture of SbF_5 and an excess of CF_3SF_3 at 35° and then removing the unreacted CF_3SF_3 from the $CF_3SF_3\cdot SbF_5(s)$ by pumping at room temperature.

Properties.—$CF_3SF_3\cdot PF_5$ showed 1 atm decomposition pressure

---

[1] E. A. Tyczkowski and L. A. Bigelow, *J. Amer. Chem. Soc.*, **75**, 3523 (1953).

[2] W. A. Sheppard, *ibid.*, **84**, 3058 (1962).

[3] L. C. Duncan, *Inorg. Chem.*, **9**, 987 (1970).

[4] V. F. Seel and O. Detmer, *Z. Anorg. Allg. Chem.*, **301**, 113 (1959).

[5] N. Bartlett and R. L. Robinson, *J. Chem. Soc.*, 3417 (1961).

[6] K. O. Christie and W. Sawodny, *Inorg. Chem.*, **8**, 212 (1969).

[7] R. J. Gillespie and A. Whitla, *Can. J. Chem.*, **48**, 657 (1970).

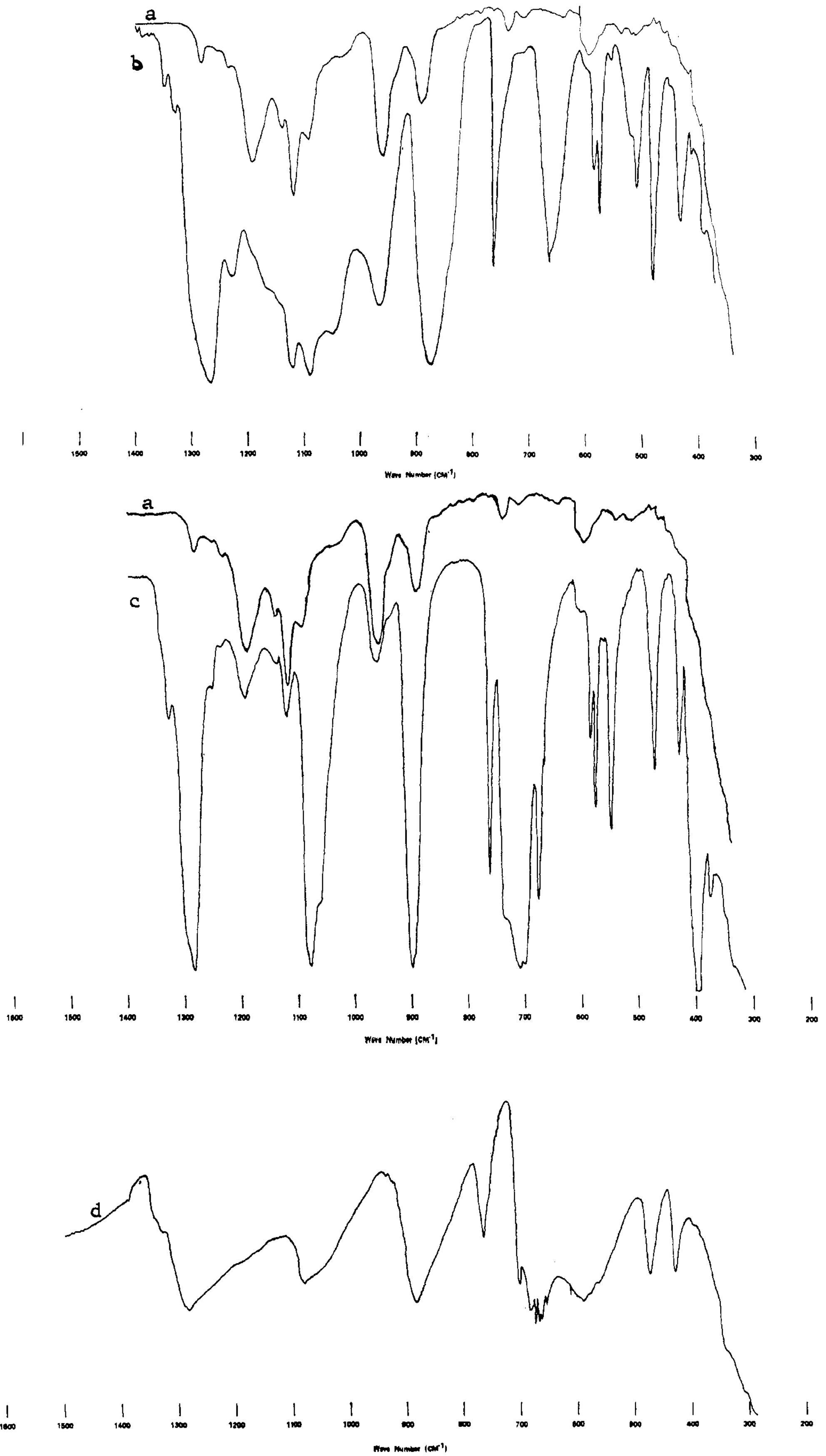

Figure 1.—Infrared spectra of CF_3SF_3 adducts: (a) Halocarbon 25-5S grease background; (b) $CF_3SF_3 \cdot BF_3$(s) (low temperature); (c) $CF_3SF_3 \cdot AsF_5$ (low temperature); (d) $CF_3SF_3 \cdot SbF_5$ (room temperature).

at −12°. The **vapor density** of a sample of the volatiles above the adduct at −12° was determined: calcd mol wt for a 1:1 mixture of CF_3SF_3 and PF_5, 142.0; found, 139.9. The **infrared spectrum** of the volatiles above the adduct at −12° showed only bands characteristic of PF_5 and CF_3SF_3.[8,9]

Analyses.—A sample of the volatiles above the adduct at −12° was hydrolyzed in 0.5 *N* KOH and the P present was determined as $Mg_2P_2O_7$. *Anal.* Calcd for $CF_{11}PS$: P, 10.88. Found: P, 10.6. Attempts were made to measure the equilibrium dissociation pressure of the adduct, but reproducible data were not obtained.

$CF_3SF_3 \cdot BF_3$ showed 207 Torr decomposition pressure at 0°. The **vapor density** of the volatiles above the solid at 100 Torr was determined: calcd mol wt for a 1:1 mixture of CF_3SF_3 and BF_3, 112.9; found, 113.9. The **infrared spectrum** of a sample of the gaseous materials above the adduct showed only bands characteristic of CF_3SF_3 and BF_3. The low-temperature spectrum obtained on $CF_3SF_3 \cdot BF_3(s)$ is shown in Figure 1. Assignments are indicated in Table I.

TABLE I

INFRARED FREQUENCIES (CM^{-1}) AND ASSIGNMENTS FOR $CF_3SF_2{}^+BF_4{}^-$, $CF_3SF_2{}^+AsF_6{}^-$, AND $CF_3SF_2{}^+SbF_6{}^-$

CF_3-$SF_2{}^+BF_4{}^-$ (low temp)	$CF_3SF_2{}^+AsF_6{}^-$ (low temp)	$CF_3SF_2{}^+SbF_6{}^-$ (room temp)	Assignment
1280	1290	1282	$CF_3SF_2{}^+$-(CF)
1090	1078	1078	$CF_3SF_2{}^+$-(CF)
1050			$BF_4{}^-$ [a,b]
875	898	885	$CF_3SF_2{}^+$(SF)
765	761	766	$CF_3SF_2{}^+$
	709		$AsF_6{}^-$ [c,d]
		702 675 665	$SbF_6{}^-$ [c,d]
668	678		$CF_3SF_2{}^+$
590 580	588 578	590	$CF_3SF_2{}^+$
	550		$AsF_6{}^-$ [c,d]
522 513			$BF_4{}^-$ [a,b]
484	474	472	$CF_3SF_2{}^+$
438	430	429	$CF_3SF_2{}^+$

[a] K. O. Christe and W. Sawodny, *Inorg. Chem.*, **6,** 313 (1967). [b] R. J. Gillespie and M. J. Morton, *ibid.*, **9,** 616 (1970). [c] G. M. Begun and H. C. Rutenberg, *ibid.*, **6,** 2212 (1967). [d] R. J. Gillespie and A. Whitla, *Can. J. Chem.*, **48,** 657 (1970).

Analysis.—A sample of the adduct was hydrolyzed and the $BF_4{}^-$ present was determined as nitron tetrafluoroborate. *Anal.* Calcd for CF_6SBF_4: BF_4, 38.4. Found: BF_4, 39.8.

Dissociation Pressure and Thermodynamic Data.—The variation in dissociation pressure with temperature was studied in the metal system between −21 and 18°. For each measurement, the sample-containing portion of the system was surrounded with a bath of approximately the desired temperature. When equilibrium was achieved, the pressure and bath temperature were recorded. The least-squares fit of the dissociation pressure measurements can be expressed by the equation $\log P_{\text{Torr}} = (-2.690 \times 10^3/T) + 12.161$. Assuming the dissociation process is of the type $CF_3SF_3 \cdot BF_3(s) \rightleftharpoons CF_3SF_3(g) + BF_3(g)$, $K_p = P_{CF_3SF_3}P_{BF_3} = P_{\text{atm}}{}^2/2$ and $\Delta G = -2.303\ RT \log K_p = \Delta H - T\Delta S$. Converting the experimental $\log P_{\text{Torr}}$ expression to $\log P_{\text{atm}}$ and substitution in the free energy expression yields $\Delta H = 24.6$ kcal/mol and $\Delta S = 82.2$ cal/mol deg.

$CF_3SF_3 \cdot AsF_5$ was prepared quantitatively; CF_3SF_3 (0.665 mmol) when contacted with AsF_5 (1.141 mmol) consumed 0.634 mmol of the AsF_5. Hence the product mole ratio CF_3SF_3:AsF_5 was 1.05:1. The ambient temperature dissociation pressure of this adduct was less than 1 Torr, but the adduct could be transferred by sublimation under high vacuum. The low-temperature **infrared spectrum** of the solid $CF_3SF_3 \cdot AsF_5$ is shown in Figure 1. Assignments are included in Table I.

Analysis.—A sample of the adduct was hydrolyzed and the resulting $AsF_6{}^-$ content was determined as nitron hexafluoroarsenate.[10] *Anal.* Calcd for CF_6SAsF_6: AsF_6, 57.6. Found: AsF_6, 58.2.

$CF_3SF_3 \cdot SbF_5$ was prepared quantitatively; SbF_5 (1.412 mmol) when held at 35° with CF_3SF_3 (2.832 mmol) consumed 1.411 mmol of CF_3SF_3. Hence the product CF_3SF_3:SbF_5 mole ratio was 0.9993:1.000. The white solid was not volatile at room temperature and showed mp 96–97°. The **infrared spectrum** of the solid is shown in Figure 1 and assignments are included in Table I.

Discussion

Trifluoromethylsulfur trifluoride forms addition compounds when contacted with the fluorides PF_5, BF_3, AsF_5, and SbF_5. The order of stability inferred from the magnitude of dissociation pressures is $CF_3SF_3 \cdot SbF_5 > CF_3SF_3 \cdot AsF_5 > CF_3SF_3 \cdot BF_3 > CF_3SF_3 \cdot PF_5$. This trend in stabilities has been reported for the respective SF_4 adducts and other "fluoronium" type adducts formed with the same acceptors.[4]

The infrared spectra of the three solid compounds $CF_3SF_3 \cdot BF_3$, $CF_3SF_3 \cdot AsF_5$, and $CF_3SF_3 \cdot SbF_5$ are interpreted to indicate that the adducts exist as ionic solids of the type $CF_3SF_2{}^+MF_{n+1}{}^-$ (where MF_n is the acceptor). The actual structure may involve fluorine bridging or considerable cation–anion interaction. The spectra show, in each case, peaks which can be assigned to the respective anions. In the $CF_3SF_3 \cdot BF_3$ case, the broad band centered at 1050 cm^{-1} and the doublet occurring at 522 and 513 cm^{-1} are assigned to the $BF_4{}^-$ ion.[11,12] In the $CF_3SF_3 \cdot AsF_5(s)$ spectrum, the peaks appearing at 709 and 550 cm^{-1} are attributed to the $AsF_6{}^-$ moiety. The band at 709 cm^{-1} is in the region expected for the ν_3 fundamental of the $AsF_6{}^-$ ion[13] and the peak centered at 550 cm^{-1} is believed to arise from a ν_2 band of $AsF_6{}^-$. The ν_2 bands are normally degenerate and infrared inactive but have been observed and assigned in the ir spectra of $AsF_6{}^-$ salts where it was assumed that the site symmetry was low or interaction was occurring.[7] The $CF_3SF_3 \cdot SbF_5$ spectrum shows an intense band centered at 680 cm^{-1}. This band is believed to arise from the ν_3 fundamental of $SbF_6{}^-$.[7,13] Excluding bands assigned to the anions, the three spectra are similar (see Figure 1). This common residual pattern is believed due to the $CF_3SF_2{}^+$ ion in the adduct lattice.

The vapor density and infrared spectra of the volatiles above the adducts $CF_3SF_3 \cdot PF_5$ and $CF_3SF_3 \cdot BF_3$ indicate the adducts are dissociated in the gas phase. In the BF_3 case the overall process of adduct formation and dissociation can be described by $CF_3SF_3(g) + BF_3(g) \rightleftarrows CF_3SF_2{}^+BF_4{}^-(s)$.

---

(8) E. W. Lawless and L. D. Harmon, *Inorg. Chem.*, **7**, 391 (1968).

(9) C. T. Ratcliffe and J. M. Shreeve, *J. Amer. Chem. Soc.*, **90**, 5403 (1968).

(10) W. Lange and E. Muller, *Ber.*, **63**, 1058 (1930).

(11) K. O. Christe and W. Sawodny, *Inorg. Chem.*, **6**, 313 (1967).

(12) R. J. Gillespie and M. J. Morton, *ibid.*, **9**, 616 (1970).

(13) G. M. Begun and A. C. Rutenberg, *ibid.*, **6**, 2212 (1967).

The enthalpy of dissociation of $CF_3SF_3 \cdot BF_3(s)$ (24.6 kcal/mol) is of the same magnitude as that reported for the $SF_4 \cdot BF_3$ dissociation (25.5,[4] 24.8 kcal/mol[5]) while the entropy of $CF_3SF_3 \cdot BF_3$ dissociation (82.2 eu) is considerably larger than that reported for the $SF_4 \cdot BF_3$ adduct (74.5,[5] 72.5 eu[4]). Consequently the equilibrium dissociation pressure above the CF_3SF_3 adduct at 0° (207 Torr) is greater than that of $SF_4 \cdot BF_3$ at the same temperature (20 Torr).[5]

Acknowledgments.—We wish to thank Dr. W. Emken for the use of the low-temperature ir cell and for his helpful advice. This research was supported under National Science Foundation Grant GP 11274.

Correspondence

A Potentially Hazardous Reaction between Dimethylmercury and Tetrachlorodiborane(4)

Sir:

At the recent American Chemical Society National Meeting, Kuo and Wartik[1] alluded to a private communication from us describing the preparation of trichloromethyldiborane(4) by the reaction $B_2Cl_4 + Hg(CH_3)_2 \rightarrow B_2Cl_3CH_3 + HgClCH_3$. At the time Kuo and Wartik mentioned this work we had without incident carried out this reaction some 23 times. Each of our next two attempts to repeat the preparation, however, resulted in violent explosions, and we are writing to warn any who heard the talk and might wish to use this reaction that it is potentially hazardous.

The most disturbing aspect of this work is that the reagents and conditions used for the two reactions which culminated in explosions were, to the best of our knowledge, in no way different from those employed earlier. The tetrachlorodiborane(4) used[2] in the explosive reactions was taken from the same supply used for prior successful preparations. All of the dimethylmercury used for these studies was prepared at one time according to the method of Marvel and Gould.[3] The identity and purity of the diboron compound were confirmed by its infrared spectrum and its vapor pressure; those of the mercurial were established by its infrared spectrum and by gas chromatographic analysis.

In all cases, equimolar quantities (from 1 to 4 mmol) of the two reagents were condensed at liquid nitrogen temperatures into Pyrex reaction vessels whose volumes varied from about 15 to 60 ml, depending on the particular experiment. (The two ill-starred reactions involved about 4 mmol of each reagent, and the volumes of the reaction vessels were about 30 ml.) After they had been sealed from the vacuum system, the reaction vessels were allowed to warm until the dimethylmercury melted (about −63°). In the first 23 cases the reaction, which commenced at about −63°, was vigorous but well under control, and, about 2 min after the initial melting of the dimethylmercury, the vessel was cooled to liquid nitrogen temperatures prior to opening the tube to the vacuum system for removal and separation of products. Reaction 24 exploded just prior to opening the tube to the vacuum system. Reaction 25 (the last one we have attempted to date) exploded at the onset of melting of the dimethylmercury. Both explosions were accompanied by bright flashes and both were of sufficient force to pose a serious hazard from the standpoint of flying glass, fire, and volatile mercurials.

We are currently attempting to account for this erratic behavior. Until and unless a set of conditions can be specified for which the reaction is entirely safe, we would advise others not to attempt to reproduce this reaction unless they are fully prepared to cope with the explosion that may result.

DEPARTMENT OF CHEMISTRY
THE PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PENNSYLVANIA 16802

BRUCE GASSENHEIMER
THOMAS WARTIK*

RECEIVED OCTOBER 15, 1970

---

[1] H. S. Kuo and T. Wartik, "Some New Boron-Carbon Heterocyclics," presented before the Division of Inorganic Chemistry at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, Abstract INOR 64.

[2] Tetrachlorodiborane(4) was prepared by the method of T. Wartik, R. Moore, and H. Schlesinger, *J. Amer. Chem. Soc.*, **71**, 3265 (1949).

[3] C. S. Marvel and V. L. Gould, *ibid.*, **44**, 153 (1922).