Contribution from the Department of Chemistry and Biochemistry,
Utah State University, Logan, Utah 84322

Dehydrohalogenation of Adducts of Dichloro(pentafluorophenyl)borane with Mesidine and *p*-Anisidine: A Reinvestigation

JOSEPH G. MORSE* and W. KENT GLANVILLE

The pyrolysis of dichloro(pentafluorophenyl)borane with mesidine or *p*-anisidine, originally reported to yield monomeric boron imides, has been restudied. Rather than boron imides, the reactions give aminoboranes, (aminoboranyl)aminoboranes, or bis(amino)boranes depending on the duration of pyrolysis. The dimer structure represents an intermediate proposed in the pyrolysis of dichlorophenylborane with aromatic amines to give diazadiboranaphthalenes. Chemical dehydrohalogenation with 1,8-bis(dimethylamino)naphthalene leads directly to the bis(amino)boranes.

After a large number of erroneous reports of their formation, monomeric boron imides were first isolated by Paetzold and co-workers.[1] An earlier report of success by means of the pyrolysis of mesidine and *p*-anisidine adducts of dichloro-(pentafluorophenyl)borane[2] led us to attempt to explore some reaction chemistry of these species. When we attempted to reproduce that reported synthesis, it became clear that a highly reactive product was indeed formed but that it was not a monomeric boron imide. This paper reports our investigation of the actual course of that reaction.

Results

The reaction studied was that of dichloro(pentafluorophenyl)borane, $C_6F_5BCl_2$, with equimolar quantities of an aromatic amine, either mesidine, 2,4,6-trimethylaniline, or *p*-anisidine, *p*-methoxyaniline. Both the reported solution pyrolysis reaction and an alternate chemical dehydrohalogenation procedure were attempted. Both gave the same ultimate product. The most detailed results were obtained for mesidine. The anisidine reaction appeared to follow the same general pathway, but the product was extremely sensitive to hydrolysis, was extremely difficult to purify, and was less successfully characterized as a consequence.

Dehydrohalogenation by Pyrolysis. When toluene solutions of mesidine, and $C_6F_5BCl_2$ are mixed, a white precipitate forms, presumably the amine–borane adduct. This solid appears to dissolve when the toluene is brought to reflux and HCl is evolved. If reflux is terminated upon complete dissolution of the solid, the aminoborane (I) is isolable.

I
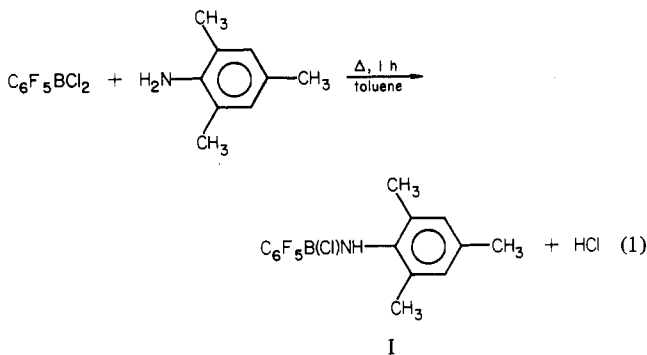
Product I is a white crystalline solid stable toward moist air. The mass spectrum is quite definitive for this structure with the *m/e* value and isotope envelope in excellent agreement with the molecular ion of I. A metastable peak in the mass spectrum at *m/e* 279 apparently arises from ready dehydrohalo-

genation of I in the spectrometer to give a transient boron imide observed as a cluster of peaks about *m/e* 311.

After reflux overnight, the principal product is a white crystalline solid that corresponds to a proposed intermediate structure in the formation of diazadiboranaphthalene compounds from similar experiments.[3]

II
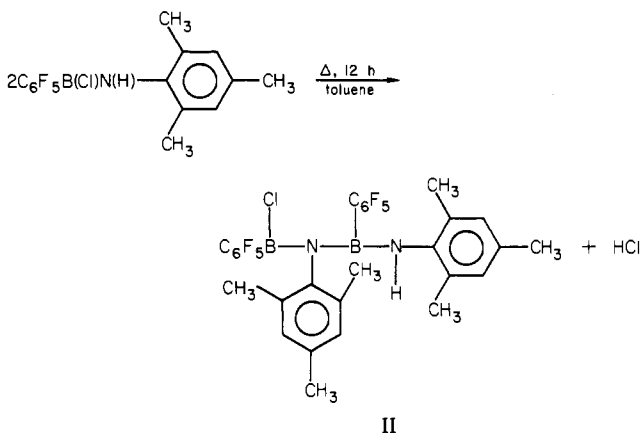
Product II was characterized by osmometric molar mass, IR, and ^1H and ^{19}F NMR data as well as elemental analysis. The analytical data deserve comment. The experimental value for chloride is consistently high though all other data are in agreement with structure II. On the conjecture that this may be a consequence of the presence of some hydrochloride salt or aminoborane contaminant, HCl gas was added to the toluene solution. The crystalline product obtained therefrom gave analysis in excellent agreement with that expected for those products (identical with one another analytically). Adjusting the analytical data by assuming the error in chloride is due to contamination gives good agreement with calculation. An attempt to obtain ^{11}B NMR data gave a featureless *very* broad signal of no utility. The formation of II is consistent with the reported ready loss of 1.5 mol of HCl/mol of reactant in the pyrolysis of $PhBCl_2 \cdot H_2NPh$.[3]

Continued pyrolysis for a period of 1 week results in the formation of III as the principal isolable product:

III
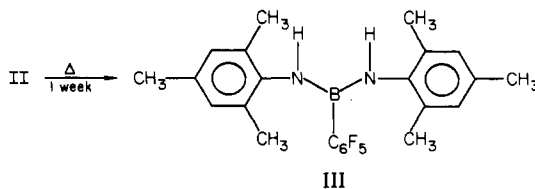
Product III is identical with that obtained upon chemical

(1) Paetzold, P.; Richter, A.; Thijssen, T.; Wurtenberg, S. *Chem. Ber.* **1979**, *112*, 3811.
(2) Paetzold, P.; Simpson, W. M. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 842. Paetzold, P. *Ibid.* **1967**, *6*, 572. Paetzold, P.; Stohr, G.; Maisch H.; Lenz., H. *Chem. Ber.* **1968**, *101*, 2881 and references therein.

(3) Blackborow, J. R.; Lockhart, J. C. *J. Chem. Soc., Dalton Trans.* **1973**, 1303.

dehydrohalogenation, and its identification is discussed below.

The corresponding reactions with anisidine proceed similarly but with some significant differences. A significant evolution of HCl is noted upon mixing and standing even at 0 °C, but much less than 1 equiv is recovered and the principal component of the mixture is the amine–borane adduct (identified by IR spectroscopy). After the mixture was refluxed at reduced pressure at about 70 °C for 36 h, 1 equiv of HCl was recovered. The principal component of the reaction mixture, IV, was identified by IR spectroscopy, mass spectrometry, and C, H, N analysis as the aminoborane $CH_3OC_6H_4NHBCl-C_6H_5$. Continued reflux for 1 week under these conditions or under an atmospheric pressure of dry N_2 for 2–3 days leads consistently to recovery of approximately 1.5 equiv of HCl. The crude product was dissolved in a minimum amount of toluene and hexane added to give a white precipitate identified as the aminoborane by IR spectroscopy. The remaining solution was reduced to an oil under vacuum and the oil heated under vacuum in a sublimation apparatus. The IR spectrum of the solid (V) collected showed a weak band in the NH region and was generally similar to that of II. Analytical data were in reasonable agreement with the dimeric structure analogous to II considering the air sensitivity of the compound. The mass spectrum displayed appropriate fragments, but the highest mass peak observable was at 467, representing the molecular ion less a C_6F_5B fragment. This particular compound was not routinely obtained.

Reflux at atmospheric pressure under dry nitrogen for 1 week gives as a product a highly reactive colorless oil, VI, which is recrystallizable, with difficulty, from hexane. The infrared spectra of crude product from the pyrolyses generally showed both VI and IV to be present. The same product is obtained as the dominant product from chemical dehydrohalogenation. Its characterization is described below.

Dehydrohalogenation with Proton Sponge.[4] Failure to isolate an iminoborane by pyrolysis led us to attempt an alternate, lower temperature route with use of a chemical agent. After no success with (dimethylamino)trimethylstannane, we chose to utilize 1,8-bis(dimethylamino)naphthalene, Proton Sponge. This compound was effective in dehydrohalogenation of the amine–boranes, giving quite rapidly the toluene-insoluble hydrochloride salt of Proton Sponge, identified by spectral comparison with an authentic sample, and a second major product. With mesidine, that product was clearly identified as dimesidino(pentafluorophenyl)borane (III). The stoichiometry of the reaction was difficult to assess due to difficulty in purification of the hydrochloride salt and complete recovery of unreacted Proton Sponge, but some of the latter was invariable recovered unreacted, consistent with the stoichiometry implied by the product. Pure product III was obtained in about 60% yield based upon mesidine charged. The remaining 1 equiv of $C_6F_5BCl_2$ was never determined quantitatively but was clearly present in the volatiles removed from the reaction vessel. Immediately upon isolation, a single strong band in the infrared spectrum, like that described in ref 2, was observed. After repeated recrystallization this resolved into three sharp peaks though no other spectral position showed detectable change. Other peaks characteristic of the C_6F_5 and mesidino moiety were also present. The ^{19}F NMR spectrum showed the 2:1 ratio of methyl peaks appropriate to the 2,4,6-trimethylaniline ring. Vapor pressure osmometry gave a molecular weight of 445 (calculated 447). The mass spectrum displayed a large molecular ion peak at about m/e 450. Because there were virtually no peaks between the molecular ion and m/e 311, an exact direct count of m/e position was impossible; however, the isotopic ratio of the peaks in the

envelope was in excellent agreement with that of structure III. The remaining pattern was consistent with the molecular components and was mainly noteworthy for the complete absence of the characteristic isotope envelope for chlorine. The elemental analysis was similarly consistent with theory.

Addition of 1 mol of HCl/mol of III in toluene led to formation of a white solid identified as the aminoborane, a reaction typical of bis(amino)boranes.[5]

When deuterated mesidine was utilized in the reaction with Proton Sponge, the NH stretch initially observed at 3380 cm^{-1} shifted to 2500 cm^{-1} demonstrating that the peak previously ascribed to the B–N overtone was in fact an NH stretch.

The reaction using anisidine in place of mesidine proceeds in an apparently similar way to give a product whose infrared spectrum is identical with that of VI. The stoichiometry of the reaction based upon recovered Proton Sponge hydrochloride appears to be 1:1 with anisidine. A peak at 3380 cm^{-1} in the IR spectrum is the same in frequency and relative intensity to that found for III, though upon crystallization comparable fine structure was never noted. Beyond this feature, little solid comparison can be made because of very great difficulty in obtaining pure samples. Repeated attempts at recrystallization led generally to dramatic losses of material. Column chromatography (silica, even very dry silica) was totally unsuccessful. Exposure to dry Utah air for seconds led to near complete loss of the sample. The compound is substantially more reactive than III. We assign VI a structure like that of III primarily on the basis of the similarity of infrared spectra and the consistent stoichiometry. The mass spectrum showed very weak peaks above m/e 400 and near m/e 250, which could correspond to a molecular ion (calculated 422) and loss of C_6H_5, but the assignment is very tenuous. Remaining fragments are consistent with the functional groups presumed present. The analytical data were high in C, H, and N but much higher than for any formulation containing equal numbers of C_6F_5 and $C_6H_4OCH_3$ functions. The high values suggest contamination by Proton Sponge, and this is supported by a shoulder at 2770 cm^{-1} in the IR spectrum of the analytical sample.

Discussion

As has become clear recently,[1,6] iminoboranes are highly reactive and best retained under conditions of low temperature. In addition the presence of considerable steric bulk (e.g., *tert*-butyl) on the B–N substituents is advantageous. Iminoboranes having several different boron substituents have been isolated, but their relative reactivities are dramatically influenced by the steric bulk of those substituents. The electronic effect of the C_6F_5 group does not appear to be essential though it is present in the first reported instance.[1] It is clear from the present work that its presence is not sufficient. The reagents used here would appear to lead potentially to iminoboranes, but the higher temperatures required for isolation of products from this or similar solvent systems (sufficient to remove the solvent under vacuum) apparently precludes their isolation. Surprisingly no clearly identified borazine products were obtained in either case though this appears to be the dominant mode of decay of monomeric boron imides.[6]

The reactions studied here lend credence to the suggestion of Blackborow and Lockhart[3] of the intermediacy of an (aminoboranyl)aminoborane in formation of diazadiboranaphthalene products characteristic of the pyrolysis of aromatic amines and aromatic dichloroboranes. The methyl groups in the 2- and 6-positions of the nitrogen substituent ring of mesidine preclude its formation, but it is of some surprise that

(4) Proton Sponge is a registered trademark of Aldrich Chemical Co, Inc.

(5) Niedenzu, K.; Dawson, J. "Boron-Nitrogen Compounds"; Academic Press: New York, 1965.

(6) Paetzold, P.; Plotho, C. *Chem. Ber.* **1982**, *115*, 2819.

we do not obtain the diazadiboranaphthalene from anisidine. Our data for VI, especially the IR spectrum and elemental analysis, are quite inconsistent with that formulation as is its very great sensitivity to moisture. Perhaps the C_6F_5 group does play a role in this regard.

Experimental Section

All starting materials were reagent grade and were purified before use by distillation, recrystallization, or sublimation as appropriate. Solvent toluene was dried over Linde 3-Å molecular sieves and vacuum distilled before use. 1,8-Bis(dimethylamino)naphthalene was obtained from Aldrich Chemical Co., Inc., to whom the term Proton Sponge is registered. All manipulations were carried out under a dry nitrogen atmosphere, in a glovebag, or on a Stock high-vacuum line. Dichloro(pentafluorophenyl)borane was prepared from the pentafluoro Grignard reagent, dibromo(dimethyl)tin, and boron trichloride as described previously.[7]

Spectral data were obtained by using Beckman IR-20A (IR spectroscopy) Hitachi Perkin-Elmer RMU-6E (mass spectroscopy), and Varian XL-100 (NMR) instruments. Solution molecular weights were obtained with use of a Mechrolab vapor pressure osmometer, Model 301-A. Microanalyses were performed by Chemalytics, Inc., Tempe, AZ.

Pyrolysis Reactions. A typical reaction was carried out in a Schlenk flask equipped with a magnetic stirrer and attached by its side arm to a vacuum line. Dry toluene was distilled in with a measured quantity of mesidine or p-anisidine. While the resulting solution was maintained at −78 °C, a weighed equimolar quantity of pure liquid $C_6F_5BCl_2$ was poured slowly into the solution through a high-vacuum Teflon stopcock. After reaction at −78 °C for about 1 h, the mixture was allowed to warm to room temperature and the flask was fitted, under N_2, with a reflux condenser. The solution was refluxed under various conditions, as earlier described, for periods up to 10 days. Hydrogen chloride evolved was measured either by *PVT* in the vacuum line or by passing the effluent through a solution of triethylamine in methanol and weighing the resulting solid. Solvent was removed from the reaction mixture under vacuum to leave a pale amber oil. Products were purified by recrystallization from toluene/hexane or by very short-path distillation or sublimation under high vacuum.

Chemical Dehydrohalogenation. In a typical experiment 4.0 mmol of amine and 8.0 mmol of Proton Sponge were dissolved in dry toluene in a Schlenk flask. After the solution was frozen under a blanket of dry N_2, the Teflon-valved weighing tube containing 4.2 mmol of $C_6F_5BCl_2$ was attached, the system evacuated, the solution degassed under vacuum, and the reagent added slowly to the stirred solution at −78 °C. The solution gave a bright yellow-orange color almost immediately. The solution was allowed to warm with stirring to room temperature. After about 30 min the color was gone, the solution was chilled to ice temperature, a filter tube and receiver flask were attached under a flow of dry N_2, and the cold solution was filtered under vacuum. The solid was washed with solvent condensed in the upper flask. The solvent was then removed by distillation under vacuum. The solid precipitate was identified as Sponge hydrochloride (6.7 mmol) by IR spectroscopy. A cold-finger device with a small glass bucket suspended from its tip was then inserted under dry N_2, the flask was evacuated, and the oil bath was heated to ca. 45 °C. Under continuous pumping, excess Proton Sponge (and some of its hydrochloride?) condensed on the cold finger and the condensed oil dripped into the bucket. No quantitative measure of this mass was accomplished. The oily solid remnant in the flask was washed twice with warm heptane, by using cannula techniques[8] to maintain an inert

atmosphere, and then dissolved in toluene; the resultant mixture was transferred via cannula to a second dry flask and recrystallized with heptane. The product was finally sublimed under vacuum to give a colorless crystalline material on the cold finger. The purified product was obtained in 60% yield from mesidine based on mesidine charged. With anisidine, satisfactorily pure compound was never obtained in more than minimal amounts for analysis or IR or mass spectrometry.

Compound Characterization. *p*-**Anisidine–Dichloro(pentafluorophenyl)borane.** IR spectrum (KBr pellet): ν_{NH} 3270, 3240, 3190 cm^{-1} (s).

Mesidinochloro(pentafluorophenyl)borane (I). IR spectrum: ν_{NH} 3300 cm^{-1} (s). Mass spectrum (principal peaks; assignments and relative intensities in parentheses): 349 ($C_{15}H_{12}^{11}B^{37}ClF_5N^+$, 20.7), 348 ($C_{15}H_{12}^{10}B^{37}ClF_5N^+$, 15.8), 347 ($C_{15}H_{12}^{11}B^{35}ClF_5N^+$, 65.8), 346 ($C_{15}H_{12}^{10}B^{35}CClF_5N^+$, 16.4) (ratio in molecular ion calcd 33:33:100:25, found 31:24:100:25), 332 (347 − CH_3, 4.5), 327 (347 − HF, 7.9), 311 (347 − HCl, 20.0), 296 (311 − CH_3, 10.7), 279 (metastable, 347 − 311), 168 ($C_6F_5H^+$, 13.3), 135 ($C_9H_{11}NH_2^+$, 100).

p-**Anisidinochloro(pentafluorophenyl)borane (IV).** IR spectrum: ν_{NH} 3300 cm^{-1} (s). Mass spectrum: 337 ($C_{13}H_8^{11}B^{37}ClF_5NO^+$, 34), 336 ($C_{13}H_8^{10}B^{37}ClF_5NO^+$, 26), 335 ($C_{13}H_8^{11}B^{35}ClF_5NO^+$, 100), 334 ($C_{13}H_8^{10}B^{35}ClF_5NO^+$, 26) (ratio in molecular ion calcd 33:33:100:25, found 34:26:100:26). Anal. Calcd: C, 46.54; H, 2.40; N, 4.18. Found: C, 46.75; H, 2.66; N, 4.43.

[*N*-[**Mesidino(pentafluorophenyl)boranyl]mesidino]chloro(pentafluorophenyl)borane (II).** IR spectrum: ν_{NH} 3280 cm^{-1} (m). ^{1}H NMR: δ 2.36 (3.88), 3.30 (1), 6.70 (20.3) (calcd intensities 4:1:18). ^{19}F NMR: −162 (2), −152 (1), −132 (2) ppm (from CCl_3F (external)). Mol wt: calcd 658, found 650. Anal. calcd: 54.71; H, 3.52; N, 4.24; Cl, 5.38. Found: C, 53.34; H, 4.13; N, 4.47; Cl, 8.32. Corrected (vide supra): C, 53.17; H, 3.69; N, 4.13; Cl, 5.38.

[*N*-[(*p*-**Methoxyanilino)(pentafluorophenyl)boranyl]-*p*-methoxyanilino]chloro(pentafluorophenyl)borane (V).** IR spectrum: ν_{NH} 3350 cm^{-1} (m, br). Mass spectrum: 467 (V − $C_6F_5^+$, 0.4), 186 ($C_6F_6^+$, 24), 168 ($C_6F_5H^+$, 9), 149 ($C_6F_4H^+$, 15), 123 ($H_2NC_6H_4OCH_3^+$, 95), 108 (123 − CH_3 and/or NH^+, 100), 37 ($^{37}Cl^+$, 0.5), 35 ($^{35}Cl^+$, 1.3). Anal. Calcd: C, 49.22; H, 2.38; N, 4.42. Found: C, 49.26; H, 2.86; N, 4.32.

Dimesidino(pentafluorophenyl)borane (III). IR spectrum: ν_{NH} 3380 (oil), 3430, 3380, 3360 cm^{-1}. (KBr pellet, m). ^{19}F NMR: −162 (2), −154 (1), −131 (2) ppm (from $CFCl_3$ (external)). ^{13}NBR: 24 (CH_3, 2), 26 (CH_3, 1) ppm (from Me_4Si (external)). Mass spectrum: 447 ($C_{23}^{13}CH_{24}^{11}BF_5N_2^+$, 3.6), 446 ($C_{24}H_{24}^{11}BF_5N_2^+$, Me_4Si 12.7), 445 ($C_{24}H_{24}^{10}BF_5N_2^+$, 4.2), 135 ($C_9H_{11}NH_2^+$, 100) (ratio in molecular ion calcd 3.5:12.7:3.2). Mol wt: calcd 446.4, found 445. Anal. Calcd: C, 64.57; H, 5.38; N, 6.28; B, 2.47. Found: C, 64.35; H, 5.44; N, 6.17; B, 2.61.

Di-*p*-anisidino(pentafluorophenyl)borane (VI). IR spectrum: ν_{NH} 3380 cm^{-1}. Mass spectrum: 186 ($C_6F_6^+$, 22), 168 ($C_6F_5H^+$, 10), 149 ($C_6F_4H^+$, 63), 123 ($C_6H_7ONH_2^+$, 72), 108 (123 − CH_3 and/or NH, 100). Anal. Calcd: C, 56.9; H, 3.82; N, 6.64. Found: C, 57.0; H, 4.28; N, 7.28.

(7) Chambers, R. D.; Chivers, T. *J. Chem. Soc.* **1965**, 3933. Nield, E.; Stephens, R.; Tatlow, J. C. *Ibid.* **1959**, 166.

(8) Shriver, D. F. "The Manipulation of Air Sensitive Compounds"; McGraw-Hill: New York, 1969; Chapter 7.