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Dehydrofluorination of Amine-Metalloid Fluorides. III. The Dehydrofluorination of Primary Amine-Boron Trifluoride Adducts[1a]

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Primary amine adducts of boron trifluoride or salts of fluoroboric acid are readily dehydrofluorinated by the adducts of hindered, preferably tertiary amines with boron trifluoride. The procedure has been applied primarily to the preparation of B-fluoroborazines $(RNBF)_3$, R = CH_3, C_2H_5, i-C_3H_7, t-C_4H_9, C_6H_5, *p*-phenylazophenyl, and *p*-phenylcarboxyethyl. The same procedure is indicated to be useful for the preparation of tris(amino)boranes, bis(amino)boron fluorides, and aminoborazines by variation of the stoichiometry of the reaction. Other methods of attempted dehydrofluorination are described. Thermodynamic aspects are discussed to explain the marked difference in the relative ease of dehydrohalogenation of primary amine adducts of boron trifluoride and boron trichloride.

Formation of covalent boron–nitrogen bonds by aminolysis of boron trifluoride with primary or secondary amines is difficult.[2,3] Present procedures for dehydrofluorination of boron trifluoride–amine adducts using metals,[4] metal hydrides,[5] or organometallic compounds,[6] at times under vigorous conditions, are not suited to general synthetic applications. Lack of a ready means of causing aminolysis of boron–fluorine bonds has hindered the development of fluoroboron–nitrogen chemistry. For example, the B-trifluoroborazines were virtually unknown prior to 1962 when Niedenzu[7,8] and later Laubengayer[9] described their indirect preparation by fluorination of B-trichloroborazines. Prior methods using high temperatures[10-12] or difficultly obtained reagents[13] gave low to fair yields.

Results

We now report a convenient procedure for the dehydrofluorination of primary amine–boron trifluoride adducts to B-trifluoroborazines, aminoboranes, or B-aminoborazines depending upon reaction stoichiometry. The method is also applicable to primary amine salts of fluoroboric acid. Dehydrofluorination is caused by the adduct of boron trifluoride with a sterically hindered, preferably tertiary amine in an aprotic solvent; the dehydrofluorinating adduct is converted to its fluoroborate salt. Direct synthesis of B-trifluoroborazines in 90% yields is possible in 2–5 hr at room temperature if a favorable amine is used. Equally satisfactory results were obtained by treating the amines and boron trifluoride in any order or adding either preformed adduct to the other. The insoluble by-product salt is readily separated from the normally soluble dehydrofluorination product. Synthesis of aminoboranes and aminoborazines by the process, studied only briefly since they are readily synthesized by other means,[14] appeared facile.

Given below is the reaction stoichiometry required for the conversion of adduct (eq 1) and salt (eq 2) to B-trifluoroborazines and adduct to bis(amino)boron fluoride (eq 3), tris(amino)boranes (eq 4), and B-tris(amino)borazines (eq 5).

$$3R'NH_2\cdot BF_3 + 6R_3N\cdot BF_3 \longrightarrow (R'NBF)_3 + 6R_3NH^+BF_4^- \quad (1)$$

$$3R'NH_3^+BF_4^- + 9R_3N\cdot BF_3 \longrightarrow (R'NBF)_3 + 9R_3NH^+BF_4^- \quad (2)$$

$$R'NH_2\cdot BF_3 + R'NH_2 + 2R_3N\cdot BF_3 \longrightarrow (R'NH)_2BF + 2R_3NH^+BF_4^- \quad (3)$$

$$R'NH_2\cdot BF_3 + 2R'NH_2 + 3R_3N\cdot BF_3 \longrightarrow (R'NH)_3B + 3R_3NH^+BF_4^- \quad (4)$$

$$3R'NH_2\cdot BF_3 + 3R'NH_2 + 9R_3N\cdot BF_3 \longrightarrow (R'NHBNR')_3 + 9R_3NH^+BF_4^- \quad (5)$$

The amine used to form the dehydrofluorinating adduct, of critical importance to the reaction, must contain R groups large enough to reduce the stability of the adduct. The adduct instability required for effective reactivity was not defined in terms of dissociation constants, but effective ones had a tendency to fume in the atmosphere. The sterically hindered diisopropylethylamine gave an adduct effective for dehydrofluorination at room temperature while the less sterically hindered trimethylamine gave poor results even at 210°. The adduct of a hindered secondary amine gave fair results while a hindered primary amine gave poor results. Diisopropylethylamine gave the best results and was used in most reactions. The amines used to cause dehydrofluorination of the reference system aniline–boron trifluoride are listed in Table I.

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[2] H. Steinberg and R. J. Brotherton, "Organoboron Chemistry," Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1966.

[3] N. N. Greenwood and R. L. Martin, *Quart. Rev.* (London), **8**, 1 (1954).

[4] C. A. Kraus and E. H. Brown, *J. Am. Chem. Soc.*, **52**, 4414 (1930).

[5] K. Lang and F. Schubert (Farbenfabriken-Bayer A.-G.), U. S. Patent 3,090,809 (May 23, 1963).

[6] A. Dornov and H. H. Gehrt, *Z. Anorg. Allgem. Chem.*, **294**, 81 (1958).

[7] K. Niedenzu, *Inorg. Chem.*, **1**, 943 (1962).

[8] K. Niedenzu, H. Beyer, and H. Jenne, *Chem. Ber.*, **96**, 2649 (1963).

[9] A. W. Laubengayer, K. Watterson, D. R. Bidinosti, and R. F. Porter, *Inorg. Chem.*, **2**, 519 (1963).

[10] E. Wiberg and G. Horeld, *Z. Naturforsch.*, **6b**, 338 (1951).

[11] R. K. Pearson and J. W. Frazer, *J. Inorg. Nucl. Chem.*, **21**, 188 (1961).

[12] H. I. Schlessinger, A. Finch, J. Kerrigan, and J. Murich, ONR Annual Technical Report PB 128079, Aug 1, 1956, U. S. Office of Technical Services, Washington, D. C.

[13] S. Sujishi and S. Witz, *J. Am. Chem. Soc.*, **79**, 2447 (1957).

[14] W. Gerrard, "The Organic Chemistry of Boron," Academic Press, London, 1961.

TABLE I

EFFECT OF THE AMINE ON DEHYDROFLUORINATION OF ANILINE–BORON TRIFLUORIDE TO N-TRIPHENYL-B-TRIFLUOROBORAZINE

Adduct of	Temp, °C	Solvent	Yield of $(C_6H_5NBF)_3$, %
$(CH_3)_3N$	25	Benzene	0
	210	None	10
$(C_2H_5)_3N$	25	Benzene	5–10
	160	None	90
$(i\text{-}C_3H_7)_2C_2H_5N$	25	Benzene	99
$(sec\text{-}C_4H_9)_2NH$	25	Benzene	65
$C_6H_5N(C_2H_5)_2$	80	Benzene	90
$(CH_3)_3CNH_2$	80	Benzene	20
Quinaldine	25	Benzene	90

The dehydrofluorination of primary amine–boron trifluoride adducts proceeded with a variety of amines as shown in Table II. An exception was *o*-nitroaniline which gave an oily mixture, although dehydrofluorination had occurred. In certain instances the products are unique. A borazine was obtained from ethyl *p*-aminobenzoate. Reaction of boron trichloride with ethyl *p*-aminobenzoate gives a complex mixture of products because of the reactivity of the ester with boron trichloride. A borazine was obtained from *t*-butylamine; reaction of *t*-butylamine with boron trichloride gave a tetramer.[15] The sterically hindered 2,6-diethylaniline did not give a borazine, but a product indicated to be the bis(amino)boron fluoride.

TABLE II

PRIMARY AMINE–BORON TRIFLUORIDE ADDUCTS DEHYDROFLUORINATED

Amine	Product
Aniline	1,3,5-Triphenyl-2,4,6-trifluoroborazine
Aniline	1,3,5-Triphenyl-2,4,6-tris(anilino)-borazine
Aniline	Bis(anilino)boron fluoride (impure)
2,6-Diethylaniline	Bis(2,6-diethylanilino)boron fluoride
Methylamine	1,3,5-Trimethyl-2,4,6-trifluoroborazine
Ethylamine	1,3,5-Triethyl-2,4,6-trifluoroborazine
t-Butylamine	1,3,5-Tri-*t*-butyl-2,4,6-trifluoroborazine
Isopropylamine	1,3,5-Triisopropyl-2,4,6-trifluoroborazine
p-Phenylazoaniline	1,3,5-Tris(*p*-phenylazophenyl)-2,4,6-trifluoroborazine
Ethyl *p*-aminobenzoate	1,3,5-Tris(*p*-carbethoxyphenyl)-2,4,6-trifluoroborazine
1,1-Dimethylhydrazine Phenylhydrazine 1,1-Diphenylhydrazine	Adducts completely dehydrofluorinated but products not well defined

Intermediates of the type $RNHBCl_2$, postulated to occur in the formation of B-trichloroborazine, have eluded attempts at isolation.[16,17] Similarly, an attempt by us to prepare $ArNHBF_2$ (Ar = C_6H_5, 2,6-$(C_2H_5)_2C_6H_4$) failed, only $(C_6H_5NBF)_3$ and $(2,6\text{-}(C_2H_5)_2C_6H_4NH)_2BF$ being found in complex mixtures of products. A small quantity of $t\text{-}C_4H_9NHBF_2$ was found as a by-product during synthesis of $(t\text{-}C_4H_9NBF)_3$. Other workers[18] studying the redistribution of $(RNH)_3B$ and BF_3 obtained only inseparable mixtures of $RNH_2 \cdot BF_3$ and B-alkyl- or B-fluoroborazines if R was unhindered alkyl but also found $t\text{-}C_4H_9NHBF_2$. We did find evidence for products of the type $(ArNH)_2BF$ when high ratios of primary amines were used to prepare $(ArNH)_3B$ and $(ArNHBNAr)_3$.

Attempts were made to effect dehydrofluorination with a variety of other reagents. Pyridine partially decomposed the adduct while diisopropylethylamine (without boron trifluoride) gave $(C_6H_5NH)_3B$ and $(i\text{-}C_3H_7)_2C_2H_5NH^+BF_4^-$ and free aniline according to

$$4C_6H_5NH_2 \cdot BF_3 + 4(i\text{-}C_3H_7)_2C_2H_5N \longrightarrow (C_6H_5NH)_3B + 3(i\text{-}C_3H_7)_2C_2H_5NH^+BF^- + C_6H_5NH_2 + (i\text{-}C_3H_7)_2C_2H_5N \quad (6)$$

Cesium fluoride, reported[19] to cause dehydrofluorination of NH_3 and sulfur oxytetrafluoride, decomposed the primary amine–boron trifluoride adduct as did potassium *t*-butoxide. An attempt to prepare B-trifluoroborazines according to eq 7 failed. Heating

$$3C_6H_5NH_2 \cdot BF_3 + 2AlCl_3 \longrightarrow (C_6H_5NBF)_3 + Al_2F_6 + 6HCl \quad (7)$$

the aniline or ethylamine adduct of boron trifluoride to 200° under N_2 or vacuum gave some decomposition but no clearly definable products other than small quantities of the tetrafluoroborate salt.

Dehydrofluorination of silicon tetrafluoride and alcohols with sulfides of metals such as calcium which form stable fluoride salts[20] or with alkali or alkaline earth salts of Cl^-, CO_3^{2-}, carbides, or oxides[21] has been claimed. However, neither calcium sulfide nor aluminum carbide reacted with aniline–boron trifluoride.

Infrared Spectra

The infrared spectra of some N-trialkyl-B-trifluoroborazines have been reported.[8] The B–N ring vibration was assigned at 1480–1500 cm^{-1}, the B–F stretching frequency at 1150–1170 cm^{-1}, and the out-of-plane ring vibration at 740 cm^{-1}. The absorptions near these frequencies are listed in Table III for the compounds in this paper. The absorption at 735–728 μ[22,23] confirms the trimeric form for the product from *t*-butylamine indicated by molecular weight determination. The tetrameric borazocines do not give this absorption.[24] The products from the dehydrofluorination of 1,1-dimethylhydrazine and phenylhydrazine did not have the band at 730 cm^{-1} but did have a band at 680 cm^{-1}. The product from 1,1-diphenylhydrazine had a band at 730 and 1430 cm^{-1} perhaps indicating the reaction mixture contained some of the substituted borazine. Since N-aminoborazines have not been previously re-

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[15] H. S. Turner and R. J. Warne, *Proc. Chem. Soc.*, 69 (1962).

[16] B. R. Curwell, W. Gerrard, and M. Khodabocus, *J. Organometal. Chem.* (Amsterdam), **8**, 411 (1967).

[17] H. S. Turner and R. J. Warne, *J. Chem. Soc.*, 6421 (1965).

[18] N. N. Greenwood, K. A. Hooten, and J. Walker, *ibid.*, *A*, 21 (1966).

[19] G. W. Parshall, *Inorg. Chem.*, **1**, 677 (1962).

[20] J. M. Pollock (Imperial Chemical Industries, Ltd.), U. S. Patent 3,055,926 (Sept 25, 1962).

[21] J. M. Pollock (Imperial Chemical Industries, Ltd.), U. S. Patent 3,055,927 (Sept 25, 1962).

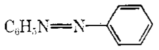
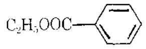
[22] H. Beyer, J. B. Hynes, H. Jenne, and K. Niedenzu, "Boron–Nitrogen Chemistry," Advances in Chemistry Series, No. 42, K. Niedenzu, Ed., American Chemical Society, Washington, D. C., 1964.

[23] D. W. Aubrey, M. F. Lappert, and H. Pyszora, *J. Chem. Soc.*, 1931 (1961).

[24] B. R. Curwell, W. Gerrard, and M. Khodabocus, *Chem. Commun.*, 77 (1966).

TABLE III

INFRARED ABSORPTION OF N-SUBSTITUTED B-TRIFLUOROBORAZINES (cm^{-1})

R	B–N (ring)	B–F (str)	B–N (out-of-plane def)
C_6H_5	1430, 1450	1201, 1030, 1000	719
	1430, 1405	1155	712, 718
C_6H_5	1470, 1450	1150	731, 722
$(CH_3)_3C$	1420 vs	1052, 1200	735, 725
i-C_3H_7	1485, 1453	1140	737, 728
	1410, 1450	1100, 1180	715

ported, the effect of the nitrogen group substituted on the ring nitrogen atom is not known.

Discussion

Of the primary adducts of the boron halides only those of boron trifluoride are difficult to dehydrohalogenate. To our knowledge, the reasons for the relative stability of the primary amine–boron trifluoride adducts to dehydrofluorination have not been well defined. However, stability must be due to kinetic and/or thermodynamic considerations. The boron–fluorine bond strength is much greater than that of the other boron halides.[25] For example, $E(\text{B–F}) = 154$ kcal/mol while $E(\text{B–Cl}) = 109$ kcal/mol, and, other considerations being equal, the boron–fluorine bond would have a higher activation energy for cleavage. The greater bond strength of the boron–fluorine bond also contributes to relatively unfavorable thermodynamics of dehydrofluorination as shown below.

Although the energy change of eq 8 has not been

$$3RNH_2 + 3BX_3 \longrightarrow (RNBX)_3 + 6HX \quad (X = Cl, F) \qquad (8)$$

measured, reasonable estimates may be made from bond strengths. Taking bond strengths as $E(\text{B–F}) = 154$ kcal/mol,[25] $E(\text{N–H}) = 93.4$ kcal/mol,[25] $E(\text{H–F}) = 135$ kcal/mol,[25] $E(\text{B–N (B-trichloroborazine)}) = 108.5$ kcal/mol,[26] $E(\text{B–Cl}) = 109$ kcal/mol,[25] $E(\text{H–Cl}) = 103$ kcal/mol,[25] the energy change for eq 8 may be estimated. We find for X = F the energy change is +23.4 kcal/mol, whereas for X = Cl the energy change is −55.5 kcal/mol. Thus, the reaction with boron trifluoride is endothermic, but with boron trichloride it is exothermic. (The actual values are somewhat more endothermic than this since calculations started with the free amine and boron halide rather than the lower energy adduct actually present in the reaction. However this does not affect the above conclusion.) Treating the primary amine–boron trifluoride adduct with the tertiary amine–boron trifluoride adduct adds reaction 9. The thermodynamics of reaction 9 are not

$$R_3N + BF_3 + HF \longrightarrow R_3NH^+BF_4^- \qquad (9)$$

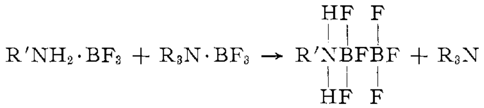
known but can be assumed to be similar to that of an equivalent reaction with NH_3 in which the energy change can be estimated from the appropriate thermodynamic cycle to be −91.3 kcal/mol. Thus, the energy change for eq 1 is estimated to be +23.4 + (6)(−91.3) or −524.4 kcal/mol.

The dehydrofluorination procedure is accomplished by a neutral species, *i.e.*, an adduct of a base and an acid which in this instance acts as a powerful hydrogen fluoride acceptor. Bases tested by us failed to effect dehydrofluorination. Thus, one may tentatively conclude that the adduct participates in the release of hydrogen fluoride from the primary amine–boron trifluoride adduct rather than merely driving the release of hydrogen fluoride from the primary amine–boron trifluoride adduct (eq 10) to completion by accepting

$$C_6H_5NH_2\cdot BF_2 \rightleftharpoons C_6H_5NHBF_2 + HF \qquad (10)$$

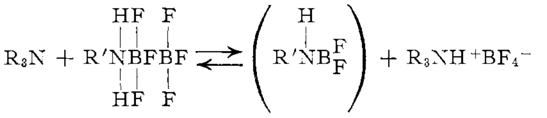
hydrogen fluoride irreversibly. The mechanism suggested below attributes the reaction to the effect the dehydrofluorinating adduct has on (1) the activation energy necessary for cleavage of the strong boron–fluorine bonds and (2) the over-all thermodynamics of dehydrofluorination.

We postulate the formation of a loose complex of boron trifluoride (from the dissociative equilibrium of the dehydrofluorinating complex) with the primary amine–boron trifluoride adduct to be dehydrofluorinated according to eq 11. A complex such as this has



$$R'NH_2\cdot BF_3 + R_3N\cdot BF_3 \rightarrow R'\overset{H}{\underset{H}{N}}\overset{F}{\underset{F}{B}}F\overset{F}{\underset{F}{B}}F + R_3N \qquad (11)$$

been observed[27] for boron trifluoride–amine complexes in the presence of excess boron trifluoride. Since some dissociation of the dehydrofluorinating complex is necessary, tightly bound adducts were not effective. Separation of the tetrafluoroborate anion followed by or with the simultaneous reaction of the free amine with the acidic hydrogen on the nitrogen atom completes the reaction



$$R_3N + R'\overset{H}{\underset{H}{N}}\overset{F}{\underset{F}{B}}F\overset{F}{\underset{F}{B}}F \rightleftharpoons \left(R'\overset{H}{N}B^{F}_{F} \right) + R_3NH^+BF_4^- \qquad (12)$$

A low activation energy path for cleavage of the boron–fluorine bond has been provided since another boron–fluorine bond is formed simultaneously. Although precise bond strengths are not known, both the B–F bond broken and the B–F bond formed are to tetrahedral boron atoms; hence, bond strengths are probably similar. A mechanism similar to the one above has been postulated for the reaction of titanium tetrafluoride with secondary amines.[28]

Experimental Section

All reagents were obtained from laboratory supply houses. Standard laboratory equipment was used, with the usual precautions necessary for moisture-sensitive compounds being

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[25] R. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Butterworth and Co. Ltd., London, 1958.

[26] B. C. Smith, L. Thakur, and M. A. Wasserf, *J. Chem. Soc., A*, 1616 (1967).

[27] H. C. Brown, P. F. Stehle, and P. A. Tierney, *J. Am. Chem. Soc.*, **79**, 2020 (1957).

[28] J. E. Wuller, Ph.D. Dissertation, University of Illinois, Urbana, Ill., 1962.

employed. However, very little drybox or vacuum-line manipulations were necessary. Amines, obtained from laboratory reagent suppliers, were refluxed over and distilled onto calcium hydride before use. Boron trifluoride etherate or boron trifluoride was used as received.

Preparation of B-Trifluoroborazines.—In a typical reaction, boron trifluoride etherate (50 ml, 0.396 mol) was added in 10 min to a stirred solution of 33.6 g (0.26 mol) of diisopropylethylamine and 12.1 g (0.13 mol) of aniline in 200 ml of benzene. The reaction mixture was stirred 3 hr at autogeneous temperature (30–40°), the white solids originally formed being replaced by fine white needles. Recovered was 55.45 g (0.258 mol, 99%) of benzene-insoluble diisopropylethylammonium tetrafluoroborate[29] and as residue after evaporating solvent from filtrate 16.3 g (0.045 mol, 100%) of N-triphenyl-B-trifluoroborazine. Similar results were obtained by treating the preformed adducts in benzene, adding the amines to boron trifluoride etherate, or using ether as a solvent. Replacing boron trifluoride etherate with excess gaseous boron trifluoride gave poor results since a two-layer liquid system formed. The top layer contained some borazine dissolved in benzene, but the remaining borazine was dissolved in an oil, $(i\text{-}C_3H_7)_2C_2H_5NH^+B_2F_7^-$,[29] and complete separation was difficult.

The preparation and properties of the adducts, salts, and B-trifluoroborazines studied are described below. All dehydrofluorinations, except those involving aniline, which was dehydrofluorinated by a variety of amines as shown in Table I, were run with diisopropylethylamine–boron trifluoride.

N-Triphenyl-B-trifluoroborazine.—This was prepared as described above, or in 70% yield from anilinium tetrafluoroborate. It melted at 207–210°, lit.[30] 212°. *Anal.* Calcd for $C_{18}H_{15}N_3B_3F_3$: C, 59.39; H, 4.17; N, 11.58; B, 8.95; F, 15.71. Found: C, 59.79; H, 4.27; N, 11.60; B, 8.81; F, 15.70.

N-Trimethyl-B-trifluoroborazine.—Reaction for 10 hr at 25°, followed by sublimation of the crude product, gave 70% yield of $(CH_3NBF)_3$, mp 88–89°, lit.[8] 90.5°. The infrared absorptions were identical with those in the literature.[9]

N-Triethyl-B-trifluoroborazine.—Crude product was isolated in 100% yield by reaction at 25° for 8 hr. Distillation gave a 75% yield of $(C_2H_5NBF)_3$, bp 140° (723 mm), 91–92° (51 mm), and 74–75° (25 mm), lit.[8] 26° (3 mm); $n^{24}D$ 1.3993; $d^{25}{}_4$ 1.0596. *Anal.* Calcd for $C_6H_{15}N_3B_3F_3$: C, 32.96; H, 6.92; N, 19.22; B, 14.84; F, 26.07. Found: C, 33.09; H, 6.92; N, 19.28; B, 14.71; F, 25.91. The distillation residue was completely dehydrofluorinated (no N–H bands in the infrared spectrum) and had infrared absorptions similar to the borazine. Its molecular weight in benzene was 237 indicating it to be a condensation product.

N-Triisopropyl-B-trifluoroborazine.—Reaction for 3 hr at 25° followed by distillation gave 80% $(i\text{-}C_3H_7NBF)_3$, mp 36–38°. It distilled at 94–97° (12 mm), 82° (6.5 mm), and 54° (1.2 mm). *Anal.* Calcd for $C_9H_{21}N_3B_3F_3$: C, 41.46; H, 8.12; N, 16.12; B, 12.45; F, 21.86. Found: C, 41.05; H, 8.20; N, 16.10; B, 11.85; F, 21.66.

N-Tri-*t*-butyl-B-trifluoroborazine.—Crude product was isolated in 100% yield by reaction at 50° for 8 hr. Heating the crude product caused sublimation of $t\text{-}C_4H_9NHBF_2$, mp 137°, lit.[18] 140°, and distillation of unreacted $(i\text{-}C_3H_7)_2C_2H_5N\cdot BF_3$. The $(t\text{-}C_4H_9NBF)_3$ after sublimation at 60–70° (0.5 mm) or 110–120° (740 mm) melted at 148–148.5°. The molecular weight (ebullioscopic, benzene) was 302; theory, 302.8. Proton nmr indicated a single resonance due to the *t*-butyl group; hence rearrangement of the *t*-butyl group had not occurred. *Anal.* Calcd for $C_{12}H_{27}N_3B_3F_3$: C, 47.59; H, 8.99; N, 13.88; B, 10.72; F, 18.82. Found: C, 46.47; H, 9.21; N, 12.42; B, 10.25; F, 19.10.

N-Tris(*p*-phenylazophenyl)-B-trifluoroborazine.—Reaction for 8 hr at 80° gave a 90% yield of $(p\text{-}C_6H_5N{=\!=}NC_6H_4NBF)_3$, mp 205–221°. The molecular weight (ebullioscopic, benzene) was 654; theory, 675. The deep color of the product implies conjugation of the borazine with the aromatic system. *Anal.* Calcd for $C_{36}H_{27}N_3B_3F_3$: N, 18.67; B, 4.81; F, 8.44. Found: N, 18.50; B, 4.55; F, 8.59.

N-Tris(*p*-carbethoxyphenyl)-B-trifluoroborazine.—Refluxing the reaction 15 hr in benzene gave 100% yield of slow crystallizing oil. Crystallization gave tan $(C_2H_5OOCC_6H_4NBF)_3$, mp 147–165°. The molecular weight (ebullioscopic, benzene) was 583; theory, 579. *Anal.* Calcd for $C_{27}H_{27}O_6N_3B_3F_3$: N, 7.26; B, 5.61; F, 9.85. Found: N, 6.70; B, 5.80; F, 9.40.

B-Trifluoroborazine.—Reaction in $(C_2H_5)_2O$ or neat for 4 hr gave 60% yield of $(HNBF)_3$, 121–122°, lit.[7] 122°. The infrared spectrum of the product was identical with that in the literature.[22] Nonvolatile residue from the crude product indicated the formation of condensed products accounting for the relatively low yield.

Adducts and Salts.—The melting points of the amine–boron trifluoride adducts and amine tetrafluoroborate salts (not previously reported) are given in Table IV. Analysis of the tetrafluoroborate salt was with the nitron reagent.[31]

TABLE IV

	Mp, °C		% BF_4^- salt	
Amine	Adduct	Salt	Theoret	Found
$(C_2H_5)_2NC_6H_5$		104–108	36.62	36.46
Quinaldine		105–110	37.58	37.22
$(sec\text{-}C_4H_9)_2NH$	38–42	142–144	39.99	39.66
$t\text{-}C_4H_9NH_2$	144–149	118–128	53.93	53.46
$p\text{-}C_6H_5N{=\!=}NC_6H_4NH_2$	178–180			
$C_2H_5OOCC_6H_4NH_2$	170–173			
$C_6H_5NHNH_2$	90–97			

Dehydrofluorination of Hydrazine Adducts of Boron Trifluoride.—1,1-Dimethylhydrazine was treated with 1 and 2 equiv of $BF_3\cdot(C_2H_5)_2O$ to give $BF_3\cdot(CH_3)_2NNH_2$ and $BF_3\cdot(CH_3)_2NNH_2\cdot BF_3$. Infrared examination indicated the 1:1 adduct was formed at the substituted nitrogen atom since the N–H vibrations were not affected by complex formation. Dehydrofluorination of 7.8 g (0.13 mol) of the 1:1 adduct with 51.2 g (0.26 mol) of $(i\text{-}C_3H_7)_2C_2H_5N\cdot BF_3$ proceeded very slowly (32-hr reflux). Recovered was 58.5 g (100%+ yield) of $(i\text{-}C_3H_7)_2C_2H_5NH^+BF_4^-$ containing impurities and 5.7 g of benzene-soluble liquid–solids. Since the benzene-soluble product was almost free of N–H bands, dehydrofluorination was essentially complete. The product was partially volatile but not purified at 160–180° (1 mm). It did not contain the 720–740-cm^{-1} band characteristic of borazines[22,23] but did have a band at 685 cm^{-1}.

Treating 26.8 g (0.198 mol) of $(CH_3)_2NNH_2\cdot 2BF_3$ with 107.4 g (0.396 mol) of $(i\text{-}C_3H_7)_2C_2H_5N\cdot BF_3$ for 10 hr at 25° gave 79.1 g (0.364 mol, 92%) of $(i\text{-}C_3H_7)_2C_2H_5NH^+BF_4^-$ and a two-layer filtrate (46.5 g). Removal of volatiles from each layer gave viscous liquids identical by ir spectra. Again, there was no absorption at 730 cm^{-1}, but there was a band at 680 cm^{-1}. Pure products could not be obtained by distillation or solvent extraction.

Treating 17.6 g (0.100 mol) of $C_6H_5NHNH_2\cdot BF_3$ with 39.4 g (0.198 mol) of $(i\text{-}C_3H_7)_2C_2H_5N\cdot BF_3$ and then stirring 8 hr at 25° gave 40.6 g (0.187 mol, 95%) $(i\text{-}C_3H_7)_2C_2H_5NH^+BF_4^-$ and 12.5 g of soluble solids [theory for $(C_6H_5NHNBF)_3$ is 13.6 g]. Purification from benzene–petroleum ether (bp 30–60°) gave a tan powder. As with the product from 1,1-$(CH_3)_2NNH_2$, no significant bands were present at 730 cm^{-1}, but there was a strong absorption at 675 cm^{-1} distinct from the monosubstituted benzene band at 690 cm^{-1}. The sample, when heated to 150°, partially decomposed to $C_6H_5NH_2\cdot BF_3$. The ebullioscopic molecular weight (benzene), which was somewhat concentration dependent, varied from 550 to 650, indicating either association or that the product is not a borazine since $(C_6H_5NHNBF)_3$ exhibits a molecular weight of 407.8.

Refluxing 15.8 g (0.0857 mol) of 1,1-diphenylhydrazine, 23.3

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(29) J. J. Harris, *Inorg. Chem.*, **5**, 1627 (1966).

(30) A. Meller, M. Wechsberg, and V. Gutmann, *Monatsh. Chem.*, **97**, 619 (1966).

(31) C. A. Lucchesi and D. D. Deford, *Anal. Chem.*, **29**, 1169 (1957).

TABLE V

Adduct	Agent	Conditions	Results
$C_6H_5NH_2 \cdot BF_3$	$(i\text{-}C_3H_7)_2C_2H_5N$	Stoichiometric	$(C_6H_5NH)_3B$, $i\text{-}C_3H_7C_2H_5NH^+BF_4^-$
$C_6H_5NH_2 \cdot BF_3$	$(i\text{-}C_3H_7)_2C_2H_5N$	Fivefold excess of $(i\text{-}C_3H_7)_2C_2H_5N$	$(C_6H_5NH)_3B$, $i\text{-}C_3H_7C_2H_5NH^+BF_4^-$
$C_6H_5NH_2 \cdot BF_3$	Heat	Reflux, chlorobenzene	No definitive products other than a small quantity of $C_6H_5NH_3^+BF_4^-$
$C_6H_5NH_2 \cdot BF_3$	Heat	Vacuum or N_2, 150°	No definitive products other than a small quantity of $C_6H_5NH_3^+BF_4^-$
$C_2H_5NH_2 \cdot BF_3$	Heat	Vacuum or N_2, 200°	No definitive products other than a small quantity of $C_2H_5NH_3^+BF_4^-$
$i\text{-}C_3H_7NH_3NH_2$	Heat	Vacuum or N_2, 200°	No definitive products other than a small quantity of $i\text{-}C_3H_7NH_3^+BF_4^-$
$C_6H_5NH_2 \cdot BF_3$	CsF	Reflux, benzene	Aniline and $CsBF_4$ formed
$C_6H_5NH_2 \cdot BF_3$	CaS	Reflux, C_6H_5Cl	No reaction
$C_6H_5NH_2 \cdot BF_3$	CaS and excess BF_3	Reflux, C_6H_5Cl	No reaction
$C_6H_5NH_2 \cdot BF_3$	Al_4C_3	Reflux, benzene	No reaction
$C_6H_5NH_2 \cdot BF_3$	$KO\text{-}t\text{-}C_4H_9$	Reflux, benzene	Aniline and potassium fluoroborate salts
$C_6H_5NH_2 \cdot BF_3$	$AlCl_3$	Relux, benzene, to cessation of HCl evolution	Viscous liquid recovered from the solvent[a]

[a] The viscous liquid contained a small quantity of $C_6H_5NH_3BCl_4$ but was mainly a rubbery solid having strong borazine absorptions in the infrared spectrum but none of B-fluoro- or B-chloroborazines. Condensation of haloborazines to polymeric types of products as has previously been reported at 400–500° is indicated: W. Gerrard, *J. Appl. Chem.* (London), **13,** 127 (1963).

g (0.18 mol) of diisopropylethylamine, and 38.4 g (0.27 mol) of boron trifluoride etherate in 250 ml of benzene for 24 hr gave 25.8 g (0.119 mol) of $(i\text{-}C_3H_7)_2C_2H_5NH^+BF_4^-$ and 33.8 g of soluble oil. Further reflux of the soluble oil in benzene gave little additional dehydrofluorination. Heating the oil to 100° at reduced pressure caused distillation of unreacted $(i\text{-}C_3H_7)_2C_2H_5N \cdot BF_3$ and left a tan solid, 18.0 g. Recrystallization of the solid from benzene–heptane left 14.0 g of white powder, very air-sensitive, mp 75–85°. The ebullioscopic molecular weights (benzene) of several samples varied from 500 to 800. Analytical data indicated a B:N ratio of 1:4 and a B:F ratio of 4:1 to 2:1, depending on the sample. The product had the 720-cm^{-1} infrared absorption characteristic of borazines.[22,23] It seems probable that the product is a mixture of 1,1-diphenylhydrazinoboranes and N-tris(diphenylamino)-B-(1,1-diphenylhydrazino)borazines containing unreacted fluorine atoms.

Preparation of Tris(anilino)borane.—A stirred solution of 37.5 g (0.29 mol) of diisopropylethylamine and 27.0 g (0.29 mol) of aniline in 250 ml of benzene was treated for 15 min with 57.1 g (0.396 mol) of boron fluoride etherate. The mixture was heated to 60° for 4 hr and then filtered. Total recovery of tris(anilino)borane after two extractions of the insoluble $(i\text{-}C_3H_7)_2C_2H_5NH^+BF_4^-$ was 28.1 g, 100%; mp 164–168°, lit.[32] 166–169°. *Anal.* Calcd for $C_{18}H_{18}N_3B$: C, 75.28; H, 6.32; N, 14.63; B, 3.77. Found: C, 75.03; H, 6.50; N, 14.69; B, 4.08.

Preparation of Bis(anilino)boron fluoride.—A mixture of 50 ml (0.396 mol) of $BF_3 \cdot (C_2H_5)_2O$, 18.1 g (0.194 mol) of $C_2H_5NH_2$, and 37.5 g (0.29 mol) $(i\text{-}C_3H_7)_2C_2H_5N$ in 250 ml of benzene was refluxed 1.5 hr at 70° and then filtered, giving 53.6 g of $(i\text{-}C_3H_7)_2C_2H_5NH^+BF_4^-$ and 20.8 g of soluble slurry. A small amount of $(C_6H_5NH)_3B$ was recovered from the slurry.

Fractionation of the remainder with mixtures of benzene and petroleum ether gave a product having the composition $N_2B_{1.07}F_{1.0}$, near that expected for bis(anilino)boron fluoride. *Anal.* Calcd for $C_{12}H_{12}N_2BF$: N, 13.1; B, 5.06; F, 8.88. Found. N, 12.20; B, 5.01; F, 8.11. The ebullioscopic molecular weight (benzene) was 297; theory, 214, indicating considerable association, commonly occurring in similar structures.[2]

Preparation of N-Triphenyl-B-tris(anilino)borazine.—Repeating the above reaction except for refluxing an additional 8 hr gave a 97% yield of $(i\text{-}C_3H_7)_2C_2H_5NH^+BF_4^-$ and a soluble fraction, 80%, identical with an authentic sample of $(C_6H_5NHBNC_6H_5)_3$ prepared by other means.[33]

Attempted Preparation of $C_6H_5NHBF_2$.—Mixtures of 50 ml (0.396 mol) of $BF_3 \cdot (C_2H_5)_2O$, 24.6 g (0.19 mol) of $(i\text{-}C_3H_7)_2C_2H_5N$, and 17.7 g (0.19 mol) of $C_6H_5NH_2$ were allowed to react for 6 hr at 30–45° in benzene by adding the amines to the $BF_3 \cdot (C_2H_5)_2O$ or *vice versa;* a two-layer system formed in each case. The top-layer solids weighed 15.0 g and contained $(C_6H_5NBF)_3$ and other products. The oil layer, 55 g, contained some $(i\text{-}C_3H_7)_2C_2H_5NH^+BF_4^-$ plus another component, possibly $(i\text{-}C_3H_7)C_2H_5NH^+C_6H_5NHBF_3^-$. Separation by various solvents was not possible. A similar oil was formed by reaction of $(i\text{-}C_3H_7)_2C_2H_5NH^+BF_4^-$ and $C_6H_5NH_2 \cdot BF_3$.

Dehydrofluorination of 2,6-Diethylaniline Adducts.—Mixtures of $2,6\text{-}(C_2H_5)_2C_6H_3NH_2 \cdot BF_3$ were treated with $(i\text{-}C_3H_7)_2C_2H_5N \cdot BF_3$, sometimes in the presence of excess $2,6\text{-}(C_2H_5)_2C_6H_3NH_2$. Complex mixtures resulted. For example, reaction of the reagents in the stoichiometry required for $(ArNH)_3B$ gave a product contaminated by unreacted $2,6\text{-}(C_2H_5)_2C_6H_3NH_2$. The material, precipitated from heptane, gave an analysis similar to that expected for $(ArNH)_2BF$. *Anal.* Calcd for $C_{20}H_{28}N_2BF$: C, 73.62; H, 8.65; N, 8.59; B, 3.32; F, 5.82. Found: C, 72.60; H, 9.22; N, 8.76; B, 3.15; F, 4.26. Mixing the reagents in the stoichiometry required for $(ArNHBNAr)_3$ resulted in the reaction of only sufficient $(i\text{-}C_3H_7)_2C_2H_5N \cdot BF_3$ to form $(ArNH)_2BF$. Some additional reaction was obtained by heating the reactants, neat, to 130°. The slow-to-crystallize oil finally obtained had a composition of $(ArNH)_{1.44}BF_{0.8}$ and was obviously a mixture of $(ArNH)_{3-n}BF_n$ and its condensation products.

Mixing the reagents in the stoichiometry necessary for formation of $ArNHBF_2$ gave incomplete utilization of the $BF_3 \cdot (C_2H_5)_2O$. Attempts to crystallize the crude product resulted in recovery of $ArNH_2 \cdot BF_3$ at several stages. The major product was that given above as impure $(ArNH)_2BF$. These results are quite similar to those of other workers during attempted syntheses of aliphatic $RNHBF_2$ compounds.[18]

Miscellaneous Attempts at Dehydrofluorination.—Several attempts to cause dehydrofluorination of amine–boron trifluoride by a variety of other agents were made, as outlined in Table V.

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(32) R. G. Jones and C. R. Kinney, *J. Am. Chem. Soc.*, **61**, 1378 (1939).

(33) D. W. Aubrey and M. F. Lappert, *J. Chem. Soc.*, 2927 (1959).