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A DIRECT SYNTHETIC ROUTE TO *B*-TRIFLUOROBORAZINES

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SUMMARY

B-Tris(alkylamino)-*N*-trialkyl-borazines and *B*-tris(arylamino)-*N*-triaryl-borazines may be prepared almost quantitatively by employing the appropriate stoichiometry in the reaction between boron trichloride and an alkyl- or aryl-amine. The borazines so formed react with boron trifluoride or boron trifluoride etherate to give good yields of the *B*-trifluoro-*N*-trialkyl- and *B*-trifluoro-*N*-triaryl-borazines. Using this method, $(CH_3NBF)_3$, $(p\text{-}ClC_6H_4NBF)_3$ and $(C_6F_5NBF)_3$ have been prepared. The analogous reaction using $(C_6F_5)_3B$ as a route to *B*-tris(pentafluorophenyl)borazines was unsuccessful.

INTRODUCTION

New synthetic routes to *B*-trifluoroborazines have received little attention during the years since Niedenzu[1,2] and Laubengayer[3] described their preparation employing the transhalogenation reaction between *B*-trichloroborazines and TiF_4 or SbF_3. This indirect route was generally accepted, since whereas the aminolysis of B–Cl bonds is a convenient route to the *B*-trichloroborazines, analogous reactions to give the *B*-trifluoro derivatives occur only to a minor extent[4]. It was later shown[5], however, that aminolysis of BF_3 gives good yields of the *B*-trifluoroborazines when a suitable dehydrofluorinating agent (usually a sterically-hindered tertiary amine) is included in a reaction mixture of selected stoichiometry. More recent, but less direct routes include the reactions of BF_3 with either silylamines of the type $(CH_3)_3SiNHR$[6] or $[(CH_3)_3Si]_2NMe$[7] to give the *B*-trifluoroborazines, along with $(CH_3)_3SiF$, and in the former case, $RNH_2{\bullet}BF_3$ as well.

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We have been interested in finding a convenient route to *B*-trifluoroborazines so as to observe their behavior under electron impact; Boenig and Niedenzu[8] describe a time-saving method for the preparation of *B*-trichloro-*N*-trimethylborazine in which BCl_3 is allowed to react with $(CH_3NHBNCH_3)_3$. The *B*-triaminoborazine is prepared using the stoichiometry depicted in equation (1).

$$3BCl_3 + 15CH_3NH_2 \rightarrow (CH_3NHBNCH_3)_3 + 9CH_3NH_2{\cdot}HCl \quad (1)$$

With the report by Beachley[9] that *B*-monofluoroborazine is obtained from the interaction of $H_2(CH_3)_2NB_3N_3H_3$ with $BF_3{\cdot}O(C_2H_5)_2$, it seemed likely that *B*-trifluoroborazines could be prepared by allowing BF_3 or $BF_3{\cdot}O(C_2H_5)_2$ to react with *B*-triaminoborazines as prepared by the stoichiometry of reaction (1).

RESULTS AND DISCUSSION

The identities of the borazines prepared were determined by mass spectrometry. The presence of polyisotopic atoms leads to unique mass-spectral isotopic patterns which when compared to computed patterns offer the ready identification of molecular formulae. Fragmentation patterns and routes assigned with the aid of metastable ions confirmed the presence of the borazine ring[10, 11].

The reactions of CH_3NH_2 and p-$ClC_6H_4NH_2$ with BCl_3, using the stoichiometry of reaction (1), proceeded smoothly to give a product, which on reaction with $BF_3{\cdot}O(C_2H_5)_2$ yielded the corresponding *B*-trifluoroborazine [equation (2)].

$$(RNHBNR)_3 + 3BF_3 \rightarrow (RNBF)_3 + 3RNHBF_2 \quad (2)$$
$$(R = CH_3,\ p\text{-}ClC_6H_4)$$

The aminodifluoroborane produced is unstable[6] and decomposes to give the primary-amine$\cdot BF_3$ adduct and *B*-trifluoroborazine [equation (3)].

$$6RNHBF_2 \rightarrow (RNBF)_3 + 3RNH_2{\cdot}BF_3 \quad (3)$$

The preparation of $(CH_3NBF)_3$ seems to have strictly followed the routes depicted in equations (1)–(3) with the borazine and $CH_3NH_2{\cdot}BF_3$ being the sole products. The $CH_3NH_2{\cdot}BF_3$ recovered in the reaction showed a mass spectrum consistent with the amine$\cdot BX_3$ adducts[12]; no parent ion (M) was observed, the base peak and highest mass value occurring at M—19 and corresponding to the $RNH_2BF_2^+$ ion. In the preparation of $(p\text{-}ClC_6H_4NBF)_3$, however, the initial precipitate obtained, following the addition of $BF_3{\cdot}O(C_2H_5)_2$ and refluxing procedure, was found to contain unreacted p-$ClC_6H_4NH_2$ as well as a trace of p-$ClC_6H_4NHBF_2$. Gradual concentration of the mother liquor yielded $(p\text{-}ClC_6H_4NH)_2BF$ and $(p\text{-}ClC_6H_4N)_3B$ before the borazine was observed to precipitate together with a small amount of $(p\text{-}ClC_6H_4N)_3B$. Indeed, it has been observed that arylamine$\cdot BCl_3$ adducts require refluxing temperatures in excess of 100 °C for long periods (24 h) to give the *B*-trichloro-*N*-triarylborazines[13], and it may be that the best route to the *B*-trifluoro-*N*-triarylborazines is through the

aminolysis of the *B*-trichloro-*N*-triarylborazines[4] followed by their reaction with $BF_3{\bullet}O(C_2H_5)_2$.

$(C_6F_5NBF)_3$ has been prepared previously by the fluorination of $(C_6F_5NBCl)_3$ with either NaF in acetonitrile[14] or TiF_4[15]. Our reaction procedure to give $(C_6F_5NBF)_3$ was varied in order to conserve the use of the more expensive $C_6F_5NH_2$. Since one function of the amine in the initial reaction to give the *B*-triaminoborazine is to act as a hydrogen-halide acceptor, the appropriate amount of $(C_2H_5)_3N$ was used in place of the $C_6F_5NH_2$ required for this function [equation (4)].

$$3(C_2H_5)_3N{\bullet}BCl_3 + 6(C_2H_5)_3N + 6C_6F_5NH_2 \rightarrow (C_6F_5NHBNC_6F_5)_3 + 9(C_2H_5)_3N{\bullet}HCl \quad (4)$$

The required ratio of base:BCl_3 remains at 5:1 as in equation (1) and the reaction proceeds smoothly to give $(C_6F_5NHBNC_6F_5)_3$. No $(C_6F_5NH)_3B$ was observed to be present in the product and its reaction with $BF_3{\bullet}O(C_2H_5)_2$ readily gave $(C_6F_5NBF)_3$.

Encouraged by the success of these procedures, an attempt to prepare $(C_6F_5BNC_6F_5)_3$ was made by allowing $(C_6F_5)_3B$ to react with $(C_6F_5NHBNC_6F_5)_3$. However, only $(C_6F_5)_3B$ was recovered from the reaction mixture after refluxing in toluene for 19 h. The thermal stability of $(C_6F_5)_3B$ has been noted by Massey and Park[16] and resistance to cleavage of the B–C bond is noted in this work as in theirs, where the pyrolysis of $(C_6F_5)_3B{\bullet}NH_3$ at 70 °C for 21 days produced only 14.2% of the theoretically obtainable C_6F_5H. The success of the reaction to give *B*-tris(pentafluorophenyl)borazines may depend on more rigorous conditions than attempted here.

EXPERIMENTAL

All materials were handled using a high-vacuum system or a dry, inert-atmosphere system. CH_3NH_2, BF_3 and BCl_3 (Matheson) were used directly as supplied, as were $C_6F_5NH_2$ (Pierce Chemical) and $BF_3{\bullet}O(C_2H_5)_2$ (Eastman Organic). *p*-$ClC_6H_4NH_2$ (Chem Service), however, was dried over P_2O_5 in a vacuum dessicator prior to use. $(C_2H_5)_3N$ (Eastman Organic) was dried and stored over anhydrous $CaCl_2$, while n-pentane, benzene and toluene were dried and stored over sodium metal. All were purified by vacuum fractionation prior to use. $(C_6F_5)_3B$ was prepared by the method of Pohlmann and Brinckmann[17] and purified by vacuum sublimation.

The mass-spectral measurements were made using an A.E.I. MS-30 double-beam, double-focusing mass spectrometer with 4 kV accelerating voltage, 1000 resolution, 70 eV electron bombardment and 100 μA filament emission. Spectra were recorded at 30 s decade^{-1}. Samples for analysis were loaded into capillary sample cups under a dry, inert atmosphere and introduced into beam 1 of the MS-30 *via* a

variable-temperature direct probe. Utilizing the double-beam feature of the mass spectrometer, chemical mass marking was achieved by running perfluorokerosene in beam 2.

Preparation of $(CH_3NBF)_3$

In a typical synthesis, a solution of BCl_3 (14.20 g) in n-pentane (*ca.* 75 cm^3) was slowly added to a solution of CH_3NH_2 (18.95 g) in n-pentane (*ca.* 100 cm^3). The reaction mixture was maintained at −78 °C by immersion in a Dry Ice/acetone bath. The solution was allowed to reach room temperature, filtered and the n-pentane removed from the filtrate using a rotary evaporator. Benzene (*ca.* 100 cm^3) was added to the remaining syrupy material and a solution of $BF_3{\bullet}O(C_2H_5)_2$ (17.16 g) in benzene (*ca.* 75 cm^3) added slowly. The mixture was refluxed for 4 h*, filtered (when $CH_3NH_2{\bullet}BF_3$ was removed) and the filtrate fractionated under high vacuum through traps at 0 °C, *ca.* −22 °C and *ca.* −196 °C. Material recovered from the trap at 0 °C contained traces of benzene and $BF_3{\bullet}O(C_2H_5)_2$, and required repeated fractionation to yield $(CH_3NBF)_3$ [4.09 g, 58%; m.p. 85 °C (lit. value[4]: 90.5 °C)].

An improved procedure removed $BF_3{\bullet}O(C_2H_5)_2$ as a product contaminant by treating $(CH_3NHBNCH_3)_3$, formed in the first step, with BF_3 in benzene, contained in an addition flask large enough to prevent an over-pressure at room temperature. The mass spectrum of the product showed a parent-ion cluster corresponding to $(CH_3NBF)_3$[18] (although the parent-ion-cluster base peak may be expected at *m/e* 81, corresponding to the ^{11}B-mono-isotopic species, large contributions from M−H, M−2H, *etc.* are also observed) and a fragmentation pattern characteristic for borazines[10,11].

Preparation of $(p\text{-}ClC_6H_4NBF)_3$

A solution of BCl_3 (0.91 g) in benzene (*ca.* 75 cm^3) was added slowly to a room-temperature solution of $p\text{-}ClC_6H_4NH_2$ (4.94 g) in benzene (*ca.* 100 cm^3). The solution was refluxed for 10 h, allowed to cool, filtered and the filtrate transferred to a second reaction flask. A solution of $BF_3{\bullet}O(C_2H_5)_2$ (8.61 g) was added slowly and the reaction mixture refluxed for 4 h. After cooling to room temperature, an initial precipitate was found to consist of a mixture of unreacted $p\text{-}ClC_6H_4NH_2$ together with a trace of $p\text{-}ClC_6H_4NHBF_2$ (mass-spectral analysis). Removal of the solvent was accomplished gradually; crystals filtered concurrently from the solution were found to be $(p\text{-}ClC_6H_4NH)_2BF$ and $(p\text{-}ClC_6H_4NH)_3B$. Further concentration of the mother liquor yielded $(p\text{-}ClC_6H_4NBF)_3B$. Sublimation at 85 °C gave a small amount (0.40 g, 24%) of the mass-spectroscopically pure product $(p\text{-}^{35}Cl^{12}C_6{}^1H_4{}^{14}N^{11}B^{19}F)_3$, *m/e* 465.

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* For all of the reactions reported, during all procedures requiring the addition of one solution to another, as well as during reflux, the reaction mixture was vigorously stirred.

Preparation of $(C_6F_5NBF)_3$

BCl_3 (3.90 g) was condensed under vacuum into a reaction flask, followed by toluene (*ca.* 100 cm^3) and $(C_2H_5)_3N$ (10.03 g). The mixture was warmed to room temperature and stirred to give a homogeneous solution. A solution of $C_6F_5NH_2$ (12.18 g) in toluene (*ca.* 75 cm^3) was then added over a period of 10 min and the contents of the reaction vessel brought to a pressure of 1 atm with dry N_2. The solution was refluxed for 27 h, cooled and filtered. Removal of the solvent yielded a thick maroon-coloured liquid which showed a mass-spectral parent-ion-cluster base peak at *m/e* 1122, $(C_6F_5NHBNC_6F_5)_3$. $BF_3{\bullet}O(C_2H_5)_2$ (2.13 g) in benzene (*ca.* 75 cm^3) was slowly added to a solution of $(C_6F_5NHBNC_6F_5)_3$ (5.17 g) in benzene (*ca.* 100 cm^3) and the final solution refluxed for 17 h. The mixture was cooled, filtered and the remaining solution concentrated to yield a crop of clear amber crystals. Following high-vacuum removal of all traces of benzene, sublimation at 120 °C gave a white solid $(C_6F_5NBF)_3$ (3.85 g, 88%) having a mass-spectral parent-ion-cluster base peak at *m/e* 633.

The attempted reaction between $(C_6F_5)_3B$ *and* $(C_6F_5NHBNC_6F_5)_3$

A solution of $(C_6F_5)_3B$ (2.85 g) in toluene (*ca.* 75 cm^3) was added slowly to a solution of $(C_6F_5NHBNC_6F_5)_3$ (2.30 g) in toluene (*ca.* 100 cm^3). The final solution was refluxed for 19 h and cooled. No precipitates were observed. The solvent was removed under vacuum leaving a viscous brown liquid which yielded $(C_6F_5)_3B$ (1.95 g) on sublimation at 85 °C.

CONCLUSIONS

Through the use of the reaction between $BF_3{\bullet}O(C_2H_5)_2$ and *B*-triaminoborazines, as prepared by the method of Boenig and Niedenzu, $(CH_3NBF)_3$, $(p\text{-}ClC_6H_5NBF)_3$ and $(C_6F_5NBF)_3$ have been prepared. This method may be applicable to many *N*-alkyl- and *N*-aryl-borazine systems. Although the cleavage of B–C bonds in $(C_6F_5)_3B$ was not observed to give rise to *B*-tris(pentafluorophenyl)borazines by this method, investigations as to the reactivity of trialkylboranes as alkylating agents in the preparation of *B*-trialkylborazines are underway in this laboratory.

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