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Molecular Addition Compounds. 5. Interaction of *N,N,N′,N′*-Tetramethylethylenediamine with Boron Trifluoride and Monoalkylboranes

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Received September 7, 1978

N,N,N′,N′-Tetramethylethylenediamine (TMED) reacts instantly with boron trifluoride ethyl etherate to give the highly insoluble product TMED·$2BF_3$. This development made it of interest to synthesize and study the addition compounds of TMED with representative monoalkylboranes. TMED reacts readily with typical monoalkylboranes to form both the TMED–monoalkylborane TMED·BH_2R and the corresponding bis adducts TMED·$2BH_2R$. These are air stable and can be stored without apparent change for long periods of time. Boron trifluoride removes TMED from these adducts, rapidly and completely, precipitating TMED·$2BF_3$. In this way the monoalkylboranes can be conveniently purified and stored as their stable adducts with TMED, with rapid convenient generation of the parent monoalkylborane as desired.

Introduction

Recent studies in this laboratory have resulted in a simple procedure for the preparation of triethylamine–monoalkylborane adducts, $Et_3N{\cdot}BH_2R$, starting from triethylamine–thexylborane, $Et_3N{\cdot}BH_2Th$ (**1**),[1] and have led to the discovery of promising new applications for these derivatives. The triethylamine component could be removed from these adducts by treatment with either THF·BH_3[2] or $Et_2O{\cdot}BF_3$[3] to produce the free monoalkylboranes for reduction and hydroboration applications. However, this procedure suffers from certain difficulties. Both $Et_3N{\cdot}BH_3$ and $Et_3N{\cdot}BF_3$ are highly soluble in the usual THF medium, making them difficult to separate from the desired product.[2,3] This problem can be circumvented in part by changing to a pentane solution from which $Et_3N{\cdot}BF_3$ can be precipitated at −50 °C.[3] Furthermore, the $Et_3N{\cdot}BH_2R$ adducts are liquids of uncertain purity which cannot be purified readily. Moreover, the versatile monoalkylboranes, thexylborane, $ThBH_2$,[4] and 2,4,4-trimethyl-3-pentylborane, diisobutylborane ≡ $(DIB)BH_2$,[5] possess limited stability upon storage in THF at 0 °C or at 25 °C.[5] Consequently they must be synthesized and used shortly thereafter. Hence it appeared highly desirable to develop a derivative which could be stored either neat or in solution for extended periods of time and then conveniently converted to the free borane as and when needed.

In the course of our work on amine–boranes,[6] we discovered that the reaction of *N,N,N′,N′*-tetramethylethylenediamine (TMED) with $Et_3O{\cdot}BF_3$ affords a white solid which is highly insoluble in the usual organic solvents (THF, Et_2O, $CHCl_3$, pentane, benzene) and only slightly soluble in acetone or water. Despite the fact that many studies have been published concerning addition compounds of polyamines with boron trifluoride, no results on the reaction between $Et_2O{\cdot}BF_3$ and TMED appear to have been recorded in the literature previously.[7-13] Therefore, it appeared desirable to investigate the reaction between $Et_2O{\cdot}BF_3$ and TMED and to explore the possibility of utilizing TMED as a stabilizing addendum for monoalkylboranes.

This paper reports the isolation and characterization of TMED adducts of BF_3, $ThBH_2$, $(DIB)BH_2$, and monoisopinocampheylborane, $(IPC)BH_2$, and the facile quantitative removal of the TMED complexing agent from these adducts as the highly insoluble TMED·$2BF_3$ compound.

Experimental Section

The reaction flasks and other glass equipment used for experiments were dried in an oven and assembled in a stream of dry nitrogen gas. Special experimental techniques used in handling air-sensitive material are described in detail elsewhere.[14] All melting points are uncorrected and were determined in evacuated sealed capillary tubes using the Thomas-Hoover capillary melting point apparatus. $Et_2O{\cdot}BF_3$ and TMED were distilled from calcium hydride. ^1H NMR and ^{11}B NMR spectra were recorded on Varian T-60 and FT-80A instruments, respectively. The ^1H and ^{11}B chemical shifts are in δ relative to Me_4Si and $Et_2O{\cdot}BF_3$ standards, respectively.

Preparation of Complexes.[15] ***N,N,N′,N′*-Tetramethylethylenediamine Complex with Boron Trifluoride, TMED·$2BF_3$ (2). (a) Determination of Stoichiometry by ^1H NMR Spectroscopy.** Three different reactions were carried out in individual reaction flasks maintained at 25 °C. The flasks were charged with TMED (2.0 mmol), benzene (2.0 mmol, internal standard), and $CDCl_3$ (2.0 mL). An aliquot was taken from the first flask and the amount of TMED was estimated via ^1H NMR spectroscopy. To the second flask, 2.0 mmol of $Et_2O{\cdot}BF_3$ was added with stirring. The ^1H NMR spectrum of the supernatant liquid indicated that 1.0 mmol of TMED remained unreacted. To the third flask was added with vigorous stirring 4.0 mmol of $Et_2O{\cdot}BF_3$. The supernatant liquid was withdrawn and its ^1H NMR spectrum determined. No signals attributable to TMED were visible.

(b) Determination of Stoichiometry by GLC. The same reactions were carried out in the THF, Et_2O, and pentane at 25 °C. The following procedure in THF is representative. In a 50-mL centrifuge vial 5.0 mmol of TMED and 3.0 mmol of *n*-dodecane (internal standard) were dissolved in 4.0 mL of THF. The amount of TMED present in the solution was determined by GLC analysis with a 6 ft × 0.25 in. column packed with 10% Carbowax 20M on Chromosorb W. The solution was then treated with 5.0 mmol of $Et_2O{\cdot}BF_3$ with stirring; a white solid precipitated. GLC analysis of the supernatant liquid indicated that 2.5 mmol of the TMED remained unreacted. The reaction mixture was treated further with 5.0 mmol of $Et_2O{\cdot}BF_3$.

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The GLC analysis now revealed that none of the TMED was present in the solution. The adduct was collected by centrifugation, washed several times with *n*-pentane, and dried. There was obtained 1.254 g (99.5% yield): mp 210–212 °C (recrystallized from acetonitrile); ^{1}H NMR (acetone-d_6) δ 2.97 (s, 12 H), 3.53 (s, 4 H); ^{11}B NMR δ −0.74 (s).

The same adduct precipitated when $Et_2O{\cdot}BF_3$ was added to excess TMED. The results were identical with reverse addition.

TMED·BH_2(DIB) (3). In a 50-mL centrifuge vial 10.0 mmol of borane–methyl sulfide (BMS) was placed. To this reagent 1.57 mL of 2,4,4-trimethyl-2-pentane (10.0 mmol) was added dropwise with stirring. Stirring was continued for another 0.5 h at 25 °C. To the reaction product 1.5 mL of TMED (10.0 mmol) was added slowly. The solid adduct was washed with cold *n*-pentane to remove methyl sulfide and then dried. There was obtained 2.39 g (98.7% yield) of the 1:1 adduct: mp 92–95 °C (recrystallized from *n*-pentane); ^{1}H NMR ($CDCl_3$) δ 0.12 (small hump, 1 H), 0.95–1.05 (s and a, 15 H), 1.83 (m, 1 H), 2.22 (s, 6 H), 2.50 (s, 6 H), 2.60–3.20 (m, 4 H); ^{11}B NMR δ −1.74 (br t).

TMED·BH_2Th (4). Thexylborane (10.0 mmol) with methyl sulfide was prepared according to the literature procedure.[16] To this product 1.5 mL of TMED (10 mmol) was added at 25 °C with stirring. Following completion of the vigorous reaction, methyl sulfide was removed under reduced pressure (12 mmHg) to afford 1.98 g of TMED·BH_2Th as a viscous liquid (92% yield). The compound was purified by distillation under reduced pressure: bp 38–40 °C (12 mmHg); n^{20}D 1.4240; ^{1}H NMR ($CDCl_3$) δ 0.83–0.93 (s and d, 12 H), 1.08–1.60 (m, 1 H), 2.25 (s, 6 H), 2.65 (s, 6 H), 2.65–3.00 (m, 4 H); ^{11}B NMR δ −1.38 (t).

TMED·$2BH_2$Th (5). The procedure is the same as above, except that only 5 mmol of TMED (0.75 mL), instead of 10 mmol, was used to form the addition compound. Removal of methyl sulfide under reduced pressure (12 mmHg) provided the adduct as a semisolid: 1.46 g (93% yield). It was then purified by recrystallization from *n*-pentane at −50 °C: mp 43–45 °C; ^{1}H NMR ($CDCl_3$) δ 0.83 (s, 12 H), 0.87 (d, J = 6 Hz, 12 H), 1.47 (septet, J = 6 Hz, 2 H), 2.63 (s, 12 H), 3.2 (s, 4 H); ^{11}B NMR δ −0.77.

TMED·BH_2(IPC) (6). With the usual experimental setup, neat $Et_3N{\cdot}BH_2$(IPC) (5 mmol) was prepared as described earlier.[1] To this reagent 0.75 mL of TMED (5.0 mmol) was added at 25 °C and the mixture was stirred for 1.5 h. The heavy white precipitate of TMED·BH_2(IPC) was collected by centrifugation, washed with cold *n*-pentane, and dried. There was obtained 1.01 g (75% yield) of the 1:1 adduct: mp 113–115 °C (recrystallized from *n*-pentane); ^{1}H NMR ($CDCl_3$) δ 1.00 (d, J = 6 Hz, 3 H), 1.10 (s, 3 H), 1.17 (s, 3 H), 2.27 (s, 6 H), 2.60 (s, 6 H), 3.2 (s, 2 H); ^{11}B NMR δ +2.20.

TMED·$2BH_2$(IPC) (7). A solution of TMED·BH_2(IPC) (10 mmol) in Et_2O (10 mL) was taken in a 50-mL centrifuge vial and 1.23 mL of $Et_2O{\cdot}BF_3$ (10 mmol) was added to it with constant stirring. On completion of the addition, the solid TMED·$2BF_3$ was centrifuged and the supernatant liquid was transferred to another centrifuge tube and cooled. The crystalline adduct was collected in the usual manner and dried. There was obtained 1.69 g of the 1:2 adduct (80% yield): mp 140–141 °C (recrystallized from Et_2O); ^{1}H NMR ($CDCl_3$) δ 1.0 (d, J = 6 Hz, 6 H), 1.1 (s, 6 H), 1.16 (s, 6 H), 2.63 (s, 12 H), 3.2 (s, 4 H); ^{11}B NMR δ +1.80.

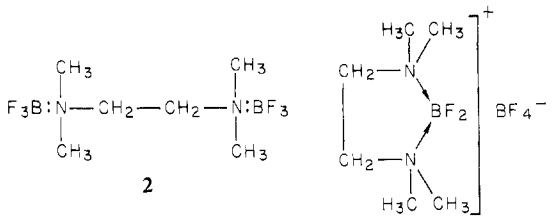
Liberation of Free Monoalkylborane. The following procedure for the liberation of free (DIB)BH_2 from TMED·BH_2(DIB) in THF is representative. To a solution of 10 mmol of TMED·BH_2(DIB) in 10 mL of THF was added 20 mmol of $Et_2O{\cdot}BF_3$ with stirring at 25 °C. A heavy white solid precipitated almost immediately. Stirring was continued for 15 min. The mixture was diluted with 10 mL of THF and the solid centrifuged down. The supernatant solution was decanted. Examination by IR revealed that it contained essentially 10 mmol of free (DIB)BH_2.

Results and Discussion

Our primary interest was to establish the stoichiometry of the reaction between $Et_2O{\cdot}BF_3$ and TMED and the nature of the solid obtained. The reaction proceeds simply to the formation of 1:2 complex (eq 1), with no evidence for the

$$\text{TMED} + 2Et_2O{\cdot}BF_3 \xrightarrow[25\ ^\circ C]{\text{THF}} \text{TMED}{\cdot}2BF_3\downarrow \qquad (1)$$

formation of the intermediate 1:1 complex. The course of the reaction could be followed conveniently by ^{1}H NMR spectroscopy and GLC. Methyl protons in TMED resonate at δ 2.25, and by integration of this peak the amount of unreacted amine could be calculated using an internal standard. Similarly the amount of uncomplexed amine could be determined also through GLC analysis. The solid is readily isolated. Upon recrystallization from acetonitrile large crystals are obtained. Elemental analysis revealed a molecular formula $C_6H_{16}B_2N_2F_6$ for the adduct. ^{1}H NMR spectroscopy indicated that the adduct could be represented either as the symmetrical bis adduct (**2**) or as the boronium tetrafluoroborate (**8**).



2 **8**

Since structure **2** is highly symmetrical, its ^{11}B NMR spectrum will have a single resonance line. On the other hand, the ^{11}B NMR spectrum of a compound represented by structure **8** would consist of two boron resonance lines. Actually the spectrum of the adduct displayed a single boron resonance line, thereby supporting structure **2** for the adduct. To the best of our knowledge, TMED·$2BF_3$ has not been previously reported in the literature. In this way, $Et_2O{\cdot}BF_3$ can be utilized to remove TMED quantitatively from solution in a wide variety of solvents. Alternatively, TMED can be used to precipitate BF_3 quantitatively from solutions in these solvents.

Any excess TMED over the 1:2 stoichiometry remains unreacted. Thus, the addition of $Et_2O{\cdot}BF_3$ to an equimolar amount of TMED in THF precipitates precisely half of the amine as the adduct with half of the amine remaining in solution (eq 2). Identical results were obtained in Et_2O and

$$\text{TMED} + Et_2O{\cdot}BF_3 \xrightarrow[25\ ^\circ C]{\text{THF}} {}^1/_2\text{TMED}{\cdot}2BF_3\downarrow + {}^1/_2\text{TMED} \qquad (2)$$

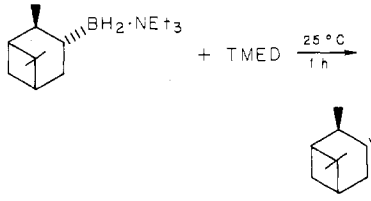
n-pentane. The same results were realized with reverse addition.

This development made the TMED adducts of monoalkylboranes of considerable interest. Accordingly, we turned our attention to the preparation and characterization of representative TMED–monoalkylborane adducts. TMED·BH_2(DIB) and TMED·BH_2Th were quantitatively prepared by direct reaction of (DIB)BH_2 and ThBH_2, respectively, with TMED in 1:1 molar ratio (eq 3 and 4).

$$(\text{DIB})BH_2 + \text{TMED} \xrightarrow[25\ ^\circ C]{\text{THF}} \text{TMED}{\cdot}BH_2(\text{DIB}) \qquad (3)$$

$$\text{Th}BH_2 + \text{TMED} \xrightarrow[25\ ^\circ C]{\text{THF}} \text{TMED}{\cdot}BH_2\text{Th} \qquad (4)$$

Since TMED can displace other amines from their adducts,[9] we utilized $Et_3N{\cdot}BH_2$(IPC) for the preparation of TMED·BH_2(IPC) (eq 5). Triethylamine was removed under reduced



6

pressure (12 mmHg) to yield the 1:1 adduct. The 1:2 adducts could be prepared by combining 2 mol of the monoalkylborane

with 1 mol of TMED. In this way, TMED·2BH_2Th was prepared (eq 6).

$$2ThBH_2 + TMED \xrightarrow[neat]{25\ °C} TMED{\cdot}2BH_2Th \quad (6)$$

5

Treatment of the 1:1 addition compounds with an equimolar quantity of $Et_2O{\cdot}BF_3$ precipitates half of the TMED and forms the 1:2 complex in solution (eq 7). This reaction was used

$$2TMED{\cdot}BH_2R + 2Et_2O{\cdot}BF_3 \xrightarrow[25\ °C,\ 0.5\ h]{THF} TMED{\cdot}2BH_2R + TMED{\cdot}2BF_3\downarrow \quad (7)$$

for the preparation of TMED·2BH_2(IPC) (eq 8).

$$2TMED{\cdot}BH_2(IPC) + 2Et_2O{\cdot}BF_3 \xrightarrow[25\ °C,\ 0.5\ h]{THF} TMED{\cdot}2BH_2(IPC) + TMED{\cdot}2BF_3\downarrow \quad (8)$$

Both the 1:1 and 1:2 addition compounds of these monoalkylboranes and TMED are air stable and can be stored neat or in THF solution for several weeks at 25 °C without noticeable hydride loss, isomerization, or redistribution. Treatment of the adducts in THF solution with 2 equiv of $Et_2O{\cdot}BF_3$ rapidly regenerates the free monoalkylboranes in solution with the complete precipitation of TMED·2BF_3 (eq 9).

$$TMED{\cdot}BH_2R + 2Et_2O{\cdot}BF_3 \xrightarrow[25\ °C,\ 0.5\ h]{THF} RBH_2 + TMED{\cdot}2BF_3\downarrow \quad (9)$$

Conclusion

The fast, complete reaction of boron trifluoride with TMED to form the highly insoluble TMED·2BF_3 provides a convenient means to remove either TMED or BF_3 from solution. Monoalkylboranes are readily stabilized as their TMED adducts, TMED·BH_2R and TMED·2BH_2R. Treatment of appropriate solutions of these adducts with an equivalent quantity of $Et_2O{\cdot}BF_3$ rapidly precipitates TMED·2BF_3 quantitatively, providing pure solution of the monoalkylboranes. This development makes such monoalkylboranes readily available for study and utilization.

Acknowledgment. We are grateful to the National Institutes of Health (Grant GM 10937) for financial support.

Registry No. **2**, 67813-45-0; **3**, 67826-88-4; **4**, 67826-89-5; **5**, 67826-90-8; **6**, 68297-73-4; **7**, 68297-74-5; TMED, 110-18-9; $Et_2O{\cdot}BF_3$, 109-63-7; BMS, 13292-87-0; 2,4,4-trimethyl-2-pentene, 107-40-4; $Me_2S{\cdot}BH_2$Th, 68297-75-6; $Et_3N{\cdot}BH_2$(IPC), 64065-16-3.

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Molecular Addition Compounds. 6. Addition Compounds of Ethylenediamine with Boron Trifluoride and Dialkylboranes[1]

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Received September 7, 1978

Ethylenediamine (EDA) reacts readily with boron trifluoride in ether to give the insoluble mono adduct $NH_2CH_2CH_2NH_2{\cdot}BF_3$. The amine also reacts with dialkylboranes in a 1:2 molar ratio to provide the bis adducts EDA·2BHR_2. The latter adducts are quite stable and can be stored at 0 °C without detectable isomerization or redistribution. In ether or THF, boron trifluoride readily and quantitatively removes EDA from these adducts liberating the free dialkylboranes. Thus this procedure provides a new valuable means for storing dialkylboranes as their stable EDA adducts, with rapid regeneration of the parent dialkylborane as desired.

Introduction

One of the intriguing problems in borane chemistry has been the relative instability of many of the borane reagents.[3-5] Workers in this area have usually been acutely aware of the possibilities for isomerization and redistribution. Consequently, they have often been limited to the use of freshly prepared reagents and very mild reaction conditions.

We recently observed the stabilization of monoalkylboranes using *N,N,N',N'*-tetramethylethylenediamine (TMED). In the hope of achieving a similar stabilization of dialkylboranes, we extended our study of the possible stabilization of these derivatives as addition compounds.

For example, dicyclohexylborane ($(cHx)_2BH$), disiamylborane (Sia_2BH), and diisopinocampheylborane ($(IPC)_2BH$) all possess limited stability upon storage. Anomalous results are obtained when hydroboration is carried out using an aged sample of these dialkylboranes.[6-8] Unfortunately, our attempts to stabilize these dialkylboranes with TMED were unfruitful. The adducts appear to be dissociated, so that the dialkylboranes undergo the usual redistribution reactions. Presumably the dissociation is the result of conflicting steric requirements of the dialkylborane and the tertiary amine. Among less hindered diamines, ethylenediamine (EDA) appeared to be a promising candidate for a complexing agent for such dialkylboranes.

The reaction between EDA and $Et_2O{\cdot}2BF_3$ is reported to afford either the mono or the bis adduct depending on the solvents used.[9] The mono adduct has not been isolated in pure form and the structures of these adducts have not been unambiguously established.[9,10]

This paper deals therefore with the isolation and characterization of the mono adduct of BF_3 and EDA, the stabili-

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