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Preliminary communication

MOLECULAR ADDITION COMPOUNDS OF *N,N,N',N'*-TETRAMETHYLETHYLENEDIAMINE WITH BORON TRIFLUORIDE AND MONOALKYLBORANES*

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Summary

N,N,N',N'-Tetramethylethylenediamine (TMED) reacts with $Et_2O{:}BF_3$ to give the highly insoluble adduct TMED:2 BF_3. TMED also reacts with representative monoalkylboranes to form both TMED-monoalkylborane (TMED:BH_2R) and the corresponding bis-adducts (TMED:2BH_2 R). These are air stable and can be stored for long periods. Boron trifluoride rapidly removes TMED from these adducts, liberating the corresponding monoalkylboranes. This procedure provides a new valuable means of storing monoalkylboranes as their stable adducts with TMED, with rapid regeneration of the parent monoalkylboranes as desired.

The discovery, here reported, that *N,N,N',N'*-tetramethylenediamine (TMED) reacts quantitatively with boron trifluoride to give the highly insoluble adducts TMED:2BF_3 offers promise for solving a large number of persistent problems in the preparation, storing and application of monoalkylboranes.

For example, recently the reaction of triethylamine-thexylborane ($Et_3N{:}ThBH_2$) with hindered olefins was reported to yield the corresponding triethylamine-monoalkylborane ($Et_3N{:}BH_2R$) adducts [1]. The triethylamine could be removed with either THF:BH_3 [2] or $Et_2O{:}BF_3$ [3] to produce the respective free monoalkylboranes. Unfortunately, there are several difficulties with this procedure. Both $Et_3N{:}BH_3$ and $Et_3N{:}BF_3$ are highly soluble in the usual THF medium and are difficult to separate from the desired product [2, 3]. This difficulty can be partially overcome by using a pentane solution. From such a solution, $Et_3N{:}BF_3$ can be crystallized out at −5°C [3]. A further difficulty is the fact that the $Et_3N{:}BH_2R$ adducts are liquids and cannot be purified readily. Moreover, the versatile monoalkylboranes, thexylborane ($ThBH_2$) [4] and 2,4,4-trimethyl-3-pentylborane ($DIBBH_2$) [5] possess limited stability** upon storage in THF at

*Dedicated to Prof. H.C. Brown in recognition of his contributions to chemistry.

**The term "stability" refers to oxidative and hydrolytic stabilities of the compounds ($DiBBH_2$ ≡ diisobutylborane).

0°C or at 25°C [5]. The triethylamine-monoisopinocampheylborane ($Et_3N:BH_2IPC$), from which the new chiral hydroborating agent is prepared [2], is a liquid of undetermined stability. 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.

During the course of our study we discovered that the reaction of *N,N,N',N'*-tetramethylethylenediamine (TMED) with $Et_2O:BF_3$ 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. This prompted us to explore the possibility of using TMED as a stabilizing addendum for monoalkylboranes.

This work describes the isolation and characterization of TMED adducts of BF_3, $ThBH_2$, $DIBBH_2$ and $IPCBH_2$ and the facile and quantitative removal of the complexing agent, from the latter adducts, as the highly insoluble TMED : 2 BF_3 compound.

First attention was focused on the reaction between $Et_2O:BF_3$ and TMED and the nature of the solid obtained.

With two equivalents of $Et_2O:BF_3$, TMED quickly and quantitatively produces TMED : $2BF_3$ (eq. 1). The solid is readily isolated and upon recrystallization

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

from acetonitrile gave large crystals (m.p. 210—212°C). Elemental analysis, ^1H NMR and ^{11}B NMR are consistent with the symmetrical molecular bis-adduct. To the best of our knowledge, TMED : 2 BF_3 has not been previously reported in literature [6—12]. In this way BF_3 can be utilized to precipitate TMED quantitatively from solution. Alternatively, TMED can be utilized to precipitate BF_3 quantitatively from ether solutions.

The bis-adduct precipitates cleanly even in the presence of excess amine. Thus the addition of $Et_2O:BF_3$ to an equimolar amount of TMED in THF precipitates half of the amine as the adduct, with half of the amine remaining in solution (eq. 2).

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

Identical results were realized in ethyl ether and pentane. The same results were obtained utilizing reverse addition.

In the second phase of our study we prepared and characterized certain TMED-monoalkylborane adducts. TMED : BH_2Th and TMED : BH_2DIB were quantitatively prepared by the direct reaction of $ThBH_2$ and $DIBBH_2$ respectively with TMED in 1/1 molar ratio (eq. 3, 4).

$$ThBH_2 + \text{TMED} \xrightarrow[25^\circ C]{\text{THF}} \text{TMED}:BH_2Th \qquad (3)$$

$$DIBBH_2 + \text{TMED} \xrightarrow[25^\circ C]{\text{THF}} \text{TMED}:BH_2DIB \qquad (4)$$

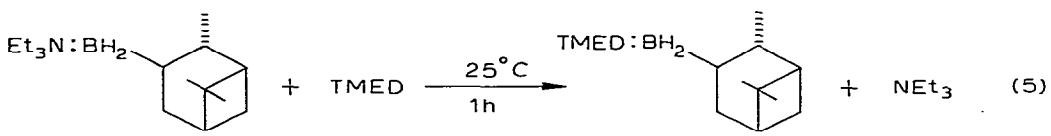
TABLE 1

TMED ADDUCTS OF BORON TRIFLUORIDE AND MONOALKYLBORANES

Compound	Recrystallization solvent [a]	M.p. (°C) [b]	Elemental Analyses (Found (calcd.) (%))			
			C	H	B	N
TMED · 2 BF_3 [c]	Acetonitrile	210—212	28.66 (28.62)	6.53 (6.40)	8.84 (8.59)	11.09 (11.12)
TMED · BH_2DIB [d]	Pentane	92—95	69.20 (69.41)	14.61 (14.56)	4.22 (4.46)	11.29 (11.56)
TMED · BH_2Th	[e]	—	67.34 (67.29)	14.54 (14.59)	4.95 (5.05)	12.90 (13.08)
TMED · 2 BH_2Th	Pentane [f]	43—45	68.96 (69.24)	14.88 (14.86)	6.71 (6.93)	8.88 (8.97)
TMED · BH_2IPC	Pentane	113—115	72.25 (72.17)	13.50 (13.25)	4.21 (4.06)	10.29 (10.52)
TMED · 2 BH_2IPC [g]	Pentane	140—141	74.70 (75.00)	13.19 (13.01)	5.21 (5.20)	6.69 (6.73)

[a] Dry, olefin-free pentane. [b] Uncorrected melting points in a sealed capillary. [c] F found 45.10, calcd. 45.27%. ^{1}H NMR (Acetone-d_6 TMS): δ 2.97 (s, 12H), 3.53 ppm (s, 4H); ^{11}B NMR (DMSO): δ −0.74 ppm (s, relative to $Et_2O \cdot BF_3$). [d] The reaction between TMED and $DIBBH_2$ in 1/2 molar ratio was not explored. ^{1}H NMR ($CDCl_3$, TMS): δ 0.12 (small hump, 1H), 0.95—1.05 (s and d, 15H), 1.83 (m, 1H), 2.22 (s, 6H), 2.50 (s, 6H), 2.60—3.20 ppm (m, 4H); ^{11}B NMR (THF): δ −1.74 ppm (broad t, relative to $Et_2O \cdot BF_3$). [e] Compound is a viscous liquid even at −78°C. [f] Recrystallized at −50°C. [g] Prepared by treating TMED · BH_2IPC with one equivalent of $Et_2O \cdot BF_3$.

TMED : monoisopinocampheylborane was prepared by the displacement of triethylamine from $Et_3N : BH_2$IPC [1] with TMED (eq. 5). The triethylamine was removed under vacuum (12 mmHg).



(5)

These addition compounds are air stable and can be stored neat or in THF solution for several weeks at 25°C without noticeable hydride loss, isomerization and redistribution. Treatment of the adducts in THF with two equivalents of $Et_2O : BF_3$ rapidly regenerates the free monoalkylboranes with the precipitation of TMED : 2 BF_3 (eq. 6).

$$\text{TMED} : BH_2R + 2\ Et_2O : BF_3 \xrightarrow[25^\circ C,\ 15\ min]{THF} RBH_2 + \text{TMED} : 2\ BF_3\downarrow \qquad (6)$$

With one equivalent of $Et_2O : BF_3$ the reaction proceeds according to eq. 7.

$$\text{TMED} : BH_2R + Et_2O : BF_3 \xrightarrow[25^\circ C,\ 15\ min]{THF} \tfrac{1}{2}\ \text{TMED} : 2\ BH_2R + \tfrac{1}{2}\ \text{TMED} : 2\ BF_3\downarrow \qquad (7)$$

The isolation and characterization of these TMED adducts are given in Table 1.

The following procedure is representative. All operations were carried out under nitrogen [13]. A solution of $DIBBH_2$ in THF was prepared by adding

1.6 ml of 2,4,4-trimethyl-2-pentene (DIB-2; 10 mmol) to a 4 ml of a 2.5 *M* solution of THF:BH_3 (10 mmol) at 0°C [5]. To this solution maintained at 0°C, 1.6 ml of TMED (10 mmol) was quickly added and the reaction mixture brought to 25°C and stirred for 1 h to provide a solution ot TMED·BH_2DIB. Evaporation of THF (25°C, 12 mmHg) followed by recrystallization from pentane (dry, olefin free) at –25°C afforded TMED:BH_2DIB as a solid in 90% yield, m.p. 92—95°C, IR, ^{1}H NMR, ^{11}B NMR and elemental analysis are in agreement with the proposed structure (Table 1). The compound was stable for at least two weeks when stored as the solid and at least four weeks as the 1.0 *M* solution in THF at 25°C. For the liberation of free $DIBBH_2$, 2.46 ml of $Et_2O:BF_3$ (20 mmol) was added with stirring at 25°C, to 10 ml of a 1.0 *M* solution of TMED:BH_2DIB (10 mmol) in THF. A heavy white solid precipitated almost immediately and stirring was continued for 15 min at 25°C. The mixture was diluted with 10 ml THF and the solid centrifuged down. The supernatant solution was decanted off [13] and found to contain essentially 10 mmol of free $DIBBH_2$ via IR. The white solid was dried and weighed (2.50 g; 10 mmol). After a recrystallization from acetonitrile (7 ml), the solid melted at 210—212°C. The spectral data (^{1}H NMR and ^{11}B NMR) and elemental analysis are in accord with the formation of TMED:2 BF_3 (Table 1).

Conclusions

The fast, complete reaction of boron trifluoride with TMED provides a means to remove TMED from solution. The reaction is also suitable to remove BF_3 from solution. In the present study, it has been established that monoalkylboranes are readily stabilized as their TMED adducts. The reaction with BF_3 provides a rapid quantitative means of removing TMED from the adducts, generating the monoalkylboranes for further utilization and study.

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