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.

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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.

References and Notes

(1) H. C. Brown, N. M. Yoon, and A. K. Mandal, *J. Organomet. Chem.*, **C10**, 135 (1977).
(2) H. C. Brown and N. M. Yoon, *J. Am. Chem. Soc.*, **99**, 5514 (1977).
(3) H. C. Brown and A. K. Mandal, *Synthesis*, **2**, 146 (1978).
(4) E. Negishi and H. C. Brown, *Synthesis*, **2**, 77 (1974).
(5) Manuscript in progress with Dr. John R. Schwier.
(6) S. U. Kulkarni and H. C. Brown, *Inorg. Chem.*, **16**, 3092 (1977).
(7) J. M. Van Paasschen and R. A. Geanangel, *Can. J. Chem.*, **53**, 723 (1975).
(8) J. R. McDivitt and G. L. Humphrey, *Spectrochim. Acta, Part A*, **30a**, 1021 (1974).
(9) A. R. Gatti and T. Nortik, *Inorg. Chem.*, **5**, 2075 (1966).
(10) A. R. Gatti and T. Nortik, *Inorg. Chem.*, **5**, 329 (1966).
(11) R. A. Geanangel and S. G. Shore, "Preparative Inorganic Reactions", Vol. 3, Wiley-Interscience, New York, N.Y., 1966, p 123.
(12) L. T. Murray, Ph.D. Thesis, Purdue University, 1963.
(13) H. C. Kelly and J. O. Edwards, *Inorg. Chem.*, **2**, 226 (1963).
(14) H. C. Brown, G. W. Kramer, A. B. Levy, and M. M. Midland, "Organic Syntheses via Boranes", Wiley-Interscience, New York, N.Y., 1975.
(15) All compounds gave satisfactory elemental analyses.
(16) H. C. Brown, A. K. Mandal, and S. U. Kulkarni, *J. Org. Chem.*, **42**, 1392 (1977).

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

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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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zation of certain dialkylboranes as their EDA addition compounds, and the ready regeneration of the pure dialkylboranes by treatment of the adducts with BF_3.

Experimental Section

The reaction flasks and other glass equipment used for experiments were oven-dried and assembled in a stream of dry nitrogen gas. The special techniques for the manipulation of air-sensitive materials are described elsewhere.[4] $Et_2O{\cdot}BF_3$ and ethylenediamine 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. All of the EDA–dialkylborane adducts were stored at least 15 days at 0 °C before they were utilized in organic syntheses.

Preparation of Complexes. EDA·BF_3 (1). To a solution of 0.67 mL of ethylenediamine (10 mmol) in 8 mL of diethyl ether was added 1.23 mL of $Et_2O{\cdot}BF_3$ (10 mmol) with constant stirring at 25 °C. A white dense solid separated. This precipitate was collected by centrifugation, washed several times with *n*-pentane, and dried. There was obtained 1.27 g: mp 70–72 °C; ^{11}B NMR δ −0.92 (q, J_{BF} = 16 Hz). Anal. Calcd for $C_2H_8BN_2F_3$: C, 18.78; H, 6.30; B, 8.46; N, 21.90; F, 44.56. Found: C, 18.60; H, 6.56; B, 8.72; N, 21.60; F, 44.80.

In contrast to ethyl ether, the monoadduct (**1**) is soluble in THF. When THF is used for the above reaction, 2 equiv of $Et_2O{\cdot}BF_3$ react with ethylenediamine to give the bis adduct (**2**), which remains in solution:[9] mp 169–171 °C (recrystallized from water); ^{11}B NMR δ −0.92 (q, J_{BF} = 16 Hz).

EDA·2BH(cHx)$_2$ (4). A suspension of dicyclohexylborane (20 mmol) in THF was prepared according to the published procedure.[11] To this, 0.67 mL of EDA (10 mmol) was added dropwise at 0 °C. Within 30 min the solid dicyclohexylborane disappears and a clear solution results. The ^{11}B NMR spectrum of the solution consists of a single boron resonance line at δ −1.62. The stock solution was stored at 0 °C and analyzed periodically via ^{11}B NMR. It was found that the adduct could be stored without any isomerization or redistribution for at least 30 days at 0 °C.

When the reaction was carried out in diethyl ether, the bis adduct of EDA and dicyclohexylborane precipitated out. The solid was collected by centrifugation, washed well with *n*-pentane, and dried. There was obtained 3.46 g (85% yield): mp 93–96 °C; ^{11}B NMR δ −1.62. Anal. Calcd for $C_{26}H_{54}B_2N_2$: C, 75.0; H, 13.1; B, 5.2; N, 6.7. Found: C, 74.84; H, 13.28; B, 5.31; N, 6.65.

EDA·2BHSia$_2$ (5). 2,3-Dimethyl-2-butene (40 mmol) was reacted with borane–methyl sulfide (20 mmol) in Et_2O to give disiamylborane (20 mmol).[11] To this solution, cooled at 0 °C, 0.67 mL of EDA (10 mmol) was added. The reaction mixture was stored at 0 °C, and aliquots were withdrawn from time to time and the ^{11}B NMR spectrum was determined. The ^{11}B NMR spectrum displayed a broad singlet at δ −4.54 as the major peak. The adduct was stored for 15 days at 0 °C without any detectable change.

EDA·2BH(IPC)$_2$ (6). A slurry of diisopinocampheylborane (20 mmol) in THF was prepared in the usual manner.[11] The reaction flask was cooled to 0 °C and 0.67 mL of EDA (10 mmol) was added with stirring. Within 30 min a clear solution was obtained. The solution was stored at 0 °C and analyzed via ^{11}B NMR spectroscopy as described above. The adduct exhibited a ^{11}B resonance peak at δ −7.70. The adduct was stored as a THF solution for at least 30 days at 0 °C without any detectable isomerization or redistribution.

Application of EDA·2BH(cHx)$_2$ (4). Zweifel's *cis*-1-Cyclohexyl-1-hexene Synthesis. To a solution of the adduct **4** (25 mmol) in THF (50 mL), cooled at 0 °C, was added 6.2 mL of $Et_2O{\cdot}BF_3$ (50 mmol) with constant stirring. Dicyclohexylborane precipitated out within 1 h. Hydroboration of 1-hexyne (50 mmol) with this reagent in a ratio of 1:1, produces the vinylborane. The product is treated with iodine following Zweifel's procedure.[12] There was produced *cis*-1-cyclohexyl-1-hexene, purified by distillation: 6.0 g (72% yield); bp 112 °C (12 mmHg), n^{20}_D 1.4585.

Application of EDA·2BHSia$_2$ (5). Hydroboration of Styrene. Free disiamylborane (10 mmol) was generated from **5** by treating it with $Et_2O{\cdot}BF_3$ (10 mmol) in Et_2O at 0 °C. Hydroboration with this reagent was carried out as recommended in the literature.[13] After the usual oxidation of the hydroboration product, analysis by GLC showed 82% of alcohol (97% 2-phenylethanol and 3% 1-phenylethanol).

Application of EDA·2BH(IPC)$_2$ (6). Hydroboration of *cis*-2-Butene at 25 °C. $(IPC)_2BH$ (50 mmol) was precipitated from a solution of EDA·2BH(IPC)$_2$ in THF by treating the adduct with 6.2 mL of $Et_2O{\cdot}BF_3$ (50 mmol) at 0 °C. The reaction flask was then cooled to −25 °C and 3.2 g (~50 mmol) of *cis*-2-butene was added to the reaction mixture. Stirring was continued for 8 h at −25 °C, and the reaction mixture was worked up as described earlier[11] to give 2.43 g (65% yield) of (−)-2-butanol: $[\alpha]^{25}_D$ −12.6° (93% optical purity).

Results and Discussion

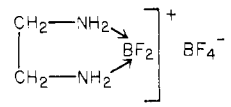
Reaction between a monofunctional Lewis acid and a difunctional Lewis base usually affords an adduct involving 2 mol of acid/mol of the base.[1] Very few instances are recorded in the literature where a mono adduct has been isolated in pure condition from the reaction between a difunctional Lewis base and a monofunctional Lewis acid.[14,15] However, addition of 1 mol of $Et_2O{\cdot}BF_3$ to 1 mol of EDA in diethyl ether results in the precipitation of a solid adduct which is the pure 1:1 addition compound. The adduct was collected, washed several times with *n*-pentane, and dried to afford an analytically pure sample of EDA·BF_3, mp 70–72 °C. Elemental analyses and the ^1H NMR and ^{11}B NMR spectra are consistent with structure **1** for the adduct. Addition of excess $Et_2O{\cdot}BF_3$ to

$$NH_2CH_2CH_2NH_2{\cdot}BF_3$$
1

the reaction mixture fails to alter the nature of the precipitate.

When a THF solution of ethylenediamine is used for the reaction with $Et_2O{\cdot}BF_3$, a bis adduct is obtained. This adduct may have structure **2** or **3**. The presence of a single ^{11}B NMR resonance supports the symmetrical structure **2** for the bis adduct.

$BF_3{:}NH_2CH_2CH_2NH_2{:}BF_3$ (**2**)



3

For the preparation of the complexes, the dialkylboranes were treated with ethylenediamine in 2:1 molar ratio (eq 1–3).

$$2(cHx)_2BH + EDA \xrightarrow[0\ °C,\ 0.5\ h]{THF} EDA{\cdot}2BH(cHx)_2 \quad (1)$$

$$2Sia_2BH + EDA \xrightarrow[0\ °C,\ 0.5\ h]{Et_2O} EDA{\cdot}2BHSia_2 \quad (2)$$

$$2(IPC)_2BH + EDA \xrightarrow[0\ °C,\ 0.5\ h]{THF} EDA{\cdot}2BH(IPC)_2 \quad (3)$$

Only dicyclohexylborane forms a solid adduct with EDA which precipitates when the reaction is carried out in Et_2O medium. Disiamylborane and diisopinocampheylborane form liquid products with EDA. These adducts were characterized through ^{11}B NMR spectroscopy, and their stability in THF solution was followed by determining their ^{11}B NMR spectrum periodically. These complexes were stored for at least 30 days at 0 °C without any detectable isomerization or redistribution. A facile reaction takes place in Et_2O or in THF between $Et_2O{\cdot}BF_3$ and these adducts, resulting in the liberation of the corresponding dialkylboranes in pure form (eq 4 and 5). The

$$EDA{\cdot}2BHR_2 + Et_2O{\cdot}BF_3 \xrightarrow[25\ °C,\ 1\ h]{Et_2O} 2R_2BH + EDA{\cdot}BF_3\downarrow \quad (4)$$

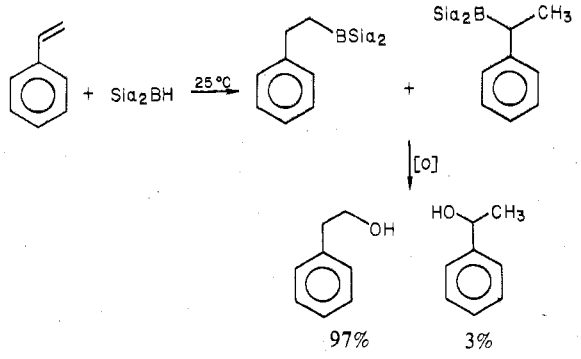
$$EDA{\cdot}2BHR_2 + 2Et_2O{\cdot}BF_3 \xrightarrow[25\ °C,\ 1\ h]{THF} 2R_2BH + EDA{\cdot}2BF_3 \quad (5)$$

choice of the solvent for the above reaction is dictated by the nature of the dialkylborane liberated. If the dialkylborane is highly soluble in the usual organic solvent, then Et_2O is used as the solvent. In this solvent the dialkylborane is soluble whereas the other product, viz., EDA·$2BF_3$, is insoluble. Hence

the two components are readily separated from each other. On the other hand, if the organoborane is highly insoluble, such as dicyclohexylborane, then THF is preferred as the reaction medium. Under this condition, the dialkylborane is thrown out of solution, whereas the EDA·$2BF_3$ is retained. EDA·$2BF_3$ is inert. Consequently its presence in the reaction mixture does not interfere with the utilization of these dialkylboranes for subsequent applications.

We encountered no difficulty in storing these adducts as their EDA complexes at 0 °C, in regenerating the dialkylborane, and in utilizing such dialkylboranes for typical applications.

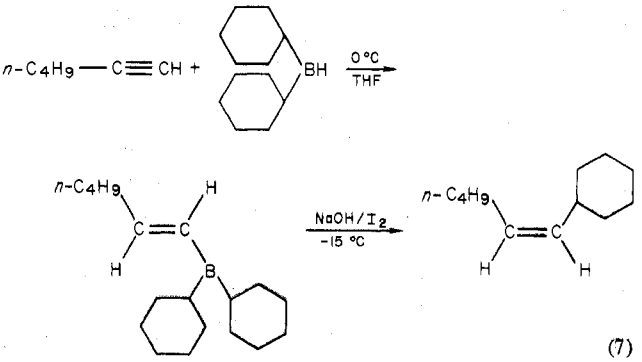
Application of EDA·2BHSia$_2$ for the Regiospecific Hydroboration of Styrene. Free disiamylborane was liberated in Et_2O from the adduct **5** and was utilized for the hydroboration of styrene[13] at room temperature. The reaction was complete within 2 h. The reaction mixture was then oxidized and the composition of the product, as determined by GLC, is shown in eq 6.



(6)

Application of EDA·BH(cHx)$_2$ in the Zweifel Cis Olefin Synthesis.[12] Dicyclohexylborane was precipitated in THF from compound **4** and 1-hexyne was added to it at 0 °C. The vinylborane thus formed was treated with aqueous sodium hydroxide and iodine to yield *cis*-1-cyclohexyl-1-hexene (72% isolated yield) (eq 7).

Application of EDA·2BH(IPC)$_2$ to Asymmetrical Hydroboration. A slurry of diisopinocampheylborane in THF was prepared from EDA adduct **6**. To this reagent at −25 °C *cis*-2-butene was added in slight excess. The reaction was allowed to proceed for 8 h. The product was then oxidized in the usual manner with alkaline hydrogen peroxide. Distillation provided (−)-2-butanol in a yield of 65%. The material was followed by GC and exhibited a rotation of $[\alpha]^{25}_D$ −12.6°, an optical purity of 93%.



(7)

Conclusions

The reaction of boron trifluoride with EDA in Et_2O provides the mono adduct EDA·BF_3 which was isolated and characterized. In the present study, it has also been established that certain dialkylboranes are readily stabilized at 0 °C as their EDA adducts. Reaction with Et_2O·BF_3 provides a rapid and quantitative means of removing EDA from the adducts, generating the dialkylborane for further study and utilization.

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Registry No. **1**, 590-10-3; **2**, 590-09-0; **4**, 68307-65-3; **5**, 68307-66-4; **6**, 68366-09-6; dicyclohexylborane, 61484-01-3; 1-hexyne, 693-02-7; *cis*-1-cyclohexyl-1-hexene, 17301-35-8; styrene, 100-42-5; disiamylborane, 42199-94-0; $(IPC)_2BH$, 16997-72-1; *cis*-2-butene, 590-18-1; (−)-2-butanol, 14898-79-4; Et_2O·BF_3, 109-63-7; 2,3-dimethyl-2-butene, 563-79-1; borane–methyl sulfide, 13292-87-0.

References and Notes

(1) For part 5 of this series, see H. C. Brown, B. Singaram, and J. R. Schwier, *Inorg. Chem.*, preceding paper in this issue.
(2) Postdoctoral research associate on Grant No. GM 10937 from the National Institutes of Health.
(3) H. C. Brown, "Boranes in Organic Chemistry", Cornell University Press, Ithaca, New York, 1972.
(4) H. C. Brown, G. W. Kramer, A. B. Levy, and M. M. Midland, "Organic Syntheses via Boranes", Wiley-Interscience, New York, N.Y., 1975.
(5) H. C. Brown, "Hydroboration", W. A. Benjamin, New York, N.Y., 1962.
(6) H. C. Brown and G. J. Klender, *Inorg. Chem.*, **1**, 204 (1962).
(7) C. A. Henrick, *Tetrahedron*, **33**, 1848 (1977).
(8) D. J. Sandman, K. Mislow, W. P. Giddings, J. Dirlam, and G. C. Hanson, *J. Am. Chem. Soc.*, **90**, 4877 (1968).
(9) C. A. Brown, E. L. Muetterties, and E. G. Rochow, *J. Am. Chem. Soc.*, **76**, 2537 (1954).
(10) J. M. Van Paasschen and R. A. Geanangel, *Can. J. Chem.*, **53**, 725 (1975).
(11) H. C. Brown, A. K. Mandal, and S. U. Kulkarni, *J. Org. Chem.*, **42**, 1392 (1977).
(12) G. Zweifel, H. Arzoumanian, and C. C. Whitney, *J. Am. Chem. Soc.*, **89**, 3652 (1967).
(13) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 1241 (1961).