Molecular Addition Compounds. 18. Borane Adducts with Hydroxydialkyl Sulfide Borates for Hydroboration. New, Essentially Odorless, Water-Soluble Sulfide Borane Acceptors for Hydroboration†

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Hydroxydialkyl sulfides of general formula $RS(CH_2CH_2)_nH$ (R = Et, *t*-Bu, *i*-Am; *n* = 1−3) and thiodiethanol monomethyl ether (**9**) have been synthesized and used as borane carriers. The compounds **3** and **6** (R = Et, *n* = 2, 3), **7** (R = *t*-Bu, *n* = 3), and **9** are completely miscible with water and exhibit only very mild odor. The sulfides were transformed into the corresponding borates by treatment either with boric acid or with diborane. The borates complex 3 mol of borane per 1 mol of borate to give highly reactive, stable, liquid adducts, hydroborating 1-octene in 15 min at room temperature. The adducts derived from water soluble sulfides **3** and **9**, selected for the hydroboration of more hindered olefins, reacted readily with (−)-*β*-pinene, 1-methylcyclohexene, and 2,3-dimethyl-2-butene. The carrier borates liberated from the adducts during hydroboration are readily hydrolyzed to give **3** and **9**, which can be washed off with water from trialkylboranes or oxidation products. Consequently, hydroxydialkyl sulfides **3** and **9** are the first completely water-soluble sulfide borane carriers that can be washed off in the workup of hydroboration products. The adducts derived from **3** and **9** are new, highly promising reagents suitable for large scale hydroborations and reductions.

Borane carriers are of increasing importance with the growing applications of diborane in the synthesis of pharmaceuticals and other compounds.[3,4] Borane−tetrahydrofuran and borane−dimethyl sulfide (BMS), the two most widely used borane adducts, are excellent reagents for laboratory use; however, they have certain limitations for larger scale applications. Thus, the commercially available borane−tetrahydrofuran is a dilute solution (1 M in BH_3), unstable over prolonged periods and, hence, inconvenient for transportation and storage, and its use is limited to one solvent. Borane dimethyl sulfide, a neat adduct, 10 M in borane, stable indefinitely, and soluble in various solvents, is free from these inconveniences. Unfortunately, dimethyl sulfide has an obnoxious odor and is water-insoluble, highly volatile, and flammable, creating environmental and safety problems. To circumvent some of these limitations, borane adducts with 1,4-thioxane[5] and bis-sulfides[3] have been introduced. These carriers are less volatile and odoriferous than dimethyl sulfide. However, none of the presently used sulfides for borane complexation is miscible with water. A water-soluble borane carrier would facilitate product isolation in hydroboration and reduction reactions. Its volatility would also be lowered at the workup stage when it is dissolved in the aqueous phase.

Among lower molecular weight sulfides, certain hydroxydialkyl sulfides, e.g., 2-(methylthio)ethanol, are miscible with water, and 2-(isoamylthio)ethanol has an agreeable odor and is partially soluble in water.[7] Consequently, we decided to prepare and examine selected hydroxydialkyl sulfides for borane complexation with the objective of developing a borane carrier of low volatility, odorless or of very mild odor, and completely miscible with water.

Results and Discussion

First, the commercially available 2-(methylthio)ethanol was examined as a model compound. The borane adduct is readily prepared by passing diborane into the neat sulfide. Hydrogen is evolved, and the borate ester formed complexes with borane to give a liquid adduct, 7.5 M in borane at room temperature (eq 1). The ^{11}B NMR spectrum shows a quartet at δ −20 (borane adduct), a singlet at δ +18 (borate ester), and a small doublet at δ +38 ppm, attributed to $(MeSCH_2CH_2O)_2BH$. The adduct hydroborates 1-octene quantitatively at room temperature to give trioctylborane and borate ester (eq 2).

$$3\ CH_3SCH_2CH_2OH + 2\ B_2H_6 \longrightarrow (CH_3SCH_2CH_2O)_3B\cdot BH_3 + 3\ H_2 \quad (1)$$

$$9\ C_6H_{13}CH{=}CH_2 + (CH_3SCH_2CH_2O)_3B\cdot BH_3 \longrightarrow 3\ n\text{-}Oct_3B + (CH_3SCH_2CH_2O)_3B \quad (2)$$

These observations indicate that hydroxydialkyl sulfides can serve as borane carriers for hydroboration.

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(3) Follet, M. *Chem. Ind.* **1986**, 123.

(4) Renn, O.; Meatres, C. F. *Bioconjugate Chem.* **1992**, *3*, 563.

(5) Brown, H. C.; Mandal, A. K. *J. Org. Chem.* **1992**, *57*, 4970.

(6) Brown, H. C.; Zaidlewicz, M.; Dalvi, P. *Organometallics* **1998**, *19*, 4202.

(7) Scherlin, S. M.; Jakubowitsch, A. I. *J. Prakt. Chem.* **1933**, *138*, 23.

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Table 1. Odor and Miscibility with Water of Hydroxydialkyl Sulfides 1−9

hydroxydialkyl sulfides		odor	miscibility with water[a]
t-BuSCH$_2$CH$_2$OH	**1**	mild	50
i-AmSCH$_2$CH$_2$OH	**2**	agreeable;strong	<100
EtS(CH$_2$CH$_2$O)$_2$H	**3**	very mild	miscible
t-BuS(CH$_2$CH$_2$O)$_2$H	**4**	mild	15
i-AmS(CH$_2$CH$_2$O)$_2$H	**5**	agreeable; weak	<100
EtS(CH$_2$CH$_2$O)$_3$H	**6**	very mild	miscible
t-BuS(CH$_2$CH$_2$O)$_3$H	**7**	mild	miscible
i-AmS(CH$_2$CH$_2$O)$_3$H	**8**	agreeable; weak	~100
CH$_3$OCH$_2$CH$_2$SCH$_2$CH$_2$OH	**9**	mild	miscible

[a] Milliliters of water required to dissolve 1.0 g of hydroxydialkyl sulfide.

Unfortunately, 2-(methylthio)ethanol is not useful because of its unpleasant odor. Similarly, 2-(ethylthio)-ethanol is only partially soluble in water and possesses an unpleasant odor. On the other hand, 3-ethylthio-1,2-propanediol has a mild odor and low volatility and is completely miscible with water. However, it reacts with diborane to give a very viscous, glassy product. The adduct formation under neat conditions is not complete, and its high viscosity makes difficult the introduction and absorption of diborane.

To circumvent these difficulties we decided to prepare a series of hydroxydialkyl sulfides **1**−**9** (Table 1), the corresponding borate esters **1a**−**9a** and their borane adducts **1b**−**9b** (Table 2). The hydroxydialkyl sulfides **1**−**8** were readily prepared as shown in eq 3, and thiodiethanol monomethyl ether (**9**) was obtained according to eq 4.

$$\mathrm{RSNa} + \mathrm{Cl(CH_2CH_2O)_nH} \xrightarrow[\mathrm{CH_3OH}]{} \mathrm{RS(CH_2CH_2O)_nH} + \mathrm{NaCl} \quad (3)$$

$$\mathrm{CH_3OCH_2CH_2Cl} + \mathrm{NaSCH_2CH_2OH} \xrightarrow[\mathrm{CH_3OH}]{} \mathrm{CH_3OCH_2CH_2SCH_2CH_2OH} + \mathrm{NaCl} \quad (4)$$

The yields are above 90%, and the product isolation is simple. All of these hydroxydialkyl sulfides have a mild or very mild odor (Table 1). Compounds **3**, **6**, **7**, and **9** are miscible with water.

Initially, pure borates were prepared by refluxing the sulfides with boric acid in toluene, removing the water azeotropically. The formation of borates was confirmed by ^{11}B NMR (δ 17−18) and ^{1}H NMR analysis, showing a downfield shift of the methylene protons of the hydroxymethyl group from δ ~3.7 to δ ~3.9 for the corresponding esters. Alternatively, the borates **1a**−**9a** were simply synthesized by the reaction of borane−tetrahydrofuran with hydroxydialkyl sulfides **1**−**9** in the molar ratio 1:3. The product formation is easily followed by measuring the hydrogen evolved. Warming the reaction mixture to 50 °C is necessary to complete the reaction.

On the basis of these observations, an efficient one-pot synthesis of borane adducts **1b**−**9b** was developed. Thus, diborane, conveniently generated using a procedure recently reported,[6] was passed into a neat hydroxydialkyl sulfide at 50 °C to form the corresponding borate ester, and then it was absorbed by the ester till saturation. The adducts **1b**−**9b,** readily prepared by this procedure, are liquids of high hydride content, stable at room temperature (Table 2). The adducts are soluble in diethyl ether, tetrahydrofuran, and dichloromethane. No change in molarity after 1 week at room temperature was observed.

To examine the complexing ability of the borates as compared to dimethyl sulfide, exchange between BMS and the borates was followed by ^{11}B NMR analysis. The amount of borane taken by borates from BMS at equilibrium for 1:3 mixtures is presented in Table 2. Borates **3a** and **6a** with an ethyl substituent at the sulfur atom take 28% and 23% of borane, respectively. Substitution of a *tert*-butyl group for the ethyl group decreases the complexing ability, whereas borates containing an isoamyl group do not undergo any significant exchange. In general, the borates **1a**−**9a** take less than 30% of borane from BMS, indicating a relatively weaker complexing ability compared to dimethyl sulfide. As follows from Table 2, the complexing ability of the borates decreases in the following order: **3a**, **6a** > **1a**, **4a**, **7a** > **2a**, **5a**, **8a**, **9a**.

For the exchange with 1 M borane−tetrahydrofuran solution, the values can be considered only as qualitative since the solution contains tetrahydrofuran in large excess. As expected, the borates **1a**−**9a** take more borane (62−83%) from borane−tetrahydrofuran, a weaker adduct than BMS (Table 2).

Hydroboration. Hydroboration of 1-octene with the borane adducts **1b**−**9b** under neat conditions was carried out at room temperature. The results are shown in Table 2. As revealed by ^{11}B NMR analysis, the adducts hydroborate 1-octene in 15 min to yield trioctylborane.

On the basis of simple synthesis, mild odor, water solubility of the parent hydroxydialkyl sulfides, and high molarity of adducts, **3b** and **9b** were selected for preparative scale hydroboration of terminal olefins. Thus, hy-

Table 2. Borane Adducts with Borate Esters of Hydroxydialkyl Sulfides

				borane adducts with borate esters					
		exchange[a] (%)				[BH$_3$][d]	^{11}B NMR[e] (δ)		HB of 1-octene[f]
borate ester		BMS	BH$_3$/THF	adduct[b]	state[c]	(M)	borate ester	adduct	(time, h)
(*t*-BuSCH$_2$CH$_2$O)$_3$B	**1a**	8	68	**1b**	liquid	6.4	17.67	−26.03	0.25
(*i*-AmSCH$_2$CH$_2$O)$_3$B	**2a**	0	67	**2b**	liquid	5.9	18.05	−22.27	0.25
[EtS(CH$_2$CH$_2$O)$_2$]$_3$B	**3a**	28	83	**3b**	liquid	5.7	18.16	−22.68	0.25
[*t*-BuS(CH$_2$CH$_2$O)$_2$]$_3$B	**4a**	11	70	**4b**	liquid	5.5	17.94	−26.21	0.25
[*i*-AmS(CH$_2$CH$_2$O)$_2$]$_3$B	**5a**	0	75	**5b**	liquid	5.0	18.09	−23.03	0.25
[EtS(CH$_2$CH$_2$O)$_3$]$_3$B	**6a**	23	81	**6b**	liquid	5.2	18.07	−23.48	0.25
[*t*-BuS(CH$_2$CH$_2$O)$_3$]$_3$B	**7a**	9	68	**7b**	liquid	4.2	18.28	−26.20	0.25
[*i*-AmS(CH$_2$CH$_2$O)$_3$]$_3$B	**8a**	0	66	**8b**	liquid	4.0	18.13	−23.22	0.25
(CH$_3$OCH$_2$CH$_2$SCH$_2$CH$_2$O)$_3$B	**9a**	0	62	**9b**	liquid	6.0	18.50	−21.49	0.25

[a] BMS or BH$_3$/THF and borate ester mixed at 3:1 molar ratio. [b] Adducts contain three borane molecules per ester molecule, e.g., [H$_3$B:S(*t*-Bu)CH$_2$CH$_2$O]$_3$B (**1b**). [c] At 20 °C. [d] Estimated by hydrolysis in water/glycerol/THF, 1:1:1, and measurement of the hydrogen evolved. [e] Neat. [f] Hydroboration with a neat adduct at room temperature.

droboration of 1-octene with **9b** was carried out in dichloromethane at room temperature. ^{11}B NMR analysis showed completion of the reaction in 15 min. The intermediate trioctylborane was oxidized with alkaline hydrogen peroxide, and the oxidation product was stirred with water at room temperature for 0.5 h or with warm water for 15 min, to wash off thiodiethanol monomethyl ether (**9**). GC analysis of the product showed 1-octanol (94%) and 2-octanol (6%), free of **9**.

Similarly, (−)-*β*-pinene (91% ee) was hydroborated with the adducts **3b** and **9b** in dichloromethane. Both adducts reacted in 0.5 h as showed by ^{11}B NMR. The usual oxidative workup and water wash gave (−)-*cis*-myrtanol in 90% yield, free of **3** and **9**, respectively.

To further test the reactivity of the borane adducts, the hydroboration of representative tri- and tetrasubstituted olefins was also examined. Thus, 1-methylcyclohexene was hydroborated under neat conditions using **3b** and **9b** (olefin/borane ratio 2:1). After 0.5 h, the reaction mixture was treated with ethanol. The ^{11}B NMR analysis showed a signal at *δ* 17 (borate ester) and at *δ* 53 (dialkylborinate), indicating quantitative conversion. Similarly, hydroboration of 2,3-dimethyl-2-butene with **9b** (olefin/borane ratio 1:1) gave thexylborane in 0.5 h (^{11}B NMR *δ* 24). The reactivity of **3b** toward 2,3-dimethyl-2-butene was lower and only 80% of the olefin reacted in 24 h. The lower reactivity of **3b** toward 2,3-dimethyl-2-butene, as compared with **9b**, reflects the higher complexing ability of **3**.

Conclusions

The borane adducts derived from hydroxydialkyl sulfides **1**−**9** are liquids of high hydride content at room temperature. The adducts **3b** and **9b** hydroborate terminal, di-, tri-, and tetrasubstituted olefins, and the corresponding hydroxydialkyl sulfides **3** and **9** can be washed off easily in workup of the hydroboration−oxidation products. Consequently, **3b** and **9b** are highly promising, efficient, new hydroborating agents of high potential for large scale applications in hydroborations and reductions.

Experimental Section

All manipulations and reactions with air-sensitive compounds were carried out under nitrogen atmosphere. The glassware was oven-dried for several hours, assembled while hot, and cooled in a stream of nitrogen. Syringes were assembled and fitted with needles while hot. ^{1}H and ^{11}B NMR spectra were recorded on a 300 MHz multinuclear instrument. The ^{11}B NMR shifts are in *δ* relative to $BF_3{\cdot}OEt_2$. GC analyses were carried out on a chromatograph using a 12 ft × 0.125 in. column packed with 10% Carbowax 20M or SE-30 on Chromosorb W (100−120 mesh). Microanalyses were performed at the Microanalytical Laboratory, Purdue University.

Materials. Borane-methyl sulfide (BMS), 2-mercaptoethanol, chlorohydrins, and boric acid were commercial products (Aldrich). 1-Octene and (−)-*β*-pinene were distilled prior to use from a small amount of lithium aluminum hydride under vacuum.

Synthesis of Hydroxydialkyl Sulfides (1a−8a). General Procedure. Sodium methoxide (10.80 g, 200 mmol) was dissolved in methanol (100 mL), thioalcohol (200 mmol) was added, and the mixture was left at room temperature for 1 h. Chlorohydrin (200 mmol) was added, and the mixture was refluxed for 1 h. Precipitated sodium chloride was filtered off and washed with methanol. The solvent was removed from the filtrate under vacuum. Diethyl ether (50 mL) was added, and a small amount of sodium chloride was filtered off. The product was isolated by distillation under vacuum.

Data for 1. Yield 22.35 g (90%); bp 46−48 °C/0.1 mmHg (lit.[8] 101.5−102.5 °C/27 mmHg). ^{1}H NMR ($CDCl_3$) *δ* 1.34 (s, 9H, CH_3), 2.77 (t, *J* = 6.1, 2H, CH_2), 3.93 (q, *J* = 6.1, 2H, CH_2). ^{13}C NMR ($CDCl_3$) *δ* 31.13 (CH_3), 42.32 (C), 31.68 (CH_2), 61.51 (CH_2). MS (70 eV CI EI) 134(M^+, 17), 57(100).

Data for 2. Yield 27.00 g (917); bp 55−56 °C/0.5 mmHg (lit.[7] 110−111 °C/10 mmHg). ^{1}H NMR ($CDCl_3$) *δ* 0.90 (d, *J* = 6.6, 6H, CH_3), 1.49 (q, *J* = 6.6, 2H, CH_2), 1.63 (nonet, *J* = 6.6, 1H, CH), 2.52 (t, *J* = 6.9, 2H, CH_2), 2.73 (t, *J* = 5.9, 2H, CH_2), 3.72 (q, *J* = 5.9, 2H, CH_2). ^{13}C NMR ($CDCl_3$) *δ* 22.28 (CH_3), 27.44 (CH), 29.65 (CH_2), 35.21 (CH_2), 38.74 (CH_2), 60.26 (CH_2). MS (70 eV EI CI) 148(M^+), 70(86), 61(100), 55(65), 47(21).

Data for 3. Yield 28.00 g (93%); bp 61−65 °C/0.1 mmHg (lit.[9] 88 °C/3 mmHg). ^{1}H NMR ($CDCl_3$) *δ* 1.27 (t, *J* = 7.3, 3H, CH_3), 2.59 (q, *J* = 7.3, 2H, CH_2), 2.74 (t, *J* = 6.7, 2H, CH_2), 3.59 (t, *J* = 6.7, 2H, CH_2), 3.67 (t, *J* = 6.7, 2H, CH_2), 3.73 (m, *J* = 6.7, 2H, CH_2. ^{13}C NMR ($CDCl_3$) *δ* 14.81 (CH_3), 26.23 (CH_2), 31.06 (CH_2), 61.47 (CH_2), 70.40 (CH_2), 72.15 (CH_2). MS (70 eV EI CI), 150(M^+), 89(100), 75(57), 60(27), 47(27).

Data for 4. Yield 32.8 g (92%); bp 70−72 °C/0.1 mmHg. ^{1}H NMR ($CDCl_3$) *δ* 1.34 (s, 9H, CH_3), 2.66 (t, *J* = 6.2, 2H, CH_2), 3.58 (t, *J* = 6.2, 2H, CH_2), 3.68 (t, *J* = 6.2, 2H, CH_2), 3.74 (m, *J* = 6.2, 2H, CH_2). ^{13}C NMR ($CDCl_3$) *δ* 28.07 (CH_3), 42.09 (C), 30.96 (CH_2), 61.54 (CH_2), 70.77 (CH_2), 72.11 (CH_2). MS (70 eV EI CI), 179(M^+ + 1), 61(20), 57(100). Anal. Calcd for $C_8H_{18}O_2S$: C, 53.89; H, 10.17; S, 17.98. Found: C, 53.54; H, 10.03; S, 17.71.

Data for 5. Yield 17.30 g (90%); bp 90−92 °C/0.2 mmHg. ^{1}H NMR ($CDCl_3$) *δ* 0.90 (d, *J* = 6.7, 6H, CH_3), 1.48 (q, *J* = 6.7, 2H, CH_2), 1.62 (nonet, *J* = 6.7, 1H, CH), 2.54 (t, *J* = 7.0, 2H, CH_2), 2.72 (t, *J* = 6.7, 2H, CH_2), 3.58 (t, *J* = 6.2, 2H, CH_2), 3.66 (t, *J* = 6.2, 2H, CH_2), 3.72 (m, *J* = 6.2, 2H, CH_2). ^{13}C NMR ($CDCl_3$) *δ* 22.29 (CH_3), 27.42 (CH), 30.55 (CH_2), 31.64 (CH_2), 38.73 (CH_2), 61.70 (CH_2), 70.52 (CH_2), 72.09 (CH_2). MS (70 eV EI CI), 192(M^+), 131(90), 75(20), 61(100), 55(35). Anal. Calcd for $C_9H_{20}O_2S$: C, 56.20; H, 10.48; S, 16.67. Found: C, 55.97; H, 10.49; S, 16.32.

Data for 6. Yield 35.36 g (91%); bp 95−97 °C/0.1 mmHg (lit.[10] 131 °C/4 mmHg). ^{1}H NMR ($CDCl_3$) *δ* 1.26 (t, *J* = 7.0, 3H, CH_3), 2.58 (q, *J* = 7.0, 2H, CH_2), 2.64 (t, *J* = 6.8, 2H, CH_2), 3.66 (m, *J* = 6.8, 6H, CH_2), 3.74 (m, *J* = 6.8, 4H). ^{13}C NMR ($CDCl_3$) *δ* 14.85 (CH_3), 26.32 (CH_2), 30.87 (CH_2), 61.55 (CH_2), 70.25 (CH_2), 70.86 (CH_2), 72.56 (CH_2), (one peak overlaps and only seven appear). MS (70 eV EI CI), 195(M^++ 1), 106(23), 89(100), 75(20), 61(36).

Data for 7. Yield 41.35 g (93%); bp 100−105 °C/0.1 mmHg. ^{1}H NMR ($CDCl_3$) *δ* 1.34 (s, 9H, CH_3), 2.75 (t, *J* = 6.1, 2H, CH_2), 3.64 (m, *J* = 6.2, 6H, CH_2), 3.74 (m, *J* = 6.2, 4H, CH_2). ^{13}C NMR ($CDCl_3$) *δ* 21.87 (CH_3), 30.98 (CH_2), 42.09 (C), 61.65 (CH_2), 70.28 (CH_2), 70.32 (CH_2), 71.10 (CH_2), 72.56 (CH_2). MS (70 eV EI CI), 223(M^++ 1), 134(20), 117(27), 61(26), 57(100). Anal. Calcd for $C_{10}H_{22}O_3S$: C, 54.01; H, 9.97; S, 14.42. Found: C, 53.65; H, 10.27; S, 14.09.

Data for 8. Yield 15.51 g (92%); bp 115−117 °C/0.1 mmHg. ^{1}H NMR ($CDCl_3$) *δ* 0.91 (d, *J* = 6.4, 6H, CH_3), 1.45 (q, *J* = 6.4, 2H, CH_2), 1.63 (nonet, *J* = 6.4, 1H, CH), 2.54 (t, *J* = 6.9, 2H, CH_2), 2.71 (t, *J* = 6.9, 2H, CH_2), 3.65 (m, *J* = 7.1, 6H, CH_2), 3.72 (m, *J* = 7.1, 4H, CH_2). ^{13}C NMR ($CDCl_3$) *δ* 22.29 (CH_3), 27.42 (CH), 30.55 (CH_2), 31.33 (CH_2), 38.73 (CH_2), 61.68 (CH_2), 70.30 (CH_2), 70.36 (CH_2), 70.94 (CH_2), 72.56 (CH_2). MS (70 eV EI CI), 237(M^++ 1), 71(30), 70(91), 69(21), 61(100) 55(34), 46-(25). Anal. Calcd for $C_{11}H_{24}O_3S$: C, 55.89; H, 10.23; S, 13.65. Found: C, 55.52; H, 10.55; S, 13.31.

Thiodiethanol Monomethyl Ether (9). Sodium methoxide (10.88 g, 0.22 mol) was dissolved in methanol (100 mL), 2-mercaptoethanol (15.63 g, 0.2 mol) was added, and the mixture was left for 1 h at room temperature. 2-Chloroethyl

(8) Strauss, C. R.; Guay, H. G.; Hardwood, H. J. *J. Org. Chem.* **1964**, *29*, 1945.

(9) Shostakovskii, M. F.; Atavin, A. S.; Nikitin, V. M.; Triofimov, B. A.; Keiko, V. V.; Lavrov, V. I. *Izv. Akad. Nauk SSSR. Ser. Khim.* **1965**, *11*, 2049−2051.

(10) Atavin, A. S.; Triofimov, B. A.; Lavrov, V. I.; Orlova, S. E. *Zh. Org. Khim.* **1966**, *2*, 14.

methyl ether (20.80 g, 0.22 mol) was added, and the mixture was refluxed for 1 h. Sodium chloride was filtered off, and the product was isolated by distillation: 25.06 g, (92%); bp 64−65 °C/0.1 mmHg (lit.[11] 104−107 °C/6 mmHg). ^{1}H NMR ($CDCl_3$) δ 2.76 (m, J = 6.0, 4H, CH_2), 3.38 (s, 3H, CH_3), 3.57 (t, J = 6.1, 2H, CH_2), 3.74 (t, J = 6.0, 2H, CH_2). ^{13}C NMR ($CDCl_3$) δ 31.53 (CH_2), 35.84 (CH_2), 58.76 (CH_2), 61.04 (CH_2), 72.30 (CH_3). MS (70 eV EI CI), 136(M^+), 118(27), 75(32), 58(100), 47(37), 46-(34).

Synthesis of Borate Esters. Typical Procedure for 1a. Method A. *tert*-Butyl 2-hydroxyethyl sulfide (4.02 g, 30 mmol) and boric acid (0.6183 g, 10 mmol) were added to toluene (40 mL). The reaction mixture was refluxed for 6 h with azeotropic removal of water. Toluene was removed by distillation under vacuum. The borate ester was dried over anhydrous magnesium sulfate and decanted. Magnesium sulfate was washed with dichloromethane, and the organic solutions were combined with the borate ester. Dichloromethane was distilled off to give the pure borate ester: 3.73 g (91%).

Method B. A round-bottom flask (25 mL) was charged with *tert*-butyl 2-hydroxyethyl sulfide (4.82 g, 36 mmol). A 1 M borane−tetrahydrofuran (12 mL, 12 mmol) was added with stirring at room temperature. The reaction mixture was refluxed for 0.5 h. Tetrahydrofuran was pumped off, and pure borate ester was obtained: ^{11}B NMR δ 18.26, in tetrahydrofuran.

Method C. Diborane (12 mmol), generated as described earlier,[6] was absorbed in neat *tert*-butyl 2-hydroxyethyl sulfide (4.70 g, 35 mmol) at room temperature. After the addition was completed, the reaction mixture was stirred at 50 °C for 0.5 h under a slow stream of nitrogen to obtain the borate ester: ^{11}B NMR δ 17.67.

Data for 1a. ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 9H, CH_3), 2.69 (t, J = 6.9, 2H, CH_2), 3.89 (t, J = 6.9, 2H, CH_2). ^{13}C NMR ($CDCl_3$) δ 29.80 (CH_3), 31.12 (CH_2), 42.02 (C), 63.41 (CH_2). MS (70 eV EI CI) 411(M + 1, 25), 277(58), 221(54), 135(64).

Data for 2a. ^{1}H NMR ($CDCl_3$) δ 0.90 (d, J = 6.6, 6H, CH_3), 1.48 (q, J = 6.6, 2H, CH_2), 1.62 (nonet, J = 6.6, 1H, CH), 2.55 (t, J = 6.8, 2H, CH_2), 2.70 (t, J = 6.8, 2H, CH_2), 3.92 (t, J = 6.8, 2H, CH_2). ^{13}C NMR ($CDCl_3$) δ 22.32 (CH_3), 27.41 (CH), 30.28 (CH_2), 33.19 (CH_2), 38.78 (CH_2), 62.84 (CH_2). MS (70 eV EI CI) 453(M + 1, 28), 305(100), 131(52).

Data for 3a. ^{1}H NMR ($CDCl_3$) δ 1.25 (t, J = 7.1, 3H, CH_3), 2.59 (q, J = 7.1, 2H, CH_2), 2.72 (t, J = 6.8, 2H, CH_2), 3.57 (t, J = 6.8, 2H, CH_2), 3.65 (t, J = 6.8, 2H, CH_2), 3.94 (t, J = 6.8, 2H, CH_2). ^{13}C NMR ($CDCl_3$) δ 14.89 (CH_3), 26.35 (CH_2), 31.03 (CH_2), 62.71 (CH_2), 70.93 (CH_2), 71.27 (CH_2). MS (70 eV EI CI) 459(M + 1), 309(60), 89(100).

Data for 4a. ^{1}H NMR ($CDCl_3$) δ 1.32 (*s*, 9H), 2.62 (t, J = 6.9, 2H, CH_2), 3.54 (t, J = 6.9, 2H, CH_2), 3.62 (t, J = 6.7, 2H, CH_2), 3.92 (t, J = 6.7, 2H, CH_2). ^{13}C NMR ($CDCl_3$) δ 28.04 (CH_3), 41.03 (CH_2), 32.01 (C), 62.75 (CH_2), 71.01 (CH_2), 71.33 (CH_2). MS (70 eV EI CI) 543(M + 1), 365(24), 117(100).

Data for 5a. ^{1}H NMR ($CDCl_3$) δ 0.90 (d, J = 6.8, 6H, CH_3), 1.49 (q, J = 6.7, 2H, CH_2), 1.64 (nonet, J = 6.7, 1H, CH), 2.54 (t, J = 6.7, 2H, CH_2), 2.70 (t, J = 6.7, 2H, CH_2), 3.54 (t, J = 6.5, 2H, CH_2), 3.64 (t, J = 6.5, 2H, CH_2), 3.91 (t, J = 6.5, 2H, CH_2). ^{13}C NMR ($CDCl_3$) δ 22.30 (CH_3), 27.36 (CH), 30.53 (CH_2), 31.44 (CH_2), 38.75 (CH_2), 62.73 (CH_2), 70.91 (CH_2), 71.29 (CH_2). MS (70 eV EI CI) 585(M + 1, 14), 393(97), 131(100).

Data for 6a. ^{1}H NMR ($CDCl_3$) δ 1.25 (t, J = 6.9, 3H, CH_3), 2.56 (q, J = 6.9, 2H, CH_2), 2.70 (t, J = 6.3, 2H, CH_2), 3.65 (m, J = 5.7, 8H, CH_2), 3.93 (t, J = 6.7, 2H, CH_2). ^{13}C NMR ($CDCl_3$) δ 14.90 (CH_3), 26.30 (CH_2), 30.90 (CH_2), 62.68 (CH_2), 70.34 (CH_2), 70.47 (CH_2), 71.02 (CH_2), 71.64 (CH_2). MS (70 eV EI CI) 591(M + 1, 2), 397(100), 89(25).

Data for 7a. ^{1}H NMR ($CDCl_3$) δ 1.32 (*s*, 9H, CH_3), 2.74 (t, J = 6.3, 2H, CH_2), 3.64 (m, J = 6.3, 8H, CH_2), 3.91 (t, J = 6.3, 2H, CH_2). ^{13}C NMR ($CDCl_3$) δ 27.89 (CH_3), 31.01 (CH_2), 42.02 (C), 62.67 (CH_2), 70.33 (CH_2), 70.44 (CH_2), 71.17 (CH_2), 71.64 (CH_2). MS (70 eV EI CI) 675(M + 1), 453(19),117(100).

Data for 8a. ^{1}H NMR ($CDCl_3$) δ 0.90 (d, J = 6.3, 6H, CH_3), 1.46 (q, J = 6.3, 2H, CH_2), 1.64 (nonet, J = 6.3, 1H, CH), 2.52 (t, J = 6.6, 2H, CH_2), 2.71 (t, J = 6.6, 2H, CH_2), 3.64 (m, J = 6.6, 8H, CH_2), 3.91 (t, J = 6.6, 2H, CH_2). ^{13}C NMR ($CDCl_3$) δ 22.29 (CH_3), 27.38 (CH), 30.52 (CH_2), 31.31 (CH_2), 38.76 (CH_2), 62.68 (CH_2), 70.35 (CH_2), 70.47 (CH_2), 71.06 (CH_2), 71.65 (CH_2). MS (70 eV EI CI) 717(M + 1), 482(22), 481(100), 131(85).

Data for 9a. ^{1}H NMR ($CDCl_3$) δ 2.71 (m, J = 6.2, 4H, CH_2), 3.38 (*s*, 3H), 3.56 (t, J = 6.2, 2H, CH_2), 3.92 (t, J = 6.2, 2H, CH_2). ^{13}C NMR ($CDCl_3$) δ 31.58 (CH_2), 33.55 (CH_2), 58.68 (CH_2), 62.83 (CH_2), 72.19 (CH_3). MS (70 eV EI CI) 417(M + 1, 14), 385(15), 281(33), 137(24), 119(20).

Borane Adducts with Borate Esters of Hydroxydialkyl Sulfides (1b−9b). Typical Procedure for Borane Adduct of Borate Ester of *tert*-Butyl 2-Hydroxyethyl Sulfide (1b). A 100-mL one-neck, round-bottom flask equipped with a septum inlet, magnetic stirring bar, and an adapter with a stopcock was charged with boron trifluoride−diglyme (20 mmol). A 2 M solution of sodium borohydride in triglyme (7.5 mL, 15 mmol) was added dropwise by means of a hypodermic syringe. Generation of diborane is smooth, and the reaction is not exothermic. Diborane was absorbed in neat *tert*-butyl 2-hydroxyethyl sulfide (7.94 g, 60 mmol) at room temperature. After the addition was completed, the reaction mixture was stirred at 50 °C for 15 min under a slow stream of nitrogen. ^{11}B NMR analysis, δ 17.67, indicated the formation of borate ester. Diborane was then passed into the borate ester at room temperature till saturation. The borane adduct thus obtained was a colorless liquid, 6.4 M in borane, estimated by a standard procedure for active hydride analysis using a water/glycerol/THF 1:1:1 hydrolyzing mixture:[12] ^{11}B NMR δ −26.03.

Trioctylborane. A 6.9 M borane adduct **9b** (3 mL, 18 mmol) was dissolved in dichloromethane (18 mL), and 1-octene (6.0 g, 54 mmol) was added dropwise with cooling to keep the temperature at 20−25 °C. The reaction was complete in 15 min, as indicated by ^{11}B NMR. The reaction mixture was oxidized with 3 M sodium hydroxide (6 mL, 18 mmol) and 30% hydrogen peroxide (3 mL, 28 mmol) and stirred at room temperature overnight. The organic layer was separated, stirred with water for 0.5 h, and dried over anhydrous magnesium sulfate, and octanol was isolated by distillation: 6.24 g (89%), bp 99−100 °C/20 mmHg. GC analysis (Carbowax 20M) showed 1-octanol 94% and 2-octanol 6%.

(−)-*cis*-Myrtanol. A 6.0 M borane adduct **9b** (2.0 mL, 12 mmol) was dissolved in dichloromethane (12 mL), and (−)-β-pinene (5.0 g, 36 mmol), $[\alpha]^{23}_D$ −20.8° (neat), 91% ee, was added at 0 °C. The reaction was completed in 0.5 h, as indicated by ^{11}B NMR. The mixture was kept at room temperature for 1 h and oxidized by the addition of 3 *M* sodium hydroxide (5.6 mL, 17 mmol) and 30% hydrogen peroxide (4.0 mL, 40 mmol), keeping the temperature during the addition below 30 °C, and then stirring at room temperature overnight. The dichloromethane layer was separated, stirred with water (20 mL) for 0.5 h, and distilled to give 5.05 g (91%) of pure product: bp 116−118 °C/15 mmHg (lit.[12] bp 65−67 °C/0.2 mmHg); $[\alpha]^{20}_D$ −19.4°.

Hydroboration of 1-Methylcyclohexene. A 6.0 M borane adduct **9b** (1 mL, 6 mmol) was taken in a sample vial, and 1-methylcyclohexene (1.15 g, 12 mmol) was added dropwise with cooling to keep the temperature at 20−25 °C. The reaction mixture was allowed to stir at room temperature for 0.5 h. Ethanol (1 mL) was added slowly with stirring at 0 °C: ^{11}B NMR δ 53.

Hydroboration of 2,3-Dimethyl-2-butene. A 6.0 M borane adduct **9b** (1 mL, 6 mmol) was taken in a sample vial, and 2,3-dimethyl-2-butene (0.504 g, 6 mmol) was added dropwise with cooling to keep the temperature at 20−25 °C. The reaction mixture was allowed to stir at room temperature for 0.5 h: ^{11}B NMR δ 24.33.

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(11) Stevens, J. P. *Pat. Belg.* **1963**, *626*, 797.; Chem. Abstr. **1964**, *61*, 8493*e*.

(12) Brown, H. C.; Kramer, G. W.; Levy A. B.; Midland, M. M. *Organic Syntheses via Boranes*, J. Wiley: New York, 1975. A reprinted edition is currently available: *Organic Syntheses via Boranes;* Aldrich Chemical Co., Inc.: Milwaukee, WI, 1997; Vol. 1.