Molecular Addition Compounds. 17. Borane and Chloroborane Adducts with Organic Sulfides for Hydroboration†

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The following sulfides have been examined as borane carriers in comparison with dimethyl sulfide and 1,4-oxathiane: *tert*-butyl methyl sulfide, isoamyl methyl sulfide, ethyl isoamyl sulfide, *tert*-butyl isoamyl sulfide, diisoamyl sulfide, tetrahydrothiophene, tetrahydro-thiopyran, thioanisole, 3-ethylthiotetrahydrofuran, bis(3-tetrahydrofuryl) sulfide, and bis(2-methoxyethyl) sulfide. Their complexing ability toward borane increases in the following order: thioanisole < ether−sulfides < dialkyl sulfides < dimethyl sulfide. Borane adducts of the sulfides are liquids above 0 °C. The thioanisole adduct loses diborane at room temperature. The reactivity of the adducts toward 1-octene increases in the reversed order of the complexing ability of the sulfides. Diisoamyl sulfide has a mild, ethereal, agreeable aroma, its synthesis is economical and the borane adduct, 4.2 M in BH_3, is stable over prolonged periods at room temperature. The sulfide can be recovered from hydroboration−oxidation products by distillation. Consequently, diisoamyl sulfide is a new promising borane carrier. Bis(2-methoxyethyl) sulfide, easily synthesized from the low cost thiodiethanol, is three times more soluble in water than 1,4-oxathiane. Its borane adduct is 6.0 M in BH_3 and can substitute for more expensive borane-1,4-oxathiane in hydroboration reactions. Applications of these new borane adducts in the synthesis of mono- and dichloroborane adducts was also studied. The equilibrium ratios observed for the new chloroborane adducts were similar to that observed for dimethyl sulfide adducts. However, the hydroboration of 1-octene with these new chloroborane adducts are much faster than the corresponding adducts of dimethyl sulfide, which are currently used extensively.

Diborane is a versatile reagent with a multitude of applications in organic and inorganic synthesis. Since it is a pyrophoric gas, borane complexes with suitable carriers are used. Borane−tetrahydrofuran (H_3B:THF) and borane−dimethyl sulfide (BMS) are the reagents of choice for most hydroborations and reductions carried out with diborane.[2−4] It is used in a growing number of syntheses of pharmaceuticals and other important compounds.[5−7] However, its large-scale applications are hampered by some inconveniences of H_3B:THF and BMS. Thus, the commercially available H_3B:THF is a dilute solution (1.0 M in BH_3) undergoing slow but significant decomposition (cleavage of tetrahydrofuran with the loss of hydride) creating storage and transportation problems.

BMS is free from these inconveniences. It is a neat complex, 10.0 M in BH_3, stable indefinitely. However, the odoriferous, water insoluble, highly volatile, and flammable dimethyl sulfide creates environmental and safety problems. Recently, it has been demonstrated that 1,4-oxathiane, having lower volatility and milder odor than dimethyl sulfide, is a convenient borane carrier.[8] It has a limited solubility in water and can be easily oxidized to the corresponding sulfoxide, which is miscible with water. Borane-1,4-oxathiane is a liquid adduct, 8.0 M in BH_3, stable over prolonged periods. Unfortunately, the commercially available reagent is relatively costly, as compared to H_3B:THF and BMS. Solid borane adducts with bis-sulfides have also been reported.[7] Clearly, there is a need for economical, environmentally safe, and easy to handle borane adducts. Consequently, this study has been undertaken with an objective of developing a sulfide for borane complexation meeting the following requirements: odorless or mild odor, low volatility, economical synthesis, stable liquid borane adducts of high molarity in BH_3, soluble in various solvents.

Results and Discussion

Dialkyl sulfides of low molecular weight are attractive for borane complexation since they may be expected to form adducts of similar reactivity and stability to BMS. Unfortunately, these compounds do not meet our requirements because of high volatility and unpleasant odor. However, it has been noted in the early literature that pure diisoamyl sulfide is exceptional among the lower alkyl sulfides in having a pleasant, ethereal odor.[9] Since the isoamyl group also exhibits a profound fragrance effect in other classes of compounds, e.g., esters and ethers,[10] we decided to prepare a series of isoamyl alkyl

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Table 1. Borane Adducts with Organic Sulfides

sulfide	odor	exchange with BMS[a] (%)	borane adduct $[BH_3]$[b]	borane adduct ^{11}B NMR δ[c] (ppm)	borane adduct hydroboration[d] (min)
dimethyl sulfide	stench		10.0	−20.3	45
isoamyl methyl sulfide	ethereal, very strong	46	5.8	−21.3	10
tert-butyl methyl sulfide	stench	39	6.6	−24.6	10
ethyl isoamyl sulfide	ethereal, strong	44	5.2	−23.1	10
tert-butyl isoamyl sulfide	ethereal, mild	32	4.3	−25.9	10
diisoamyl sulfide	ethereal, mild, agreeable	40	4.2	−22.5	15
tetrahydrothiophene	stench	46[e]	8.1	−20.6	15
tetrahydrothiopyran	stench	45	7.5	−22.8	15
3-ethylthiotetrahydrofuran	stench	21	5.8	−24.5	5
bis(2-methoxyethyl) sulfide	stench	16	6.0	−22.6	5
1,4-oxathiane	stench, mild	17	8.0	−23.0	5
bis(3-tetrahydrofuryl) sulfide	stench	0	4.6	−26.0	5
thioanisole	stench	0[e]	3.0[f]	−20.6	

[a] BMS and sulfide mixed at 1:1 molar ratio. [b] Estimated by hydrolysis in water−glycerol−methanol (1:1:1), measuring hydrogen evolved. [c] Neat. [d] Hydroboration of 1-octene in THF at 20−25 °C. Concentration of the adduct 1 M. [e] Calculated from the exchange with borane−*tert*-butyl methyl sulfide. [f] Unstable over longer periods.

sulfides and compare their odor and borane complexing ability. The following sulfides which can be prepared from readily available, low cost, starting materials have been selected: diisoamyl sulfide, isoamyl methyl sulfide, ethyl isoamyl sulfide, and *tert*-butyl isoamyl sulfide. Commercially available *tert*-butyl methyl sulfide, tetrahydrothiophene, tetrahydrothiopyran and thioanisole have also been included in the study.

Diisoamyl sulfide was prepared in high yield (90%) by the reaction of isoamyl bromide with an aqueous solution of sodium sulfide in the presence of a phase-transfer catalyst (eq 1).

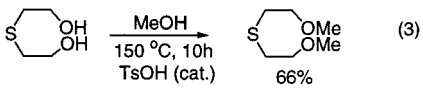
$$2\ i\text{-AmBr} + Na_2S \xrightarrow[n\text{-}Bu_4NBr\ \text{reflux, 6 h}]{H_2O} i\text{-}Am_2S \qquad (1)$$

The product is isolated by simple distillation in >99% purity. It has an agreeable, mild, ethereal aroma and low volatility. The mixed alkyl isoamyl sulfides were prepared in high yields by a routine methodology according to eq 2.[11] *tert*-Butyl isoamyl sulfide has a mild, but less agreeable odor than diisoamyl sulfide. Methyl and ethyl isoamyl sulfides have a strong ethereal odor.

$$RSH + NaOMe \xrightarrow{MeOH} RSNa \xrightarrow[MeOH,\ \text{reflux, 1h}]{R^1X} RSR^1 \qquad (2)$$

R = Et, *t*-Bu; R = *i*-Am
R^1X = *i*-AmBr; R^1X = MeI

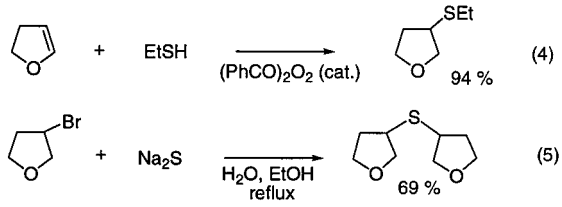
In contrast to the dialkyl sulfides, which are insoluble in water, the lower molecular weight ether−sulfides, e.g., 1,4-oxathiane,[8] are more hydrophilic. Since water soluble carrier would be advantageous in various applications of its borane adduct, the following ether−sulfides were prepared. Bis(2-methoxyethyl) sulfide, structurally related to 1,4-oxathiane, was prepared in an improved yield from low cost thiodiethanol by the literature procedure[12] (eq 3). The product is isolated by simple distillation and the unreacted starting material can be recycled.



(3)

Bis(2-methoxyethyl) sulfide is three times more soluble in water than 1,4-oxathiane and can be considered a cheaper alternative to 1,4-oxathiane for borane complexation. It possesses a less obnoxious odor and is much less volatile than dimethyl sulfide.

The tetrahydrofuryl sulfides were also prepared. 3-Ethylthiotetrahydrofuran was obtained by the free radical addition of ethyl mercaptan to 2,3-dihydrofuran,[13] and bis(3-tetrahydrofuryl) sulfide by the reaction of 3-bromotetrahydrofuran with sodium sulfide (eqs 4 and 5).



However, 3-ethylthiotetrahydrofuran is only sparingly soluble in water. Bis(3-tetrahydrofuryl) sulfide is twice as soluble in water as 1,4-oxathiane, but both sulfides have a typically unpleasant odor.

Borane Adducts. Exchange reactions between BMS and the sulfides were followed by ^{11}B NMR. Except for thioanisole and tetrahydrothiophene, BMS and the borane−sulfide adducts showed different chemical shifts, enabling direct calculation from the spectrum of the amount of borane taken by a sulfide at equilibrium of 1:1 mixtures. The results presented in Table 1 reveal the following order of borane complexing ability: thioanisole < ether−sulfides < dialkyl sulfides < dimethyl sulfide. No uptake of borane from BMS was observed for bis(3-tetrahydrofuryl) sulfide and thioanisole.

Borane adducts were prepared by saturating the neat sulfides with diborane at 0 °C. All the adducts are liquids above 0 °C. Their molarities are shown in Table 1. The adducts are soluble in tetrahydrofuran, diethyl ether, and dichloromethane, solvents typically used for hydroboration.

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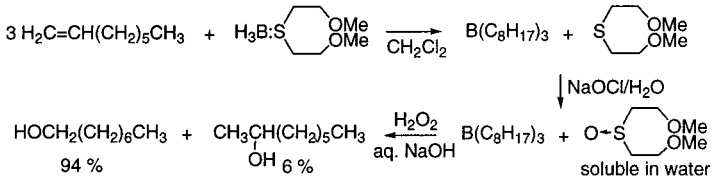
(13) Hillers, S.; Viskne, S.; Kurgane, B.; Veinbergs, A.; Braukame, M. USSR Pat. 525,312, 1977; *Chem. Abstr.* **1977**, *88*, 6703.

Scheme 1



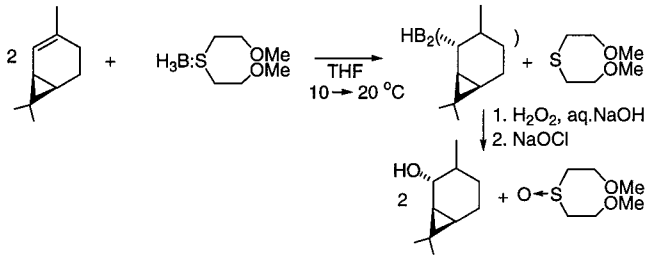
Dialkyl sulfide adducts are stable over prolonged periods at room temperature. No change in molarity and the ^{11}B NMR spectrum of borane−diisoamyl sulfide adduct and borane−ethyl isoamyl sulfide adduct over 10 months at room temperature was observed. The ^{11}B NMR spectra of the borane−ether−sulfide adducts showed only a single absorption (quartet) in the range −20 to −26 ppm, indicating coordination of borane with the sulfur atom. Thioanisole absorbs diborane to give a solution 5.0 M in BH_3 at 0 °C. However, at room temperature the solution loses diborane, the molarity decreasing to 3.0 M in a few days and then slowly further over a prolonged period.

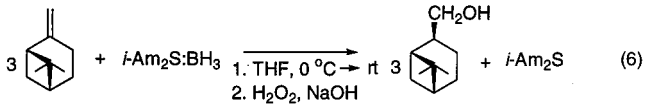
A convenient procedure for small-scale generation of diborane (5−50 mmol) modified from an earlier method,[14] was developed for this study. Thus, a commercially available 2.0 M sodium borohydride solution in triglyme is added to the boron trifluoride adduct with diglyme or triglyme at room temperature. Both reagents are liquids, convenient to handle. Generation of diborane is smooth and the yield is high (95%). No other gaseous products are formed, making possible a visual observation of diborane absorption in sulfides. The boron trifluoride complexes with diglyme and triglyme are prepared by mixing equimolar amounts of the boron trifluoride etherate with diglyme or triglyme, and removing diethyl ether under vacuum. The complexes are pale yellow liquids, darkening slowly when kept at 0 °C. The darkening exerted no significant effect on the yield of diborane realized.

Hydroboration. The hydroboration of 1-octene with the adducts was carried out in tetrahydrofuran solution (1.0 M) at room temperature following the progress of the reaction by ^{11}B NMR. The results are shown in Table 1. The reactivity of the adducts corresponds to the complexing ability of the sulfides, the borane adducts with ether−sulfides being more reactive than the adducts with dialkyl sulfides. The hydroborations with the ether−sulfide adducts were practically instantaneous. The ^{11}B NMR spectrum taken in 5 min showed complete transformation of 1-octene into trioctylborane. The adducts with dialkyl sulfides required 10−15 min to complete the hydroboration, whereas, with the strongest adduct (BMS), the reaction took 45 min.

Hydroborations on a preparative scale were carried out with borane-diisoamyl sulfide adduct and borane-bis(2-methoxyethyl) sulfide adduct. Thus, (−)-*β*-pinene was reacted with borane-diisoamyl sulfide adduct and the organoborane intermediate was oxidized with standard 30% hydrogen peroxide and 3.0 *M* sodium hydroxide used in excess to suppress oxidation of the sulfide.[15] It should be noted that diisoamyl sulfide is less reactive toward hydrogen peroxide than dimethyl sulfide.[16] (−)-*cis*-Myrtanol was isolated by distillation in 82% yield and the sulfide was readily recovered (eq 6).

Scheme 2





Hydroboration of 1-octene with borane-bis(2-methoxyethyl) sulfide adduct was carried out in dichloromethane. The sulfide could not be completely removed from the organic phase by several washings with water. It was oxidized to the corresponding sulfoxide with 5% aqueous sodium hypochlorite (Chlorox). ^{1}H and ^{11}B NMR spectra taken after removing the solvent showed only trioctylborane, which was isolated in 96% yield. The organoborane was oxidized under standard conditions to give a mixture of 1- and 2-octanol (94:6) in 94% yield (Scheme 1).

(+)-2-Carene was hydroborated with borane-bis(2-methoxyethyl) sulfide adduct in THF at room temperature. A white precipitate of diisocaranylborane was formed in a few minutes after mixing the reagents. It can be removed by filtration at this stage. Oxidation of the organoborane with hydrogen peroxide/sodium hydroxide and distillation gave a mixture of (−)-2-isocaranol and the sulfide, which was removed by oxidation with Chlorox. (−)-2-Isocaranol was isolated in 81% yield (Scheme 2).

Preparation of Monochloroborane and Dichloroborane Adducts of Various Dialkyl Sulfides. Synthesis of mono- and dichloroborane adducts from methyl sulfide−borane constitutes one of its most valuable synthetic application, as these chloroborane adducts hydroborate unhindered olefins with much improved regioselectivities.[4,17] Methyl sulfide forms very stable monochloroborane adduct that hydroborate representative olefins at room temperature.[18] The corresponding

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dichloroborane is less reactive, but hydroboration can be carried out with some procedural modifications such as the addition of 1 equiv of BCl_3.[19] Unfortunately, these synthetically important chloroborane adducts exist as equilibrium mixtures and only ~73% pure monochloroborane and ~85% pure dichloroborane (by ^{11}B NMR) can be obtained. Also, the unpleasant odor and volatility of dimethyl sulfide make these reagents less convenient for large-scale applications. Having prepared less volatile and less odoriferous dialkyl sulfide-borane adducts, it was of interest to see whether these adducts can be used for the synthesis of the corresponding mono- and dichloroborane adducts. For this study the following dialkyl sulfides were examined as chloroborane carriers in comparison with methyl sulfide: ethyl sulfide, *n*-propyl sulfide, isoamyl sulfide, 1,4-thioxane, thioanisole, *tert*-butyl methyl sulfide, *tert*-butyl isoamyl sulfide.

The dialkyl sulfide−BCl_3 adducts were prepared by slowly passing boron trichloride gas into neat sulfide at − 20 °C and warming the reaction flask slowly to room temperature.

$$R_2S + BCl_3 \xrightarrow{-20\ ^\circ C \rightarrow rt} R_2S{:}BCl_3 \qquad (7)$$

The adducts thus obtained show clean sharp signals in ^{11}B NMR and are stable at 0 °C indefinitely. Initially, the preparation of mono- and dichloroborane−dialkyl sulfide complexes was attempted by bubbling a sufficient amount of diborane into a solution of dialkyl sulfide−BCl_3 complex in dialkyl sulfide according to the following equations.

$$R_2S{:}BCl_3 + 2\ R_2S + B_2H_6 \xrightarrow{0\ ^\circ C} 3\ R_2S{:}BH_2Cl$$

$$4\ R_2S{:}BCl_3 + 2\ R_2S + B_2H_6 \xrightarrow{0\ ^\circ C} 6\ R_2S{:}BHCl_2 \qquad (8)$$

However, using this procedure the chloroborane adducts were not obtained cleanly. Alternatively, the adducts were prepared by mixing dialkyl sulfide−BH_3 and dialkyl sulfide−BCl_3 in appropriate ratios at room-temperature according to the following equations.

$$R_2S{:}BCl_3 + 2\ R_2S{:}BH_3 \xrightarrow{rt} 3\ R_2S{:}BH_2Cl$$

$$2\ R_2S{:}BCl_3 + R_2S{:}BH_3 \xrightarrow{rt} 3\ R_2S{:}BHCl_2 \qquad (9)$$

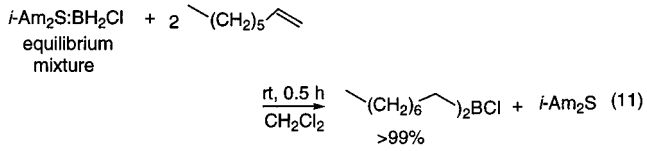
Using this procedure, the corresponding mono- and dichloroborane adducts were obtained as major products. The required monochloroborane adduct were in equilibrium with dialkyl sulfide−BH_3 and dialkyl sulfide−$BHCl_2$ (similar to that reported for dimethyl sulfide). For example, during the preparation of isoamyl sulfide−BH_2Cl preparation, the product isoamyl sulfide−BH_2Cl (75%) is in equilibrium with the corresponding $BHCl_2$ (12%) and BH_3 (13%) adducts.

$$\underset{(1.0\ \text{equiv})}{i\text{-}Am_2S{:}BCl_3} + \underset{(2.0\ \text{equiv})}{i\text{-}Am_2S{:}BH_3} \rightarrow \underset{(2.25\ \text{equiv})}{i\text{-}Am_2S{:}BH_2Cl} + \underset{(0.36\ \text{equiv})}{i\text{-}Am_2S{:}BHCl_2} + \underset{(0.39\ \text{equiv})}{i\text{-}Am_2S{:}BH_3} \qquad (10)$$

(19) Brown, H. C.; Ravindran, N.; Kulkarni, S. U.; *J. Org. Chem.* **1980**, *45*, 2533.

$$i\text{-}Am_2S{:}BH_2Cl \rightleftharpoons i\text{-}Am_2S{:}BHCl_2 + i\text{-}Am_2S{:}BH_3$$

These equilibrium ratios did not change drastically with the change in dialkyl sulfide. Though the adduct exits in equilibrium, hydroboration of 1-octene and α-pinene gave the corresponding dialkylchloroborane cleanly. Also, the monochloroborane adducts of *i*-Am_2S, *t*-BuSMe, and *t*-BuSAm[*i*] hydroborate 1-octene much faster than the borane adduct of dimethyl sulfide and can even be carried out at 0 °C. The results are summarized in Table 3.



(11)

Similarly, dichloroborane−dialkyl sulfide adducts also exist in equilibrium with the corresponding dichloroborane and boron trichloride adducts. In most of the cases, the dichloroborane adduct can be obtained in ~85% purity (by ^{11}B NMR). Table 3 summarizes the ratios of various peaks observed in ^{11}B NMR.

$$\underset{(2.0\ \text{equiv})}{i\text{-}Am_2S{:}BCl_3} + \underset{(1.0\ \text{equiv})}{i\text{-}Am_2S{:}BH_3} \rightarrow \underset{(2.55\ \text{equiv})}{i\text{-}Am_2S{:}BHCl_2} + \underset{(0.24\ \text{equiv})}{i\text{-}Am_2S{:}BH_2Cl} + \underset{(0.21\ \text{equiv})}{i\text{-}Am_2S{:}BCl_3} \qquad (12)$$

$$i\text{-}Am_2S{:}BHCl_2 \rightleftharpoons i\text{-}Am_2S{:}BH_2Cl + i\text{-}Am_2S{:}BCl_3$$

However, the hydroboration of 1-octene using these dichloroborane adducts is much slower than that of the corresponding monochloroborane adducts (see Table 3). These hydroboration can be made faster by the addition of one equivalent of boron trichloride as reported for dimethyl sulfide−dichloroborane.[19]

Conclusions

The complexing ability of the sulfides toward borane increases in the following order: thioanisole < ether−sulfides < dialkyl sulfides < dimethyl sulfide. The reactivity of the corresponding borane adducts toward 1-octene increases in the reversed order. Diisoamyl sulfide has a mild, ethereal agreeable aroma. Its synthesis is simple and the borane adduct, 4.2 M in BH_3, is a liquid above 0 °C, stable over prolonged periods at room temperature. Consequently, it is a new promising borane carrier. Bis(2-methoxyethyl) sulfide can be used for borane complexation as a less costly alternative to 1,4-oxathiane. The mono- and dichloroborane adducts of these dialkyl sulfides can be prepared, however, these adducts exists in equilibrium as in the case of dimethyl sulfide−chloroborane adducts. The equilibrium distributions are slightly better for isoamyl sulfide *tert*-butyl methyl sulfide and *tert*-butyl isoamyl sulfides. The hydroboration of 1-octene with these monochloroborane adducts is very fast and complete within 30 min. Also, isoamyl sulfide−BH_2Cl does not possess the unpleasant odor of typical sulfur compounds. Accordingly, the present study provides dialkyl sulfides that are nonvolatile, with a more agreeable smell that are advantageous as borane and chloroborane carriers, with improved reactivities,

Table 2. Preparation of Monochloroborane Adducts of Dialkyl Sulfides[a]

dialkyl sulfide	$R_2S:BH_2Cl$ % (^{11}B NMR)	$R_2S:BHCl_2$ % (^{11}B NMR)	$R_2S:BH_3$ % (^{11}B NMR)	hydroboration[b] (h)
methyl sulfide	73 (−7.2, t)	15 (+1.6, d)	12 (−20.6, q)	2.0
ethyl sulfide	74 (−9.8, t)	14 (+2.8, d)	12 (−24.1, q)	1.5
n-propyl sulfide	76 (−9.1, t)	14 (+1.2, d)	10 (−23.1, q)	1.5
isoamyl sulfide	75 (−9.3, t)	13 (+1.2, d)	11 (−23.2, q)	0.5
1,4-oxathiane	63 (−7.9, t)	18 (+8.1, d)	19 (−23.4, q)	0.5
thioanisole	62 (−5.7, t)	20 (+3.0, d)	18 (−21.2, q)	0.25
tert-butyl methyl sulfide	73 (−7.5, t)	15 (+1.3, d)	12 (−20.9, q)	0.25
tert-butyl isoamyl sulfide	76 (−9.5, t)	12.5 (+2.5, d)	11.5 (−25.3, q)	0.25
methyl sulfide[c]	75 (−7.2, t)	13 (+1.6, d)	12 (−20.6, q)	2.0

[a] Equilibrium ratios observed after 48 h at room temperature. [b] Hydroboration of 1-octene in CH_2Cl_2 at 20−25 °C. Concentration of the adduct 1 M. [c] Peaks observed for a commercial sample of dimethyl sulfide−monochloroborane adduct.

Table 3. Preparation of Dichloroborane Adducts of Dialkyl Sulfides[a]

dialkyl sulfide	$R_2S:BHCl_2$ % (^{11}B NMR)	$R_2S:BH_2Cl$ % (^{11}B NMR)	$R_2S:BCl_3$ % (^{11}B NMR)	hydroboration[b] (h)
methyl sulfide	86 (+1.7, d)	6.4 (−7.2, t)	7.6 (+7.0, s)	24.0
ethyl sulfide	85 (+0.9, d)	11 (−9.9, t)	4 (+6.9, s)	24.0
n-propyl sulfide	84 (+1.1, d)	10 (−9.3, t)	6 (+7.0, s)	12.0
isoamyl sulfide	83 (+1.1, d)	10 (−9.4, t)	7 (+7.1, s)	6.0
1,4-oxathiane	83 (+8.1, d)	7 (−7.9, t)	8 (+8.2, s)	4.0
thioanisole	86 (+3.0, d)	6 (−5.7, t)	8 (+8.1, s)	6.0
tert-butyl methyl sulfide	85 (+1.5, d)	7.4 (−7.3, t)	7.6 (+6.8, s)	3.0
tert-butyl isoamyl sulfide	86 (+2.4, d)	7.5 (−9.5, t)	6.5 (+7.0, s)	3.0
methyl sulfide[c]	86 (+1.8, d)	7 (−7.1, t)	8 (+7.2, s)	24.0

[a] Equilibrium ratios observed after 48 h at room temperature. [b] Hydroboration of 1-octene in CH_2Cl_2 at 20−25 °C. Concentration of the adduct 1 M. [c] Peaks observed for a commercial sample of dimethyl sulfide−monochloroborane adduct.

and should therefore be able to substitute for the corresponding dimethyl sulfide compounds.

Experimental Section

All glassware was oven-dried for several hours at 120 °C, assembled while hot, and cooled in a stream of dry nitrogen gas. Syringes were assembled and fitted with needles while hot. Techniques for handling air-sensitive compounds described elsewhere were followed.[20] All manipulations and reactions with air-sensitive compounds were carried out under nitrogen atmosphere. ^1H and ^{11}B NMR spectra were recorded on a 300 MHz multinuclear instrument. The ^{11}B chemical shifts are in δ relative to boron trifluoride diethyl etherate. Optical rotations were measured on an automatic polarimeter. GC analyses were carried out on a chromatograph equipped with FID and CI-100A integrator. The following columns were used, 12 ft × 0.125 in column packed with 10% Carbowax 20M, SE-30 on Chromosorb W (100−120 mesh). Microanalyses were performed at the Microanalytical Laboratory, Purdue University.

Materials. Borane−methyl sulfide (BMS), *tert*-butyl methyl sulfide, tetrahydrothiophene, tetrahydrothiopyran, dimethyl sulfide, thioanisole, 1,4-oxathiane, thiodiethanol, and boron trichloride were commercial products. Tetrahydrofuran was freshly distilled from a small quantity of benzophenone ketyl prior to use. Diglyme, (+)-2-carene $[\alpha]^{23}_D = +92.0°$ (neat), and (−)-β-pinene $[\alpha]^{23}_D = -20.8°$ (neat) were distilled from a small amount of lithium aluminum hydride under vacuum. Boron trifluoride diethyl etherate was distilled from a small amount of calcium hydride under vacuum.

Isoamyl Methyl Sulfide. Typical Procedure. Sodium methoxide (5.90 g, 0.11 mol) was dissolved in methanol (50 mL). Isoamyl mercaptan (10.42 g, 0.10 mol) was added and the mixture was left at room temperature for 1 h. Methyl iodide (15.61 g, 0.11 mol) was added and the mixture was refluxed for 2 h. Water was added and the mixture was extracted with pentane. The extracts were combined and dried over anhydrous magnesium sulfate. The product was isolated by distillation and redistilled from lithium aluminum hydride: 10.64 g, bp 54−55 °C/35 mmHg (lit.[21] bp 136−138 °C), 90%, $n^{20}_D = 1.4465$; ^1H NMR ($CDCl_3$), δ, 9.05 (d, $J = 6$ Hz, 6H, CH_3), 1.47 (q, $J = 6$ Hz, 2H, CH_2), 1.67 (septet, $J = 6$ Hz, 1H, CH), 2.09 (s, 3H, CH_3), 2.49 (t, $J = 6$ Hz, 2H, CH_2).

Ethyl Isoamyl Sulfide. Prepared from isoamyl bromide and ethyl mercaptan: yield 75%, bp 54−55/15 mmHg (lit.[22] bp 158−159 °C), $n^{20}_D = 1.4488$; ^1H NMR ($CDCl_3$), δ, 0.92 (*d*, $J = 6$ Hz, 6H, CH_3), 1.25 (*t*, $J = 6$ Hz, 2H, CH_2), 1.47 (q, $J = 6$ Hz, 2H, CH_2), 1.67 (septet, $J = 6$ Hz, 1H, CH), 2.54 (q, $J = 6$ Hz, 2H, CH_2).

***tert*-Butyl Isoamyl Sulfide.** Prepared from isoamyl bromide and *tert*-butyl mercaptan: 86% yield, bp 55−56 °C/7 mmHg, $n^{20}_D = 1.4460$; ^1H NMR ($CDCl_3$), δ, 0.92 (*d*, $J = 6$ Hz, 6H, CH_3), 1.32 (*s*, 9H, CH_3), 1.45 (*q*, 2H, CH_2), 1.68 (septet, 1H, CH), 2.52 (*t*, $J = 6$ Hz, 2H, CH_2).

Diisoamyl Sulfide. Isoamyl bromide (21.88 g, 0.21 mol) and tetrabutylammonium bromide (1.61 g, 5 mmol) were added to a solution of sodium sulfide nonahydrate (24.02 g, 0.10 mol) in water (50 mL), and the mixture was refluxed with stirring for 6 h. The organic layer was separated, and the aqueous layer was extracted with pentane. The extract was combined with the organic layer and dried with anhydrous magnesium sulfate. Distillation gave 15.85 g, 91% of a colorless liquid: bp 49−50 °C/0.1 mmHg, $n^{20}_D = 1.4514$ (lit.[23] bp (corr) 214.3−214.8 °C, $n^{20}_D = 1.4520$), >99% GC pure; ^1H NMR ($CDCl_3$), δ, 0.95 (d, $J = 6$ Hz, 12H, CH_3), 1.47 (q, $J = 6$ Hz, 4H, CH_2), 1.68 (septet, $J = 6$ Hz, 2H, CH), 2.51 (t, $J = 6$ Hz, 4H, CH_2).

3-Ethylthiotetrahydrofuran. Ethyl mercaptan (12.43 g, 0.1 mol) was added to a mixture of 2,3-dihydrofuran (7.00 g, 0.1 mol) and benzoyl peroxide (0.1 g) at room temperature. An increase in temperature was observed after 5 min and the mixture was kept at 25−30 °C by cooling with water. After 1 h, no further increase of temperature was observed. The mixture was left overnight and the product was isolated by distillation: 24.85 g (94%), bp 46 °C/0.1 mmHg, $n^{20}_D = 1.4866$ (lit.[13] bp 106−108 °C/35 mmHg, $n^{20}_D = 1.4930$); ^1H NMR ($CDCl_3$) δ 1.28 (t, $J = 6$ Hz, 3H, CH_3), 1.83 (m, 1H, CH_2), 2.28 (m, 1H, CH_2), 2.60 (q, $J = 6$ Hz, 2H, CH_2), 3.35 (m, 1H, CH), 3.58 (dd, $J = 6$ Hz, 6.5 Hz, 1H, CH_2), 3.83 (m, 1H, CH_2), 3.91 (m, 1H, CH_2), 4.08 (dd, $J = 6$ Hz, 6.5 Hz, 1H, CH_2).

Bis(3-tetrahydrofuryl) Sulfide. 3-Bromotetrahydrofuran[22] (31.70 g, 0.21 mol) was dissolved in ethanol (70 mL), and

(20) Reference 2, p 191.
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a solution of sodium sulfide nonahydrate (24.00 g, 0.1 mol) in water (40 mL) was added. The mixture was refluxed for 1 h. Ethanol was removed under water aspirator vacuum, solid potassium carbonate was added to saturate the aqueous solution, and the product was extracted with diethyl ether. The extract was dried with anhydrous magnesium sulfate. Distillation gave 12.01 g (69%) of a colorless liquid: bp 90−91 °C/0.05 mmHg, $n^{20}_D = 1.5126$; MS EI/CI, 70 eV, 174 (M^+, 2), 73 (16), 71 (22), 70 (100), 69 (15); ^{1}H NMR (mixture of diastereomers) ($CDCl_3$) δ 1.84 (m, 2H, CH_2), 2.30 (m, 2H, CH_2), 3.35 (quintet, $J = 6$ Hz, 2H, CH), 3.57 (m, 2H, CH_2), 3.83 (m, 4H, CH_2), 4.04 (m, 2H, CH_2). Anal. Calcd for ($C_8H_{14}O_2S$) (174.27) 55.18%: C, 8.10; H, 18.40. Found: 54.79%; C, 8.11; H, 18.78.

Bis(2-methoxyethyl) Sulfide. A solution of thiodiethanol (12.22 g, 0.1 mol) and *p*-toluenesulfonic acid monohydrate (0.95 g, 5 mmol) in methanol (12.82 g, 0.4 mol) was heated for 10 h at 150 °C in an autoclave provided with a glass liner. The product was isolated by distillation: 9.91 g (66%), bp 55−56 °C/0.1 mmHg (lit.[12] bp 202.2−202.6 °C), $n^{20}_D = 1.4609$; ^{1}H NMR ($CDCl_3$) δ 2.75 (t, $J = 6$ Hz, 4H, CH_2), 3.37 (s, 6H, CH_3), 3.57 (t, $J = 6$ Hz, 4H, CH_2).

Borane−Sulfide Adducts. Borane−Diisoamyl Sulfide. Typical Procedure. Diborane generated as described elsewhere[2] was passed at 0 °C through a bubbler containing a magnetic stirring bar and neat diisoamyl sulfide (8.67 g, 50 mmol). Excess diborane was absorbed in the next bubbler containing tetrahydrofuran (10 mL) over mercury until the borane concentration in tetrahydrofuran reached 1.0 M. The borane−sulfide adduct, a colorless liquid, was stirred overnight at room temperature prior to disconnecting the bubblers and then analyzed for active hydride by a standard procedure using water−glycerol−methanol (1:1:1) hydrolyzing mixture. Borane concentration 4.2 M in BH_3: ^{11}B NMR δ −22.5 ppm.

(−)-*cis*-Myrtanol. A 4.2 M borane−diisoamyl sulfide adduct (5.0 mL, 21 mmol) was dissolved in THF (20 mL) and (−)-β-pinene (8.86 g, 64 mmol), $[\alpha]^{23}_D = -20.8°$ (neat), 91% ee, was added at 0 °C. The mixture was kept at room temperature for 1 h and oxidized by the addition of 3.0 *M* sodium hydroxide (10 mL, 30 mmol) and 30% hydrogen peroxide (7 mL, 70 mmol) keeping the temperature during the addition below 30 °C and then stirring at room temperature for 3 h. The mixture was saturated with potassium carbonate, the THF layer was separated and the aqueous layer was extracted with diethyl ether. The extracts were combined with the THF solution, dried over magnesium sulfate and distilled using a Widmer column to give a first fraction, 4.25 g, bp 45−58 °C/0.1 mmHg composed of diisoamyl sulfide (77%) and *cis*-myrtanol (23%) and a second fraction which is pure *cis*-myrtanol, 7.96 g (82%), bp 58−60 °C/0.1 mmHg, $n^{20}_D = 1.4907$, $[\alpha]^{20}_D = -19.4°$ (neat) (lit.[26] bp 65−67 °C/0.2 mmHg, $n^{20}_D = 1.4911$, $[\alpha]^{22}_D = -19.5°$).

Trioctylborane. A 6.0 M borane bis(2-methoxyethyl) sulfide adduct (5.0 mL, 30 mmol) was dissolved in dichloromethane (30 mL) and 1-octene (10.10 g, 90 mmol) was added dropwise with cooling to keep the temperature at 20−25 °C. The reaction was complete in 5 min as indicated by ^{11}B NMR. The solution was vigorously stirred with water, dried over magnesium sulfate and the solvent was removed under vacuum. ^{1}H NMR spectrum showed the sulfide present. Diethyl ether was added, followed by 5% sodium hypochlorite solution (Chlorox, 40 mL) and the mixture was stirred keeping the temperature at 20−25 °C. After 1 h, the organic phase was separated, washed with water and dried over magnesium sulfate. Ether was removed under vacuum to give trioctylborane: 9.84 g, 94%, ^{11}B NMR δ 86 ppm. ^{1}H NMR spectrum did not indicate bis(2-methoxyethyl) sulfide. Tetrahydrofuran (30 mL) was added, followed by 3.0 M sodium hydroxide (10 mL, 30 mmol) and 30% hydrogen peroxide (10 mL, 100 mmol). The mixture was stirred for 2 h at room temperature and then 1 h at 40 °C, saturated with potassium carbonate, the organic layer was separated and the aqueous layer was extracted with diethyl ether. The extracts were combined with the THF solution, dried over magnesium sulfate and octanol was isolated by distillation, 10.60 g, 90.5%, bp 99−100 °C/20 mmHg. GC analysis (Carbowax 20M) showed 1-octanol 94% and 2-octanol (6%).

(−)-2-Isocaranol. (+)-2-Carene (14.96 g, 0.11 mol), $[\alpha]^{23}_D = +92.0°$ (neat), was added to a solution of borane−bis(2-methoxyethyl)sulfide adduct (8.2 mL, 50 mmol) in tetrahydrofuran (50 mL) at 10−20 °C. A white precipitate was formed in 5 min. ^{11}B NMR spectrum showed no borane signal and only a signal at δ, 31.1 ppm. After 1 h, water was added and the organoborane was oxidized under nitrogen by the addition of 3.0 M sodium hydroxide (30 mL, 90 mmol) and 30% hydrogen peroxide (12 mL, 120 mmol) at 20−30 °C, stirred for 2 h and then for 1 h at 40 °C. The mixture was saturated with potassium carbonate, the organic phase was separated and the aqueous phase was extracted with diethyl ether. The extracts were combined with the THF solution, washed with saturated brine and dried over magnesium sulfate. Distillation gave a mixture of bis(2-methoxyethyl) sulfide and the product alcohol. The distillate was dissolved in diethyl ether (25 mL) and added dropwise with vigorous stirring to Chlorox (80 mL) at 20−25 °C. After 1 h, the organic solution was separated, the aqueous solution was extracted with diethyl ether, the extract was combined with the organic solution, dried over magnesium sulfate and distilled to give 12.52 g (81%) of (−)-2-isocaranol: bp 50−52 °C/0.05 mmHg, $[\alpha]^{23}_D = -31°$ (neat) (lit.[27] bp 50−52 °C/0.05 mmHg, $[\alpha]^{23}_D = -31.1°$ (neat)).

Preparation of Boron Trichloride Adducts. The procedure followed for all dialkyl sulfides is identical and the procedure followed for isoamyl sulfide is representative. An oven-dried RB flask provided with septum inlet and a stirring bar was cooled under dry nitrogen gas. The flask was charged with isoamyl sulfide (8.72 g, 50 mmol) and the reaction flask was further cooled to −18 °C. Boron trichloride (5.86 g, 50 mmol) gas was slowly condensed in to the reaction flask using a double-ended needle under nitrogen atmosphere. As soon the vigorous reaction subsides, the contents were slowly brought to room temperature to obtain a white solid that is air and moisture sensitive. The ^{11}B NMR examination in dichloromethane showed a single signal at +7.1 ppm.

Preparation of Monochloroborane Adducts of Dialkyl Sulfides. The procedure followed for all dialkyl sulfides is identical and the procedure followed for isoamyl sulfide is representative. An oven dried RB flask provided with septum inlet and a stirring bar was cooled under dry nitrogen gas. The flask was charged with isoamyl sulfide-boron trichloride complex (2.91 g, 10 mmol). and isoamyl sulfide-borane adduct (4.8 mL, 4.2 M, 20 mmol). The contents were further stirred at room temperature and the progress of reaction was followed by ^{11}B NMR examination of the reaction mixture in dichloromethane solvent. The results are presented in Table 2.

Preparation of Dichloroborane Adducts of Dialkyl Sulfides. The procedure followed for all dialkyl sulfides is identical and the procedure followed for isoamyl sulfide is representative. An oven-dried RB flask provided with septum inlet and a stirring bar was cooled under dry nitrogen gas. The flask was charged with isoamyl sulfide-boron trichloride complex (5.82 g, 20 mmol) and isoamyl sulfide-borane adduct (2.4 mL, 4.2 M, 10 mmol). The contents were further stirred at room temperature and the progress of reaction was followed by ^{11}B NMR examination of the reaction mixture in dichloromethane solvent. The results were presented in Table 3.

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