Monobromoborane: Dimethyl Sulfide; A New Stable Reagent for Hydroboration, Providing a General Synthesis of Dialkylbromoboranes and their Derivatives

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The newly synthesized addition compound of monobromoborane with dimethyl sulfide, $H_2BBr:S(CH_3)_2$ (MBBS)[1], hydroborates olefins cleanly in dichloromethane solution at 25° to give quantitatively the corresponding dialkylbromoboranes as their methyl sulfide addition compounds, $R_2BBr:S(CH_3)_2$. The parent dialkylbromoboranes are easily isolated by distillation under reduced pressure. MBBS is readily prepared in high purity and the R_2BBr realized in the hydroboration with this reagent is essentially free of other species, such as R_3B or $RBBr_2$. This development provides the first general synthesis of dialkylbromoboranes, R_2BBr. The dialkylbromoboranes thus obtained can be readily converted into methyl dialkyl borinates, into hindered alcohols, and into ketones by available reactions[2,3].

We recently described[1] a simple synthesis of monobromoborane: dimethyl sulfide (MBBS) by the redistribution of $Br_3B:S(CH_3)_2$ and $H_3B:S(CH_3)_2$, see Scheme A.

$$2\ H_3B:S(CH_3)_2 + Br_3B:S(CH_3)_2 \longrightarrow 3\ H_2BBr:S(CH_3)_2$$

Scheme A

MBBS was obtained as the neat, high purity product, free of any significant amount of other possible species, such as $H_3B:S(CH_3)_2$ or $HBBr_2:S(CH_3)_2$. MBBS is stable thermally. It was apparent that hydroboration of olefins with MBBS could provide a valuable route to the corresponding dialkylbromoboranes, providing redistribution of the various intermediates could be avoided in the course of the reaction. At the present time, no convenient, direct method is available for the synthesis of such dialkylbromoboranes[4-7].

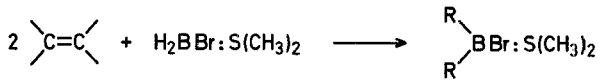
Recently we achieved successful procedures for the preparation of dialkylchloroboranes via hydroboration with the monochloroborane ethyl etherate[8]. More recently, we discovered that the more stable reagent, monochloroborane: dimethyl sulfide[1], was effective for the synthesis of these products[9]. The dialkylchloroboranes have proven to be valuable products, not merely as interesting compounds in their own right, but as valuable intermediates in organic synthesis[2,3,10]. Accordingly, it appeared to be of considerable interest to undertake an examination of the possibility of providing a convenient synthesis of R_2BBr to permit an exploration of their chemistry and of their utility as synthetic intermediates. To that end, we examined the hydroboration of representative olefins with MBBS and examined the practicality of utilizing the resulting dialkylbromoboranes for conversion to desired organic products.

The reaction of 1-octene with MBBS in dichloromethane is slow at 0°, requiring some 6 h for completion. However, at 25° the reaction is complete within 1 h. Even less reactive compounds, such as *cis*-3-octene, styrene, 2-methyl-2-butene, 2-methyl-1-pentene, and 1-methylcyclopentene, are quantitatively converted into products under these conditions.

The directive effect of the MBBS hydroboration was examined by oxidizing the reaction product with alkaline hydrogen peroxide and determining the isomeric alcohols by G.L.C. analysis. The results are summarized in Table 1 and compared with related data for borane:THF[11], monochloroborane etherate[12], and monochloroborane:dimethyl sulfide (MCBS)[9].

For olefins, such as 1-hexene, styrene, and *cis*-2-pentene, MBBS exhibits directive effects similar to those realized for monochloroborane etherate[12] and MCBS[9], more powerful than those of borane:THF[11]. However, in the case of olefins containing trisubstituted carbon-carbon double bonds, such as 2-methyl-1-pentene, 2-methyl-2-butene, and 1-methylcyclopentene, the reagent yields significantly greater amounts (2–3%) of the tertiary derivative than were realized with monochloroborane etherate[12], $H_2BCl:S(CH_3)_2$[9], and $H_3B:THF$[11]. These amounts of the minor isomer produced in this reaction are not serious synthetically, but they may be of significance diagnostically in realizing an understanding of the mechanism.

The initial product of the reaction of olefins with MBBS is the methyl sulfide addition compound of the corresponding dialkylbromoborane (Scheme **B**).

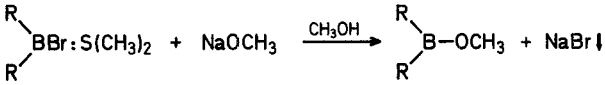


Scheme **B**

In the case of the more hindered alkyl groups, such as those formed from *cis*-2-butene, isobutene, etc., the corresponding addition compounds lose dimethyl sulfide readily during vacuum distillation, providing pure R_2BBr, free of dimethyl sulfide. However, in the case of derivatives containing less hindered alkyl groups, such as $(n\text{-}C_4H_9)_2BBr:S(CH_3)_2$, such distillation causes only partial loss of the dimethyl sulfide. However, in such cases, the pure R_2BBr can be obtained by adding 1 mol equivalent of BBr_3 to the product prior to the distillation, so that the solid $Br_3B:S(CH_3)_2$ is retained in the distillation flask (Scheme **C**).

Scheme **C**

Treatment of the reaction product, $R_2BBr:S(CH_3)_2$, with excess methanol, in the presence of an equivalent of sodium methoxide, provides the borinate (Scheme **D**).

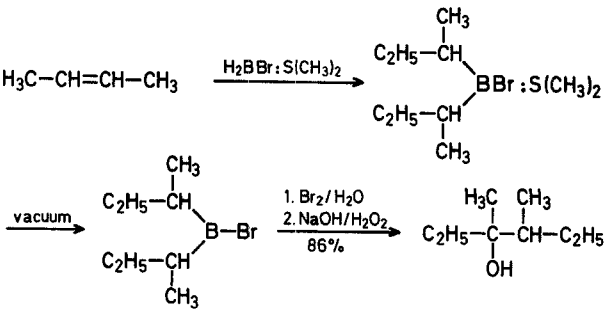


Scheme **D**

In the case of volatile derivatives, the methyl dialkyl borinates are readily recovered by distillation (Table 2).

In the case of dialkyl borinates of low volatility, the esters can be separated from the sodium bromide by extraction with a suitable solvent, such as pentane, following removal of the excess methanol.

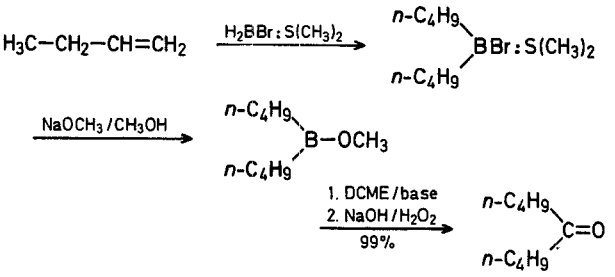
To test the usefulness of MBBS as a reagent, several R_2BBr derivatives were directly converted into the corresponding tertiary alcohols and ketones, using previously described reactions[2,3]. Thus, $(sec\text{-}C_4H_9)_2BBr$ from 2-butene was transformed into 3,4-dimethyl-3-hexanol in 86% yield by treatment with bromine in the presence of water (Scheme **E**).



Scheme **E**

Similarly, 2-methyl-2-butene was converted into 2,3,4,5-tetramethyl-3-hexanol in 84% yield.

Alternatively, di-*n*-butylbromoborane:dimethyl sulfide was converted into 5-nonanone in 99% yield utilizing the DCME reaction[3] following removal of the excess methanol with an aspirator (Scheme **F**).



Scheme **F**

The present development provides the first general synthesis of dialkylbromoboranes. The ready availability of these compounds via the hydroboration of olefins with MBBS should stimulate research on the physical and chemical characteristics of these reactive species. Evidently, these compounds are also valuable as intermediates in organic syntheses via boron chemistry. Finally, the redistribution reaction (Scheme **A**) provides MBBS in greater purity than is realized for MCBS[1]. Since it is often so difficult to purify the reactive products, this constitutes a major advantage for MBBS as a route to dialkylborane derivatives.

Preparation of Monobromoborane: Dimethyl Sulfide (MBBS):
A 100-ml reaction flask[13] cooled in ice bath, is charged with dimethyl sulfide (7.45 ml, 6.22 g, 100 mmol) under nitrogen and boron tribromide (9.5 ml, 25.34 g, 101 mmol) is added dropwise with stirring. Following the complete addition, the flask is brought to room temperature and borane:dimethyl sulfide[14] [$H_3B:S(CH_3)_2$] (20 ml, 200 mmol) is added. The formation of MBBS is completed on stirring the contents of the flask for 6 h at 65°. The resultant solution is a clear liquid, 9.1 molar in MBBS.

Hydroboration with MBBS and Recovery of the R_2BBr Products:
MBBS (50 mmol, 5.49 ml) is dissolved in dichloromethane (45 ml) in a 100-ml reaction flask under nitrogen. The flask is cooled in an ice-bath and *cis*-2-butene (~6.5 g, 115 mmol, 15% excess) is passed into the flask[13]. The mixture is stirred for 1 h at 25°. The solvent is removed using a water aspirator (2 h) and the di-*sec*-butylbromoborane is distilled; yield: 8.6 g (84%); b.p. 50–52°/6 torr.

(In the above example, an excess of the gaseous olefin was used. In the case of liquid olefins, it is adequate to add a stoichiometric quantity of the olefin.)

Table 1. The Directive Effect in the Hydroboration of Olefins with $H_2BBr:S(CH_3)_2$ in Dichloromethane at 25°

Olefin	Products	Relative Yields of Products [%]			
		$H_2BBr:S(CH_3)_2$[a]	$H_2BCl:S(CH_3)_2$[b]	$H_2BCl:O(C_2H_5)_2$[c]	$H_3B:THF$[e]
1-Hexene	1-Hexanol	99.6	99.2	>99.5	94
	2-Hexanol	0.4	0.8	< 0.5	6
Styrene	2-Phenylethanol	96	93	96	81
	1-Phenylethanol	4	7	4	19
2-Methyl-1-pentene	2-Methyl-1-pentanol	98	>99.9[d]	>99.9[d]	99[d]
	2-Methyl-2-pentanol	2	< 0.1[d]	< 0.1[d]	1[d]
cis-2-Pentene	2-Pentanol	63	—	58	55
	3-Pentanol	37	—	42	45
2-Methyl-2-butene	3-Methyl-2-butanol	97	99.5	99.7	98
	2-Methyl-2-butanol	3	0.5	0.3	2
1-Methylcyclopentene	*trans*-2-Methylcyclopentanol	97.5	—	>99.8	98.5
	1-Methylcyclopentanol	2.5	—	< 0.2	1.5

[a] Total yields were 95±5% as determined by G.L.C. Identity and purity of all products were established by comparison with authentic samples.
[b] Data from Lit.[9].
[c] Data from Lit.[12].
[d] The yields are for the corresponding alcohols from 2-methyl-1-butene.
[e] Data from Lit.[11].

Table 2. Synthesis of Dialkylbromoboranes and Methyl Dialkyl Borinates by the Hydroboration of Olefins with Monobromoborane : Dimethyl Sulfide

Product	Yield [%]	b.p./torr	Lit. b.p./torr	Physical Data
Di-*sec*-butylbromoborane	84	50–52°/6	—	—
Di-*iso*-butylbromoborane	78	49–50°/6	—	—
Di-*n*-butylbromoborane	85	59–60°/5[a]	70°/10[b]	—
Methyl di-*n*-butylborinate	85	58 60°/6	56–58°/5[c]	$n_D^{20}=1.4144$

[a] Distillation over 1 mol equivalent of BBr_3.
[b] Data from Lit.[15].
[c] Data from Lit.[16].

In the synthesis of di-*n*-butylbromoborane, the hydroboration is carried out as above. Following completion of the reaction (1 h, 25°), the reaction mixture is cooled to 0° and liquid BBr_3 (4.75 ml, 50 mmol) is added. The reaction mixture is stirred for 1 h at 25°. The solvent is removed with a water aspirator, causing solid $Br_3B:S(CH_3)_2$ to precipitate. The product, di-*n*-butylbromoborane, is recovered by distillation at 59–60°/5 torr, without allowing the temperature of the bath to rise above the m.p. of $Br_3B:S(CH_3)_2$ (106°); yield: 8.7 g (85%).

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[1] H. C. Brown, N. Ravindran, *Inorg. Chem.* in press.
[2] H. C. Brown, C. F. Lane, *Synthesis* **1972**, 303.
[3] B. A. Carlson, H. C. Brown, *J. Am. Chem. Soc.* **95**, 6876 (1973).
[4] W. Gerrard, E. F. Mooney, R. G. Rees, *J. Chem. Soc.* **1964**, 740.
[5] D. Dollimore, L. H. Long, *J. Chem. Soc.* **1953**, 3906.
[6] J. R. Johnson, H. R. Snyder, M. G. Van Campen, Jr., *J. Am. Chem. Soc.* **60**, 115 (1938).
[7] Convenient conversion of R_3B into R_2BSCH_3 has been described:
H. C. Brown, M. M. Midland, *J. Am. Chem. Soc.*, **93**, 3291 (1971).
A. G. Davies, B. P. Roberts, *J. Chem. Soc.* [B] **1971**, 1830.
Treatment of these derivatives with bromine provides an alternative route to the R_2BBr derivatives: A. Pelter, K. Rowe, D. N. Sharrocks, K. Smith, *J. Chem. Soc. Chem. Commun.* **1975**, 531.
[8] H. C. Brown, N. Ravindran, *J. Am. Chem. Soc.* **94**, 2112 (1972); **98**, 1785 (1976).
[9] H. C. Brown, N. Ravindran, *J. Org. Chem.* **42**, 2533 (1977).
[10] H. C. Brown, M. M. Midland, A. B. Levy, *J. Am. Chem. Soc.* **94**, 2114, 3662 (1972).
[11] (a) H. C. Brown, G. Zweifel, *J. Am. Chem. Soc.* **82**, 4708 (1960).
(b) H. C. Brown, *Hydroboration*, W. A. Benjamin, Inc., New York, N. Y., 1962.
(c) H. C. Brown, R. L. Sharp, *J. Am. Chem. Soc.* **88**, 5851 (1966).
[12] H. C. Brown, N. Ravindran, *J. Org. Chem.* **38**, 182 (1973).
[13] H. C. Brown, G. W. Kramer, A. B. Levy, M. M. Midland, *Organic Syntheses via Boranes*, Wiley-Interscience, New York, N. Y., 1975, Chapter 9.
[14] Borane : Methyl sulfide (BMS) is available from Aldrich Boranes, Inc., a subsidiary of Aldrich-Chemical Co., Inc.
[15] R. Köster, M. A. Grassberger, *Justus Liebigs Ann. Chem.* **719**, 169 (1968).
[16] H. C. Brown, N. Ravindran, *J. Am. Chem. Soc.* **98**, 1785 (1976).