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Table I. Directive Effect in the Hydroboration of Olefins with Dibromoborane–Methyl Sulfide in Refluxing Methylene Chloride.

Olefin	Product	Rel yields of products, % $HBBr_2$·SMe_2[a]	Rel yields of products, % H_2BBr·SMe_2[b]
1-Hexene	1-Hexanol	99.6	99.6
	2-Hexanol	0.4	0.4
Styrene	2-Phenylethanol	96	96
	1-Phenylethanol	4	4
2-Methyl-1-pentene	2-Methyl-1-pentanol	98	98
	2-Methyl-2-pentanol	2	2
cis-2-Pentene	2-Pentanol	67	63
	3-Pentanol	33	37
2-Methyl-2-butene	3-Methyl-2-butanol	93	97
	2-Methyl-2-butanol	7	3
1-Methylcyclopentene	*trans*-2-Methylcyclopentanol	98	97.5
	1-Methylcyclopentanol	2	2.5

[a] Total yields were 95 ± 5%. [b] At 25 °C in CH_2Cl_2.[6]

Direct Reaction of Dibromoborane–Methyl Sulfide, $HBBr_2$·$S(CH_3)_2$, with Alkenes. The Remarkable Reactivity of $HBBr_2$·$S(CH_3)_2$ as a Hydroborating Agent as Compared with Related Dichloroborane Derivatives

Sir:

In contrast to dichloroborane–ethyl ether and dichloroborane–methyl sulfide, which require the presence of a Lewis acid, usually boron trichloride, for the satisfactory hydroboration of alkenes, the new reagent, dibromoborane–methyl sulfide, readily hydroborates representative alkenes directly. This development makes readily available for the first time such alkyldibromoboranes and the numerous derivatives into which they can be transformed. At the same time, a fascinating theoretical question is raised. Why should $HBBr_2$·SMe_2, which theory predicts and experiment confirms to be a stabler addition compound than $HBCl_2$·SMe_2, be a more reactive hydroborating agent?

Monochloroborane–ethyl ether,[1] H_2BCl·OEt_2, and monochloroborane–methyl sulfide,[2] H_2BCl·SMe_2, readily hydroborate alkenes (eq 1).

$$RCH{=}CH_2 + H_2BCl{\cdot}SMe_2 \xrightarrow[25\ °C]{\text{pentane}} (RCH_2CH_2)_2BCl{\cdot}SMe_2 \quad (1)$$

However, the dichloroborane derivatives are much less reactive hydroborating agents.[2,3] They require the presence of a Lewis acid, generally BCl_3, to achieve simple hydroboration, without redistribution (eq 2).

$$RCH{=}CH_2 + HBCl_2{\cdot}SMe_2 + BCl_3 \xrightarrow[25\ °C]{\text{pentane}} RCH_2CH_2BCl_2 + Cl_3B{\cdot}SMe_2\downarrow \quad (2)$$

The lower reactivity of the dichloroborane derivatives was attributed to the stronger Lewis acidity of $HBCl_2$, reducing the dissociation of the addition compounds, $HBCl_2$·OEt_2 and $HBCl_2$·SMe_2, over that of the monochloroborane derivatives.[2,3]

Boron tribromide is a stronger Lewis acid than boron trichloride.[4,5] Consequently, we had anticipated that $HBBr_2$·SMe_2, would be even less reactive than the dichloroborane derivatives. Accordingly, our early experiments with this new hydroborating agent utilized BBr_3 as a coreagent. However, a fortunate blank experiment revealed the error of our theoretical extrapolation. This experiment revealed that $HBBr_2$·SMe_2 was capable of reacting directly with representative alkenes without added BBr_3. Consequently, we undertook to explore this unexpected development.

The more reactive olefins react at a satisfactory rate at 25 °C. However, the reaction times for less reactive species are undesirably long at this temperature. Fortunately, essentially all reactions go to completion in 3 to 6 h in refluxing methylene chloride, 1 M in each reactant. Accordingly, we adopted this as our standard reaction condition (eq 3).

$$RCH{=}CH_2 + HBBr_2{\cdot}SMe_2 \xrightarrow[40\ °C]{CH_2Cl_2} RCH_2CH_2BBr_2{\cdot}SMe_2 \quad (3)$$

The directive effect in the hydroboration stage was determined by oxidizing the intermediate with alkaline hydrogen peroxide and examining the product by GC. The results are summarized in Table I.

Perhaps the only unexpected feature is the formation of 7% of the tertiary derivative in 2-methyl-2-butene, enhancing the 3% previously observed for H_2BBr·SMe_2.[6] These values are considerably greater than those observed for H_2BCl·OEt_2,[1] H_2BCl·SMe_2,[2] and even H_3B·$O(CH_2)_4$.[7]

The reaction appears to be quite general (Table II). The products are formed as the $RBBr_2$·SMe_2 addition compounds, and can be isolated as such by vacuum distillation.

The alkyldibromoborane can be freed from dimethyl sulfide by distillation in the presence of 1 mol equiv of boron tribromide (eq 4).

$$RBBr_2{\cdot}SMe_2 + BBr_3 \rightarrow RBBr_2 + Br_3B{\cdot}SMe_2\downarrow \quad (4)$$

The product, $RBBr_2$·SMe_2, is readily converted into the corresponding boronate by treatment with $NaOCH_3$ in methanol (eq 5).

$$RBBr_2{\cdot}SMe_2 + 2NaOCH_3 \xrightarrow[CH_3OH]{CH_2Cl_2} RB(OCH_3)_2 + SMe_2 + 2NaBr\downarrow \quad (5)$$

The following experimental procedures are representative.

Table II. Synthesis of Alkyldibromoborane-Methyl Sulfide Addition Compounds and Their Derivatives by the Hydroboration of Olefins with Dibromoborane-Methyl Sulfide, $HBBr_2{\cdot}SMe_2$, in Refluxing Methylene Chloride

Alkyldibromoborane derivative	Isolated yield, %	Bp, °C (mm)
n-Hexyldibromoborane-methyl sulfide	91	97-100 (1)
3-Hexyldibromoborane-methyl sulfide	90	73-75 (2.2)
2-Methyl-1-pentyldibromoborane-methyl sulfide	93	82-85 (1.6)
Cyclopentyldibromoborane-methyl sulfide[a]	93	140-144 (2.1)
trans-2-Methylcyclohexyldibromoborane-methyl sulfide[b]	86	68-69 (0.5)
n-Hexyldibromoborane	71	56-58 (0.9)
Dimethyl *n*-hexylboronate	83	84-86 (35)

[a] Solid at 25 °C, contained 18% of the uncomplexed compound. [b] Contained 19% of the uncomplexed compound.

Dibromoborane was prepared by a slow, dropwise addition of 80.2 mL (212 g, 846 mmol) of BBr_3 to a mixture of 40.0 mL (423 mmol) of $H_3B{\cdot}SMe_2$ and 62.1 mL (52.6 g, 846 mmol) of methyl sulfide at 0 °C, followed by stirring at 40 °C for 12 h. Under these conditions, the redistribution is essentially complete (eq 6).

$$H_3B{\cdot}SMe_2 + 2SMe_2 + 2BBr_3 \rightarrow 3HBBr_2{\cdot}SMe_2 \quad (6)$$

The resulting colorless, viscous liquid (at 40 °C) was characterized by spectroscopic methods.[8] It was 7.8 M in active hydride. No other boron species were detected in significant amounts by ^{11}B NMR. Therefore, the material is 7.8 M in the desired reagent, $HBBr_2{\cdot}SMe_2$.

1-Hexene, 100 mmol (12.5 mL), was dissolved in 75 mL of CH_2Cl_2 in a flask fitted with a reflux condenser and maintained under nitrogen. To this flask was added 100 mmol (12.8 mL) of $HBBr_2{\cdot}SMe_2$ and the reaction mixture was heated under reflux for 3 h. After the mixture cooled to 25 °C, the solvent was removed using a water aspirator. The product, distilled at 97-100 °C (1 mm), was obtained in a yield of 29 g, 91%. Examination of the ^1H NMR spectrum revealed a CH_3 signal at δ 2.45, characteristic of the $RBBr_2{\cdot}SMe_2$ derivatives.

The following procedure was used to prepare free *n*-hexyldibromoborane. Following completion of the hydroboration stage the reaction mixture was brought to 0 °C and 105 mmol (10.0 mL) of BBr_3 was added. The reaction mixture was stirred at 25 °C for 1 h. Solvent was removed with the aid of a water aspirator. A white solid, $Br_3B{\cdot}SMe_2$, separated. Distillation gave 18.0 g (71%) of *n*-hexyldibromoborane, bp 56-58 °C (0.9 mm). (The bath temperature was maintained below 100 °C to avoid melting of $Br_3B{\cdot}SMe_2$, mp 108 °C.)

To obtain the dimethyl boronate, the hydroboration reaction mixture was cooled to 0 °C and treated with 200 mmol of CH_3ONa in methanol (4.5 M). After 2 h at 25 °C, the solvent was removed and the product distilled (without separating the precipitated sodium bromide) to obtain 13.1 g (83%) of dimethyl *n*-hexylboronate,[2] bp 84-86 °C (35 mm).

As mentioned earlier, this ability of $HBBr_2{\cdot}SMe_2$ to hydroborate alkenes directly was unexpected. The reactivities of the borane etherates and borane-methyl sulfides decrease in the order $H_3B{\cdot}OR_2 > H_2BCl{\cdot}OR_2 > HBCl_2{\cdot}OR_2$, and $H_3B{\cdot}SMe_2 > H_2BCl{\cdot}SMe_2 > HBCl_2{\cdot}SMe_2$. This was attributed to the increase in the Lewis acidity of the borane component with the number of chlorine substituents: $H_3B < H_2BCl < HBCl_2 < BCl_3$.[8] It was believed that the reaction proceeds via a prior dissociation of the addition compound. The stabler the complex, the smaller the amount of free borane, and the slower the hydroboration.

It is known that BBr_3 is a stronger Lewis acid than BCl_3, attributed to decreased resonance contributions of the boron-bromine bond.[4] According to the above interpretation, the bromoboranes should be more acidic than the corresponding chloroboranes: $BBr_3 > BCl_3$; $HBBr_2 > HBCl_2$; $H_2BBr > H_2BCl$. Since $HBCl_2{\cdot}SMe_2$ fails to react with olefins at a convenient rate, $HBBr_2{\cdot}SMe_2$ was expected to be even less reactive.

Some support for this prediction was obtained by ^1H NMR observations.[8] In CCl_4 solution, $Cl_3B{\cdot}SMe_2$ readily exchanges with excess SMe_2. On the other hand, such exchange was not observed for $Br_3B{\cdot}SMe_2$. This was attributed to the greater stability of the bromine derivative. Similarly, $HBCl_2{\cdot}SMe_2$, undergoes such exchange, whereas $HBBr_2{\cdot}SMe_2$ does not, apparently confirming the greater stability of the latter.[8]

There is evidence that π electrons, such as those in benzene, can interact strongly with the $Br_3B{\cdot}SMe_2$ addition compound.[8,9] Possibly, a similar phenomenon occurs involving the π electrons of the alkene and the dibromoborane adduct, $HBBr_2{\cdot}SMe_2$. If so, the hydroboration may involve a direct transfer of the $HBBr_2$ moiety from sulfur to the π electrons.

Irrespective of the final theoretical interpretation of this fascinating new development, it has important synthetic implications. It provides a new stable monofunctional hydroborating agent which can be used in the absence of added Lewis acids. It makes available a convenient synthetic route to the alkyldibromoboranes, not previously available. It makes possible, for the first time, the systematic exploration of their chemistry. Finally, it opens up a more convenient route to the alkylboronic acids and esters and to the many synthetic applications for which they can be utilized.

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Mechanism of Nickel(0)-Catalyzed Dimerization of 1,3-Butadiene

Sir:

We wish to report details of the mechanism of the nickel-catalyzed dimerization of butadiene. Our results, taken together with the pioneering efforts of Wilke,[1] Heimbach,[2] and co-workers, allow a complete picture to be proposed for this intriguing transformation.

For the formation of divinylcyclobutane from butadiene we propose a series of complex, but well-precedented, steps. This mechanism, an expansion of an earlier suggestion of Mango[3] and Heimbach and Traunmüller,[4] is shown in Scheme I. The proposal has as key steps preferential formation of *anti*-π-allyl[5] complex[6] **3**, and transformation of **3** via σ-allyls[1c,7] **4** and **5** to *syn*-π-allyl **6**. This latter species is clearly well disposed for the reductive elimination to yield *cis*-divinycyclobutane (**8**) via **7**.

Examination of the mechanism in detail makes it clear that