0 °C for 15 min, 1.71 g (9.0 mmol) of cuprous iodide added, and the suspension warmed to room temperature and stirred for 15 min (solution becomes homogeneous). After the mixture cooled to 0 °C, allyl bromide (1.55 mL, 17.9 mmol) was added dropwise and the solution stirred at 0 °C (1 h) followed by warming to room temperature (1 h). Water (30 mL) was added, the tetrahydrofuran was removed in vacuo, ethyl ether (50 mL) was added, and the inorganics were filtered. Standard workup afforded 3.21 g of crude product which gave 2.78 g (87%) of the product on short-path distillation (bath temperature 50–55 °C, 0.5 torr).

Electrolysis of 2-Allyl-1,4-dimethoxybenzene. The aromatic compound (0.5 g, 2.81 mmol) was dissolved in 40 mL of 1% methanolic potassium hydroxide and electrolyzed at 0 °C by using power supply C[19] at a potential of 1.95 V (760 C, 71% current efficiency) vs. a Pt electrode. Standard workup afforded 627 mg of yellow oil which on short-path distillation (bath temperature 50–55 °C, 0.1 torr) gave 546 mg (81%) of the bisketal as a colorless liquid which showed an NMR spectrum identical with that of the material prepared via the cuprate.

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Registry No. 1, 60316-51-0; **4a**, 957-78-8; **4b**, 7421-23-0; **4c**, 84-80-0; **5a**, 62008-14-4; **5b**, 62008-01-9; **5b** 3,5-dinitrobenzoate, 72205-63-1; **7**, 64648-85-7; **8a**, 72205-64-2; **8b**, 72207-14-8; **9**, 2674-34-2; **10**, 65400-01-3; **11**, 65372-74-9; **12**, 65372-76-1; **13**, 65372-77-2; **15**, 72205-65-3; **16**, 72207-15-9; **17**, 72207-16-0; **18**, 72207-17-1; **19**, 72054-81-0; 2-(cyclohexylcarbonyl)-1,1,4,4-tetramethoxy-2,5-cyclohexadiene, 72205-66-4; 2-benzoyl-1,1,4,4-tetramethoxy-2,5-cyclohexadiene, 60316-59-8; 2-benzyl-1,1,4,4-tetramethoxy-2,5-cyclohexadiene, 72205-67-5; methyl 3,3,6,6-tetramethoxy-1,4-cyclohexadiene-2-acetate, 72205-68-6; 1-bromo-3-methyl-2-butene, 870-63-3; phytyl bromide, 4444-13-7; 1,4-dimethoxybenzene, 150-78-7; geranyl bromide, 6138-90-5; allyl bromide, 106-95-6; cyclohexanecarboxylic acid chloride, 2719-27-9; benzoyl chloride, 98-88-4; benzyl bromide, 100-39-0; methyl α-bromoacetate, 96-32-2; methyl (2,5-dimethoxyphenyl)acetate, 6202-39-7; 2-allyl-1,4-dimethoxybenzene, 19754-22-4; 2-bromo-1,4-dimethoxybenzene, 25245-34-5.

Hydroboration. 54. New General Synthesis of Alkyldihaloboranes via Hydroboration of Alkenes with Dihaloborane–Dimethyl Sulfide Complexes. Unusual Trends in the Reactivities and Directive Effects[1]

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The reactions of alkenes with the dimethyl sulfide complexes of the dihaloboranes (HBX_2·SMe_2; X = Cl, Br, I) have been studied in detail. Dichloroborane–dimethyl sulfide ($HBCl_2$·SMe_2) hydroborates representative olefins relatively slowly and requires the presence of a strong Lewis acid, such as boron trichloride, to complete the hydroboration reaction rapidly. Unexpectedly, dibromoborane–dimethyl sulfide ($HBBr_2$·SMe_2) and diiodoborane–dimethyl sulfide (HBI_2·SMe_2) react readily with olefins, even in the absence of such Lewis acids. This is contrary to the trend expected on the basis of the strengths of these methyl sulfide adducts and a hydroboration mechanism involving a prior dissociation of the addition compound. The hydroboration of olefins with these reagents, followed by distillation under reduced pressure, affords alkyldihaloborane–dimethyl sulfide complexes in good yields. These are readily converted by hydrolysis into the boronic acids or by methanolysis to the corresponding esters. Oxidation with alkaline hydrogen peroxide utilizing sufficient sodium hydroxide to neutralize the hydrogen halide readily provides the corresponding alcohols. $HBBr_2$·SMe_2 and HBI_2·SMe_2 exhibit an unusual directive effect in the hydroboration of trisubstituted olefins, giving unexpected enhanced amounts of the Markovnikov (tertiary) derivatives.

Monochloroborane etherate (H_2BCl·OEt_2) hydroborates representative olefins cleanly and completely, providing pure dialkylchloroboranes in high yields.[3] The methyl sulfide complexes of monohaloboranes (H_2BX·SMe_2; X = Cl, Br, I) possess a number of advantages over the etherates.[4] These reagents have provided the first general route for the synthesis of dialkylhaloboranes from olefins. In view of the synthetic utilities of trialkylboranes (R_3B) and dialkylboron halides (R_2BX), it is anticipated that the alkyldihaloboranes (RBX_2) should also find valuable applications in organic synthesis.

We recently reported the preparation of a series of alkyldichloroboranes via the hydroboration of alkenes with dichloroborane etherate ($HBCl_2$·OEt_2).[5] However, this reagent suffers from some practical difficulties. The reagent itself is not stable over long periods of time, cleaving the ether solvent at a significant rate, even with storage at 0 °C. The reaction of $HBCl_2$·OEt_2 with alkenes in ether or in pentane is slow and incomplete. The hydroboration goes to completion when neat reagents are allowed to react, but the resulting product is predominantly the dialkylchloroborane (R_2BCl) and not the desired alkyldichloroborane ($RBCl_2$). In the presence of 1 molar equiv of BCl_3 in pentane, however, $HBCl_2$·OEt_2 reacts with alkenes quantitatively and cleanly to give the desired $RBCl_2$ (eq 1).[5] This development provided for the first

$$\text{alkene} + HBCl_2\cdot OEt_2 + BCl_3 \xrightarrow{\text{pentane}} RBCl_2 + BCl_3\cdot OEt_2\downarrow \quad (1)$$

time a convenient low-temperature procedure for the general synthesis of alkyldichloroboranes.

Since the development of this procedure, many valuable applications of $RBCl_2$ have been uncovered.[6-9] However,

(1) For preliminary reports on some aspects of this study, see: (a) Brown, H. C.; Ravindran, N. *J. Org. Chem.* **1977**, *42*, 2533. (b) Brown, H. C.; Ravindran, N. *J. Am. Chem. Soc.* **1977**, *99*, 7097.

(2) (a) Postdoctoral research associate on NSF Grant No. GP 6942X and GP 41169X (1973–1974). (b) Postdoctoral research associate on Grant GM 10937-16 from the National Institutes of Health (1978).

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Table I. Hydroboration of Representative Olefins with Dihaloborane-Dimethyl Sulfide Reagents

reagent	olefin	solvent	concn, M	temp, °C	time, h	% reaction[a]
$HBCl_2 \cdot SMe_2$ + $SnCl_4$ (1:1)	1-octene	pentane	1.0	25	0.25	86
					1.0	98
$HBCl_2 \cdot SMe_2$ + $SnCl_4$ (1:1.5)	1-octene	pentane	1.0	25	0.25	97
					0.5	99
$HBCl_2 \cdot SMe_2$ + BCl_3 (1:1)	1-octene	pentane	1.0	25	0.5	90
					1.0	97
					2.0	100
$HBCl_2 \cdot SMe_2$	1-octene	CH_2Cl_2	2.0	25	1.0	47
					2.0	61
					6.0	88
					24.0	100
			1.0	40	1.0	75
					2.0	84
					6.0	98
					8.0	100
$HBCl_2 \cdot SMe_2$	*cis*-3-octene	CH_2Cl_2	1.0	40	1.0	55
					6.0	86
					11.0	90
$HBBr_2 \cdot SMe_2$	1-octene	CH_2Cl_2	1.0	25	1.0	69
					5.0	95
					8.0	97
			2.0	25	1.0	70
					3.0	94
					5.0	97
			1.0	40	1.0	78
					2.0	96
					3.0	98
$HBBr_2 \cdot SMe_2$	*cis*-3-octene	CH_2Cl_2	1.0	40	1.0	87
					3.0	96
$HBI_2 \cdot SMe_2$	1-octene	CH_2Cl_2	1.0	25	2.0	26
					4.0	61
					10.0	96
					12.0	100
				40	1.0	38
					2.0	80
					3.0	96
$HBI_2 \cdot SMe_2$	*cis*-3-octene	CH_2Cl_2	1.0	40	1.0	36
					3.0	88
					6.0	100

[a] Determined by GC analysis on a 12 ft × 0.125 in. column packed with 5% SE-30 on Varaport.

the full potentialities of other alkyldihaloboranes (RBX_2; X = Br, I) have been rarely explored, mainly due to the unavailability of these intermediates by a direct route and their anticipated greater instabilities in ether solvents. Therefore, we undertook to explore the possibilities both of circumventing these difficulties and of achieving the preparation of such alkyldihaloboranes via the hydroboration of alkenes with dichloroborane–dimethyl sulfide ($HBCl_2 \cdot SMe_2$), dibromoborane–dimethyl sulfide ($HBBr_2 \cdot SMe_2$), and diiodoborane–dimethyl sulfide ($HBI_2 \cdot SMe_2$).

Results and Discussion

The dihaloborane–dimethyl sulfide reagents are readily prepared in high yield and purity by the exchange reaction between the commercially available borane–dimethyl sulfide ($H_3B \cdot SMe_2$, BMS) and the respective boron trihalide–dimethyl sulfides (eq 2; X = Cl or Br).[10] Diiodo-

$$H_3B \cdot SMe_2 + 2BX_3 \cdot SMe_2 \rightarrow 3HBX_2 \cdot SMe_2 \qquad (2)$$

borane–dimethyl sulfide ($HBI_2 \cdot SMe_2$) has been prepared by the action of iodine on BMS.[11] These three addition compounds have been prepared as the neat liquids. They appear to be stable indefinitely at room temperature when stored under nitrogen.

Hydroboration of Alkenes with $HBX_2 \cdot SMe_2$. For the preliminary study, 1-octene and *cis*-3-octene were chosen as the representative terminal and internal alkene, respectively. In the case of $HBCl_2 \cdot SMe_2$, the reaction was studied in pentane at 0 and 25 °C and in dichloromethane at 25 and 40 °C. The hydroboration was also carried out in pentane in the presence of $SnCl_4$ and of BCl_3. Since CH_2Cl_2 proved to be a highly convenient solvent, the reactions with $HBBr_2 \cdot SMe_2$ and $HBI_2 \cdot SMe_2$ were carried out in this solvent at 25 and 40 °C (refluxing CH_2Cl_2).

The general procedure involved the addition of the chosen Lewis acid to a mixture of $HBCl_2 \cdot SMe_2$ and the olefin in pentane. For the reaction in the absence of added Lewis acids, the neat reagent was added to a solution of the olefin in CH_2Cl_2 at the desired temperature. For the reactions in refluxing CH_2Cl_2, the reactants were mixed in the solvent at 25 °C and then heated under reflux. The initial concentration of the reaction mixture was 1 or 2 M in both the reactants. The progress of the reaction was followed by the analysis of aliquots for unreacted alkene at definite intervals of time. The results are summarized in Table I.

The reactions of $HBCl_2 \cdot SMe_2$ with the representative olefins are slow and incomplete in pentane or ether, similar

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(10) Brown, H. C.; Ravindran, N. *Inorg. Chem.* **1977**, *16*, 2938. The rate of exchange appears to vary somewhat with different samples of the commercial BMS.
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Table II. Directive Effects in the Hydroboration of Olefins with Dihaloborane-Dimethyl Sulfide Complexes

olefin	isomeric alcohols[a]	isomer distribution,[b] %			
		$HBCl_2\cdot SMe_2$[c]	$HBBr_2\cdot SMe_2$	$HBI_2\cdot SMe_2$	$H_2BBr\cdot SMe_2$[d]
1-hexene	1-hexanol	99	99.6	96	99.6
	2-hexanol	1	0.4	4	0.4
styrene	2-phenylethanol	97	96	97	96
	1-phenylethanol	3	4	3	4
2-methyl-1-pentene	2-methyl-1-pentanol	96	98	92	98
	2-methyl-2-pentanol	4	2	8	2
2-methyl-2-butene	3-methyl-2-butanol	97	93	75	97
	2-methyl-2-butanol	3	7	25	3
1-methylcyclopentene	*trans*-2-methylcyclopentanol	99	98	86	97.5
	1-methylcyclopentanol	1	2	14	2.5

[a] Determined by GC analysis on a 14 ft × 0.125 in. column packed with 5% Carbowax 20M on Varaport. Overall yields were 90 ± 5%. [b] Reactions were carried out in CH_2Cl_2. [c] These values were obtained for the reactions in CH_2Cl_2 in the absence of BCl_3 or $SnCl_4$. [d] Taken from ref 4.

to the slow reaction previously observed for $HBCl_2\cdot OEt_2$.[5] However, these olefins are hydroborated completely in refluxing CH_2Cl_2 (Table I), although the product contains considerable quantities of R_2BCl and R_3B as impurities. These undesirable impurities presumably arise from the disproportionation of $HBCl_2\cdot SMe_2$. Such difficulties, in the case of the hydroboration with $HBCl_2\cdot OEt_2$, were overcome by using a strong Lewis acid, boron trichloride, which generates nascent $HBCl_2$ with instantaneous precipitation of $BCl_3\cdot OEt_2$. Therefore, we undertook to examine the applicability of various Lewis acids on the hydroboration of alkenes with $HBCl_2\cdot SMe_2$.

The hydroboration of 1-octene with $HBCl_2\cdot SMe_2$ in the presence of anhydrous $AlCl_3$ is accompanied by considerable polymerization of the olefin, resulting in very low yields of the desired $RBCl_2$. Anhydrous $SnCl_4$ promotes the hydroboration leading cleanly to $RBCl_2$. However, the presence of the adduct offered difficulties to the isolation of pure $RBCl_2$ free of $SnCl_4$. This problem was solved by employing BCl_3, which had previously proven successful for $HBCl_2\cdot OEt_2$. Thus, 1-octene was hydroborated cleanly by $HBCl_2\cdot SMe_2$ in pentane in the presence of 1 molar equiv of BCl_3 (eq 3). The clean precipitation of the addition compound simplifies the isolation of the product.

$$n\text{-}C_6H_{13}CH{=}CH_2 + HBCl_2\cdot SMe_2 + BCl_3 \xrightarrow[25\ °C]{\text{pentane}} n\text{-}C_8H_{17}BCl_2 + BCl_3\cdot SMe_2\downarrow \quad (3)$$

We had anticipated that $HBBr_2\cdot SMe_2$ would be even less reactive than $HBCl_2\cdot SMe_2$. Accordingly, our early experiments with this reagent utilized BBr_3 as a coreagent. However, a blank experiment revealed that $HBBr_2\cdot SMe_2$ hydroborates olefins even in the absence of BBr_3 (eq 4).

$$RCH{=}CH_2 + HBBr_2\cdot SMe_2 \xrightarrow[40\ °C]{CH_2Cl_2} RCH_2CH_2BBr_2\cdot SMe_2 \quad (4)$$

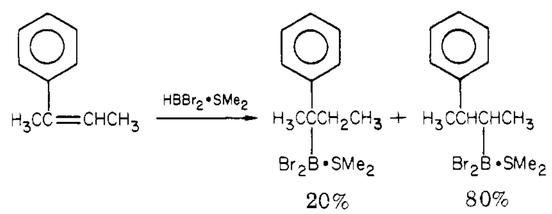
The reaction appears to be general. The products are formed as $RBBr_2\cdot SMe_2$ addition compounds and can be isolated as such by vacuum distillation. Similarly, $HBI_2\cdot SMe_2$ reacts cleanly with alkenes in refluxing CH_2Cl_2 to afford $RBI_2\cdot SMe_2$ (Table I).

Directive Effects. In view of the high regioselectivity observed in the hydroboration of alkenes with $HBCl_2\cdot OEt_2$,[5] it was of interest to explore directive effects in the hydroboration of representative alkenes with $HBX_2\cdot SMe_2$. Such information is helpful for the utilization of RBX_2 and its derivatives for further reactions. The method of investigation consisted of the hydroboration of the chosen alkene with the reagent, followed by oxidation with alkaline hydrogen peroxide. The isomeric alcohols thus generated were estimated by GC analysis (Table II).

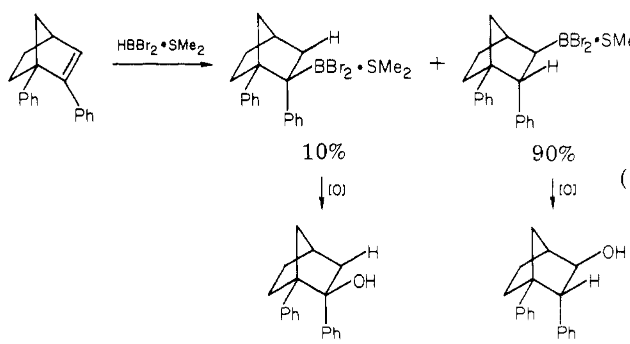
In the hydroboration of the representative alkenes selected for study, $HBCl_2\cdot SMe_2$ exhibits directive effects similar to those observed for $H_2BCl\cdot SMe_2$.[4] For unsubstituted terminal alkenes, the directive effects of $HBBr_2\cdot SMe_2$ are comparable to those of $H_2BBr\cdot SMe_2$. However, in the hydroboration of 2-methyl-2-butene with $HBBr_2\cdot SMe_2$, the formation of 7% of the tertiary derivative, a significant increase over the 3% previously observed for $H_2BBr\cdot SMe_2$, was quite unexpected. These values are considerably greater than those observed for $H_2BCl\cdot OEt_2$,[3] $H_2BCl\cdot SMe_2$,[4] and even $H_3B\cdot THF$.

This property is further enhanced in the case of $HBI_2\cdot SMe_2$, as observed by the formation of notably increased amounts of tertiary derivatives from 2-methyl-2-butene and 1-methylcyclopentene (Table II).

The hydroboration of 2-phenyl-2-butene with $HBBr_2\cdot SMe_2$ yields 20% of the tertiary derivative[12] (eq 5). Advantage was taken of this unusual directive effect of $HBBr_2\cdot SMe_2$ to hydroborate 1,2-diphenylnorbornene to obtain the highly elusive 1,2-diphenyl-*exo*-norbornanol[13] (eq 6).



(5)



(6)

Reactivities of Dihaloborane-Dimethyl Sulfide Adducts. $HBCl_2\cdot OEt_2$ and $HBCl_2\cdot SMe_2$ require the presence of a strong Lewis acid, usually BCl_3, for the

(12) Research with J. B. Campbell, Jr.

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Table III. Synthesis of Alkyldihaloboranes and Their Derivatives

alkyldihaloborane derivative	reagent	solvent	yield,[b] %	bp, °C (mmHg)
n-octyldichloroborane	$HBCl_2 \cdot SMe_2$ + BCl_3	pentane	85	92–94 (19)
n-octyldichloroborane–dimethyl sulfide[a]	$HBCl_2 \cdot SMe_2$	CH_2Cl_2	69	65–67 (2)
trans-2-methylcyclopentyldichloroborane–dimethyl sulfide	$HBCl_2 \cdot SMe_2$	CH_2Cl_2	79	45–47 (0.3)
n-hexyldibromoborane–dimethyl sulfide	$HBBr_2 \cdot SMe_2$	CH_2Cl_2	91	99–100 (1)
3-hexyldibromoborane–dimethyl sulfide	$HBBr_2 \cdot SMe_2$	CH_2Cl_2	90	73–75 (2.2)
2-methyl-1-pentyldibromoborane–dimethyl sulfide	$HBBr_2 \cdot SMe_2$	CH_2Cl_2	93	82–85 (1.6)
cyclopentyldibromoborane–dimethyl sulfide	$HBBr_2 \cdot SMe_2$	CH_2Cl_2	93	140–144 (2.1)
trans-2-methylcyclopentyldibromoborane–dimethyl sulfide	$HBBr_2 \cdot SMe_2$	CH_2Cl_2	86	68–69 (0.5)
n-hexyldibromoborane	$HBBr_2 \cdot SMe_2$	CH_2Cl_2	71	56–58 (0.9)
n-octyldiiodoborane–dimethyl sulfide	$HBI_2 \cdot SMe_2$	CH_2Cl_2	74	125–128 (0.2)
dimethyl *n*-hexylboronate	$HBCl_2 \cdot SMe_2$	pentane	83	84–86 (35)
dimethyl cyclopentylboronate	$HBBr_2 \cdot SMe_2$	CH_2Cl_2	74	76–78 (40)

[a] Contains R_2BCl and R_3B as minor impurities. [b] All are isolated yields.

satisfactory hydroboration of alkenes. However, $HBBr_2 \cdot SMe_2$ and $HBI_2 \cdot SMe_2$ hydroborate representative alkenes directly. This raises a theoretical question as to why $HBBr_2 \cdot SMe_2$, which theory predicts should be a stabler complex than $HBCl_2 \cdot SMe_2$, should be a more reactive hydroborating agent.

The Lewis acid strengths of boron halides are in the order $BCl_3 < BBr_3 < BI_3$.[10,14,15] The reactivities of the borane etherates and the borane–dimethyl sulfide adducts 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 stability of these adducts in this order, resulting from the increasing Lewis acidity of the borane component with increasing number of chlorine substituents: $H_3B < H_2BCl < HBCl_2 < BCl_3$.[10] It was believed that the hydroboration reaction proceeds via prior dissociation of the addition compounds. The more stable the complex is, the smaller the amount of free borane and the slower the hydroboration. Since BBr_3 is a stronger Lewis acid than BCl_3, the bromoboranes should be more acidic than the corresponding chloroboranes: $BBr_3 > BCl_3$, $HBBr_2 > HBCl_2$, $H_2BBr > H_2BCl$. Consequently, the addition compounds of bromoboranes should be less reactive than those of chloroboranes with respect to hydroboration. 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.

This prediction of the relative stabilities of these addition compounds is partially supported by the ^1H NMR observations.[10] In CCl_4 solution at room temperature, $BCl_3 \cdot SMe_2$, $HBCl_2 \cdot SMe_2$, and $H_2BCl \cdot SMe_2$ readily exchange complexed SMe_2 with added excess SMe_2. On the other hand, $BBr_3 \cdot SMe_2$, $HBBr_2 \cdot SMe_2$, and $H_2BBr \cdot SMe_2$ do not undergo such exchange under these conditions, in agreement with the predicted greater stability of the bromoborane complexes.

There is evidence that π electrons, such as those present in benzene, can interact strongly with $BBr_3 \cdot SMe_2$.[10] A similar phenomenon may occur involving the π electrons of the alkene and the dibromoborane or diiodoborane adducts. If so, the hydroboration may proceed through an association of the olefin and the methyl sulfide complex, followed by a direct transfer of the $HBBr_2$ and HBI_2 moiety directly from sulfur to the π electrons of the alkene. This could account for both the unexpected reactivity and the unusual directive effects exhibited by $HBBr_2 \cdot SMe_2$ and $HBI_2 \cdot SMe_2$ in their hydroboration of trisubstituted alkenes. This would mean that the hydroboration of alkenes with these reagents may follow a path significantly different from that proposed for the reagents reported earlier. However, before arriving at a final conclusion, it is desirable that this phenomenon be investigated in greater detail. For the present study, we were more interested in exploring the synthetic aspects of the reagents.

Synthesis of Alkyldihaloboranes. For the preparation of alkyldichloroboranes, $HBCl_2 \cdot SMe_2$ and the olefin are mixed in pentane, and 1 molar equiv of BCl_3 in pentane is added. The precipitated $BCl_3 \cdot SMe_2$ is removed by filtration. Following the removal of pentane, $RBCl_2$ is distilled under vacuum. In the cases of $RBBr_2$ and RBI_2, hydroboration in CH_2Cl_2, followed by distillation, affords the corresponding dimethyl sulfide complexes. The alkyldihaloborane free from SMe_2 is obtained by the addition of BBr_3 or BI_3, respectively, prior to distillation (eq 7; X = Br or I). The results are summarized in Table III.

$$RBX_2 \cdot SMe_2 + BX_3 \rightarrow RBX_2 + BX_3 \cdot SMe_2 \downarrow \quad (7)$$

Methanolysis of Alkyldihaloboranes. The alkyldichloroboranes readily undergo methanolysis to afford the methyl esters of the corresponding alkylboronic acids (eq 8). Following removal of the solvent (pentane or CH_2Cl_2),

$$RBCl_2 + 2MeOH \rightarrow RB(OMe)_2 + 2HCl \quad (8)$$

the excess of methanol, and the hydrogen chloride generated, the boronate esters can be recovered by distilling under reduced pressure. However, in the cases of $RBBr_2 \cdot SMe_2$ and $RBI_2 \cdot SMe_2$, the formation of $HBr \cdot SMe_2$ and $HI \cdot SMe_2$ complicates the isolation of the boronate esters by simple distillation. This problem is solved by using the stoichiometric amount of sodium methoxide in an excess of methanol (eq 9; X = Br or I). Simple vacuum

$$RBX_2 \cdot SMe_2 + 2NaOMe \xrightarrow{MeOH} RB(OMe)_2 + 2NaX\downarrow + SMe_2 \quad (9)$$

distillation then provides pure $RB(OMe)_2$ in good yields (Table III). Hydrolysis with water yields the corresponding boronic acids.

It has previously been demonstrated that such boronic acids and esters are readily oxidized to the corresponding alcohols with alkaline hydrogen peroxide.[16]

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Conclusion

The unusual reactivities and directive effects of these dihaloborane reagents ($HBX_2{\cdot}SMe_2$) may be suggestive of a strange phenomenon. The hydroboration of alkenes with dibromo- and diiodoborane–dimethyl sulfide adducts may proceed through a significantly different mechanism than do hydroborations with the addition compounds explored previously. However, a final theoretical interpretation requires detailed kinetic and mechanistic studies in this area.

Irrespective of the mechanistic considerations, this study has important synthetic implications. The present work provides a series of new, stable, monofunctional hydroborating agents ($HBX_2{\cdot}SMe_2$), which can be conveniently used for the first general synthesis of alkyldihaloboranes (RBX_2) under mild conditions. The alkyldibromo- and the alkyldiiodoboranes were not previously available. The synthetic applications of the alkyldihaloboranes have been rarely explored. In view of the utility of $RBCl_2$ in organic synthesis,[6-9] the present study should encourage further research in this area, using RBX_2 compounds as synthons.

Experimental Section

Materials. All the glassware used for the experiment was thoroughly dried in an oven and cooled under a stream of nitrogen. Reagent-grade methanol was used after being stored over type 3A molecular sieves. Ether, pentane, and dichloromethane were dried over molecular sieve (type 5A). The alkenes used for this study were commercial products of the highest purity available, and they were purified by distillation over $LiAlH_4$. The special experimental techniques used in handling air- and moisture-sensitive materials are described elsewhere.[16]

Gas Chromatographic Analyses. Most of the reactions were monitored by gas chromatography using a Varian 1400 series gas chromatograph. All of the GC yields were determined by utilizing *n*-decane as an internal standard. The following columns were generally used: 14 ft × 0.125 in. packed with 5% Carbowax 20M on Varaport-30; 12 ft × 0.125 in. packed with 5% SE-30 on Varaport-30.

Syntheses of Dihaloborane–Dimethyl Sulfide Complexes. The syntheses and characterization of these reagents have been described in detail elsewhere.[10,11] Considerable quantities were prepared by following these procedures. $HBI_2{\cdot}SMe_2$ was prepared from BMS and iodine.[11]

Reaction of 1-Octene with $HBCl_2{\cdot}SMe_2$. A dry, 50-mL round-bottomed flask, equipped with a side arm capped with a silicone rubber septum, a magnetic stirring bar, and a connecting tube attached to a mercury bubbler, was flushed with nitrogen. The flask was immersed in a water bath (25 °C), and 0.54 mL of $HBCl_2{\cdot}SMe_2$ (5 mmol; neat $HBCl_2{\cdot}SMe_2$ is 9.2 M), 0.2 mL of pentane (in order to make the reaction mixture 1.0 M in reactants), 0.79 mL of 1-octene (5 mmol), and 0.97 mL of *n*-decane (5 mmol, internal standard for GC analysis) were added. The mixture was stirred vigorously, and 2.5 mL of a 2 M solution of BCl_3 in pentane (5 mmol) was added dropwise. At definite intervals of time, 0.2 mL of the reaction mixture was withdrawn and quenched in an ice–water mixture in a 1-dr vial, the acidic materials were destroyed by adding sufficient NaOH, and the organic materials were extracted in 1 mL of ether. The GC analysis of this organic layer gives the amount of unreacted 1-octene, from which the extent of the hydroboration reaction was calculated.

For the reaction in the presence of $SnCl_4$, the same procedure was followed, except that the required quantity of $SnCl_4$ was added instead of BCl_3 in pentane.

For the reaction in the absence of BCl_3, pentane was replaced by CH_2Cl_2. The rates of hydroboration of 1-octene and *cis*-3-octene were determined at 1 and 2 M concentrations of the reactants, both at 25 and at 40 °C.

Reaction of 1-Octene with $HBBr_2{\cdot}SMe_2$. Employing the same experimental setup as described for the hydroboration with $HBCl_2{\cdot}SMe_2$, we added 0.79 mL of 1-octene (5 mmol) to 0.64 mL of $HBBr_2{\cdot}SMe_2$ (5 mmol; neat liquid at 40 °C is 7.8 M) in 2.6 mL of CH_2Cl_2 containing 0.97 mL of *n*-decane (5 mmol) with vigorous stirring. In the case of the reaction at 40 °C, the mixture was heated under reflux. The progress of the reaction was followed by GC, as already described.

Hydroboration of *cis*-3-octene was carried out in the same manner.

Reaction of 1-Octene with $HBI_2{\cdot}SMe_2$. A stock solution of $HBI_2{\cdot}SMe_2$ in CH_2Cl_2 was prepared and standardized by hydrolysis using a 1:1 mixture of MeOH and 6 N HCl at 35 °C. To a 2.2-mL solution of $HBI_2{\cdot}SMe_2$ in CH_2Cl_2 (2.29 M, 5 mmol) were added 0.97 mL of *n*-decane (5 mmol), 2.0 mL of CH_2Cl_2 (to make the reaction mixture 1 M in the reactants) and 0.79 mL of 1-octene. The progress of hydroboration was followed by GC, as described earlier.

The hydroboration of *cis*-3-octene was also carried out by the same procedure.

Directive Effects. The determination of directive effects in the hydroboration of 1-hexene (5 mmol) with $HBBr_2{\cdot}SMe_2$ is described as a representative case. The reaction was carried out as described for the hydroboration of 1-octene with $HBBr_2{\cdot}SMe_2$. When the reaction was complete (3 h, under reflux), the resulting *n*-hexyldibromoborane was oxidized by adding 6.7 mL of 3 N NaOH (20 mmol), 5 mL of 95% EtOH, 5 mL of THF, and 2 mL of 30% H_2O_2, followed by stirring at 25 °C for 1 h. The oxidation was completed by maintaining the reaction mixture at 50 °C, with vigorous stirring, for 1 h. The mixture was cooled to 0 °C, and the aqueous layer was saturated with anhydrous K_2CO_3. The organic layer was then analyzed by GC for the amounts of 1-hexanol and 2-hexanol.

The directive effects in the hydroboration of styrene, 2-methyl-1-pentene, 2-methyl-2-butene, and 1-methylcyclopentene with $HBCl_2{\cdot}SMe_2$, $HBBr_2{\cdot}SMe_2$, and $HBI_2{\cdot}SMe_2$ were determined by following this procedure. The results are summarized in Table II.

Synthesis of *n*-Octyldichloroborane. A 250-mL flask was equipped with a typical hydroboration setup, as described above. A solution of 7.85 mL (50 mmol) of 1-octene in 61 mL of pentane was placed in a flask, the flask was immersed in an ice-water bath, and 25 mL of a 2 M solution of BCl_3 in pentane was added dropwise while stirring the contents of the flask vigorously. Following the complete addition of BCl_3, the mixture was stirred for 2 h at 25 °C. The clear pentane solution of the resulting alkyldichloroborane was decanted through a double-ended needle into another 250-mL, round-bottomed flask. The solvent was removed by using a water aspirator and octyldichloroborane, 8.4 g (a yield of 85%), was obtained on distillation under reduced pressure; bp 92–94 °C (19 mmHg).

Synthesis of *n*-Hexyldibromoborane–Dimethyl Sulfide. In a 250-mL reaction flask, fitted with a reflux condenser, 12.5 mL of 1-hexene (100 mmol) was dissolved in 75 mL of CH_2Cl_2 under nitrogen. To this flask was added 12.8 mL (100 mmol) of $HBBr_2{\cdot}SMe_2$ slowly, and the mixture was heated under reflux for 3 h. After the mixture had cooled to 25 °C, the solvent was removed by using a water aspirator. The product, distilled at 97–100 °C (1 mmHg), 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.

Other alkyldibromoborane–dimethyl sulfides, alkyldiiodoborane–dimethyl sulfides, and some alkyldichloroborane–dimethyl sulfides were prepared by following this procedure. However, the $RBCl_2{\cdot}SMe_2$ compounds prepared in this way were contaminated with considerable quantities (5–10%) of $R_2BCl{\cdot}SMe_2$ and R_3B.

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

Methanolysis of *n*-Octyldichloroborane. To a solution of 25 mmol of *n*-hexyldichloroborane in pentane (free from $BCl_3{\cdot}SMe_2$) prepared from 1-hexene and $HBCl_2{\cdot}SMe_2$ by the same procedure as described for *n*-octyldichloroborane was added 4.1 mL (100 mmol, 100% excess) of MeOH (at 0 °C) with vigorous stirring. Following the completion of addition, the reaction mixture was stirred for 1 h at 25 °C. The solvent, excess MeOH, and the HCl generated in the reaction were removed by using a water aspirator, and the resulting product, dimethyl *n*-hexylboronate, was distilled under reduced pressure: yield 3.3 g (83%), bp 84-86 °C (35 mmHg).

The methanolysis of $RBCl_2$ or $RBCl_2 \cdot SMe_2$ can be carried out by following this procedure, and the methyl ester of alkylboronic acids can be isolated in good yields.

Methanolysis of Cyclopentyldibromoborane-Dimethyl Sulfide. The usual experimental setup was employed for the hydroboration of 8.8 mL (100 mmol) of cyclopentene with 12.8 mL (100 mmol) of $HBBr_2 \cdot SMe_2$ in 75 mL of CH_2Cl_2. The reaction mixture was heated under reflux for 5 h. The flask was cooled to 0 °C, 44.5 mL of 4.5 M solution of NaOMe in MeOH (200 mmol) was added, and the mixture was stirred for 2 h at 25 °C. The solvent was removed under vacuum, and the product, dimethyl cyclopentylboronate, 10.5 g (74% yield), bp 76-78 °C (40 mmHg), was obtained as a colorless liquid.

The methanolysis of $RBBr_2$, $RBBr_2 \cdot SMe_2$, RBI_2, and $RBI_2 \cdot SMe_2$ derivatives can be carried out according to this procedure. The results obtained with representative dihaloboranes are listed in Table III.

Registry No. 1-Octene, 111-66-0; *cis*-3-octene, 14850-22-7; 1-hexene, 592-41-6; styrene, 100-42-5; 2-methyl-1-pentene, 763-29-1; 2-methyl-2-butene, 513-35-9; 1-methylcyclopentene, 693-89-0; 1-hexanol, 111-27-3; 2-hexanol, 626-93-7; 2-phenylethanol, 60-12-8; 1-phenylethanol, 98-85-1; 2-methyl-1-pentanol, 105-30-6; 2-methyl-2-pentanol, 590-36-3; 3-methyl-2-butanol, 598-75-4; 2-methyl-2-butanol, 75-85-4; *trans*-2-methylcyclopentanol, 25144-04-1; 1-methylcyclopentanol, 1462-03-9; octyldichloroborane, 63348-82-3; octyldichloroborane-dimethyl sulfide, 72205-94-8; *trans*-2-methylcyclopentyldichloroborane-dimethyl sulfide, 72205-95-9; hexyldibromoborane-dimethyl sulfide, 64770-04-3; 3-hexyldibromoborane-dimethyl sulfide, 64770-06-5; 2-methyl-1-pentyldibromoborane-dimethyl sulfide, 72205-97-1; cyclopentyldibromoborane-dimethyl sulfide, 64770-10-1; *trans*-2-methylcyclopentyldibromobrane-dimethyl sulfide, 72205-99-3; hexyldibromoborane, 64770-03-2; octyldiiodoborane-dimethyl sulfide, 72206-01-0; dimethyl hexylboronate, 2344-23-2; dimethyl cyclopentylboronate, 41156-60-9; $HBCl_2 \cdot SMe_2$, 63462-42-0; $HBBr_2 \cdot SMe_2$, 55671-55-1; $HBI_2 \cdot SMe_2$, 55652-51-2.

Hydroboration. 55. Hydroboration of Alkynes with Dibromoborane-Dimethyl Sulfide. Convenient Preparation of Alkenyldibromoboranes

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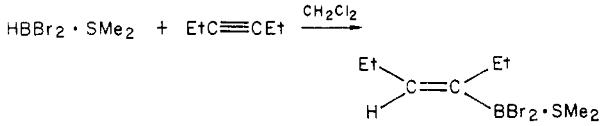
Dibromoborane-dimethyl sulfide undergoes direct hydroboration of both terminal and internal alkynes with remarkable facility to give alkenyldibromoboranes. These reactive alkenylboranes, which may be isolated, undergo many synthetically useful transformations. Oxidation provides the carbonyl compounds while protonolysis with acetic acid occurs stereospecifically to yield the corresponding alkenes. 1-Alkenyldibromoboranes can be converted easily to 1-iodo-1-alkenes by basic hydrolysis and iodination. Both internal and 1-alkenyldibromoboranes serve as convenient precursors to symmetrical conjugated dienes by reaction with 3 equiv of methylcopper. Hydroboration of alkynes with $HBBr_2 \cdot SMe_2$ is critically examined in terms of relative reactivities of both alkyne and alkene substrates. A very broad reactivity spectrum is evident, with internal acetylenes reacting with remarkable facility. The regiospecificity of the hydroboration of unsymmetrically substituted alkynes indicates $HBBr_2 \cdot SMe_2$ to be a highly selective reagent, sensitive to both steric and electronic effects. The regioselectivity is compared with that of other hindered hydroborating reagents, such as 9-BBN and disiamylborane.

Dibromoborane-dimethyl sulfide ($HBBr_2 \cdot SMe_2$) was recently reported to undergo direct reaction with alkenes in refluxing methylene chloride to give alkyldibromoboranes in high yields.[2] The enhanced reactivity of this reagent relative to dichloroborane diethyl etherate ($HBCl_2 \cdot OEt_2$)[3] and dichloroborane-dimethyl sulfide ($HBCl_2 \cdot SMe_2$)[4] was somewhat surprising since one might have predicted $HBBr_2 \cdot SMe_2$, the more stable adduct,[5] to be less reactive than $HBCl_2 \cdot SMe_2$ for hydroboration. In fact, whereas the dichloroborane adducts require a strong Lewis acid, such as BCl_3, to induce hydroboration, $HBBr_2 \cdot SMe_2$ reacts directly.[2] The unusual reactivity of $HBBr_2 \cdot SMe_2$ toward alkenes prompted an investigation of the reaction with alkynes as a possible route to alkenyldibromoboranes. These strongly acidic diheterofunctional alkenylboranes would be anticipated to be fairly reactive intermediates and hence of considerable synthetic interest. Thus, a systematic examination of the hydroboration of alkynes with $HBBr_2 \cdot SMe_2$ was undertaken as a potential route to the promising alkenyldibromoboranes.

Rate and Stoichiometry. Initially, the rate and stoichiometry of the reaction of $HBBr_2 \cdot SMe_2$ with 1-hexyne and 3-hexyne, selected as representative terminal and internal alkynes, were investigated. Stoichiometric amounts of the alkyne and $HBBr_2 \cdot SMe_2$ were employed in CH_2Cl_2 solution at 0 and 25 °C. The reaction rate was followed by monitoring the disappearance of active hydride by hydrolyzing measured aliquots at appropriate intervals of time and determining the volume of the hydrogen evolved. Simultaneously, aliquots were withdrawn, quenched with dilute alkali, and analyzed by gas chromatography for unreacted alkyne. The results, presented in Figure 1 for 3-hexyne, indicate the reaction to be proceeding to form the alkenyldibromoborane (eq 1).



(1)

Likewise, hydroboration of 1-hexyne with $HBBr_2 \cdot SMe_2$ (Figure 2) appears to form cleanly the corresponding 1-

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