added dropwise at reflux over a 1.5 h period. After 1 h of additional stirring, the reaction mixture was cooled to room temperature and quenched with a 0.2 M HCl solution (20 mL). The standard treatment gave 93% of **35**: NMR ($CDCl_3$) δ 1.30 (t, J = 7.5 Hz, 3, CH_3), 2.78 (q, J = 7.5 Hz, 2, CH_2), 6.18 (d, J = 10.6 Hz, 1, PhC=CH), 6.45 (d, J = 10.6 Hz, 1, PhCH=C), 7.10–7.58 (m, 5 H, ArH); IR (neat) 1600, 1500, 1370, 1275, 850, 775, 720, 690 cm^{-1}; mass spectrum m/e 164.

1,1-Diphenylthio-2-phenylethylene. In a 100-mL, three-necked flask, fitted with a dropping funnel, a reflux condenser, a nitrogen inlet, and a magnetic stirring bar, was placed tetrakis(triphenylphosphine)palladium (0.117 g, 0.10 mmol). The flask was alternately evacuated and filled with argon on a vacuum line. A solution of an 1,1-dichloro-2-phenylethylene (0.371 g, 2.1 mmol) in 20 mL of benzene was added, and the mixture was stirred at reflux for 30 min. To the mixture was added dropwise a solution of lithium benzenethiolate, prepared from thiophenol (0.446 g, 4.0 mmol) and butyllithium (4.0 mmol), and then the mixture was diluted with 10 mL of benzene and refluxed for 1 h. After 4 h of stirring, the reaction mixture was cooled to room temperature and quenched by adding 0.2 M HCl (20 mL). The ether extract was washed, dried, and concentrated. The GLC analysis using an internal standard showed that 1,1-diphenylthio-2-phenylethylene[62] (**36**) was obtained in 96% yield (the conversion of the dihalide is 12%): NMR (CCl_4) δ 7.05 (s, 1, PhCH=C), 7.10–7.33 (m, 13, ArH), 7.42–7.70 (m, 2, ArH); IR (Nujol) 1585, 1480, 1440, 750, 740, 690 cm^{-1}; mass spectrum m/e 320. Even when the palladium catalyst, prepared from $PdCl_2$–PPh_3–CH_3Li, was used, the conversion of dichloride did not increase. The reaction of 1,1-dibromo-2-phenylethylene[60] under the same reaction conditions gave the ketene thioacetal in 96% yield. (The conversion of the dibromide was again only 10%.)

(62) A. J. Speziale, "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., 1973, p 361.

Registry No. **1**, 766-90-5; **2**, 15325-54-9; **3**, 1657-45-0; **4**, 18138-87-9; **5**, 23516-73-6; **6**, 70197-43-2; **7**, 873-66-5; **8**, 6111-82-6; **9**, 1860-17-9; **10**, 16939-57-4; **11**, 21676-00-6; **12**, 26708-50-9; **13**, 70197-44-3; **14**, 52728-09-3; **15**, 7433-78-5; **16**, 56949-84-9; **17**, 70197-45-4; **18**, 768-00-3; **29**, 13343-78-7; **37**, 70197-46-5; **32**, 7214-56-4; **33**, 7214-53-1; **34**, 70197-34-1; **35**, 20890-79-3; **36**, 35550-81-3; (*Z*)-PhCH=CHBr, 588-73-8; (*E*)-PhCH=CHBr, 588-72-7; (*Z*)-PhCH=CHCl, 4604-28-8; (*Z*)-BuCH=CHBr, 13154-12-6; (*E*)-$Ph(CH_3)C$=CHBr, 16917-35-4; (*Z*)-1,2-dichloroethylene, 156-59-2; (*E*)-1,2-dichloroethylene, 156-60-5; (*Z*)-5-undecen-7-yne, 70197-33-0; 1,1-dichloro-2-phenylethylene, 698-88-4; (*Z*)-stilbene, 645-49-8; (*E*)-stilbene, 103-30-0; biphenyl, 92-52-4; MeLi, 917-54-4; BuLi, 109-72-8; *p*-MeC_6H_4Li, 2417-95-0; **19**, 2786-02-9; **20**, 2786-07-4; **21**, 22608-37-3; **22**, 27171-81-9; phenyllithium, 591-51-5; lithium benzenethiolate, 2973-86-6; lithium ethanethiolate, 30383-01-8; PhSNa, 930-69-8.

Supplementary Material Available: Analytical data of compounds **2–6**, **11–13**, **16**, **31**, **32**, and **34–36** (1 page). Ordering information is given on any current masthead page.

Hydroboration. 52. Monohaloborane–Methyl Sulfide Adducts as New Reagents for the Hydroboration of Alkenes. A Convenient Synthesis of Dialkylhaloboranes and Their Derivatives for Organic Synthesis[1]

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Received December 18, 1978

Reactions of alkenes with the recently discovered monochloroborane–methyl sulfide ($H_2BCl{\cdot}SMe_2$), monobromoborane–methyl sulfide ($H_2BBr{\cdot}SMe_2$), and monoiodoborane–methyl sulfide ($H_2BI{\cdot}SMe_2$) were investigated in detail in order to establish their usefulness as hydroborating agents. $H_2BCl{\cdot}SMe_2$ hydroborates alkenes rapidly and quantitatively at 25 °C. Simple distillation under low pressure affords pure R_2BCl. Similarly, the hydroboration of alkenes with $H_2BBr{\cdot}SMe_2$ followed by distillation affords pure R_2BBr in the case of hindered alkyl groups and the corresponding methyl sulfide complexes in the case of unhindered alkyl groups. Distillation of $R_2BBr{\cdot}SMe_2$ following the addition of 1 mol equiv of BBr_3 gives pure R_2BBr. The reactions of $H_2BI{\cdot}SMe_2$ are slower, but it reacts satisfactorily with alkenes in refluxing dichloromethane. Distillation affords dialkyliodoboranes almost free from SMe_2. These dialkylhaloboranes are readily converted into other dialkylboron derivatives by treatment with appropriate reagents. Such derivatives are useful as intermediates in organic synthesis.

We recently reported a detailed study of the hydroboration of alkenes with monochloroborane etherate, $H_2BCl{\cdot}OEt_2$ (MCBE).[3] This study revealed that MCBE is an excellent reagent for converting alkenes into dialkylchloroboranes. It provided for the first time a convenient general procedure for the synthesis of dialkylchloroboranes and their derivatives. Since then, such dialkylboron derivatives have been found to be excellent intermediates for a wide variety of synthetic applications.[4-7]

Unfortunately, monochloroborane etherate, although a superb hydroborating agent, suffers from some practical difficulties. The most convenient preparation of the reagent starts from lithium borohydride, a relatively expensive chemical. Moreover, the reagent can be prepared only as a dilute ether solution and, therefore, must be handled as such, since it disproportionates upon concentration. MCBE possesses only limited stability at room

(1) For preliminary reports on some aspects of the present study, see: (a) H. C. Brown and N. Ravindran, *J. Org. Chem.*, **42**, 2533 (1977); (b) H. C. Brown and N. Ravindran, *Synthesis*, 695 (1977).

(2) (a) Postdoctoral research associate (1972–1973) on National Science Foundation Grant No. 27742X; (b) Postdoctoral research associate on a grant from G. D. Searle and Co.; (c) Postdoctoral research associate on Grant No. GM 10937-16 from the National Institutes of Health (1978).

(3) H. C. Brown and N. Ravindran, *J. Am. Chem. Soc.*, **98**, 1785 (1976).

(4) H. C. Brown, M. M. Midland, and A. B. Levy, *J. Am. Chem. Soc.*, **94**, 2114, 3662 (1972); **95**, 2394 (1973).

(5) H. C. Brown and C. F. Lane, *Synthesis*, 303 (1972).

(6) B. A. Carlson and H. C. Brown, *J. Am. Chem. Soc.*, **95**, 6876 (1973).

(7) Y. Yamamoto, K. Kondo, and I. Moritani, *Tetrahedron Lett.*, 793 (1974).

0022-3263/79/1944-2417$01.00/0

temperature, thus necessitating its storage at 0 °C or the use of freshly prepared reagent for obtaining best results. Therefore, we undertook a search for new monohaloborane derivatives possessing all the desirable hydroboration properties of MCBE but, at the same time, free from most of its disadvantages.

Recently we reported that borane–methyl sulfide, $H_3B{\cdot}SMe_2$ (BMS), undergoes redistribution rapidly with boron trichloride–methyl sulfide and boron tribromide–methyl sulfide to give haloborane–methyl sulfide addition compounds in excellent yield and purity (eq 1).[8] Mo-

$$2H_3B{\cdot}SMe_2 + BX_3{\cdot}SMe_2 \rightarrow 3H_2BX{\cdot}SMe_2 \quad (1)$$

noiodoborane–methyl sulfide was prepared by a similar exchange reaction, as well as by the reaction of BMS with iodine or hydrogen iodide.[9] These SMe_2 addition compounds are stable indefinitely at room temperature when stored under nitrogen. Moreover, they can be prepared as neat compounds, in highly concentrated form. These attractive properties of the monohaloborane–methyl sulfide complexes prompted us to undertake a detailed investigation of their reaction with representative olefins. The results of our study on monochloroborane–methyl sulfide, $H_2BCl{\cdot}SMe_2$ (MCBS), monobromoborane–methyl sulfide, $H_2BBr{\cdot}SMe_2$ (MBBS), and monoiodoborane–methyl sulfide, $H_2BI{\cdot}SMe_2$ (MIBS), and the preparation of the corresponding dialkylboron halides are reported here.

Results and Discussion

Hydroboration of Alkenes with $H_2BX{\cdot}SMe_2$. The reagents MCBS, MBBS, and MIBS were prepared, characterized, and analyzed as reported earlier.[8,9] For the preliminary study, 1-octene and *cis*-3-octene were chosen as the representative terminal and internal alkene, respectively. In the case of MCBS, the reaction was studied both in ether and pentane at 0 and 25 °C and in dichloromethane at 25 °C. Since the hydroboration was slow at 0 °C in CH_2Cl_2, a convenient solvent, the reactions of MBBS and MIBS were investigated in CH_2Cl_2 at 25 °C. In the case of MIBS, the reaction was slow, even at 25 °C, so that it was carried out in refluxing CH_2Cl_2.

The general procedure involves the addition of the required amount of the neat reagent to a solution of the alkene under study in the preferred solvent. The initial concentration of the reaction mixture is 1 M in the reagent and 2 M in alkene. The reaction is carried out at the desired temperatures, and the rate is followed by the analysis of aliquots for unreacted alkene at definite intervals of time. The results are summarized in Table I.

It is evident that both terminal and internal alkenes react with MCBS completely in less than 2 h at 25 °C in pentane, ether, or CH_2Cl_2. Other representative alkenes studied at 25 °C include 1-butene, *cis*-2-butene, 1-hexene, styrene, 2-methyl-2-butene, 1-methylcyclopentene, and norbornene. In all the cases the reactions were essentially complete in less than 2 h at 25 °C with both MCBS and MBBS in the solvents used (ether, pentane, and CH_2Cl_2 for MCBS and CH_2Cl_2 for MBBS). The hydroboration with MIBS in CH_2Cl_2 is relatively sluggish at 25 °C, requiring 6 and 10 h for the complete reaction with 1-octene and *cis*-3-octene, respectively. However, these alkenes are hydroborated cleanly and completely in 2 h in refluxing CH_2Cl_2 (40 °C).

Under the stoichiometric conditions employed, the complete utilization of the alkene would give the dialkylhaloborane as the reaction product (eq 2). This was confirmed by isolation of the products and their characterization via available methods.

$$2(\text{alkene}) + H_2BX{\cdot}SMe_2 \rightarrow R_2BX{\cdot}SMe_2 \quad (2)$$
$$X = Cl, Br, I$$

Table I. Rate of Reaction of Representative Alkenes with Monohaloborane-Methyl Sulfide Complexes[a]

reagent	alkene	solvent	temp, °C	time, h	alkene reacted, %
$H_2BCl{\cdot}SMe_2$	1-octene	Et_2O	0	1	89
				2	91
				4	96
			25	1	95
				2	99
		pentane	0	2	87
				5	95
			25	2	98
		CH_2Cl_2	25	1	98
				1.5	99
	cis-3-octene	Et_2O	0	1	79
				3	87
				6	96
			25	1	94
				2	99
		pentane	0	2	63
				5	76
			25	1	97
				2	99
		CH_2Cl_2	25	1	98
				2	100
$H_2BBr{\cdot}SMe_2$	1-octene	CH_2Cl_2	25	0.25	98
				1	>99
	cis-3-octene	CH_2Cl_2	25	1	96
				2	99
$H_2BI{\cdot}SMe_2$	1-octene	CH_2Cl_2	25	1	40
				2	74
				4	98
				6	100
			40	0.5	96
				1	98
				1.5	100
	cis-3-octene	CH_2Cl_2	25	1	31
				5	78
				7	90
				10	100
			40	0.5	90
				1	94
				1.5	98
				2	100

[a] All reaction mixtures were 1.0 M in $H_2BX{\cdot}SMe_2$ and 2.0 M in alkene.

Directive Effects in the Hydroboration of Alkenes. Monochloroborane etherate (MCBE) hydroborates alkenes with a high degree of regioselectivity.[3] Therefore, it was of interest to determine directive effects in the hydroboration of representative alkenes with $H_2BX{\cdot}SMe_2$. Such information is also helpful for the utilization of R_2BX and their derivatives obtained by this route. The method of investigation followed is that described earlier for MCBE.[3] The results are summarized in Table II, along with those reported earlier for MCBE[3] and $H_3B{\cdot}THF$.[10]

For the unsubstituted terminal alkenes, such as 1-hexene and styrene, $H_2BX{\cdot}SMe_2$ reagents exhibit directive effects similar to those observed for MCBE, more powerful than those of $H_3B{\cdot}THF$. In the case of trisubstituted alkenes,

(8) H. C. Brown and N. Ravindran, *Inorg. Chem.*, **16**, 2938 (1977).
(9) K. Kinberger and W. Siebert, *Z. Naturforsch., B*, **30**, 55 (1975).
(10) (a) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 4708 (1960); (b) H. C. Brown, "Hydroboration", W. A. Benjamin, New York, N.Y., 1962.

Table II. Directive Effects in the Hydroboration of Alkenes with Monohaloborane-Methyl Sulfide Complexes[a]

alkene	isomeric alcohols	relative yields of products				
		$H_2BCl\cdot SMe_2$[b]	$H_2BBr\cdot SMe_2$[c]	$H_2BI\cdot SMe_2$[d]	$H_2BCl\cdot OEt_2$[e]	$H_3B\cdot THF$[f]
1-hexene	1-hexanol	99.2	99.6	>99.5	>99.5	94
	2-hexanol	0.8	0.4	<0.5	<0.5	6
styrene	2-phenylethanol	93	96	96	96	81
	1-phenylethanol	7	4	4	4	19
2-methyl-1-butene	2-methyl-1-butanol	99.9			99.9	99
	2-methyl-2-butanol	0.1			0.1	1
2-methyl-1-pentene	2-methyl-1-pentanol		98			
	2-methyl-2-pentanol		2			
norbornene	*exo*-2-norbornanol	>99.5			>99.8	99
	endo-2-norbornanol	<0.5			<0.2	1
cis-2-pentene	2-pentanol		63		58	55
	3-pentanol		37		42	44
2-methyl-2-butene	3-methyl-2-butanol	99.5	97		99.7	98
	2-methyl-2-butanol	0.5	3		0.3	2
1-methylcyclopentene	*trans*-2-methylcyclopentanol	99.5	97.5	>99.7	>99.8	98.5
	1-methylcyclopentanol	0.5	2.5	<0.3	<0.2	1.5
	cis-2-methylcyclopentanol	0	0	0	0	0
α-methylstyrene	2-phenyl-1-propanol	>99.9			100	100
	2-phenyl-2-propanol	<0.1			0	0

[a] Total yields were 95 ± 4%. [b] Reactions were carried out in pentane at 25 °C. [c] Reaction in CH_2Cl_2 at 25 °C. [d] Reaction in CH_2Cl_2 under reflux. [e] Taken from ref 3. [f] Taken from ref 10.

such as 2-methyl-1-pentene, 2-methyl-2-butene, and 1-methylcyclopentene, MCBS still exhibits directive effects similar to those of the etherate. However, MBBS gives significantly greater amounts of the tertiary derivatives, even greater than those given by borane–tetrahydrofuran. The relative amount of the minor product formed is still negligible, so far as the purity of the major isomer is concerned from a synthetic point of view. Although we have not further investigated this anomaly in the case of MBBS, we believe it might be suggestive of a different mechanism for the hydroboration with MBBS, as compared to hydroboration with other borane reagents. The directive effects of MIBS studied in the case of 1-octene, styrene, and 1-methylcyclopentene indicate that it resembles MCBS and MCBE more closely than MBBS.

Synthesis and Isolation of Dialkylhaloboranes. The initial products in the reaction of alkenes with $H_2BX\cdot SMe_2$ are the methyl sulfide addition compounds of the corresponding haloboranes (eq 2). In the case of the dialkylchloroborane–methyl sulfide adducts, dissociation to free dialkylchloroborane occurs in the course of their distillation under reduced pressure. Thus, free R_2BCl is easily obtained by the hydroboration of alkenes with MCBS, followed by removal of the solvent and isolation of the product by vacuum distillation. However, pure R_2BBr can be obtained by a similar procedure only in the case of products from hindered alkenes, such as *cis*-2-butene and isobutylene. In other cases, with relatively unhindered R groups, pure dialkylbromoboranes free from methyl sulfide can be obtained by adding 1 mol equiv of boron tribromide to the product prior to distillation (eq 3). $BBr_3\cdot SMe_2$ is

$$R_2BBr\cdot SMe_2 + BBr_3 \rightarrow R_2BBr + BBr_3\cdot SMe_2\downarrow \quad (3)$$

a solid, insoluble in CH_2Cl_2. Following addition of BBr_3, the solvent is removed and pure R_2BBr is recovered by distillation under low pressure, without the need for prior separation of $BBr_3\cdot SMe_2$.

Di-*n*-hexyliodoborane and dicyclopentyliodoborane obtained via the hydroboration of the corresponding olefins, followed by distillation under reduced pressure, contain only 13 and 9% of the SMe_2 complexes, respectively. However, distillation following the addition of 1 mol equiv of BI_3 affords the pure dialkyliodoboranes free from SMe_2.

Methanolysis of Dialkylhaloboranes. The dialkylhaloboranes easily undergo methanolysis to afford the corresponding methyl dialkylborinates. Thus, the dialkylchloroborane–methyl sulfides are methanolyzed simply by adding methanol, and the methyl borinates are isolated by vacuum distillation of the reaction mixtures (eq 4). In the case of $R_2BBr\cdot SMe_2$ and $R_2BI\cdot SMe_2$ the

$$R_2BCl\cdot SMe_2 + MeOH \rightarrow R_2BOMe + HCl + SMe_2 \quad (4)$$

reaction with methanol also results in the formation of the methyl borinates, but HBr and HI produced in the reaction form strong complexes with SMe_2. This causes difficulties in the isolation of pure R_2BOMe by distillation. The problem is easily overcome by using 1 mol equiv of sodium methoxide in an excess of methanol (eq 5). Simple vacuum distillation then gives pure R_2BOMe.

$$R_2BX\cdot SMe_2 + NaOMe \xrightarrow{MeOH} R_2BOMe + NaX\downarrow + SMe_2 \quad (5)$$

A number of dialkylchloroboranes, dialkylbromoboranes, dialkyliodoboranes, and methyl dialkylborinates were synthesized by using these new reagents and were isolated in pure form. They are listed in Table III.

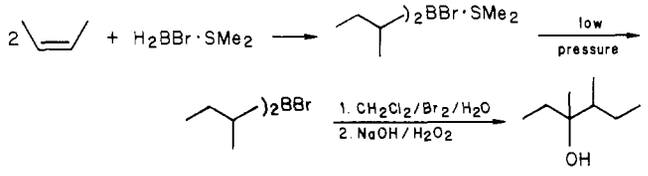
Synthetic Applications of Dialkylboron Derivatives. Since the monohaloborane–methyl sulfide adducts can be easily prepared in high purity and stored at room temperature without deterioration over a long period of time, these provide for the first time a very convenient general method for the synthesis of dialkylboron derivatives. Various dialkylboron derivatives have been shown to be valuable synthetic intermediates. For example, secondary dialkylboronic acids are converted into tertiary alcohols by free radical bromination,[5] and R_2BOR' derivatives in general are transformed into ketones by the DCME reaction.[6] In order to demonstrate the usefulness of the representative reagent MBBS for organic synthesis, we directly converted, without isolation, a few typical dialkylboron derivatives obtained by hydroboration with MBBS into the corresponding tertiary alcohols and ketones. Thus, di-*sec*-butylbromoborane, obtained by the hydroboration of *cis*-2-butene with MBBS, was directly converted into 3,4-dimethyl-3-hexanol in 86% yield by treatment in CH_2Cl_2 with bromine and water, followed by oxidation with alkaline hydrogen peroxide (Scheme I).

Table III. Synthesis of Dialkylboron Derivatives by the Hydroboration of Alkenes with Monohaloborane-Methyl Sulfide Complexes

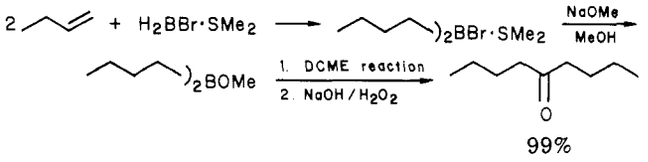
dialkylboron derivatives	reagent	yield,[a] %	bp, °C (mmHg)
di-*n*-butylchloroborane	MCBS	85	68–70 (19)
diisobutylchloroborane	MCBS	84	78–80 (62)
dicyclopentylchloroborane	MCBS	81	69–70 (1.2)
di-*n*-butylbromoborane[b]	MBBS	85	59–60 (6)
di-*sec*-butylbromoborane	MBBS	84	50–52 (6)
diisobutylbromoborane	MBBS	78	49–50 (6)
di-*n*-hexyliodoborane	MIBS	85	112–114 (0.5)
dicyclopentyliodoborane[c]	MIBS	86	109–110 (3.0)
methyl di-*n*-butylborinate	MCBS	93[d]	
methyl di-*sec*-butylborinate	MCBS	89[d]	
methyl diisobutylborinate	MCBS	93[d]	
methyl dicyclopentylborinate	MCBS	89	82–84 (2)
methyl di-*n*-butylborinate	MBBS	85	58–60 (6)
methyl dicyclopentylborinate	MIBS	82	90–92 (3)

[a] Isolated yields. [b] Distillation over 1 mol of BBr_3. [c] Distillation over 1 mol of BI_3. [d] GC yield.

Scheme I



Scheme II



99%

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

Di-*n*-butylbromoborane–methyl sulfide, obtained from 1-butene and MBBS, was directly converted into 5-nonanone in 99% yield, by first treating with methanolic sodium methoxide and removal of excess methanol, followed by the DCME reaction[6] of the resulting borinate ester (Scheme II).

Thus, monohaloborane–methyl sulfide adducts not only represent a class of stable, yet highly regioselective bifunctional hydroborating agents, but they also provide, for the first time, a simple general method for the preparation of dialkylhaloboranes. These can be readily converted into other dialkylboron derivatives which find application as useful intermediates in organic synthesis.

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 storing over type 3-Å molecular sieves without further purification. Ether, pentane, and dichloromethane were dried over type 5-Å molecular sieves. The hydrocarbons used as internal standards for GC analyses and all the gaseous alkenes used were obtained from Phillips Petroleum Co. and were labeled >99% pure. The liquid alkenes used for these studies were commercial products of the highest purity available. Their refractive indices and spectral characteristics were checked before use. Whenever necessary, the commercial samples of olefins were purified by distillation over $LiAlH_4$. In all cases, satisfactory purity was ensured.

The special experimental techniques used in handling air- and moisture-sensitive materials are described elsewhere.[11]

Gas Chromatographic Analyses. Most of the reactions were monitored by gas chromatography. GC analyses were carried out on a Varian 1400 series temperature-programmed gas chromatograph equipped with a flame ionization detector. All the GC yields were determined by utilizing a suitable internal standard and authentic synthetic mixtures. The following columns were generally used: 5% SE-30 on Aeropack-30, 5 ft × 0.125 in., 2 ft × 0.125 in.; 30% adiponitrile on firebrick, 3 ft × 0.125 in.; 5% Carbowax 20M on Varaport, 14 ft × 0.125 in. The special precautions recommended for the GC analyses of organoboranes[12] were scrupulously followed whenever such compounds were analyzed.

Syntheses of MCBS, MBBS, and MIBS. The syntheses, characterization, and stabilities of these reagents have been described in detail elsewhere.[8,9] Considerable quantities of the reagents were prepared following these procedures. MIBS was prepared from BMS and iodine.[9]

General Procedure for the Determination of the Rate of Reaction of Alkenes. The general procedure was to add 5 mmol of the neat reagent to 10 mmol of alkene taken in sufficient quantity of the solvent containing a known quantity of a saturated hydrocarbon (generally 5 mmol of *n*-decane to serve as internal standard for GC analyses), so that the concentrations were 1 M in the reagent and 2 M in the alkene. The reaction mixture was stirred at 0 °C (ice bath), at 25 °C (room temperature), or at 40 °C (refluxing CH_2Cl_2), as described, by using a magnetic stirrer. Aliquots of the reaction mixtures were withdrawn at specific intervals and quenched in ice–water mixture in a small vial. The acidic materials in the mixture were destroyed with aqueous NaOH at 0 °C. The organic materials in the vial were extracted into pentane or ether and analyzed by GC for the amount of unreacted alkene. From the amount of alkene remaining, the extent of the reaction was calculated. The detailed procedure for the determination of the rate of reaction of 1-octene is described as a representative example.

Rate of Reaction of 1-Octene (2.0 M) with MCBS (1.0 M) in Ether at 0 and 25 °C. A dry 100-mL round-bottom 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 an ice bath and 1.9 mL of ether was injected into the flask by using a hypodermic syringe, followed by 1.57 mL of 1-octene (10 mmol) and 0.974 mL of *n*-decane (5 mmol). The mixture was stirred, and 0.58 mL of MCBS (5 mmol) was injected into the flask all at once. Stirring was continued keeping the flask in the ice bath for reaction at 0 °C. For reaction at 25 °C, the ice bath was removed immediately after adding the MCBS. The total volume of the mixture was 5 mL (2 M in alkene and 1 M in MCBS). At definite intervals of time, 0.5-mL aliquots were withdrawn and analyzed for residual 1-octene as described in the general procedure. From these data the percent reaction was calculated.

The reaction of MBBS with 1-octene was also followed in the same manner except that 0.55 mL of MBBS (5 mmol) and 1.9 mL of CH_2Cl_2 were used in place of MCBS and ether, respectively. The experiment was repeated with other alkenes. In the case of MIBS, the reactants were mixed in CH_2Cl_2 at 25 °C and then maintained under reflux.

Directive Effects in the Hydroboration of 1-Hexene with MCBS. The same experimental setup as above was used. The flask was charged with 1.5 mL of pentane, 1.26 mL of 1-hexene (10 mmol), and 1.63 mL of *n*-octane (10 mmol). The mixture was cooled to 0 °C and 0.58 mL of MCBS (5 mmol) was added and stirred at room temperature for 2 h to complete the hydroboration. The dihexylchloroborane formed in the reaction was oxidized by adding 6 mL of 3 N aqueous NaOH and 2 mL of 30% H_2O_2, followed by 10 mL of 95% ethanol as cosolvent. After 1 h of stirring at 25 °C, the oxidation was completed by warming the

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mixture to 50 °C and stirring for 1 h. The organic layer was then analyzed by GC for the amounts of 1-hexanol and 2-hexanol formed in the reaction by using the Carbowax-20M column. The total yield of alcohols was 97%, of which 99.2% was 1-hexanol and 0.8% was 2-hexanol. The reactions in CH_2Cl_2 were carried out similarly. The results were comparable. The experiment was repeated for other representative alkenes listed in Table II, and the alcohols produced following oxidation were determined.

Directive Effects in the Hydroboration of 1-Hexene with MBBS in CH_2Cl_2 at 25 °C. The experimental setup and procedure were the same as above, except that ether was substituted by CH_2Cl_2 and 0.55 mL of MBBS (5 mmol) was used. Otherwise the procedure was the same. Hexanol was formed in 98% yield, of which 99.6% was 1-hexanol and 0.4% was 2-hexanol. The directive effects were established for other olefins in the same way.

Directive Effects in the Hydroboration with MIBS. The same experimental setup was used to react 0.53 mL of MIBS (5 mmol) with 10 mmol of 1-hexene in refluxing CH_2Cl_2. After 2 h the mixture was oxidized and analyzed by GC.

The same procedure was followed to determine directive effects in the hydroboration of styrene and 1-methylcyclopentene with MIBS.

Synthesis of Dialkylchloroboranes and Methyl Dialkylborinates via Hydroboration of Alkenes with MCBS. The syntheses of dicyclopentylchloroborane and methyl dicyclopentylborinate are described as typical procedures. A clean dry 600-mL round-bottom flask, fitted with a side arm capped with a silicone rubber septum, a magnetic stirring bar, and a connecting tube attached to a mercury bubbler, was cooled in an ice bath and charged with 90 mL of pentane or ether. Cyclopentene (18.5 mL, 210 mmol) was added, followed by 11.6 mL of MCBS (100 mmol). The mixture was stirred for 2 h at 25 °C. The solvent was then removed by using a water aspirator. Distillation provided 14.9 g of pure dicyclopentylchloroborane, bp 69–70 °C (1.2 mmHg), a yield of 81%.

Methyl dicyclopentylborinate was synthesized as follows. The above procedure was followed for hydroboration. After 2 h of reaction at 25 °C, 8.11 mL of methanol (200 mmol) was added and stirred at 25 °C for 15 min. The solvent, excess methanol, and HCl formed by methanolysis of dicyclopentylchloroborane were removed under vacuum by using a water aspirator. Methyl dicyclopentylborinate, 16.0 g (89% yield), was obtained by distillation at 82–84 °C (2 mmHg).

Synthesis of Di-*sec*-butylbromoborane by the Hydroboration of *cis*-2-Butene with MBBS. A 100-mL round-bottom flask set up as in the above experiment was charged with 45 mL of CH_2Cl_2 and 5.5 mL of MBBS (50 mmol). The flask was cooled in an ice bath. While the mixture was stirred, 6.5 g (115 mmol, 15% excess) of *cis*-2-butene was passed into the flask from a cylinder through the rubber septum by using a syringe needle. The mixture was then stirred for 1 h at 25 °C. The solvent was removed with a water aspirator. Then 8.6 g (84% yield) of di-*sec*-butylbromoborane was isolated by distillation at 50–52 °C (6 mmHg). The same procedure was used for other hindered olefins. In the case of liquid alkenes, only the stoichiometric amount of alkene need be used.

Synthesis of Di-*n*-butylbromoborane by the Hydroboration of 1-Butene with MBBS. The experimental setup was the same as above, with 6.5 g of 1-butene used in place of *cis*-2-butene. After the hydroboration had been completed by stirring the mixture for 1 h at 25 °C, the flask was cooled in an ice bath and 4.75 mL of liquid BBr_3 (50 mmol) was added and the mixture stirred for 1 h at 25 °C. The solvent was then removed with a water aspirator (at this time solid $BBr_3{\cdot}SMe_2$ starts to separate). Di-*n*-butylbromoborane, 8.7 g (85% yield), was distilled at 59–60 °C (5 mmHg) without allowing the heating bath temperature to rise above 100 °C ($BBr_3{\cdot}SMe_2$ melts at 106 °C). No difficulty was encountered because of the presence of solid $BBr_3{\cdot}SMe_2$ in the flask during distillation. The same procedure was used in the case of other unhindered alkenes.

Synthesis of Methyl Di-*n*-butylborinate by the Hydroboration of 1-Butene with MBBS. The above procedure was followed. After the hydroboration was complete, the mixture was cooled in an ice bath and 55 mmol of NaOMe in 15 mL of methanol was added slowly. The mixture was stirred for 1 h at 25 °C. The solvent was then removed and the methyl di-*n*-butylborinate was distilled at 58–60 °C (6.0 mmHg) without prior separation of solid NaBr. The yield was 85%.

Synthesis of 3,4-Dimethyl-3-hexanol via Hydroboration with MBBS. A 100-mL flask was set up as in the above experiments and 10 mL of CH_2Cl_2 was added, followed by 1.1 mL of MBBS (10 mmol). The mixture was cooled in an ice bath and 25 mmol of *cis*-2-butene was passed in while stirring. Stirring was continued for 1 h at 25 °C. The solvent and SMe_2 were removed by using a water aspirator and then cooled to 0 °C, followed by the addition of 11 mL of CH_2Cl_2, 6 mL of water, and 0.65 mL of bromine (12.5 mmol). The reaction mixture was stirred under laboratory light for 20 min at 25 °C by which time the bromine color had disappeared. After the solution was cooled to 0 °C, 10 mL of 6 N NaOH was added; the mixture was then stirred for 15 min, 12 mL of EtOH and 3 mL of 30% H_2O_2 were then added, and stirring was continued at 25 °C for 30 min, followed by heating at 55–58 °C for 1 h. After the reaction mixture had cooled to room temperature, 12 mL of ether was added, and the aqueous phase was saturated with NaCl. The ether layer was analyzed by GC using n-$C_{11}H_{24}$ as the internal standard on a Carbowax-20M column. The 3,4-dimethyl-3-hexanol was formed at 86% yield.

Similarly 20 mmol of 2-methyl-2-butene was hydroborated with 10 mmol of MBBS and converted into 2,3,4,5-tetramethyl-3-hexanol in 84% yield by the same procedure.

Synthesis of 5-Nonanone via Hydroboration of 1-Butene with MBBS. Into a flask containing 10 mmol of MBBS in CH_2Cl_2 was passed 25 mmol of 1-butene. After the hydroboration was complete, the mixture was cooled to 0 °C and 10.5 mmol of $NaOCH_3$ in 25 mL of CH_3OH was slowly added. The mixture was stirred at 0 °C for 30 min. The solvent and methanol were removed with a water aspirator at 25 °C. The mixture was again cooled in an ice bath and 10 mL of THF was added, followed by 1.0 mL of 1,1-dichloromethyl methyl ether (DCME, 1.306 g, 11 mmol), followed by the slow addition of 11.2 mL of 1.8 M Et_3COLi in hexane (20 mmol). The mixture was stirred at 25 °C for 30 min. Then 1 g of NaOH dissolved in 12 mL of EtOH (containing the minimum amount of water to dissolve the NaOH) was added to the reaction flask after cooling to 0 °C. Then 3 mL of 30% H_2O_2 was added dropwise. The mixture was maintained at 50–60 °C for 1 h. The aqueous layer was saturated with NaCl. The organic phase was analyzed by GC for 5-nonanone after 10 mmol of dodecane was added as the internal standard. 5-Nonanone was formed in 99% yield.

Synthesis of Dicyclopentyliodoborane and Methyl Dicyclopentylborinate from MIBS. The same experimental setup described for the preparation of dicyclopentylchloroborane was employed except that a reflux condenser was used in this case. To a solution of 8.8 mL (100 mmol) of cyclopentene in 40 mL of CH_2Cl_2 was added 5.3 mL (50 mmol) of MIBS at room temperature. The reaction mixture was refluxed for 2 h. The solvent was pumped off and the product distilled under reduced pressure. Dicyclopentyliodoborane, 12.4 g (88% yield), was obtained, bp 109–111 °C (3 mmHg). This product contained 9% of the SMe_2 complex.

In order to obtain dicyclopentyliodoborane free from SMe_2, we carried out the hydroboration in the same manner, but 50 mmol of BI_3 was added prior to distillation. Pure dicyclopentyliodoborane was obtained in 86% yield.

For the preparation of methyl dicyclopentylborinate, hydroboration was carried out as described above. To the reaction mixture at room temperature was added 12.5 mL of a 4 N solution of NaOMe in MeOH with stirring. Solvent and excess methanol were pumped off. Distillation under reduced pressure provided 7.4 g of methyl dicyclopentylborinate, bp 90–92 °C (3 mmHg), a yield of 82%.

Registry No. $H_2BCl{\cdot}SMe_2$, 63348-81-2; $H_2BBr{\cdot}SMe_2$, 55652-52-3; $H_2BI{\cdot}SMe_2$, 55652-50-1; 1-octene, 111-66-0; *cis*-3-octene, 14850-22-7; 1-hexene, 592-41-6; styrene, 100-42-5; 2-methyl-1-butene, 563-46-2; 2-methyl-1-pentene, 763-29-1; norbornene, 498-66-8; *cis*-2-pentene, 627-20-3; 2-methyl-2-butene, 513-35-9; 1-methylcyclopentene, 693-89-0; 1-hexanol, 111-27-3; 2-phenylethanol, 60-12-8; 2-methyl-1-butanol, 137-32-6; 2-methyl-1-pentanol, 105-30-6; *exo*-2-norbornanol, 497-37-0; 2-pentanol, 6032-29-7; 3-pentanol, 584-02-1; 2-methyl-2-butanol, 75-85-4; *trans*-2-methylcyclopentanol, 25144-04-1; α-methylstyrene,

98-83-9; 2-phenyl-1-propanol, 1123-85-9; dibutylchloroborane, 1730-69-4; diisobutylchloroborane, 13317-64-1; dicyclopentylchloroborane, 36140-18-8; dibutylbromoborane, 5674-70-4; di-*sec*-butylbromoborane, 13317-63-0; diisobutylbromoborane, 13317-59-4; dihexyliodoborane, 70116-83-5; dicyclopentyliodoborane, 70116-84-6; methyl dibutylborinate, 2344-21-0; methyl di-*sec*-butylborinate, 32705-45-6; methyl diisobutylborinate, 17832-17-6; methyl dicyclopentylborinate, 36140-24-6; cyclopentene, 142-29-0; *cis*-2-butene, 590-18-1; 3,4-dimethyl-3-hexanol, 19550-08-4; 2,3,4,5-tetramethyl-3-hexanol, 36633-44-0; 1-butene, 106-98-9; 5-nonanone, 502-56-7.

Hydroboration. 53. Cyclic Hydroboration of 1,5-Cyclooctadiene with Monohaloborane Complexes. A Simple, Convenient Synthesis of *B*-Halo-9-borabicyclo[3.3.1]nonanes[1]

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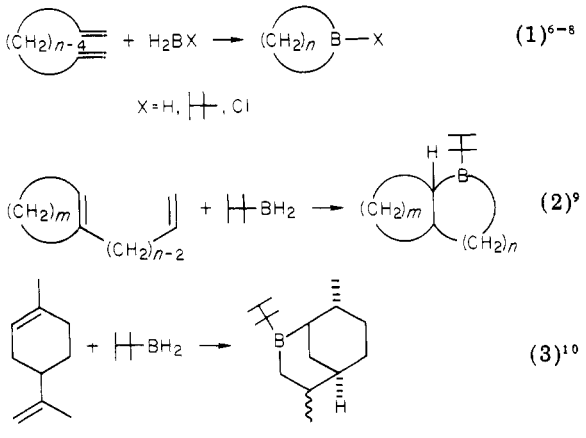
Received December 18, 1978

The hydroboration of 1,5-cyclooctadiene with stable methyl sulfide complexes of monochloro-, monobromo-, and monoiodoboranes ($H_2BX{\cdot}SMe_2$) gives a mixture of *B*-halo-9-borabicyclo[3.3.1]nonane (*B*-X-9-BBN) and its [4.2.1] isomer. The thermodynamically less stable [4.2.1] isomer predominates in the mixture. This can be readily converted to the more stable isomer *B*-X-9-BBN by gentle heating. The methyl sulfide complexes are isolated as stable crystalline solids. Distillation, following the addition of 1 equiv of the respective boron trihalide, provides *B*-X-9-BBN free from SMe_2. These compounds have been characterized by physical and chemical means. They exhibit promise as synthetic intermediates.

Cyclic hydroboration of dienes and polyenes with a variety of hydroborating agents has become increasingly important during the past few years.[3-5] Such reactions provide a valuable route to organoborane heterocycles (eq 1-3).[6-10] The hydroboration of dienes can lead to boraheterocycles or polymers depending upon the hydroborating agent and the reaction conditions employed. Monosubstituted borane reagents have definite advantages over borane itself in the cyclic hydroboration of dienes, since they give rise to much simpler products.[5] Therefore we examined some of the newly developed monosubstituted borane reagents, viz., monohaloborane complexes, for their utility as cyclic hydroborating agents.



Monochloroborane etherate ($H_2BCl{\cdot}OEt_2$, MCBE, **1**) proved to be a versatile reagent for the synthesis of 1-boracycloalkanes via cyclic hydroboration of α,ω-acyclic dienes.[8] Recently, stable methyl sulfide adducts of monochloroborane ($H_2BCl{\cdot}SMe_2$, MCBS, **2a**),[11] monobromoborane ($H_2BBr{\cdot}SMe_2$, MBBS, **2b**),[11] and monoiodoborane ($H_2BI{\cdot}SMe_2$, MIBS, **2c**)[12] were prepared and characterized. They are more stable and more convenient than **1** as hydroborating agents and have provided the first general synthesis of dialkylhaloboranes.[13,14] Therefore, it was felt desirable to explore the usefulness of these reagents for the cyclic hydroboration of representative dienes. Since the hydroboration of 1,5-cyclooctadiene (COD) has been previously studied with tetraethyldiborane ($Et_4B_2H_2$),[15] borane-tetrahydrofuran ($BH_3{\cdot}THF$),[16] thexylborane (⊢BH_2),[7] and borane-methyl sulfide ($BH_3{\cdot}SMe_2$),[17] it appeared ideal for a study of the cyclic hydroboration characteristics of the monohaloborane complexes.

Results and Discussion

Hydroboration of COD with $BH_3{\cdot}THF$ proceeds in a cyclic fashion forming a mixture of two isomeric bicyclic boron compounds, 9-borabicyclo[3.3.1]nonane (1,5 adduct) and its [4.2.1] isomer (1,4 adduct) (eq 4).[16] The relative amounts of these isomers vary with the hydroborating agent used. The monohaloborane complexes also provide a mixture of the two isomers, although the isomer distribution is quite different from those realized with borane itself.

Hydroboration with Monochloroborane Etherate (1). This reagent hydroborates COD cleanly in ethyl ether at 0 °C (eq 5). Following the removal of the solvent,

(1) Partly presented at the Joint Central-Great Lakes Regional Meeting of the American Chemical Society, May 24-26, Indianapolis, Ind., 1978.
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