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Review

HALOBORANES AND THEIR ALKYL DERIVATIVES *

HERBERT C. BROWN * and SURENDRA U. KULKARNI
Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907 (U.S.A.)

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Contents

1. Introduction

1.1. Historical developments

The study of boron halides was initiated almost 170 years ago when Gay-Lussac and Thenard first isolated the ammonia-boron trifluoride complex ($H_3N \cdot BF_3$) [1]. Since then, an enormous amount of work has been reported, especially during the past few decades. Obviously, the use of boron halides in a variety of chemical reactions has greatly encouraged explorations with these compounds. The chemistry of boron halides has been thoroughly reviewed by Massey [2].

The formation of partially hydrogenated boron chloride was first observed [3] by Schlesinger and Burg in 1931 (eq. 1).

* Dedicated to Prof. R.C. Mehrotra on the occasion of his sixtieth birthday (February 16th, 1982).

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$$2\ BCl_3 + 5\ H_2 \xrightarrow[\text{discharge}]{\text{electric}} B_2H_5Cl + 5\ HCl \quad (1)$$

However, the resulting monochlorodiborane was highly unstable, readily disproportionating into diborane and boron trichloride (eq. 2).

$$6\ B_2H_5Cl \rightarrow 5\ B_2H_6 + 2\ BCl_3 \quad (2)$$

Only by applying great experimental skill was Burg able to isolate and characterize monochlorodiborane [4].

Practical methods for the preparation and utilization of various haloboranes have been developed during the search for new hydroborating agents. Hydroboration of alkenes and alkynes with diborane or borane complexes provides a variety of organoboranes [5—8]. However, the demand for more selective reagents has been steadily increasing. Partially alkylated borane derivatives have become important as new hydroborating agents with enhanced regioselectivity and functional group tolerance. However, the desirability of a substituted borane reagent with more easily replaceable blocking groups led to the development of heterosubstituted boranes.

The alkoxy-substituted boranes, such as $ROBH_2$ and $(RO)_2BH$, are either unstable toward disproportionation, or inert toward hydroboration of alkenes and alkynes. However, catecholborane is one diheterosubstituted borane which can hydroborate unsaturated organic compounds, although under relatively harsh conditions [9]. Recent developments in the area of halogen-substituted borane derivatives (haloboranes) have revolutionized organoboron chemistry. As a result of extensive studies on the preparation and applications of haloboranes, it is now possible to obtain boron compounds containing only one or two alkyl groups. The halogen atoms on boron in haloboranes serve as blocking groups, thus permitting the formation of mono- or dialkylated boranes selectively. Besides, the presence of one or two halogen atoms influences the Lewis acidities of haloboranes so that the reagents differ considerably in their reactivities and directive effects during hydroboration.

Consequently, the haloboranes occupy an important position in the spectrum of hydroborating agents. They react readily with alkenes and alkynes, providing a highly convenient general route for the preparation of alkyl- and alkenylhaloboranes, which can be conveniently converted to the corresponding borinic or boronic acids and esters [5]. Since each of these classes of organoboranes undergo many useful transformations, the synthetic potential of the hydroboration reaction is significantly expanded by haloboranes.

1.2. Scope of this review

The chemistry of boron halides has been comparatively well worked out [2]. However, the partially hydrogenated boron halides (haloboranes) are relatively new. In this review we wish to summarize the preparation, properties and important applications of haloboranes and their alkyl derivatives.

The synthesis of organohaloboranes has been reviewed by Niedenzu [10]. Besides, organohaloboranes are discussed in a wider context of organoboron chemistry in various reviews and monographs [11—19]. However, recent developments and the increasing importance of these reagents in organic synthesis justify a more detailed discussion.

1.3. Nomenclature

The American Chemical Society has formulated rules for the nomenclature of boron compounds [20].

Organohaloboranes may be named as the derivatives of borane (BH_3), as the derivatives of boron trihalide (BX_3), as the acid halide of boron acid, or as the boryl-substituted alkanes. In heterocyclic rings, boron halides may be named as the derivatives of boracycloalkanes or borabicycloalkanes. For the acyclic compounds, the borane nomenclature is preferred. All of these forms can be found in the current literature.

2. Preparation of haloboranes

2.1. Gas-phase reactions

Haloboranes were synthesized in the gas phase by the reaction of boron trihalides with hydrogen [3,21—30] or of diborane with hydrogen halides [21] (eq. 3,4).

$$BX_3 + H_2 \xrightarrow[\text{or electric discharge}]{550\text{—}950^\circ C} HBX_2 + HX \qquad (3)$$

X = Cl, Br

$$2B_2H_6 + 6HCl \underset{\text{high press.}}{\overset{\text{room temp.}}{\rightleftharpoons}} B_2H_5Cl + HBCl_2 + BCl_3 + 6H_2 \qquad (4)$$

Facile hydride—halide exchange between diborane and boron trichloride was observed at room temperature [31,32]. The reaction of diborane with boron trifluoride proceeds at high temperatures [33,34] (eq. 5).

$$B_2H_6 + 4\ BF_3 \overset{200^\circ C}{\rightleftharpoons} 6\ HBF_2 \qquad (5)$$

For other, less significant methods, the reader is referred to a recent review [19].

Due to the inconvenience in preparation and to the instability of free haloboranes, only a few attempts to use these compounds as hydroborating agents in the gas phase have been made [32]. Fortunately, haloboranes can be stabilized by complexation with electron donors, such as amines, phosphines, ethers and sulfides [19]. The complexes of haloboranes with amines are poor hydroborating and reducing agents [35]. On the other hand, the complexes with phosphines have not been applied as hydroborating agents. However, ethers and sulfides proved to be very useful as complexing agents, both for the preparation and for the reactions of haloboranes.

2.2. Ether complexes

In the presence of ethers, such as dimethyl ether, diethyl ether, diglyme, tetrahydrofuran, and tetrahydropyran, diborane reacts readily with boron trichloride at room temperature to form chloroborane etherates [36—39] (eq. 6,7).

$$B_2H_6 + BCl_3 + 3\ R_2O \rightarrow 3\ H_2BCl \cdot OR_2 \qquad (6)$$

$$B_2H_6 + 4\ BCl_3 + 6\ R_2O \rightarrow 6\ HBCl_2 \cdot OR_2 \qquad (7)$$

A convenient version involves the use of alkali metal borohydrides [36,40—42] (eq. 8—10).

$$MBH_4 + BCl_3 + 2\ R_2O \rightarrow 2\ H_2BCl \cdot OR_2 + MCl \downarrow \quad (8)$$

$$MBH_4 + 3\ BCl_3 + 4\ R_2O \rightarrow 4\ HBCl_2 \cdot OR_2 + MCl \downarrow \quad (9)$$

$$LiBH_4 + BCl_3 \xrightarrow[0°C]{Et_2O} 2\ H_2BCl \cdot OEt_2 + LiCl \downarrow \quad (10)$$

Alternatively, the reaction of borane with hydrogen chloride provides the desired chloroborane [41,43] (eq. 11,12).

$$BH_3 \cdot THF + 2\ HCl \xrightarrow{THF} HBCl_2 \cdot THF + 2\ H_2 \quad (11)$$

$$BH_3 \cdot THF + HCl \xrightarrow{THF} H_2BCl \cdot THF + H_2 \quad (12)$$

The most useful preparative method for the synthesis of chloroborane etherate seems to be the reaction of lithium borohydride with boron trichloride [40,42]. The products are readily obtained by simply mixing the ether solutions of the reagents. Lithium chloride can be separated by decantation. Attempts to prepare other haloboranes in ethereal solutions did not meet with success [39]. The solutions of boron trifluoride and borane in THF do not react, whereas solvent cleavage was observed in the preparation of bromoboranes.

2.3. Dimethyl sulfide complexes

A facile redistribution between borane dimethyl sulfide ($BH_3 \cdot SMe_2$, BMS) and boron trihalide-dimethyl sulfide ($BX_3 \cdot SMe_2$) was observed recently [44,45] (eq. 13,14).

$$2\ BH_3 \cdot SMe_2 + BX_3 \cdot SMe_2 \rightarrow 3\ H_2BX \cdot SMe_2 \quad (13)$$

$$BH_3 \cdot SMe_2 + 2\ BX_3 \cdot SMe_2 \rightarrow 3\ HBX_2 \cdot SMe_2 \quad (14)$$

X = Cl, Br

No such exchange reaction was observed between BMS and boron trifluoride [44]. The haloborane-dimethyl sulfide complexes were also prepared by the action of halogens or hydrogen halides on BMS [45] (eq. 15,16).

$$2\ BH_3 \cdot SMe_2 + X_2 \xrightarrow{CS_2} 2\ H_2BX \cdot SMe_2 + H_2 \quad (15)$$

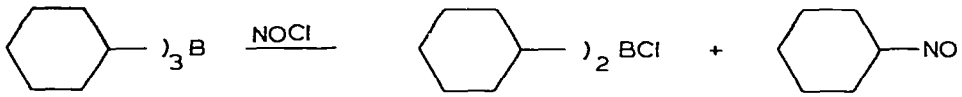
$$BH_3 \cdot SMe_2 + HX \xrightarrow{CS_2} H_2BX \cdot SMe_2 + H_2 \quad (16)$$

X = Br, I

3. Preparation of alkylhaloboranes

3.1. Early methods

Various methods have been employed for the preparation of alkylhaloboranes involving the reaction of trialkylboranes with a variety of reagents. The reaction of nitrosyl chloride [46], antimony trifluoride [47,48], halogens [49,50] and hydrogen halides [49,51,52] with trialkylboranes provided the corresponding dialkylhaloboranes (eq. 17—21).



(17)

$$(n\text{-}Bu)_3B \xrightarrow[135-180^\circ C]{SbF_3} (n\text{-}Bu)_2BF \quad (18)$$

$$R_3B \xrightarrow[100-200^\circ C]{HX} R_2BX + RH \quad (19)$$

X = Cl, Br, I

$$(n\text{-}Pr)_3B \xrightarrow[155-165^\circ C]{I_2} (n\text{-}Pr)_2BI + n\text{-}PrI \quad (20)$$

$$(n\text{-}Bu)_3B \xrightarrow{Br_2} (n\text{-}Bu)_2BBr + n\text{-}BuBr \quad (21)$$

The borate and boronate esters have been converted to the corresponding haloboranes by treatment with phosphorus pentachloride [53,54] (eq. 22,23).

$$PhB(OBu)_2 + 2\ PCl_5 \rightarrow PhBCl_2 + 2\ POCl_3 + 2\ BuCl \quad (22)$$

$$(n\text{-}BuO)_3B + PCl_5 \rightarrow (n\text{-}BuO)_2BCl + POCl_3 + n\text{-}BuCl \quad (23)$$

Recently, we have reported the preparation of dialkylhaloboranes from the corresponding borinate esters [55] (eq. 24).

$$R_2BOMe \xrightarrow{X_2, HX, BX_3} R_2BX \quad (24)$$

Direct redistribution between trialkylboranes and boron halides also provides the alkylhaloboranes [56] (eq. 25).

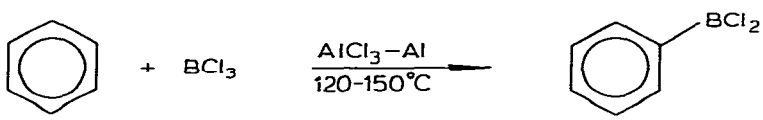
$$R_3B + 2\ BX_3 \xrightarrow{\Delta} 3\ RBX_2 \quad (25)$$

The halides of organohaloboranes can be exchanged with boron trihalide, aluminum halide and even alkali metal halides [57,58] (eq. 26,27).

$$Cl_2C{=}CCl{-}BBr_2 \xrightarrow[CCl_4]{AlCl_3} Cl_2C{=}CCl{-}BCl_2 \quad (26)$$

$$PhBCl_2 + NaF \xrightarrow{200-600^\circ C} Ph_2BCl + PhBF_2 \quad (27)$$

Friedel-Crafts-type boronation of benzene can also provide phenylhaloboranes [59–61] (eq. 28).



(28)

Recently, the conversion of dialkylboranes into the corresponding haloboranes has been successfully carried out using halogens, hydrogen halides and boron halides [55] (eq. 29).

$$R_2BH \xrightarrow{X_2, HX, BX_3} R_2BX \quad (29)$$

One of the most extensively employed method, followed prior to the applica-

tion of the hydroboration technique, for the preparation of alkylhaloboranes consists of the use of heavy metal derivatives [62—65] (eq. 30—33).

$$(CH_2{=}CH{-})_2Hg + BX_3 \rightarrow CH_2{=}CHBX_2 \quad (30)$$

$$ArHgX + BX_3 \rightarrow ArBX_2 \quad (31)$$

X = Cl, Br

$$Ph_3Sb + BCl_3 \rightarrow PhBCl_2 \quad (32)$$

$$(CH_2{=}CH{-})_4Sn + BBr_3 + Hg \rightarrow CH_2{=}CHBBr_2 \quad (33)$$

It should be noted that saturated alkyl groups other than cyclopropyl cannot be used in these reactions. However, due to the commercial availability of many organic derivatives of heavy metals, and simple preparation for many others, this method is very useful in the preparation of vinyl-, aryl-, and cyclopropyl haloboranes.

Finally, the addition of diboron tetrachlorides to alkenes represents a convenient method for the preparation of vicinal diboryl derivatives [66] (eq. 34).

$$Me_3CCH{=}CH_2 + B_2X_4 \rightarrow Me_3C\underset{BX_2}{\underset{|}{C}}H\text{——}\underset{BX_2}{\underset{|}{C}}H_2 \quad (34)$$

The chemistry of diboron tetrahalides has been extensively reviewed [11,13,67].

3.2. Hydroboration methods

Since the reaction of diborane with alkenes and alkynes is rapid and tolerant of a wide variety of functional groups, the most attractive route to the organohaloboranes should be the hydroboration of unsaturated organic compounds with mono- or di-haloboranes. The first reports on the hydroboration of alkenes with haloboranes were not encouraging. The reaction of ethylene with dichloroborane pyranate resulted in the formation of organoborane, presumably triethylborane [36]. Lynds and Stern obtained dichloroalkylboranes from the reaction of dichloroborane with propene and isobutene in the gas phase [68].

Zweifel [43] and Pasto [39] studied the hydroboration of alkenes with mono- and di-chloroboranes in THF. From the rate, stoichiometry and analysis of the methanolysis products, it was concluded that the reaction with monochloroborane proceeds to the monoalkylation stage. However, careful examination revealed that the reaction was not clean [40]. On account of low reactivity of chloroboranes in THF, hydroboration in this solvent has little synthetic potential. The low reactivity is attributed to strong complexation of the chloroboranes with THF.

3.2.1. Hydroboration with monohaloboranes

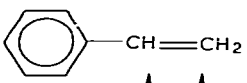
The hydroboration of alkenes with monochloroborane in a less basic solvent, such as diethyl ether and diglyme [40,69], revealed the quantitative formation of dialkylchloroboranes (eq. 35).

$$2\ RCH{=}CH_2 + \underset{(MCBE)}{H_2BCl \cdot OEt_2} \xrightarrow[0^\circ C]{Et_2O} (RCH_2CH_2)_2BCl \quad (35)$$

This reaction represents the first general synthesis of dialkylhaloboranes and their derivatives under mild conditions [40].

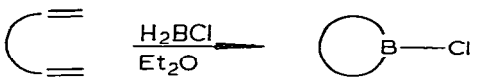
Recently monohaloborane-dimethyl sulfide complexes, $H_2BCl \cdot SMe_2$ (MCBS), $H_2BBr \cdot SMe_2$ (MBBS) and $H_2BI \cdot SMe_2$ (MIBS), were shown to possess several advantages over the etherate [70]. These are liquids, stable at room temperature under nitrogen, available in highly concentrated form and soluble in various organic solvents (CH_2Cl_2, $CHCl_3$, Et_2O, pentane). These reagents hydroborate alkenes readily with high regio- and stereo-selectivities. An unusually powerful directive effect in the hydroboration of representative alkenes with monohaloboranes is shown in Scheme 1.

SCHEME 1

	RCH=CH$_2$		$(CH_3)_2C$=CHCH$_3$			
$H_3B \cdot THF$	6	94	2	98	19	81
$H_2BCl \cdot OEt_2$	05	99 5	03	99 7	4	96
$H_2BCl \cdot SMe_2$	08	99 2	05	99 5	7	93
$H_2BBr \cdot SMe_2$	0.4	99 6	3	97	4	96
$H_2BI \cdot SMe_2$	0.5	99 5	–	–	4	96

As a result of powerful directive effects in hydroboration, dialkylhaloboranes of high isomeric purities are obtained in high yields (Table 1). Consequently, the hydroboration of alkenes with monohaloborane-dimethyl sulfide complexes provides a direct, general and highly convenient route to dialkylhaloboranes.

Since the monohaloboranes are bifunctional hydroborating agents, they serve as versatile reagents for the cyclic hydroboration of dienes. A systematic study of the cyclic hydroboration of α,ω-dienes with MCBE has provided a number of *B*-chloroboracyclanes [71] (eq. 36).



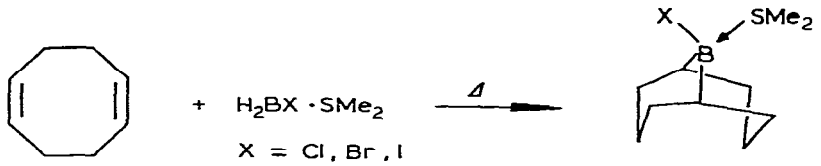
(36)

Cyclic [72] and mixed dienes [73] also afford the corresponding borabicyclanes in high yields (eq. 37, 38).

TABLE 1

PREPARATION OF DIALKYLHALOBORANES VIA HYDROBORATION

Dialkylboron derivatives	Reagent	Yield (%)	B.p. (°C (mmHg))
Di-n-butylchloroborane	MCBS	85	68—70(19)
Diisobutylchloroborane	MCBS	84	78—80(62)
Dicyclopentylchloroborane	MCBE	80	68—69(1.0)
Di-n-butylbromoborane	MBBS	85	59—60(6)
Di-sec-butylbromoborane	MBBS	84	50—52(6)
Diisobutylbromoborane	MBBS	78	49—50(6)
Di-n-hexylchloroborane	MCBE	84	74—75(0.3)
Di-n-hexyliodoborane	MIBS	85	112—114(0.5)
Dicyclopentyliodoborane	MIBS	86	109—110(3)



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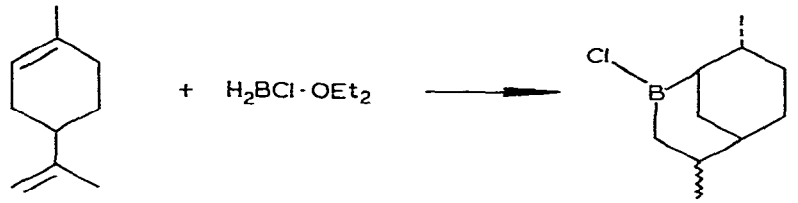
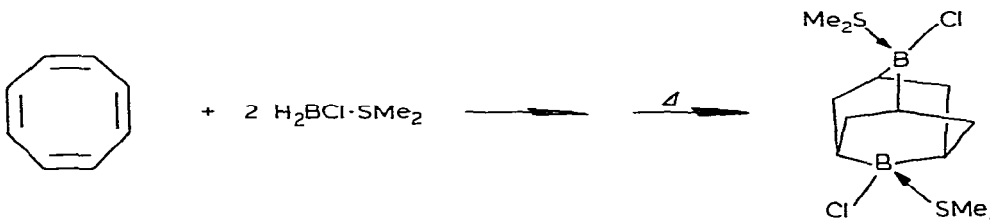


(38)

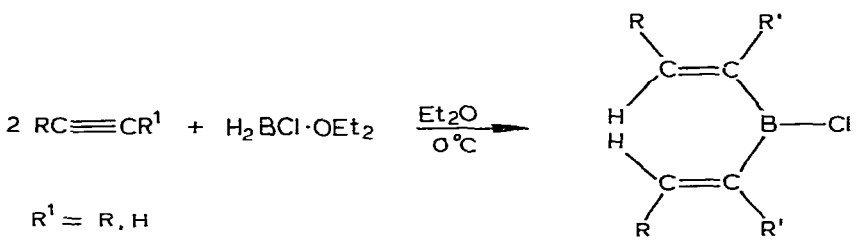
More recently, MCBS was employed for the cyclic dihydroboration of cyclooctatetraene, leading to the first synthesis of 2,6-diboraadamantane system in a simple, two-step reaction [74] (eq. 39).



(39)

These examples clearly demonstrate the importance of cyclic hydroboration with monohaloboranes in the construction of monocyclic, bicyclic and tricyclic organohaloboranes from simple diene precursors.

The dialkenylchloroboranes were prepared by the hydroboration of alkynes with monochloroborane etherate [40] (eq. 40).



(40)

Internal alkynes react in a stoichiometric ratio, whereas in the case of terminal alkynes, 30—40% excess alkynes must be used in order to avoid undesired dihydroboration. The dialkenylchloroboranes are promising synthetic intermediates.

3.2.2. Hydroboration with dihaloboranes

Dichloroborane reacts readily with alkenes in the gas phase [68]. However, the hydroboration of alkenes and alkynes with dichloroborane in THF or ether and with dichloroborane-dimethyl sulfide (DCBS) is slow and is accompanied by disproportionation [39,42,43,75]. Apparently, the strong complexation

TABLE 2

SYNTHESIS OF ALKYLDIHALOBORANES VIA HYDROBORATION

Alkyldihaloboranes	Reagent	Solvent	Yield (%)	B.p. (°C (mmHg))
n-Octyldichloroborane	$HBCl_2 \cdot SMe_2 + BCl_3$	Pentane	85	92—94(19)
n-Octyldichloroborane-dimethyl sulfide	$HBCl_2 \cdot SMe_2$	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	$HBBr_2 \cdot SMe_2 + BBr_3$	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)
n-Hexyldichloroborane	$HBCl_2 \cdot Et_2O + BCl_3$	Pentane	81	102—104(100)
3-Hexyldichloroborane	$HBCl_2 \cdot Et_2O + BCl_3$	Pentane	77	88—90(102)
exo-2-Norbornyldichloroborane	$HBCl_2 \cdot Et_2O + BCl_3$	Pentane	83	95—98(50)
Cyclopentyldichloroborane	$HBCl_2 \cdot Et_2O + BCl_3$	Pentane	79	136—138(751)

with ethers or dimethyl sulfide decreases the reactivities of these reagents significantly. This difficulty was circumvented by the addition of a strong Lewis acid, boron trichloride (eq. 41)

$$HBCl_2 \cdot OEt_2 + \text{alkene} + BCl_3 \xrightarrow{\text{pentane}} RBCl_2 + BCl_3 \cdot OEt_2 \downarrow \quad (41)$$

The solution in pentane contains essentially pure alkyl- or alkenyl-dichloroborane, which can be used directly for further synthetic operations. Alternatively, the products can be isolated by distillation (Table 2).

Surprisingly, dibromoborane- and diiodoborane-dimethyl sulfide complexes ($HBBr_2 \cdot SMe_2$, DBBS; $HBI_2 \cdot SMe_2$, DIBS) can hydroborate alkenes and alkynes directly, even in the absence of the corresponding boron halides [75,76] (eq. 42, 43).

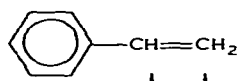
$$\text{alkene} + HBX_2 \cdot SMe_2 \xrightarrow[\Delta]{CH_2Cl_2} RBX_2 \cdot SMe_2 \quad (42)$$

X = Br, I

$$RC{\equiv}CH + HBBr_2 \cdot SMe_2 \rightarrow \begin{matrix} R \\ H \end{matrix}\!\!>\!C{=}C\!<\!\!\begin{matrix} H \\ BBr_2 \cdot SMe_2 \end{matrix} \quad (43)$$

The strong directive effects exhibited by dihaloboranes (except DIBS) in the hydroboration of alkenes (Scheme 2) indicate that alkyldihaloboranes of good isomeric purities can be prepared via hydroboration.

SCHEME 2

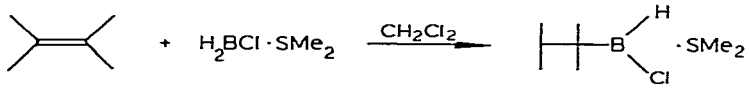
	$RCH{=}CH_2$		$(CH_3)_2C{=}CHCH_3$			
	↑	↑	↑	↑	↑	↑
$HBCl_2 \cdot OEt_2$	0.3	99.7	-	-	4	96
$HBCl_2 \cdot SMe_2$	1	99	3	97	3	97
$HBBr_2 \cdot SMe_2$	0.4	99.6	7	93	4	96
$HBI_2 \cdot SMe_2$	4	96	25	75	3	97
BH_3-THF	6	94	1	99	20	80

An excess (10—40%) of alkyne is required in the hydroboration with dichloroborane etherate ($HBCl_2 \cdot OEt_2$, DCBE) [42] in order to avoid dihydroboration. However, in the case of DBBS, stoichiometric amounts of the reagents can be used. Besides, the alkenyldibromoboranes can be conveniently distilled as stable dimethyl sulfide adducts [76].

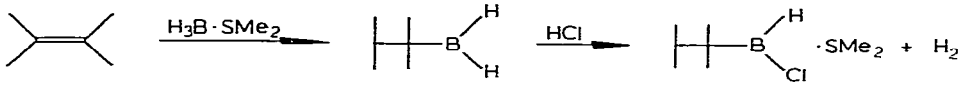
3.2.3. Hydroboration with monoalkylhaloboranes

A new class of hydroborating agents, monoalkylhaloboranes (RBHX), have been developed recently, which hydroborate suitable alkenes to provide the corresponding mixed dialkylhaloboranes. Thexylchloroborane (2,3-dimethyl-2-butylchloroborane) can be prepared either by the hydroboration of 2,3-dimethyl-2-butene with MCBS [77] or by the action of hydrogen chloride on thexylborane [78] (eq. 44, 45).

Another class of monoalkylhaloboranes has been prepared via controlled



(44)



(45)

hydridation of alkyldihaloboranes [79] (eq. 46).

$$RBX_2 \cdot SMe_2 + 1/4\ LiAlH_4 \xrightarrow{Et_2O} RBHX \cdot SMe_2 \quad (46)$$

The availability of monoalkylhaloboranes now permits the first general synthesis of mixed dialkylhaloboranes (eq. 47), which are valuable synthetic intermediates.

$$RBHX \cdot SMe_2 + \text{alkene} \rightarrow RR'BX \quad (47)$$

4. Properties of haloboranes and alkylhaloboranes

As discussed earlier, the THF complexes of mono- and di-chloroboranes are not suitable for hydroboration. The inertness of these reagents is attributed to the strong complexation of chloroboranes with THF. The following sequence of B—O bond strength was established [17].

$$BH_3 \cdot THF < BH_2Cl \cdot THF < BHCl_2 \cdot THF$$

Monochloroborane etherate does hydroborate the alkenes, but the reagent shows limited stability and must be stored at 0° C at which temperature it is stable for several weeks.

Concentration of this solution to obtain the neat reagent leads to disproportionation [40]. In contrast, dichloroborane etherate can be obtained as a neat product by concentrating the ether solution [42]. It is a colorless liquid, m.p. —25 to —30° C, miscible with benzene, carbon tetrachloride, THF, and diethyl ether, but not with pentane. The reagent is not stable over long periods of time, cleaving ether even at 0° C.

The methyl sulfide complexes of monohaloboranes, MCBS, MBBS, MIBS, are colorless liquids. Dibromoborane complex (DBBS) is a solid, m.p. 30—35° C, but DCBS and DIBS are liquids. All of these complexes are stable at room temperature when stored under an inert atmosphere. They are soluble in dichloromethane and carbon disulfide, but not in pentane. In ether solvents, they either disproportionate or cleave the ethers. Other properties, especially the ^1H and ^{11}B NMR chemical shifts, are listed in Table 3.

The proton NMR spectra [44] of the haloborane-dimethyl sulfide complexes indicate that the increase in downfield shift corresponds to the order of increase in acidities of Lewis acids: $BF_3 < BCl_3 < BBr_3$ [80]. This is supported by the extensive NMR studies of Bula and Hartman [81]. As we move along this series, an increasingly strong S → B coordinate bond is formed, as reflected in the three-bond coupling between the methyl protons and the boron atom [45,81]. This also explains the fast exchange of SMe_2 between the added SMe_2 and $F_3B \cdot SMe_2$

TABLE 3

PHYSICAL AND SPECTROSCOPIC DATA ON BORON TRIHALIDE-DIMETHYL SULFIDE AND HALOBORANE-DIMETHYL SULFIDE

Compound	M.p. (°C)	Molarity [b] (neat) (*M*)	^{1}H NMR chemical shifts [f] (δ, ppm from TMS)				^{11}B NMR (δ, ppm from $BF_3 \cdot OEt_2$) [f]		
			CCl_4 [a]	CD_2Cl_2	CS_2	C_6H_6 [b]	CCl_4 [b]	CH_2Cl_2	CS_2
$S(CH_3)_2$	–	–	2.06	2.14 [c] 2.13 [d,e]	–	1.78	–	–	–
$H_3B \cdot S(CH_3)_2$	–	10.0	2.20	–	2.06	–	–19.4	–	–19.7(q, 105)
$F_3B \cdot S(CH_3)_2$	–	–	2.21	2.42 [c]	–	1.53	2.3	–15.2	–
$Cl_3B \cdot S(CH_3)_2$	87 [b] 90 [e]	–	2.51	2.58 [c] 2.60 [d,e]	–	1.47	–7.5	–11.2	–
$Br_3B \cdot S(CH_3)_2$	107 [b] 108 [e]	–	2.56	2.64(Br) [c] 2.70(Br) [d,e]	2.76(Br)	1.51(q, 3.0)	–11.0		–11.3(Br)
$I_3B \cdot S(CH_3)_2$	137 [e]	–	–	2.65(q, 3.8) [c] 2.76(q, 3.7) [d,e]	2.84(q, 3.5)	–	–	–87.0	–68.5(Sept. 4)
$H_2BCl \cdot S(CH_3)_2$	–	9.0	2.34	–	–	–	–6.7(t, 131)	–	–
$HBCl_2 \cdot S(CH_3)_2$	–	8.1	2.42	–	–	–	2.2(d, 167)	–	–
$H_2BBr \cdot S(CH_3)_2$	–	9.1	2.38	–	2.53	–	–10.5(t, 132)	–	–10.9(t, 131)
$HBBr_2 \cdot S(CH_3)_2$	30–35 [b]	7.8	2.48	–	2.67	–	–7.3(d, 160)	–	–7.8(d, 162)
$H_2BI \cdot S(CH_3)_2$	–	–	2.38	–	2.56 2.45	–	–19.6 [a] (t, 135)	–	–20.5(t, 105) –20.3(t, 140)
$HBI_2 \cdot S(CH_3)_2$	–	–	2.50	–	2.76 2.53	–	–33.9 [a] (d, 160)	–	–34.4(d, 160) –34.7(d, 160)

[a] Observed by this investigator. [b] Taken from ref. 44. [c] D.E. Young, G.E. McAchran and S.G. Shore, J. Amer. Chem. Soc., 88 (1966) 4390. [d] M. Schmidt and H.D. Block, Chem. Ber., 103 (1970) 3075. [e] Taken from ref. 45. [f] All are singlets unless stated otherwise. The multiplicity and *J*(B—H) or *J*(B—S—C—H) (in Hz) are given in the parentheses. Positive signs represent chemical shifts downfield from the standard.

or $Cl_3B \cdot SMe_2$, but the absence of such exchange in the case of $Br_3B \cdot SMe_2$. The latter complex is strong enough to prevent the exchange at room temperature.

In benzene solution, these addition compounds exhibit dimethyl sulfide shifts opposite to those in CCl_4 solution (Table 3). The appearance of $Br_3B \cdot SMe_2$ as a quartet while methyl protons in other complexes are singlets is attributable to the fact that $Br_3B \cdot SMe_2$ is a relatively stronger complex. It has been reported that such a quartet exists in the NMR of this complex in dichloromethane solution at lower temperature (<14°C) [81]. The appearance of a clear quartet at 35°C (NMR probe temperature) in benzene solution, but not in CCl_4 nor CH_2Cl_2 solution, suggests that the complex is much more stabilized in benzene than in the latter solvents.

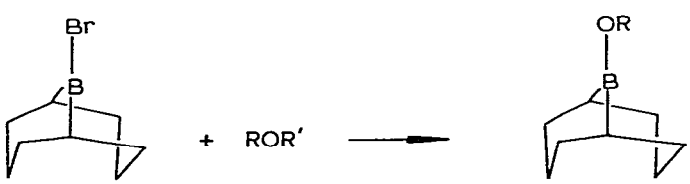
An interesting feature of haloborane-dimethyl sulfide addition compounds is the enormously different behavior of the chloroborane and bromoborane derivatives in their exchange of dimethyl sulfide molecules between themselves and the added free SMe_2. The chloroborane derivatives exchange their SMe_2 molecules very readily, whereas, the bromoborane derivatives do not undergo such exchange. Thus, in the ^1H NMR spectrum of a CCl_4 solution of a mixture of $H_3B \cdot SMe_2$, $H_2BCl \cdot SMe_2$ and $HBCl_2 \cdot SMe_2$, the methyl proton signals appear as a single peak. Upon addition of a small amount of SMe_2 to this mixture, the peak position is shifted upfield slightly. Still only a single peak is observed in the ^1H NMR spectrum. On the other hand, the CCl_4 solution of a mixture of $H_3B \cdot SMe_2$, $H_2BBr \cdot SMe_2$ and $HBBr_2 \cdot SMe_2$ gives ^1H NMR signals attributable to each individual species, establishing the absence of a rapid exchange of the methyl sulfide molecules. The addition of a small amount of SMe_2 to this mixture causes the $H_3B \cdot SMe_2$ peak to broaden, but has no effect on the signals due to the other species, showing that only the $H_3B \cdot SMe_2$ is exchanging with the methyl sulfide molecules, but not the bromoborane derivatives [44].

Like the haloboranes, their alkyl derivatives react with water, alcohols, mercaptans, phenols, silanols and alkoxides readily to afford the corresponding derivatives of boron acids (eq. 48,49).

$$R_2BX \xrightarrow{R'OH} R_2BOR' + HX \qquad (48)$$

$$RBX_2 \xrightarrow{2\,H_2O} RB(OH)_2 + 2\,HX \qquad (49)$$

Like boron trihalides [82], alkylhaloboranes cleave ethers, yielding the corresponding boron esters and organic halides [83] (eq. 50).



(50)

With ammonia or primary amines, alkyldihaloboranes give iminoboranes in the presence of a strong reductant [84], and bis-aminoboranes and borazoles in the absence of a reductant [11].

Organohaloboranes undergo replacement of halogen by hydride when treated

with a variety of hydride donors. Thus, lithium aluminum hydride, various borohydrides and alkoxy metal hydrides have been successfully employed for this purpose [85—87] (eq. 51,52).

$$PhBCl_2 \xrightarrow[\text{dioxane}]{LiAlH_4} (PhBH_2)_2 \qquad (51)$$

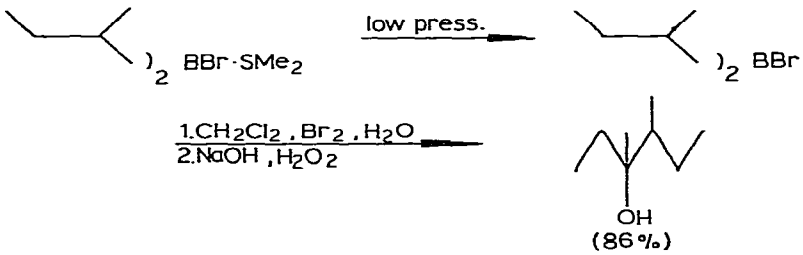
$$R_2BCl \xrightarrow[THF]{K(i\text{-}PrO)_3BH} (R_2BH)_2 \qquad (52)$$

5. Applications

A detailed discussion of the synthetic applications of alkylhaloboranes is beyond the scope of this review. However, a few representative examples will be given in order to illustrate the usefulness of these promising intermediates in organic synthesis.

5.1. Dialkylhaloboranes

Dialkylhaloboranes can be converted into tertiary alcohols by free-radical bromination when the alkyl group is secondary [88] (eq. 53).

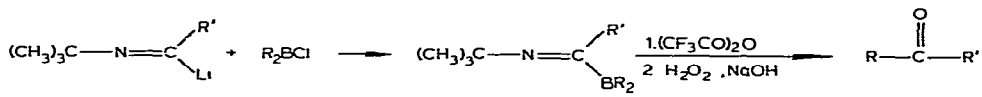


(53)

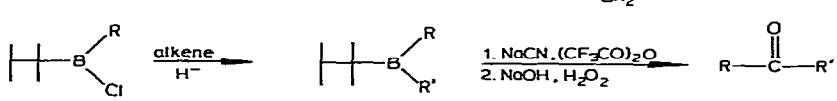
Alcoholysis, followed by treatment with α,α-dichloromethyl methyl ether (DCME), in the presence of lithium triethylcarboxide gives α-chloroboronic esters, which can be readily oxidized to ketones [70] (eq. 54).

$$R_2BX \xrightarrow[MeOH]{NaOMe} R_2BOMe \xrightarrow[2.\ [O]]{1.\ DCME} R{-}\overset{O}{\overset{\|}{C}}{-}R \qquad (54)$$

Unsymmetrical ketones can be synthesized either by the reaction of dialkylchloroboranes with lithium aldimines [89] (eq. 55) via thexyldialkylboranes [90 (eq. 56) or via the DCME reaction of mixed dialkylhaloboranes [79] (eq. 57).



(55)



(56)

(57)

Dialkylchloroboranes react with organic azides to give secondary amines [91] (eq. 58).

$$R_2BCl + R'N_3 \rightarrow RR'NHBClR \xrightarrow{NaOH} \begin{matrix} & H & \\ & | & \\ R & N & R' \end{matrix} \quad (58)$$

Facile homologation is carried out by the reaction between ethyl diazoacetate and dialkylchloroboranes [91] (eq. 59).

$$R_2BCl + N_2CHCOOEt \xrightarrow{-78^\circ C} RCH_2COOEt \quad (59)$$

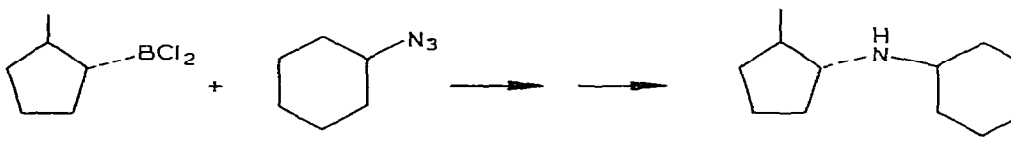
All of these reactions proceed with the retention of configuration of the alkyl group transferred from boron.

A representative dialkylhaloborane, *B*-bromo-9-BBN, proved to be a selective ether cleavage agent [83] (eq. 50).

5.2. Alkyldihaloboranes

The stronger Lewis acidity of alkyldihaloboranes and the presence of only one alkyl group on boron enables these compounds to undergo certain reactions involving initial coordination with an electron donor. Thus, ethyl diazoacetate [92] (eq. 60) and alkyl azide [93] (eq. 61) react with alkyldichloroboranes to provide the corresponding homologated esters and secondary amines, respectively.

(60)



(61)

An important application of alkyldihaloboranes is in the first general preparation of mixed trialkylboranes via stepwise hydridation-hydroboration [79].

5.3. Alkenylhaloboranes

Alkenylhaloboranes undergo many characteristic reactions of vinylboranes, such as protonolysis to alkenes, oxidation to carbonyl compounds, etc.

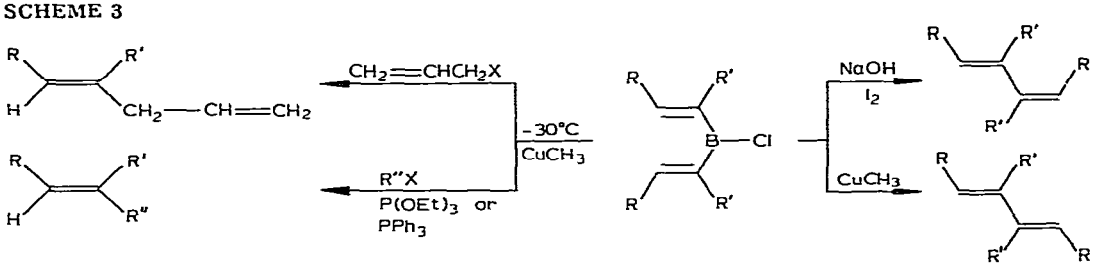
The hydroboration of alkynes with dibromoborane-dimethyl sulfide, followed by hydrolysis and iodination constitutes a one-pot synthesis of (*E*)-1-alkenyl iodides [76] (eq. 62).

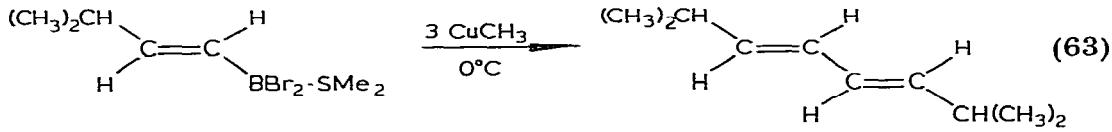
$$n\text{-BuC}{\equiv}\text{CH} \xrightarrow{HBBr_2\cdot SMe_2} \begin{matrix} n\text{-Bu} & & H \\ & C{=}C & \\ H & & BBr_2 \end{matrix} \xrightarrow[I_2]{NaOH} \begin{matrix} n\text{-Bu} & & H \\ & C{=}C & \\ H & & I \end{matrix} \quad (62)$$

Divinylchloroboranes can be transformed to a variety of dienes [40,94,95] and alkenes [95] as shown in Scheme 3.

Recently, a highly promising application of alkenyldibromoborane as a precursor of alkenylcopper compounds was reported [76] (eq. 63).

SCHEME 3





(63)

This modification is a major improvement over the procedure employing dialkenylchloroboranes [94].

Mono- and di-chloroboranes in THF were employed as selective reducing agents for a number of organic functional groups [96]. Dichloroborane in THF rapidly reduces sulfoxides to the corresponding sulfides under mild conditions [97]. Sulfones, amine oxides, esters and chlorides, nitriles and nitro compounds are inert, whereas aldehydes, ketones and amides are reduced slowly under these conditions. Diiodoborane in THF has been successfully employed in the conjugate reduction of α,β-unsaturated ketones into the corresponding saturated ketones [98]. The selective reduction characteristics of other haloborane complexes are yet to be explored. With a wide range of Lewis acidities for mono- and di-haloboranes, they will undoubtedly emerge as a new class of reducing agents possessing variable functional group selectivities. The complexes of chloroboranes with amines were used in the vulcanization of rubber [99,100]

6. Conclusions

During the past few years, haloboranes and their alkyl derivatives have been studied in detail. As a result, we now have available a whole series of mono- and di-haloboranes with chlorine, bromine and iodine atoms attached to boron. Based on the number, size and the electronegativities of these halogen atoms, these haloboranes differ in their Lewis acidities. Consequently, their complexes with ethers, sulfides and amines vary widely in their stabilities and chemical reactivities.

Mono- and di-haloboranes offer great promise as selective reducing agents, but not much effort has been put in this direction thus far. Preliminary studies indicate that they will soon represent a new class of reducing agents with wide-spectrum functional-group selectivities.

The most remarkable application of haloboranes is in the hydroboration of alkenes and alkynes. They provide for the first time general routes for a variety of mono- and di-alkylhaloboranes or alkenylhaloboranes under relatively mild conditions which can tolerate common organic functional groups.

The alkylhaloboranes greatly extend the application of organoboranes in two ways: (1) an increased Lewis acidity of alkylhaloborane facilitates those transformations involving the initial complexation of electron donors and (2) the halogen atoms serve as convenient blocking groups, readily replaceable when needed, permitting the economical utilization of alkyl groups attached to boron.

The synthetic applications of alkyl- and alkenyl-haloboranes are innumerable. We are only beginning to see some of them. One aspect, i.e., the in situ generation of dialkylboranes [87], thus far unavailable via direct hydroboration, has permitted the generalization of the syntheses of *cis*- [101], *trans*- [102], and trisubstituted alkenes [103] and ketones [79,90,104]. Simple routes now available for the conversion of alkenylhaloboranes into other organometallics, such as organocopper compounds, offer great promise for the application of such haloboranes in the synthesis of complex organic molecules.

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