Organoboranes. 29. A Convenient Synthesis of Alkyldibromoboranes and Dialkylbromoboranes via Hydroboration–Redistribution

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Trialkylboranes, obtained via hydroboration of terminal and cyclic alkenes with $BH_3{\cdot}SMe_2$, undergo redistribution with boron tribromide at room temperature under the influence of a catalytic amount (7 mol %) of $BH_3{\cdot}SMe_2$ in *n*-pentane to afford the corresponding alkyldibromoboranes or dialkylbromoboranes, depending upon the stoichiometry, thus providing a convenient method for preparing these valuable derivatives. The reaction of trialkylboranes derived from internal alkenes such as tri-3-hexylborane is much slower. However, these derivatives could be transformed into the corresponding alkyldibromoboranes at 70 °C under neat conditions without significant isomerization. The complete conversion of tri-3-hexylborane into di-3-hexylbromoborane could not be achieved.

The importance of alkyldibromoboranes and dialkylhaloboranes in organic synthesis has been well documented.[1-9] Simple procedures are now available for the synthesis of such valuable derivatives. Mono- and dichloroborane etherates ($BH_2Cl{\cdot}OEt_2$, $BHCl_2{\cdot}OEt_2$), monohaloborane–dimethyl sulfides ($BH_2X{\cdot}SMe_2$) and dihaloborane–dimethyl sulfides ($BHX_2{\cdot}SMe_2$) are the important borane reagents that were developed recently for the synthesis of alkylhaloboranes (eq 1–5).[10-15]

$$BH_2Cl{\cdot}OEt_2 + \text{alkene} \rightarrow R_2BCl \quad (1)$$

$$BHCl_2{\cdot}OEt_2 + \text{alkene} \xrightarrow{BCl_3} RBCl_2 + BCl_3{\cdot}OEt_2 \quad (2)$$

$$BH_2X{\cdot}SMe_2 + \text{alkene} \rightarrow R_2BX{\cdot}SMe_2 \quad (3)$$

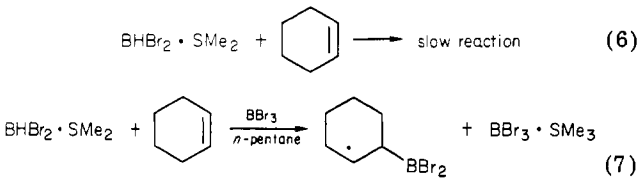
$$X = Cl, Br, I$$

$$BHCl_2{\cdot}SMe_2 + \text{alkene} \xrightarrow{BCl_3} RBCl_2 + BCl_3{\cdot}SMe_2 \quad (4)$$

$$BHX_2{\cdot}SMe_2 + \text{alkene} \rightarrow RBX_2{\cdot}SMe_2 \quad (5)$$

$$X = Br, I$$

Dibromoborane–dimethyl sulfide ($BHBr_2{\cdot}SMe_2$) proves to be a more versatile and useful reagent in organic transformations.[1-4] However, highly hindered alkenes such as cyclohexene react very sluggishly with this reagent (eq 6).[16] Addition of BBr_3 solves this problem, providing cyclohexyldibromoborane in excellent yields (eq 7).[17]



Also, in the case of gaseous alkenes like ethylene, dibromoborane–dimethyl sulfide ($BHBr_2{\cdot}SMe_2$) fails to provide the desired ethyldibromoborane–dimethyl sulfide ($EtBBr_2{\cdot}SMe_2$) (eq 8). This might be attributed to the nonavailability of ethylene to $BHBr_2{\cdot}SMe_2$ because ethylene gas escapes. However, the addition of BBr_3 helps in this case also (eq 9).[17]

$$BHBr_2{\cdot}SMe_2 + H_2C{=}CH_2 \rightarrow \text{slow reaction} \quad (8)$$

$$BHBr_2{\cdot}SMe_2 + H_2C{=}CH_2 \xrightarrow[n\text{-pentane}]{BBr_3} EtBBr_2 + BBr_3{\cdot}SMe_2 \quad (9)$$

The increasing importance of alkyldibromoboranes in organic synthesis[1-4] requires a simple method for the preparation of ethyldibromoborane and cyclohexyldibromoborane, as well as other derivatives not readily accessible by direct hydroboration with the dibromoborane.

Earlier methods for the preparation of alkylhaloboranes involve halogenation of the carbon–boron bond in trialkylboranes by either hydrogen halide or halogen or halogenation of the boron–oxygen bond in trialkylboroxines or alkylboron esters using boron trihalides.[18,19] Alternatively, alkylhaloboranes were obtained by the action of trialkylboranes with boron trihalides at high temperatures.[18,20,21] Zakharkin reported a similar reaction at 125 °C using sodium borohydride as catalyst.[22]

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Table I. Preparation of Alkylbromoboranes via Redistribution of Trialkylboranes and Boron Tribromide

borane (R_3B)	product	yield,[c] %	bp, °C (mm)
triethyl-	ethyldibromoborane–dimethyl sulfide[a]	77	112–114 (15)
	diethylbromoborane–dimethyl sulfide[b]	80	74–76 (80) [lit.[6] 70–72 (75)]
tri-*n*-propyl-	*n*-propyldibromoborane–dimethyl sulfide[a]	83	88–89 (3)
tri-*n*-hexyl-	*n*-hexyldibromoborane[a]	80	69–71 (3) [lit.[14] 56–58 (0.9)]
	di-*n*-hexylbromoborane[b]	81	102–103 (4)
tris(2-methyl-1-pentyl)-	2-methyl-1-pentyldibromoborane[a]	85	60–62 (3.7)
	bis(2-methyl-1-pentyl)bromoborane[b]	81	100–102 (4.5)
tricyclopentyl-	cyclopentyldibromoborane[a]	82	50–52 (2.8)
	dicyclopentylbromoborane[b]	82	104–105 (6)
tricyclohexyl-	cyclohexyldibromoborane[a]	78	70–72 (4)
	dicyclohexylbromoborane[b]	84	122–124 (4)
tri-3-hexyl-	3-hexyldibromoborane[a]	79	60–62 (4.6)

[a] All reactions for the preparation of alkyldibromoboranes were carried out on a 20-mmol (R_3B) scale. [b] All reactions for the preparation of dialkylbromoboranes were carried out on a 30-mmol (R_3B) scale. [c] Yields of isolated products.

Köster and Grassberger have elegantly established that the redistribution of trialkylboranes with boron trihalides, to provide alkyldihaloboranes and dialkylhaloboranes, is strongly catalyzed by tetraalkyldiboranes (eq 10 and 11).[23,24] The redistribution of trialkylboranes with boron trichloride, catalyzed by added diborane, provides a convenient synthetic route to $RBCl_2$ (eq 12).[25]

$$R_3B + 2BX_3 \xrightarrow{(R_2BH)_2} 3RBX_2 \quad (10)$$
$$X = F, Cl, Br$$

$$2R_3B + BX_3 \xrightarrow{(R_2BH)_2} 3R_2BX \quad (11)$$
$$X = F, Cl, Br$$

$$R_3B + 2BCl_3 \xrightarrow{5\%\ BH_3} 3RBCl_2 \quad (12)$$

The requirement of cyclohexyldibromoborane and ethyldibromoborane in our studies led us to explore the Köster procedure for the synthesis of alkylbromoboranes. Consequently, we examined the redistribution of representative trialkylboranes with boron tribromide under the influence of a catalytic amount of $BH_3{\cdot}SMe_2$ (BMS), a more convenient means of introducing catalytic diborane into the reaction mixture.

Results and Discussion

First, we studied the redistribution of tri-*n*-hexylborane with boron tribromide. Tri-*n*-hexylborane [free from solvent THF and SMe_2, obtained by the hydroboration of 1-hexene with $BH_3{\cdot}SMe_2$ (BMS)], reacts readily at room temperature with boron tribromide in *n*-pentane in the presence of 7 mol % $BH_3{\cdot}SMe_2$ (BMS). The product is either *n*-hexyldibromoborane (eq 13) or di-*n*-hexylbromoborane (eq 14), depending upon the amount of boron

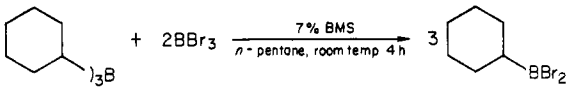
$$(n\text{-Hex})_3B + 2BBr_3 \xrightarrow[n\text{-pentane, room temp 4 h}]{7\%\ BMS} 3(n\text{-Hex})BBr_2 \quad (13)$$

$$2(n\text{-Hex})_3B + BBr_3 \xrightarrow[n\text{-pentane, room temp 4h}]{7\%\ BMS} 3(n\text{-Hex})_2BBr \quad (14)$$

tribromide used in the redistribution reaction. Thus, treatment of 1 molar equiv of tri-*n*-hexylborane, with 2 molar equiv of boron tribromide, affords *n*-hexyldibromoborane in 82% yield. The ^{11}B NMR spectrum showed a clean peak at δ 64, indicative of an alkyldibromoborane. The ^{11}B NMR spectrum of the methanolyzed product showed a clean signal at δ 32, indicative of alkyl boronate esters. Similarly, treatment of tri-*n*-hexylborane with boron tribromide, in a 2:1 molar ratio, affords di-*n*-hexylbromoborane (^{11}B NMR δ 80, after methanolysis, δ 54) in 80% yield.

Alkenes of intermediate steric requirements such a 2-methyl-1-pentene and cyclopentene could be converted under the same conditions into the corresponding alkyldibromoboranes and dialkylbromoboranes in excellent yields (Table I).

More hindered alkenes such as cyclohexene could also be transformed into the corresponding alkyldibromoboranes and dialkylbromoboranes in very high yields (eq 15, 16) (Table I).



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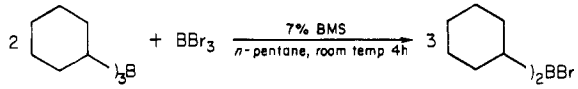

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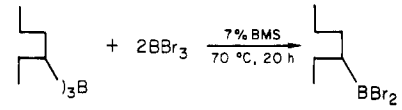
Trialkylboranes derived from gaseous alkenes such as ethylene could be readily converted into the corresponding alkyldibromoborane or dialkylbromoborane, depending upon the molar ratio of the reactants (eq 17, 18). It should

$$Et_3B + 2BBr_3 \xrightarrow[n\text{-pentane, room temp 4 h}]{7\%\ BMS} 3EtBBr_2 \quad (17)$$

$$2Et_3B + BBr_3 \xrightarrow[n\text{-pentane, room temp 4 h}]{7\%\ BMS} 3Et_2BBr \quad (18)$$

be mentioned that the preparation of $EtBBr_2$ by direct hydroboration of the gaseous alkene with $BHBr_2{\cdot}SMe_2$ offers difficulties. Thus, the present procedure surmounts this problem, providing a simple and clean synthesis of $EtBBr_2$.

We did encounter difficulties with the 3-hexyl derivative. Redistribution was very sluggish at room temperature. Attempts at intermediate temperatures such as in refluxing methylene chloride or in refluxing *n*-hexane were unsuccessful. Fortunately, the redistribution proceeded satisfactorily at 70 °C by using the neat reagents, affording 3-hexyldibromoborane in 80% yield (eq 19). No signifi-



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cant isomerization occurred, as evidenced by the formation of >99% pure 3-hexanol in the oxidation of the product by alkaline hydrogen peroxide. It was previously noted that the redistribution of tri-3-hexylborane with boron

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trichloride produces products in which the boron atom has migrated in part from its original position.[25]

Unfortunately, the further formation into di-3-hexylbromoborane was very slow, even at still higher temperatures (85 °C), requiring 48 h for only 30% completion. We did not pursue this redistribution further since di-3-hexylbromoborane can be easily prepared by hydroboration of 3-hexene with $BH_2Br{\cdot}SMe_2$.

Thus the present procedure supplements the direct synthesis of alkyldibromo- and dialkylbromoboranes via hydroboration of alkenes with $BHBr_2{\cdot}SMe_2$ and $BH_2Br{\cdot}SMe_2$. Particularly, this method demonstrates its utility for the synthesis of ethyldibromoborane and cyclohexyldibromoborane, two derivatives which cannot be obtained easily from $BHBr_2{\cdot}SMe_2$. Internal alkenes such as 3-hexene work well for the synthesis of the alkyldibromoboranes but fail to provide the corresponding dialkylbromoboranes. Presently we are exploring the applications of these alkylbromoboranes for organic transformations.

Experimental Section

All glassware used for the experiments were dried in an oven at 140 °C for several hours, assembled hot, and cooled under a stream of nitrogen. The alkenes used for the study were obtained from Aldrich Chemical Co. or Chemical Samples Co. and were purified by distillation over a small quantity of $LiAlH_4$. Triethylborane was obtained from Callery Chemical Co. Reagent grade methanol was used after being stored over 3-Å molecular sieves and *n*-pentane was dried over molecular sieves, type 5 Å. The special experimental techniques used in handling air and moisture sensitive materials are described elsewhere.[26] ^1H NMR and ^{11}B NMR spectra were recorded on Varian T-60 and Varian FT-80A spectrometers, respectively. ^{11}B NMR chemical shifts are with reference to $BF_3{\cdot}OEt_2$ (δ 0), and the resonances upfield from the standard are assigned negative signs. GC analyses were carried out on a Varian 1200 FID gas chromatograph (column 12 ft × $^1/_8$ in. packed with 10% Carbowax 1540 on Chromosorb W 100/120).

Preparation of *n*-Hexyldibromoborane. Tri-*n*-hexylborane (20 mmol) was prepared from 1-hexene and $BH_3{\cdot}SMe_2$ in the usual way.[26] Solvent THF and SMe_2 were removed under reduced pressure. The residual tri-*n*-hexylborane was dissolved in 30 mL of *n*-pentane. Boron tribromide (40 mmol, 3.80 mL) was added, followed by a slow addition of 1.4 mmol of $BH_3{\cdot}SMe_2$ (BMS) in pentane (1.75 mL, 0.8 M) at 0 °C. The reaction mixture was stirred at room temperature for 4 h. ^{11}B NMR of the crude product showed a single peak at δ 64, which is indicative of *n*-hexyldibromoborane. Solvent *n*-pentane was removed, and distillation afforded 12.3 g (80%) of pure *n*-hexyldibromoborane: bp 69–71 °C (3 mm) [lit.[14] 56–58 °C (0.9 mm); ^{11}B NMR ($BF_3{\cdot}OEt_2$) δ 64 ((*n*-Hex)BBr_2). The methanolyzed product showed a single peak at δ 32 ((*n*-Hex)$B(OMe)_2$). Ethyl-, *n*-propyl-, 2-methyl-1-pentyl-, cyclopentyl-, and cyclohexyldibromoboranes were prepared in identical fashion to the above procedure.

Preparation of Di-*n*-hexylbromoborane. Tri-*n*-hexylborane (30 mmol) was treated with boron tribromide (15 mmol, 1.42 mL) under the same conditions as in the preparation of *n*-hexyldibromoborane to afford 9.52 g (81%) of di-*n*-hexylbromoborane: bp 102–103 °C (4 mm); ^{11}B NMR ($BF_3{\cdot}OEt_2$) δ 82 ((*n*-Hex)$_2$BBr). Diethyl-, bis(2-methyl-1-pentyl)-, dicyclopentyl-, and dicyclohexylbromoboranes were prepared in an identical manner.

Preparation of 3-Hexyldibromoborane. To 20 mmol of neat tri-3-hexylborane was added 40 mmol of BBr_3 (3.80 mL) at 0 °C, followed by a slow addition of 0.16 mL of neat $BH_3{\cdot}SMe_2$ (8.8 M). The reaction mixture was stirred at 70 °C for 20 h. Distillation furnished 12.20 g (79%) of 3-hexyldibromoborane: bp 60–62 °C (4.5 mm); ^{11}B NMR ($BF_3{\cdot}OEt_2$) δ 67 ((3-Hex)BBr_2). The methanolyzed product showed a single peak at δ 31, indicative of (3-Hex)$B(OMe)_2$. Oxidation of 3-hexyldibromoborane was carried out in the usual way[26] by using NaOH and H_2O_2. The alcohol obtained was found to be >99% pure 3-hexanol on GC analysis.

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Registry No. $RBBr_2{\cdot}SMe2$ (R = ethyl), 83967-42-4; $R_2BBr{\cdot}SMe2$ (R = ethyl), 86646-22-2; $RBB_2{\cdot}SMe2$ (R = *n*-propyl), 86646-23-3; $RBBr_2$ (R = *n*-hexyl), 64770-03-2; R_2BBr (R = *n*-hexyl), 57476-26-3; $RBBr_2$ (R = 2-methyl-1-pentyl), 72205-96-0; R_2BBr (R = 2-methyl-1-pentyl), 86646-21-1; $RBBr_2$ (R = cyclopentyl), 64770-09-8; R_2BBr (R = cyclopentyl), 57476-09-2; $RBBr_2$ (R = cyclohexyl), 6783-09-1; R_2BBr (R = cyclohexyl), 22086-59-5; $RBBr_2$ (R = 3-hexyl), 64770-05-4; R_3B (R = ethyl), 97-94-9; R_3B (R = *n*-propyl), 1116-61-6; R_3B (R = *n*-hexyl), 1188-92-7; R_3B (R = 2-methyl-1-pentyl), 1188-50-7; R_3B (R = cyclopentyl), 23985-40-2; R_3B (R = cyclohexyl), 1088-01-3; R_3B (R = 3-hexyl), 1883-34-7; BBr_3, 10294-33-4.

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Organoboranes. 30. Convenient Procedures for the Synthesis of Alkyl- and Alkenylboronic Acids and Esters

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Alkyl- and alkenyldibromoborane–dimethyl sulfide complexes, readily obtained by the hydroboration of alkenes and alkynes with dibromoborane–dimethyl sulfide ($HBBr_2{\cdot}SMe_2$), react with water, giving the corresponding boronic acids, and with alcohols and glycols to give the corresponding esters. Various procedures have been developed for the preparation of boronic esters with primary and secondary alcohols, glycols, and tertiary alcohols. Boronic acids react with primary and secondary alcohols reversibly to form the corresponding esters. The equilibrium may be conveniently displaced in favor of ester by carrying out the reaction in pentane, from which the water component separates. This procedure does away with the necessity of azeotrope distillation of a ternary mixture, extensively used previously for the esterification of boronic acids.

Alkyl- and alkenylboronic acids and their esters have found extensive applications in organic synthesis in the last decade.[2-8] Recently, a number of chiral boronic esters have been utilized for the synthesis of optically active

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