Monochloroborane–Methyl Sulfide, $H_2BCl{\cdot}S(CH_3)_2$, and Dichloroborane–Methyl Sulfide, $HBCl_2{\cdot}S(CH_3)_2$, as New Stable Hydroborating Agents with High Regiospecificity

Summary: Monochloroborane-methyl sulfide, $H_2BCl{\cdot}SMe_2$, and dichloroborane–methyl sulfide, $HBCl_2{\cdot}SMe_2$, are new highly stable hydroborating agents with major advantages over the corresponding unstable etherates.

Sir: Monochloroborane–methyl sulfide, $H_2BCl{\cdot}SMe_2$, and dichloroborane–methyl sulfide, $HBCl_2{\cdot}SMe_2$, are readily synthesized by redistribution of $H_3B{\cdot}SMe_2$ with $Cl_3B{\cdot}SMe_2$ in the appropriate ratios (eq 1, 2). The products are stable indefinitely at room temperature. Yet they hydroborate olefins readily with high regiospecificity and provide a valuable advantageous route to the corresponding dialkylboron chlorides, R_2BCl, and monoalkylboron dichlorides, $RBCl_2$, and to the many derivatives into which these may be transformed.

$$2H_3B{\cdot}SMe_2 + Cl_3B{\cdot}SMe_2 \xrightarrow{25\ ^\circ C} 3H_2BCl{\cdot}SMe_2 \quad (1)$$

$$H_3B{\cdot}SMe_2 + 2Cl_3B{\cdot}SMe_2 \xrightarrow{25\ ^\circ C} 3HBCl_2{\cdot}SMe_2 \quad (2)$$

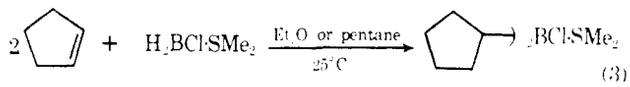
The chloroborane etherates, $H_2BCl{\cdot}OEt_2$ and $HBCl_2{\cdot}OEt_2$, are valuable hydroborating agents, achieving hydroboration with exceptionally high regiospecificity and providing important new routes to the alkylboron chlorides, $RBCl_2$ and R_2BCl.[1,2] The latter derivatives are revealing valuable versatility as intermediates for synthetic applications.[3-8]

Unfortunately, the synthesis of the chloroborane etherates proceeds from lithium borohydride,[1,2] a relatively expensive intermediate. Moreover, the chloroborane etherates must be handled as dilute solutions in ethyl ether. They possess limited stability. They must be freshly prepared and used shortly after their synthesis.

The discovery that borane–methyl sulfide and boron trichloride–methyl sulfide undergo redistribution rapidly at 25 °C[9] led us to undertake the synthesis, characterization, and examination as hydroborating reagents of the products, $H_2BCl{\cdot}SMe_2$ and $HBCl_2{\cdot}SMe_2$ (eq 1, 2). The synthesis proved exceptionally simple—it was necessary only to mix borane–methyl sulfide[10] with boron trichloride–methyl sulfide.[9,11] The neat products appeared to be stable indefinitely, as indicated by NMR observations over long periods of time. Accordingly, we examined their hydroborating characteristics. These proved excellent, achieving all of the valuable transformations previously achieved by the chloroborane etherates.

Thus, $H_2BCl{\cdot}SMe_2$ reacts with olefins rapidly at 25 °C in ether or pentane to give the corresponding dialkylboron chlorides. The reaction is general, as indicated by the quantitative reaction of the representative olefins, 1-hexene, 1-octene, *cis*-3-octene, styrene, 2-methyl-1-butene, 2-methyl-2-butene, 1-methylcyclopentene, and norbornene, in <2 h at 25 °C. The regiospecificity achieved in hydroboration with $H_2BCl{\cdot}SMe_2$ is comparable with that with $H_2BCl{\cdot}OEt_2$, as shown in Table I, where the relative yields of the isomeric alcohols produced in the hydroboration–oxidation of the representative olefins with the two reagents are summarized.

The product of the reaction of olefins with $H_2BCl{\cdot}SMe_2$ is the corresponding dialkylchloroborane–methyl sulfide addition compound, $R_2BCl{\cdot}SMe_2$ (eq 3). Pure R_2BCl is obtained



(3)

free of Me_2S by removal of the reaction solvent followed by distillation under low pressure.[12] The corresponding *B*-alkoxy derivatives are obtained by alcoholysis of the hydroboration

Table I. Isomeric Alcohols from the Hydroboration–Oxidation of Representative Olefins with $H_2BCl{\cdot}SMe_2$ at 25 °C and $H_2BCl{\cdot}OEt_2$ at 0 °C

Olefin	Solvent for $H_2BCl{\cdot}SMe_2$	Isomeric alcohols	Isomeric products, %	
			$H_2BCl{\cdot}SMe_2$[a]	$H_2BCl{\cdot}OEt_2$[b]
1-Hexene	Ether	1-Hexanol	99.2	>99.5
		2-Hexanol	0.8	<0.5
1-Hexene	Pentane	1-Hexanol	99.2	
		2-Hexanol	0.8	
Styrene	Ether	2-Phenylethanol	93	96
		1-Phenylethanol	7	4
Styrene	Pentane	2-Phenylethanol	93	
		1-Phenylethanol	7	
2-Methyl-1-butene	Pentane	2-Methyl-1-butanol	>99.9	>99.9
		2-Methyl-2-butanol	<0.1	<0.1
Norbornene	Pentane	*exo*-2-Norbornanol	>99.5	>99.8
		endo-2-Norbornanol	<0.5	<0.2
2-Methyl-2-butene	Pentane	3-Methyl-2-butanol	>99.5	99.7
		2-Methyl-2-butanol	<0.5	0.3
1-Methylcyclopentene	Pentane	*trans*-2-Methylcyclopentanol	99.5	>99.8
		1-Methylcyclopentanol	0.5	<0.2
		cis-2-Methylcyclopentanol	0	0
α-Methylstyrene	Pentane	2-Phenyl-1-propanol	>99.9	100
		2-Phenyl-2-propanol	<0.1	0

[a] Total yields were 95 ± 4%. [b] Reference 1.

Table II. Syntheses of Alkylboron Derivatives by the Hydroboration of Olefins with $H_2BCl{\cdot}SMe_2$ and $HBCl_2{\cdot}SMe_2$

Dialkylboron derivative	Solvent	Yield, %	Bp, °C (mm)
Methyl di-*n*-butylborinate	Pentane	93[a]	
Methyl di-*sec*-butylborinate	Pentane	89[a]	
Methyl diisobutylborinate	Pentane	93[a]	
Methyl dicyclopentylborinate	Ether	89[b]	
Diisobutylchloroborane	Ether	84[c]	78–80 (62)
Dicyclopentylchloroborane	Pentane	79[c]	69–70 (1.2)
Dicyclopentylchloroborane	Ether	81[c]	69–70 (1.2)
Di-*n*-butylchloroborane	Ether	85[c]	68–70 (19)
n-Octyldichloroborane	Pentane	85[c]	92–94 (19)

[a] GLC yield. [b] Yield determined by ^1H NMR using benzene as the internal standard. [c] Yields by isolation of the product.

mixture followed by distillation (eq 4). The results of the syntheses of the representative dialkylboron derivatives are given in Table II.

$$R_2BCl{\cdot}SMe_2 + R'OH \rightarrow R_2BOR' + Me_2S + HCl \quad (4)$$

The reaction of $HBCl_2{\cdot}SMe_2$ with olefins is slow and incomplete in pentane or ether, similar to the slow reaction of the etherate $HBCl_2{\cdot}OEt_2$.[2] Again, as in the case of the etherate,[2] $HBCl_2{\cdot}SMe_2$ reacts with olefins cleanly and quantitatively at 25 °C in pentane in the presence of 1 mol equiv of BCl_3 to give the corresponding alkyldichloroborane, $RBCl_2$. The $Cl_3B{\cdot}SMe_2$ precipitates from the reaction medium during the reaction (eq 5). The $RBCl_2$ is readily isolated from the reaction mixture by distillation following removal of the solid $Cl_3B{\cdot}SMe_2$ by filtration under nitrogen. *n*-Octyldichloroborane was isolated in 85% yield by this method.

$$\text{olefin} + HBCl_2{\cdot}SMe_2 \xrightarrow[BCl_3]{\text{pentane}} RBCl_2 + Cl_3B{\cdot}SMe_2\downarrow \quad (5)$$

The following experimental procedure is typical. The addition compound, $Cl_3B{\cdot}SMe_2$, mp 86–87 °C, was prepared by adding boron trichloride to an equimolar amount of methyl sulfide. The $H_2BCl{\cdot}SMe_2$ and $HBCl_2{\cdot}SMe_2$ were then prepared by mixing the two reagents, $Cl_3B{\cdot}SMe_2$ and $H_3B{\cdot}SMe_2$,[10] in the stoichiometric ratios (eq 1, 2). Cyclopentene (210 mmol) was dissolved in 90 mL of pentane or ether at 0 °C under nitrogen. While stirring at 0 °C, 100 mmol of $H_2BCl{\cdot}SMe_2$ was slowly added and the stirring continued for 2 h at 25 °C. The solvent was then removed using a water aspirator and pure dicyclopentylchloroborane[12] was obtained by distillation at 69–70 °C (1.2 mm) in 79–81% yield. The methyl dicyclopentylborinate was synthesized in 89% yield by methanolyzing the reaction mixture of cyclopentene and $H_2BCl{\cdot}SMe_2$[13] with 100% excess methanol, followed by removal of the solvent, the excess methanol, and the hydrogen chloride with a water aspirator. The regiospecificity in the hydroboration with $H_2BCl{\cdot}SMe_2$ was established as described earlier for $H_2BCl{\cdot}OEt_2$.[1]

For the synthesis of *n*-octyldichloroborane, 50 mmol of 1-octene was dissolved in 61 mL of pentane and cooled to 0 °C; 25 mL of a 2 M solution of BCl_3 in pentane was added. While the mixture stirred at 0 °C, 50 mmol of $HBCl_2{\cdot}SMe_2$ was slowly added. The mixture was stirred for 2 h at 25 °C. The procedure then follows that previously described for the isolation of the $RBCl_2$ using $HBCl_2{\cdot}OEt_2$. *n*-Octyldichloroborane was isolated in 85% yield.

Although the reactivity and usefulness of $H_2BCl{\cdot}SMe_2$ and $HBCl_2{\cdot}SMe_2$ are comparable with those of the corresponding chloroborane etherates reported previously, these new reagents are far more advantageous and convenient to use, as a consequence of their indefinite stability at room temperature and their availability as neat reagents.

Because of the thermal stability of $H_2BCl{\cdot}SMe_2$ and $HBCl_2{\cdot}SMe_2$, these reagents will surely find their major place in the laboratory along with other valuable hydride reagents. This would greatly facilitate application of the recently discovered many synthetically useful reactions of R_2BCl and $RBCl_2$ and their derivatives.[3-8]

References and Notes

(1) H. C. Brown and N. Ravindran, *J. Am. Chem. Soc.*, **98**, 1785 (1976).
(2) H. C. Brown and N. Ravindran, *J. Am. Chem. Soc.*, **98**, 1798 (1976).
(3) H. C. Brown, M. M. Midland, and A. B. Levy, *J. Am. Chem. Soc.*, **94**, 2114, 3662 (1972); **95**, 2394 (1973).
(4) A. B. Levy and H. C. Brown, *J. Am. Chem. Soc.*, **95**, 4067 (1973).
(5) M. M. Midland and H. C. Brown, *J. Am. Chem. Soc.*, **95**, 4069 (1973).
(6) J. Hooz, J. N. Bridson, J. G. Calzada, H. C. Brown, M. M. Midland, and A. B. Levy, *J. Org. Chem.*, **38**, 2574 (1973).
(7) H. C. Brown and C. F. Lane, *Synthesis*, **303** (1972).
(8) B. A. Carlson and H. C. Brown, *J. Am. Chem. Soc.*, **95**, 6876 (1973).
(9) H. C. Brown and N. Ravindran, *Inorg. Chem.*, in press.
(10) Available from Aldrich-Borane, a subsidiary of the Aldrich Chemical Co., Milwaukee, Wis.
(11) M. Schmidt and H. D. Block, *Chem. Ber.*, **103**, 3705 (1970).
(12) In the case of unhindered R_2BCl, like *n*-Bu_2BCl, the methyl sulfide addition compound breaks up completely upon vacuum distillation only, whereas in hindered cases like *sec*-Bu_2BCl, the Me_2S addition compounds breaks up completely at 25 °C under aspirator vacuum (10–20 mm).
(13) NMR examination of $H_2BCl{\cdot}SMe_2$ reveals the presence of small amounts of $H_3B{\cdot}SMe_2$ and $HBCl_2{\cdot}SMe_2$. Consequently, the maximum yields of ~93% for R_2BCl (Table II) probably correspond to the actual amount of $H_2BCl{\cdot}SMe_2$ present in the reagent. Distillation readily removes the minor components, R_3B and $RBCl_2$.
(14) Postdoctoral research associate on grants provided by G. D. Searle & Co. and the National Science Foundation (GP 6942X and 41169X).

Herbert C. Brown,* N. Ravindran[14]

Richard B. Wetherill Laboratory, Purdue University
West Lafayette, Indiana 47907

Received March 14, 1977

Lithium *B*-Isopinocampheyl-9-borabicyclo[3.3.1]nonyl Hydride. A New Reagent for the Asymmetric Reduction of Ketones with Remarkable Consistency

Summary: Lithium *B*-isopinocampheyl-9-borabicyclo-[3.3.1]nonyl hydride [Li(HB-IPC-9-BBN)], a highly hindered trialkylborohydride containing an asymmetric alkyl group, reduces rapidly and quantitatively a variety of ketones to the corresponding optically active alcohols, consistently enriched in the *R* enantiomer.

Sir: The asymmetric reduction of ketones has been examined with a number of chiral metal hydride complexes.[1] In particular, lithium aluminum hydride complexes with chiral alkaloids (ephedrine, quinine, cinchonine, etc.), chiral amino alcohols [(2*S*,3*R*)-(+)-4-dimethylamino-1,2-diphenyl-3-methyl-2-butanol], and monosaccharides (3-*O*-benzyl-1,2-cyclohexylidene-α-D-glucofuranose) have been recently explored in detail. Unfortunately, such reagents appear not reliable for stereochemical correlations. In the majority of cases, the precise structures of the reducing species are not well defined. Further, both enantiomeric forms of the complexing agent may not be available, thereby limiting the choice of the enantiomer to be synthesized.