runs (0.0011 M) to function as an oxidative scavenger (converting Co(I) to Co(III) as rapidly as formed). In control experiments the rates obtained were shown to be independent of periodate concentration in this range of molality. Furthermore, the approximate rate constants obtained anaerobically[2] (in the absence of periodate) by monitoring the accumulation of cobaloxime anion **3** did not differ significantly. In a similar set of control experiments rates were shown not to be a function of sodium chloride concentration.

Rates (Figures 1 and 2) were determined by monitoring disappearance of absorption due to the (hydroxyalkyl)aquocobaloxime at 430 nm for several half-lives. Pseudo-first-order rate constants were obtained by directly fitting absorbance readings to an exponential decay function by the method of least squares. Replicate runs were routinely made, with derived rate constants agreeing within 5%. Pyridine dependence experiments were carried out by incorporating twice-distilled pyridine in various concentrations into the cobaloxime stock solution immediately prior to the kinetic runs. Tolerances listed in the Results and Discussion sections are standard errors as obtained from nonlinear least-squares curve fitting. For the kinetic deuterium isotope effect determination, the following series of pseudo-first-order rate constants were obtained in rapid succession (0.20 N NaOH): **10**, 0.0184; **14**, 0.0168; **10**, 0.0190; **14**, 0.0185; **10**, 0.0202; **14**, 0.0192; **10**, 0.0201; **14**, 0.0189 (±0.0005) s^{-1}. Kinetic data for other substrates (i.e., for Figures 1 and 2) is recorded in the Ph.D. thesis of C.B.[24]

Registry No. **2**, 15218-81-2; **3**, 53790-02-6; **8a**, 20379-85-5; **8b**, 98065-09-9; **10**, 15218-82-3; **11**, 75716-05-1; **12**, 59598-34-4; **13**, 98065-10-2; **14**, 98065-12-4; **17**, 15228-01-0; **21**, 98065-11-3; CH_3CHO, 75-07-0; *endo*-6-methylnorcamphor, 20569-37-3; *trans*-2-bromocyclohexanol, 2425-33-4; cyclopentene oxide, 285-67-6; acetone, 67-64-1; cyclohexanone, 108-94-1; cyclopentanone, 120-92-3.

(24) Bieniarz, C. Ph.D. Thesis, University of Illinois at Chicago, 1982; *Diss. Abstr. Int. B* **1982**, *43*, 136.

Organoboranes. 42. One-Carbon Homologation of Organoboranes. Synthesis of Homologated Boronic Acids and Esters from Boronic Esters

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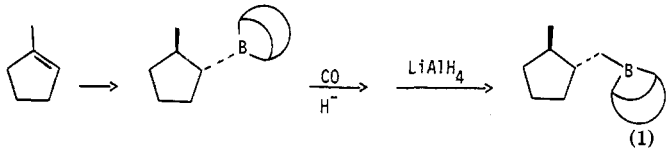
Received March 18, 1985

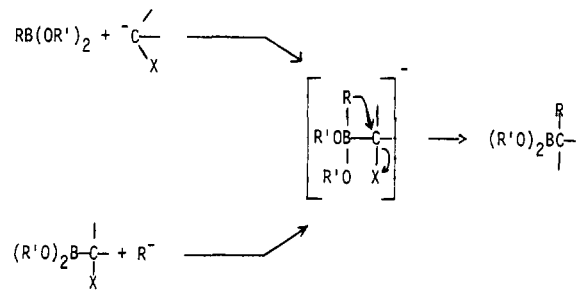
One-carbon-homologated boronic acid and esters were prepared from alkylboronic esters by the reaction with (dichloromethyl)lithium, $LiCHCl_2$, followed by reduction with KIPBH. One-carbon homologation of representative dialkylborinic esters and trialkylboranes was achieved by the reaction with $LiCHCl_2$, followed by trapping the first intermediate, the one alkyl migrated product, with KIPBH at −100 °C. Oxidation of the one-carbon-homologated organoborane intermediates, $RB(OR')_2 \rightarrow RCH_2B(OR')_2$, afforded homologated primary alcohols, RCH_2OH.

The utility of boranes in organic synthesis stems in large part from the high regio- and stereoselectivity of their transformations. Application of this chemistry hinges on the availability of regio- and stereochemically pure organoboranes. As part of an ongoing program in the synthesis of boranes not available via hydroboration,[2] we were interested in a convenient method for the one-carbon homologation of organoboranes. Recently we developed practical methods for extending the alkyl chain via carbonylation of *B*-alkyl-9-borabicyclo[3.3.1]nonane (*B*-alkyl-9-BBN) in the presence of potassium triisopropoxyborohydride (KIPBH), followed by reduction of the intermediate by lithium aluminum hydride[3] (eq 1).



(1)

Scheme I



Unfortunately, there is not available at present a simple procedure to convert the homologated *B*-alkyl-9-BBN into the homologated boronic esters, $RCH_2B(OR')_2$.

Generally, carbanionic reagents bearing potential leaving group(s), such heteroatom substituents as halogen, oxygen, or sulfur, at the α-position, homologate organoboranes. A large number of such reagents have been successfully applied for such transformations[4-6] (eq 2–4).

In many of these reactions, only one of the three alkyl groups of a trialkylborane is utilized. In some cases, the

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(2) (a) Kramer, G. W.; Brown, H. C. *J. Organomet. Chem.* **1974**, *73*, 1. (b) Brown, H. C.; Sinclair, J. A. *Ibid.* **1977**, *131*, 163. (c) Brown, H. C.; Cole, T. E. *Organometallics* **1983**, *2*, 1316.

(3) Brown, H. C.; Ford, T. M.; Hubbard, J. L. *J. Org. Chem.* **1980**, *45*, 4067.

(4) Tufariello, J. J.; Lee, L. T. C. *J. Am. Chem. Soc.* **1966**, *88*, 4757.

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(6) Musker, W. K.; Stevens, R. R. *Tetrahedron Lett.* **1967**, 995.

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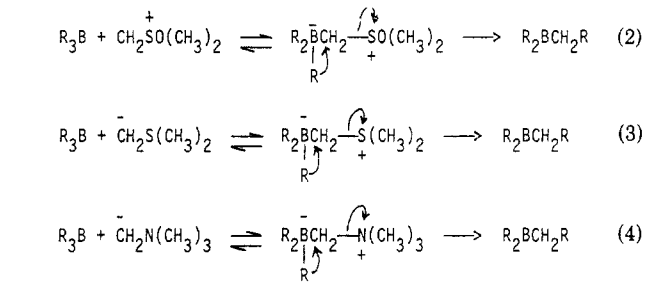
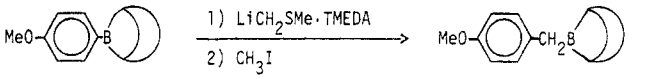


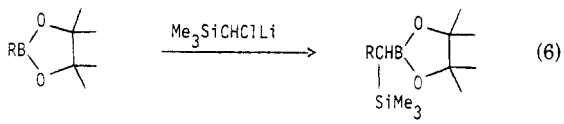
use of *B*-alkyl-9-BBN derivatives circumvents this difficulty[7] (eq 5).



(5)

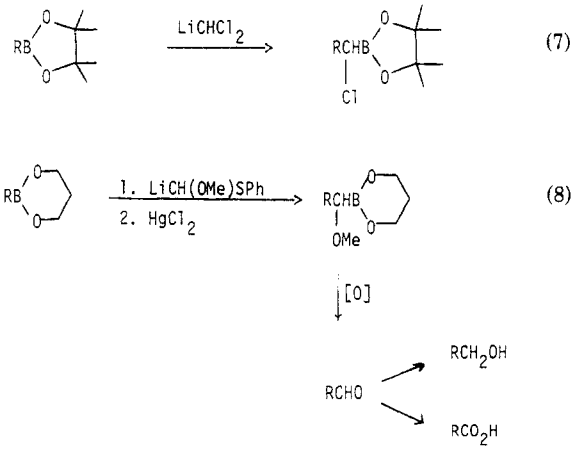
There would be major advantages in developing homologation reactions that could utilize boronic esters with their single organic group as the boron component (Scheme I). In this way those organic groups that are readily formed by the hydroboration reaction can be further incorporated into organic molecules. Unfortunately, the reagents that were used for the one-carbon homologation of trialkylboranes fail to react with boronic esters.

In 1980 Matteson and his co-workers achieved the first successful application of boronic esters in such a transfer reaction (eq 6).[8] Soon afterward he successfully utilized (dichloromethyl)lithium in a similar reaction[9] (eq 7).



(6)

We then discovered that (methoxy(phenylthio)-methyl)lithium also reacts with boronic esters, providing a valuable route to a homologated derivative readily transformed into the aldehyde, methanol, and carboxylic acid derivatives (eq 8).[10]

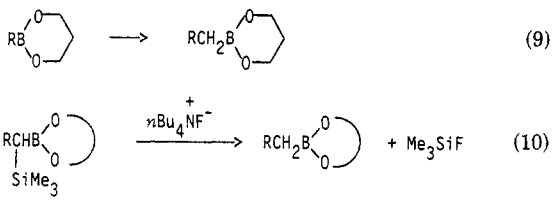


(7)

(8)

We desired a simple synthetic route to the homologated boronic ester (eq 9).

Indeed, Matteson has recently achieved such a one-carbon homologation of boronic esters by the desilylation of the α-(trimethylsilyl)boronic esters with tetrabutylammonium fluoride (eq 10).[11] Unfortunately, the reaction

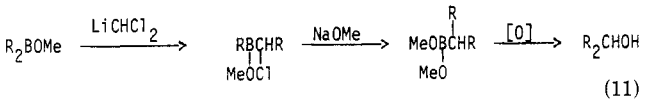


(9)

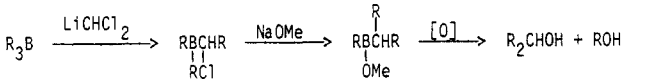
(10)

is relatively slow and appears to be sensitive to the structure of the α-(trimethylsilyl)boronic esters.

We recently reported a synthesis of homologated secondary alcohols from various dialkylborinic esters and trialkylboranes by the reaction with $LiCHCl_2$, followed by sodium methoxide treatment and oxidation[12] (eq 11 and 12).



(11)



(12)

It occurred to us that hydride reduction of the intermediate α-chloroalkyl derivatives might provide a convenient route to one-carbon-homologated boronic esters.

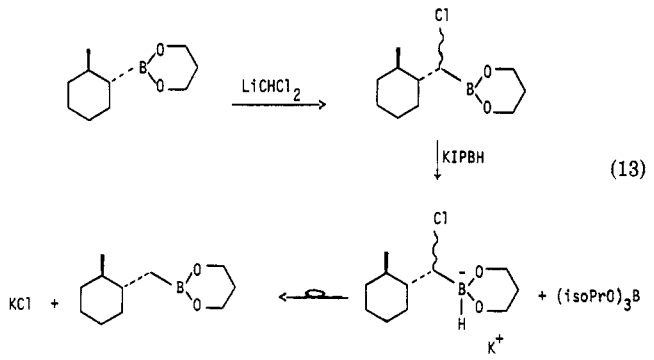
In this paper we report the synthesis and isolation of one-carbon-homologated boronic esters $RCH_2B(OR')_2$ from boronic esters $RB(OR')_2$. We were also successful in reducing the first alkyl-migrated intermediate from borinic esters and trialkylboranes, providing a route to singly homologated borinic esters $RCH_2BR(OMe)$ and RCH_2BR_2. In these cases we were content to identify the products by quantitative oxidation to the alcohols.

Results and Discussion

Representative boronic esters, 2-alkyl-1,3,2-dioxaborinanes, selected for this study, were prepared by procedures described previously.[10] A slurry of (dichloromethyl)lithium ($LiCHCl_2$) in tetrahydrofuran (THF) was prepared[9] at −100 °C, and the boronic esters were added dropwise, maintaining the temperature at −100 °C. After the addition, the reaction mixture became clear and it was allowed to warm to 25 °C. Usually the reaction mixture turned dark at −50 °C due to the decomposition of the excess (10%) $LiCHCl_2$. The reaction mixture was stirred at 25 °C for 3 h. The ^{11}B NMR spectrum of the reaction mixture showed cleanly one peak at δ +27–28, due to the formation of the α-chloro boronic esters. The intermediate α-chloro boronic esters were not isolated but were reduced by using KIPBH at 25 °C. The reaction was facile and was complete within 1.0 h. The ^{11}B NMR spectrum of the reaction mixture showed the formation of boronic ester (δ +30–32), triisopropoxyborane (δ +18), and the presence of a small amount of potassium tetraisopropoxyborate (δ +1–2), originally present as an impurity in the commercial KIPBH solution. The reduction of α-chloro boronic ester presumably proceeds through the intermediate formation of the corresponding borohydride, followed by a fast transfer (eq 13).

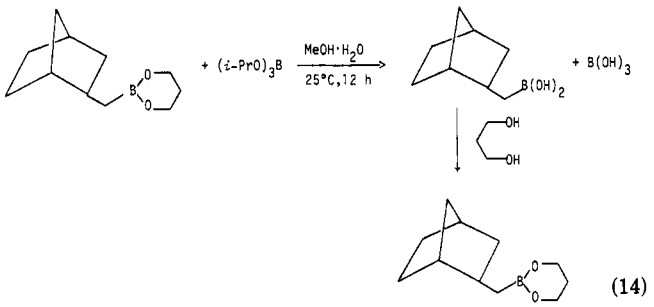
The byproduct triisopropoxyborane is readily removed by washing the ether solution of the reaction mixture with water, selectively hydrolyzing $(i\text{-PrO})_3B$, and extracting the boric acid into water. Although the 1,3-propanediol esters

(7) Negishi, E.; Yoshida, T.; Silveira, Jr., A.; Chiou, B. L. *J. Org. Chem.* **1975**, *40*, 814.
(8) Matteson, D. S.; Majumdar, D. *J. Organomet. Chem.* **1980**, *184*, C41.
(9) (a) Matteson, D. S.; Majumdar, D. *J. Am. Chem. Soc.* **1980**, *102*, 7588. (b) *Organometallics* **1983**, *2*, 1529.
(10) Brown, H. C.; Imai, T. *J. Am. Chem. Soc.* **1983**, *105*, 6285.
(11) Tasi, D. J. S.; Matteson, D. S. *Organometallics* **1983**, *2*, 236.
(12) Brown, H. C.; Imai, T.; Perumal, P. T.; Singaram, B. *Organometallics*, in press.



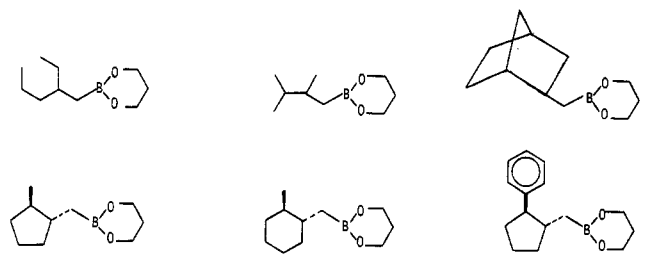
(13)

were partially hydrolyzed, the resulting boronic acid–ester mixture still remained in ether phase and could be readily reesterified with 1,3-propanediol prior to distillation. Alternatively, the reaction product was completely hydrolyzed with MeOH–H_2O (1:1) and the resulting homologated boronic acids were esterified[13] with 1,3-propanediol and purified by distillation (eq 14).

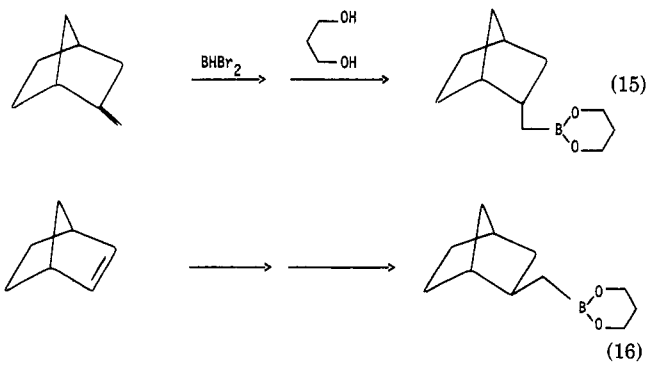


(14)

Using the general procedure, the following one-carbon homologated boronic esters were synthesized (Table I).



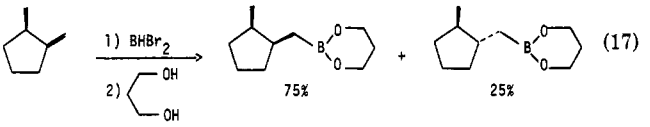
The sequence described here is particularly attractive for those cases where stereoisomers are possible. The stereochemistry is determined by the hydroboration step and the homologation proceeds with retention of configuration. Thus, although hydroboration of 2-methylenenorbornane would be expected to proceed predominantly from the exo face to give the endo derivative, application of our methodology to norbornene provides exo derivative (eq 15 and 16).



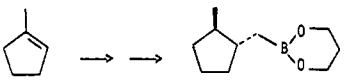
(15)

(16)

Similarly, hydroboration of 2-methylenecyclopentane yields a mixture predominating in the cis isomer whereas the above procedure procedures only the trans isomer (eq 17 and 18).

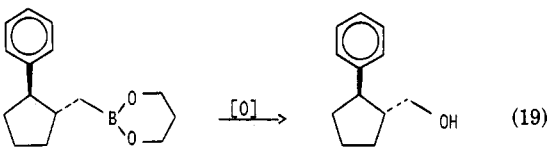


(17)



(18)

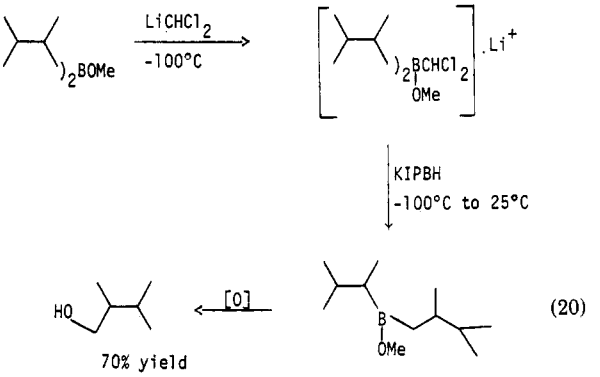
The homologated boronic esters, on oxidation, afforded the corresponding homologated primary alcohols (eq 19).



(19)

The cyclic homologated alcohols were analyzed by capillary GC using 50m Methylsilicon and 20m Supelcowax columns and were found to be diastereomerically pure.[3,14] The diastereomeric purity of these alcohols in turn reflect the diastereomeric purity of the corresponding boronate esters.

Following the general procedure, dialkylborinic esters were reacted with $LiCHCl_2$ at −100 °C. The reaction mixture was allowed to warm to −70 °C and reacted with KIPBH at −70 °C in the hope of trapping the single alkyl-migrated product, avoiding the formation of the double alkyl-migrated product (eq 8). The reaction mixture was warmed to 25 °C, oxidized, and analyzed by GC using *n*-hexadecane as the internal standard. The analysis showed only 40% formation of the desired one-carbon-homologated primary alcohol, the rest being the corresponding secondary alcohol formed due to a double alkyl migration.[12] The best yields (70–75%) of homologated primary alcohols were obtained when KIPBH was added to the reaction mixture at −100 °C, followed by the usual oxidative workup (eq 20).



(20)

Experimental Section

All operations were carried out under a nitrogen atmosphere with oven-dried glassware.[15] ^1H NMR spectra were obtained with a Perkin-Elmer R32 spectrometer. ^{13}C NMR and ^{11}B NMR spectra were obtained with a Varian FT-80A spectrometer. The chemical shift values are in δ relative to Me_4Si for ^1H and ^{13}C NMR

(13) Brown, H. C.; Bhat, N. G.; Somayaji, V. *Organometallics* **1983**, *2*, 1311.

(14) Liotta, R. Ph.D. Thesis, Purdue University, 1976.

(15) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975.

Table I. One-Carbon-Homologated Boronic Esters

boronic esters $RBO_2(CH_2)_3$, R	isolated yield, %	bp, °C (torr)	^{11}B NMR chem shift[a] δ
2,3-dimethyl-1-butyl	70	100–102 (7)	+30.9
2-ethyl-1-pentyl	75	112–114 (17)	+31.0
(*trans*-2-methylcyclopentyl)methyl	75	45–46 (0.05)	+30.5
(*trans*-2-methylcyclohexyl)methyl	85	78–80 (0.05)	+31.0
exo-norbornylmethyl	72	66–68 (0.01)	+30.5
(*trans*-2-phenylcyclopentyl)methyl	80	110–112 (0.01)	+31.0

[a] Relative to EE·BF_3 (δ 0).

spectra. The ^{11}B NMR chemical shifts are in δ relative to EE·BF_3 with chemical shifts downfield from EE·BF_3 assigned as positive. Gas chromatographic analyses were carried out with a Hewlett-Packard 5750 chromatograph with a TC detector using *n*-tridecane or *n*-hexadecane as the internal standard. Capillary gas chromatographic analyses were carried out with a Hewlett-Packard 5890 chromatograph.

Materials. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl prior to use. Dichloromethane, purchased from J. T. Baker Chemical Co., was dried over 4-Å molecular sieves. Butyllithium (Alfa) in hexane was estimated to be 2.3 M. Potassium triisopropoxyborohydride (KIPBH, 1.0 M) in THF was purchased from Aldrich Chemical Co.

The boronic esters,[10] borinic esters,[16] and the trialkylboranes[17] were prepared by procedures described previously.

Homologation of 2-Alkyl-1,3,2-dioxaborinanes. General Procedure. A solution of dichloromethane (2 mL) in 30 mL of freshly distilled THF was cooled to −105 to +100 °C in a 1:1 diethyl ether–*n*-pentane/liquid-nitrogen bath and stirred magnetically during the dropwise addition of 22 mmol of *n*-butyllithium (2.1 M in hexane) from a syringe. The butyllithium was chilled before contacting the dichloromethane solution by bringing the tip of the syringe needle very close to the surface of the cold solution. After the addition, the reaction mixture was stirred at −100 °C for 15 min. The reaction mixture should remain colorless or pale yellow. Darkening is a sign of decomposition. A solution of 2-alkyl-1,3,2-dioxaborinanes (20 mmol) in 10 mL of THF was then added dropwise, maintaining the temperature below −100 °C. The reaction mixture was allowed to reach 25 °C slowly. The reaction mixture was stirred for 3 h at 25 °C. The 2-(chloroalkyl)-1,3,2-dioxaborinanes thus obtained were not isolated but were reduced in situ by using KIPBH (20 mmol) in THF. The exothermic reaction was controlled by the rate of addition of KIPBH and by water-bath cooling to maintain the temperature below 30 °C. Reaction was complete within 1.0 h, as indicated by the ^{11}B NMR analysis. The solvent was evaporated at 25 °C under reduced pressure (12 torr), and the residue was stirred with 40 mL of 1:1 MeOH–H_2O at 25 °C for 12 h to hydrolyze triisopropoxyborane and the product. The reaction mixture was extracted with EE (2 × 20 mL), washed with water (2 × 10 mL), and dried over anhydrous $MgSO_4$. Evaporation (25 °C, 12 torr) of the solvent gave the crude homologated boronic acid which was esterified with 1,3-propanediol and purified by distillation (Table I).

2-(2,3-Dimethylbutyl)-1,3,2-dioxaborinane: ^{1}H NMR ($CDCl_3$) δ 0.53 (br d, *J* = 7 Hz, 2 H), 0.8 (d, *J* = 7 Hz, 6 H), 1.1–2 (m, 2 H), 1.9 (q, *J* = 6 Hz, 2 H), 3.93 (t, *J* = 6 Hz, 4 H).

2-(2-Ethylpentyl)-1,3,2-dioxaborinane: ^{1}H NMR ($CDCl_3$) δ 0.6 (d, *J* = 7 Hz, 2 H), 0.8–1.6 (m, 13 H), 1.9 (q, *J* = 7 Hz, 2 H), 3.97 (t, *J* = 7 Hz, 4 H).

2-((*trans*-2-Methylcyclopentyl)methyl)-1,3,2-dioxaborinane: ^{1}H NMR ($CDCl_3$) δ 0.35–0.7 (m, 2 H), 0.8–1.1 (m, 3 H), 1.2–2.2 (m, 10 H), 3.97 (t, *J* = 7 Hz, 4 H).

2-((*trans*-2-Methylcyclohexyl)methyl)-1,3,2-dioxaborinane: ^{1}H NMR ($CDCl_3$) δ 0.53 (m, 2 H), 0.8–2.1 (m, 15 H), 4.0 (t, *J* = 7 Hz, 4 H).

2-(*exo*-Norbornylmethyl)-1,3,2-dioxaborinane: ^{1}H NMR ($CDCl_3$) δ 0.65 (br d, *J* = 6 Hz, 2 H), 0.9–2.4 (m, 13 H), 3.97 (t, *J* = 7 Hz, 4 H).

2-((*trans*-2-Phenylcyclopentyl)methyl)-2,3,2-dioxaborinane: ^{1}H NMR ($CDCl_3$) δ 0.67 (br d, *J* = 6 Hz, 2 H), 1.1–2.4 (m, 10 H), 3.83 (t, *J* = 7 Hz, 4 H), 7.2 (s, 5 H).

Oxidation of these boronic esters with alkaline hydrogen peroxide[15] afforded the corresponding homologated primary alcohols which were isolated and purified by distillation.

2,3-Dimethyl-1-butanol: 85% yield; bp 64–66 °C (25 torr); ^{1}H NMR ($CDCl_3$) δ 0.82–0.96 (m, 9 H), 1.2 (br s, 1 H), 1.4–1.8 (m, 2 H), 3.4–3.6 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 12.5, 17.9, 20.6, 28.9, 41.4, 66.4.

2-Ethyl-1-pentanol: 90% yield; bp 78–80 °C (20 torr); ^{1}H NMR ($CDCl_3$) δ 0.6–1.0 (m, 6 H), 1.1–1.6 (m, 7 H), 3.0 (br s, 1 H), 3.3–3.7 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 10.9, 14.3, 20.2, 23.3, 32.8, 41.8, 64.9.

(*trans*-2-Methylcyclopentyl)methanol: 90% yield; bp 110–112 °C (80 torr); ^{1}H NMR ($CDCl_3$) δ 1.04 (t, *J* = 7 Hz, 3 H), 1.2–1.9 (m, 8 H), 3.4–3.8 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 20.0, 24.0, 29.5, 35.0, 37.0, 49.7, 66.8.

(*trans*-2-Methylcyclohexyl)methanol: 92% yield; bp 106–108 °C (20 torr); ^{1}H NMR ($CDCl_3$) δ 0.93 (t, *J* = 7 Hz, 3 H), 1.2–1.9 (m, 10 H), 4.1–4.4 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 20.1, 26.2, 26.4, 29.7, 33.7, 35.7, 46.6, 65.9.

(*trans*-2-Phenylcyclopentyl)methanol: 88% yield; bp 92–94 °C (0.01 torr); ^{1}H NMR ($CDCl_3$) δ 1.1–2.2 (m, 7 H), 2.65 (m, 1 H), 3.3–3.65 (m, 2 H), 7.2 (s, 5 H); ^{13}C NMR ($CDCl_3$) δ 24.6, 29.5, 35.7, 48.8, 50.2, 65.5, 126.0, 127.4, 128.4, 145.5.

Preparation of Primary Alcohols from Dialkylborinic Esters. General Procedure. A slurry of (dichloromethyl)lithium (12 mmol) in freshly distilled THF was prepared as described previously and reacted with a THF solution of dialkylborinic ester (10 mmol) at −100 °C. The reaction mixture was stirred at −100 °C for 0.25 h, and a THF solution of KIPBH (10 mmol) was added through the inner surface of the flask. The reaction mixture was allowed to reach 25 °C and stirred at that temperature for 6 h. The reaction mixture was oxidized by successive addition of 3 N NaOH (10 mmol) and 8.0 M H_2O_2 (30 mmol). The product was analyzed by GC on a 10% Carbowax 20M column using *n*-hexadecane as the internal standard (Table II).

Preparation of Primary Alcohols from Trialkylboranes. All reactions of trialkylboranes with $LiCHCl_2$·KIPBH were done on a 10-mmol scale following the general procedure as described for the reaction of dialkylborinic esters. The product alcohols RCH_2OH and ROH obtained following oxidation were analyzed by GC using either *n*-tridecane or *n*-hexadecane as the internal standard.

Table II. Primary Alcohols from Borinic Esters and Trialkylboranes[a]

organoborane	primary alcohol[b]	GC yield,[d] %
methyl di-2-butylborinate	2-methyl-1-butanol	75
methyl di-3-methyl-2-butylborinate	2,3-dimethyl-1-butanol	70
tri-*n*-butylborane	*n*-pentyl alcohol	87
tri-2-butylborane	2-methyl-1-butanol	80
B-*n*-butyl-9-borabicyclo[3.3.1]nonane	1-pentyl alcohol	2
	cis-5-hydroxymethylcyclooctanol[c]	85[e]

[a] All reactions were done on a 10-mmol scale. [b] Each alcohol was identified by GC coinjection with an authentic sample. [c] An authentic sample was prepared by literature procedure. See ref 18. [d] Obtained by using *n*-hexadecane as the internal standard. [e] The alcohol was silylated by using *bis*(trimethylsilyl)acetamide and analyzed on a SE-30 column using *n*-tridecane as the internal standard.

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Registry No. KIPBH, 42278-67-1; $RBO_2(CH_2)_3$ (R = 2,3-dimethyl-1-butyl), 98303-39-0; $RBO_2(CH_2)_3$ (R = 2-ethyl-1-pentyl), 98303-40-3; $RBO_2(CH_2)_3$ (R = (*trans*-2-methylcyclopentyl)methyl), 98303-41-4; $RBO_2(CH_2)_3$ (R = (*trans*-2-methylcyclohexyl)methyl), 98303-42-5; $RBO_2(CH_2)_3$ (R= *exo*-norbornylmethyl), 98303-43-6; $RBO_2(CH_2)_3$ (R = (*trans*-2-phenylcyclopentyl)methyl), 98303-44-7; $LiCHCl_2$, 2146-67-0; $BHBr_2$, 13709-65-4; $RBO_2(CH_2)_3$ (R = 1,2-dimethyl-1-propyl), 98303-38-9; $RBO_2(CH_2)_3$ (R = 1-ethyl-1-butyl), 86290-28-0; $RBO_2(CH_2)_3$ (R = *trans*-2-methylcyclopentyl), 86290-31-5; $RBO_2(CH_2)_3$ (R = *trans*-2-methylcyclohexyl), 98392-60-0; $RBO_2(CH_2)_3$ (R = *exo*-norbornyl), 30154-25-7; $RBO_2(CH_2)_3$ (R = *trans*-2-phenylcyclopentyl), 98392-61-1; $RBO_2(CH_2)_3$ (R = *endo*-norbornylmethyl), 98303-45-8; $RBO_2(CH_2)_3$ (R = *cis*-2-methylcyclopentyl)methyl), 98303-46-9; norbornene, 498-66-8; 2-methyl-1-methylene cyclopentane, 41158-41-2; 2-methylenenorbornane, 497-35-8; 1,3-propanediol, 504-63-2; 1-methyl cyclopentene, 693-89-0; (*trans*-2-phenylcyclopentyl)-methanol, 98392-62-2; 2,3-dimethyl-1-butanol, 19550-30-2; 2-ethyl-1-pentanol, 27522-11-8; (*trans*-2-methylcyclopentyl)-methanol, 63241-06-5; (*trans*-2-methyl cyclohexyl)methanol, 3937-46-0; methyl di-2-butylborinate, 32705-45-6; methyl di-3-methyl-2-butyl borinate, 43209-69-4; tri-*n*-butylborane, 122-56-5; tri-2-butylborane, 1113-78-6; B-*n*-butyl-9-borabicyclo[3.3.1]nonane, 23532-74-3; 2-methyl-1-butanol, 137-32-6; *n*-pentyl alcohol, 71-41-0; *cis*-5-hydroxymethylcyclooctanol, 98303-47-0.

Thermolysis, Photolysis, and Deuterium Exchange Studies of Dinuclear Zirconocene Hydride Complexes

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Parallel thermolysis (at 75 °C in solution) and photolysis (20 °C) studies of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$, **1**, and $\{[SiR_2(C_5H_4)_2]ZrH(\mu\text{-}H)\}_2$ (R = CH_3, **2a**; R = C_2H_5, **2b**; R = $n\text{-}C_3H_7$, **2c**) have shown that these dinuclear zirconocene hydride complexes reductively eliminate H_2. In each case, this process is accompanied by the initial formation of a paramagnetic zirconocene hydride species, which exhibits a hydride doublet with $A(^1H)$ = 6.8 G in the corresponding solution EPR spectrum. The results from a low temperature gas chromatographic analysis of the gas mixture containing H_2, HD, and D_2 generated during the thermolysis of **1** in the presence of a large excess of D_2 are consistent with deuterium incorporation into the methylcyclopentadienyl rings and the hydride positions. Further evidence for the involvement of the methylcyclopentadienyl rings during the thermolysis of **1** is provided by the fact that 3 equiv of H_2 are eliminated per equivalent of **1**. Comparable experiments conducted on **2**, however, clearly reveal that the chelating $[SiR_2(C_5H_4)_2]^{2-}$ ligand significantly restricts the chemical participation of the rings. Linking the rings with a dialkylsilyl bridge reduces the number of equivalents of H_2 evolved per equivalent of **2** to ca. two upon prolonged thermolysis and stabilizes the corresponding paramagnetic zirconocenophane hydride species produced during the initial reductive elimination step. A series of consecutive solution EPR experiments have demonstrated that this Zr(III)–H intermediate undergoes reversible H/D exchange at the hydride position. Complementary NMR measurements have further confirmed that deuterium incorporation is restricted to only the hydride positions of **2**. The role of paramagnetic zirconocene hydride species in these H/D exchange reactions is discussed.

Introduction

The reactivity patterns associated with zirconocene hydrides have attracted considerable interest due to the hydridic nature of the $Zr^{\delta+}\text{–}H^{\delta-}$ bond(s) in these compounds.[1-7] Bercaw and co-workers[1] have studied extensively the chemistry of $(\eta^5\text{-}C_5Me_5)_2ZrH_2$, which generally is initiated by nucleophilic attack at the vacant valence orbital of this 16-electron species. In contrast the dinuclear structure of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$,[8] **1**, requires that all nine metal hybrid orbitals of each Zr be involved in bonding. Consequently, to provide a vacant coordination site a suitable pathway leading to the degradation of its dinuclear structure must be available for **1**. The involvement of a dimer $\rightleftarrows$ monomer equilibrium process, however, appears to be minimal on the basis that **1** is stereochemically rigid at 25 °C on a NMR time scale. An alternative possibility involves the reductive elimination of H_2 with concomitant formation of reduced zirconocene hydride species. Preliminary results, as communicated earlier,[9] indicate that both photolysis (at 20 °C) and the

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