a water bath (25 °C) to 25 mL with a rotary evaporator. After being cooled at -5 °C for 5 h, the precipitated solid was filtered and washed with an ether-pentane mixture (1:1; v/v) which had previously been cooled to dry ice-acetone temperatures. The crude material (3.35-3.75 g) was recrystallized from ether to give 2.9-3.5 g (26-30.7%) of the pure dione 3 as white needles: mp 114-115 °C; IR (CHCl₃) 1780 (sh), 1740 cm⁻¹ (C=O); ¹H NMR (CDCl₃) δ 1.47 (s, 3, CH₃), 2.08 (s, 3, CH₃CO), 2.34 (m, 4, CH₂), 3.10 (m, 2, CHCH₂), 5.90 (m, 2, =CH); MS (80 eV), *m/e* 222 (parent); ¹³C NMR (CHCl₃) 210.4 (ketonic C=O), 169.3 (ester C=O), 127.3 (vinylic carbons), 81.1 (COCOCH₃), 42.3 (CH₂CHCO), 22.2 (CH₂), 19.1 (CH₃COO), 18.4 (CH₃COCOCH₃).

An analytical sample was prepared by recrystallization from ether followed by sublimation at 85 °C (0.3 mm), mp 114.5–115 °C.

Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.86; H, 6.45.

2-Acetoxy-2-methylindan-1,3-dione (4). A mixture of 0.66 g of 3, 1.18 g of N-bromosuccinimide, and a few grains of benzoyl peroxide in 20 mL of CCl₄ (spectrum grade) was refluxed with magnetic stirring under N2 for 40 min. Since the reaction had not been initiated by this time, a second portion of benzoyl peroxide was added and refluxing was continued. Within 40 min the reaction was initiated as evidenced by the appearance of a brown color and the evolution of HBr. When the brown color had disappeared, heating was continued for an additional hour. Succinimide was removed by filtration, and the filtrate was diluted with 25 mL of CH_2Cl_2 and washed with four 15-mL portions of saturated NaHCO₃ solution and four 20-mL portions of H_2O . The solution was dried (MgSO₄) and rotary evaporated at 25 °C. The residue was dissolved in a small amount of ether, and hexane was added to the cloud point. After the solution was cooled in a dry ice-acetone bath at -40 to -35 °C for several hours, 0.21 g of solid. mp 91-93 °C, was obtained. A second crop (0.05 g) was obtained from the mother liquor. Sublimation of the combined material gave 0.23 g (36%) of 4, mp 94-96 °C (lit.⁵ mp 100.5-101 °C), identified by infrared and NMR spectral comparisons with an authentic sample: IR (CHCl₃) 1760 (sh), 1730 cm⁻¹ (C=O); ¹H NMR (CDCl₃) δ 1.52 (s, 3, CH₃), 2.11 (s, 3, CH₃CO), 7.96 (m, 4, aryl); ¹³C NMR (CHCl₃) δ 196.5 (ketonic C=O), 169.4 (ester C=O), 138.2 (CH-C-CO), 135.9 and 123.6 (remaining aryl carbons), 78.6 (COCOCH₃), 19.2 (CH₃COO), 18.4 (CH₃COCOCH₃); MS (80 eV), m/e 218 (parent).

Anal. Calcd for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 66.19; H, 4.71.

8-Acetoxy-3,4-trans-dibromo-8-methylbicyclo[4.3.0]nona-7,9-dione (6). To a magnetically stirred solution of 0.67 g of 3 in 25 mL of CCl_4 (spectrum grade) and 5 mL of dry CH_2Cl_2 maintained between -35 and -25 °C with a dry ice-acetone bath was added 2-3 drops of Br_2 under an atmosphere of N_2 . After a short induction period, the bromine color disappeared and the remaining Br₂ (total 0.48 g) was added over a period of 1 h. After the solution was warmed to room temperature, 35 mL of CH_2Cl_2 was added, and the solution was washed with 30 mL of saturated $NaHCO_3$ solution, 30 mL of H_2O , and 30 mL of saturated NaCl solution. Removal of solvent from the dried (CaSO₄) solution left 1.05 g of white solid, mp 118-120 °C dec. Recrystallization from ether gave 0.75 g (65%) of 6 as white crystals: mp 125.5-126.5 °C dec; IR (CHCl₃) 1780 (sh), 1740 cm⁻¹ (C=O); NMR (CDCl₃) δ 1.48 (s, 3, CH_3), 2.1 (s, 3, CH_3CO), 2.25–2.96 (m, 4, CH_2), 3.3 (m, 2, CH_2CHCO), 4.5 (m, 2, CHBr). The analytical sample was obtained by two recrystallizations from CH_2Cl_2 -ether (1:12; v/v), mp 127-127.5 °C.

Anal. Calcd for C₁₂H₁₄O₄Br₂: C, 37.73; H, 3.69; Br, 41.83. Found: C, 37.84; H, 3.71; Br, 41.79.

When this reaction was carried out in CH₂Cl₂, and the crude product was recrystallized from CH₂Cl₂-ether (1:5; v/v), there was obtained a mixture which consisted of white granules and green-white needles which could be separated manually. The white granules were shown to be 6, obtained in 11% yield. Repeated recrystallization of the green-white needles from CH₂Cl₂-ether (1:5; v/v) gave 10% of 5: mp 183-186 °C; IR (CHCl₃) 1740, 1715 cm⁻¹ (C=O); NMR (CDCl₃) δ 1.45 (s, 3, CH₃). 2.05 (s, 3, CH₃CO), 3.35 (m, 4, CH₂), 4.7 (m, 2, CHBr), which was identified by treatment with 2 equiv of 1,5-diazabicyclo[4.3.0]-5-nonene (DBN) in CH₂Cl₂ at room temperature (16 h). There

was obtained compound 4, mp 100-102 °C, in 91% yield.

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Registry No. 1, 36461-33-3; **3**, 70355-38-3; **4**, 17190-78-2; **5**, 70355-39-4; **6**, 70355-40-7; acetyl chloride, 75-36-5.

Proton Nuclear Magnetic Resonance Studies of Alkenylboranes. On the Presence of Diastereomers in Certain Alkenylboranes

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Previously we reported the relative importance of mesomeric B–C π -bonding forms in alkenyl- and alkynylboranes.¹ An unanswered question remained concerning the ¹³C chemical shifts for (1-hexenyl)disiamylborane (1): two kinds of signals appeared in the C² region



 $Sia = CHMeCHMe_{z}$

(δ 155.2 and 154.4, in parts per million from Me₄Si; converted by using $\delta_C(C_6D_6)$ 128.7). Other alkenylboranes, such as butyl (1-hexenyl)boronate, methyl bis(1-hexenyl)borinate, and (1-hexenyl)(1,2-phenylenedioxy)borane, exhibited one signal in their C² regions as would be expected. We now decipher the origin of the two kinds of signals by investigating the ¹H NMR spectra of alkenyl-disiamylboranes and related boranes.

To solve this problem, we examined ¹H NMR spectra of various types of (5-decenyl)- and (1-hexenyl)boranes. (5-Decenyl)disiamylborane (2) exhibited a triplet-triplet signal in the olefinic H² region as shown in Figure 1. The corresponding H² signal of 1 became more complex due to long-range coupling (Figure 2). On the other hand, (5-decenyl)dicyclohexylborane (3) exhibited a simple triplet signal as shown in Figure 3. Irradiation of the methylene protons helped to analyze the olefinic proton. Chemical shifts of alkenylboranes which exhibit two kinds of olefinic signals are summarized in Table I, and those which exhibit one olefinic signal are summarized in Table II.

Two reasons may be considered for the two kinds of olefinic signals (Table I). First, there is the possibility that two stereoisomers are present on the NMR time scale at room temperature due to the restricted rotation around the boron-carbon bonds.² The ¹H NMR spectrum of 1 at various temperatures (-76 to +83 °C) remained essentially unchanged. Second, the present observation may be rationalized by the presence of diastereomers (racemic

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		chemical shift (δ in CCl_4)				
borane	H1	H²	ΔH^1	ΔH^2	other	
H ² C==C (Sia) ₂ (Sia) ₂		6.02 5.92		0.1	2.40-2.04 (4 H, m), 2.00-1.60 (4 H, m), 1.60-1.15 (8 H, m), 1.08-0.72 (24 H, m)	
2						
1	$6.30 \\ 6.25$	$\begin{array}{c} 6.81 \\ 6.76 \end{array}$	0.05	0.05	2.35-2.10 (2 H, m), 1.85-1.50 (4 H, m), 1.50-1.15 (4 H, m), 1.05-0.70 (21 H, m)	
r^{-Bu} $c = c < H_{B}$	$\begin{array}{c} 6.22 \\ 6.16 \end{array}$	$\begin{array}{c} 6.74 \\ 6.68 \end{array}$	0.06	0.06	2.40-2.12 (2 H, m), 1.80-1.04 (24 H, m), 0.94 (3 H, t J = 6 Hz), 0.76-0.60 (6 H, m)	

 Table I.
 Alkenylboranes Which Exhibit Two Kinds of Olefinic Signals^a

^a The methylene protons adjacent to the double bond were irradiated. The decoupled spectrum of 2 showed two kinds of singlet in the H² region, and the spectra of the (1-hexenyl)boranes showed two kinds of doublet in both H¹ and H² regions. Δ Hⁿ indicates the difference between two chemical shifts in the Hⁿ region.

	chemical shift (δ in CCl ₄)		
borane	H1	H²	other
		5.60 ^b	с
		6.72	7.25-6.85 (4 H, m), 2.42-2.00 (4 H, m), 1.60-1.12 (8 H, m), 1.04-0.90 (6 H, m)
		6.54	2.40-2.14 (4 H, m), $2.08-1.72$ (12 H, m), 1.60-1.16 (10 H, m), 0.94 (6 H, t, $J = 6$ Hz)
$\frac{n-Bu}{H^2} c = c \frac{n-Bu}{BMe_2}$		6.42	2.50-1.88 (4 H, m), $1.63-1.13$ (8 H, m), 0.98 (6 H, t, $J = 7$ Hz), 0.79 (6 H, s)
$\frac{n - Bu}{H^2} > C = C < \frac{n - Bu}{BC_{12}}$		7.06	2.50-2.10 (4 H, m), 1.66-1.13 (8 H, m), 0.93 (6 H, t, $J = 6$ Hz)
a = Bu H^2 $C = = C + BC = BC$		6.17	2.25-1.83 (8 H, m), 1.83-1.08 (16 H, m), 1.08-0.68 (12 H, bs)
n-Bu H ² ⊂ == ○ ∫ B		5.80 ^b	c
H^2 $C == C \left(H^1 \right)_2$	6.19 ^b	6.78 ^b	с
	5.60	d	7.15-6.80 (5 H, m), 2.40-2.10 (2 H, m), 1.70-1.30 (4 H, m), 0.94 (3 H, t, J = 6 Hz)
r-Bu →2 C==c H' B	6.10	6.72	2.28-2.08 (2 H, m), 2.00-1.60 (12 H, m), 1.44-1.08 (6 H, m), 0.90 (3 H, t, $J = 6$ Hz)
^{7-Ви} с=с н ² н ¹ с=с всі	6.08	6.98	2.48-1.85 (4 H, m), 1.68-1.08 (8 H, m), 0.91 (6 H, t, $J = 6.8$ Hz)

Table II. Alkenylboranes Which Exhibit One Olefinic Signal^a

^a Irradiation was performed as in Table I. The decoupled spectra of the (5-decenyl)boranes showed a singlet in the H² region and those of the (1-hexenyl)boranes showed a doublet in both the H¹ and H² regions. ^b THF solution. ^c The solvent (THF) signals masked the methyl and methylene protons. ^d Phenyl proton signals masked the H¹ signal.

and meso compounds) since the alkenylboranes in Table I possess two asymmetric carbons (Scheme I). Indeed, the boranes in Table II do not possess any asymmetric centers.

Accordingly, we prepared (1-hexenyl)diisopinocamphenylboranes (**6a,b**) from optically pure (+)- α -pinene and from racemic (\pm) - α -pinene and examined their ¹H NMR spectra. The data are listed in Table III. As would be expected, two kinds of olefinic signals appeared in **6b**. One type of signal (δ 6.60 and 6.24) must be ascribed to the meso isomer (such as 5) and the other (δ 6.24 and 6.28) to the enantiomers (such as 4a and 4b).

In conclusion, it is now clear that diastereomeric alkenylboranes can be distinguished by the two kinds of chemical shifts of the alkenyl protons. Although the other protons of such isomers should also appear in different regions, complex overlapping of methyl or methylene protons prevents clear analysis.







Figure 2. (a) ¹H NMR spectrum of the olefinic region of 1. (b) The decoupled spectrum of 1.





Figure 3. ¹H NMR spectrum of the olefinic region of 3.

Experimental Section

Most of the boranes were prepared according to the standard procedure.³ (5-Decenyl)dimethylborane,⁴ (5-decenyl)dichloro-borane,⁵ bis(5-decenyl)chloroborane,⁶ and bis(1-hexenyl)chloroborane⁶ were prepared as previously described. Some of the boranes were distilled under reduced pressure, and others were used after evaporation of the solvent. Boiling ranges at reduced pressures are as follows: 5-decenyl-9-BBN, 152-154 °C (0.02 mmHg); bis(5-decenyl)chloroborane, 110–115 °C (0.005 mmHg); (5-decenyl)dimethylborane, 43–45 °C (1 mmHg); (5-decenyl)dichloroborane, 64-70 °C (2 mmHg); bis(1-hexenyl)chloroborane, 70-72 °C (0.05 mmHg); (1-hexenyl)(1,2-phenylenedioxy)borane,



Table III. 'H NMR Spectra of (1-Hexenyl)diisopinocamphenylboranes^a



^a See footnote *a* to Table I. The NMR spectra were recorded in THF.

60-70 °C (0.01 mmHg); 1-hexenyl-9-BBN, 52-55 °C (0.01 mmHg). ¹H NMR spectra were measured on a JEOL PS-100 spectrometer. Chemical shifts are in parts per million, referenced to Me₄Si.

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Registry No. 1, 55168-92-8; 2, 69082-89-9; 3, 69082-90-2; 6a, 70179-28-1; (±)-6b, 70223-51-7; meso-6, 70223-52-8; (E)-(1-hexenyl)bis(trans-2-methylcyclohexyl)borane, 70223-53-9; (Z)-(5-decenyl)(1,2-phenylenedioxy)borane, 70179-29-2; (Z)-(5-decenyl)-9-borabicyclo[3.3.1]nonane, 69322-52-7; (Z)-(5-decenyl)dimethylborane, 64285-24-1; (Z)-(5-decenyl)dichloroborane, 64285-25-2; bis[(Z)-(5decenyl)]chloroborane, 64323-54-2; tris[(Z)-(5-decenyl)]borane, 70179-30-5; (E)-(1-hexenyl)dicyclohexylborane, 37609-12-4; (E)-(2hexenyl)(1,2-phenylenedioxy)borane, 37490-22-5; (E)-(1-hexenyl)-9-borabicyclo[3.3.1]nonane, 69322-45-8; bis[(E)-(1-hexenyl)]chloroborane, 41929-38-8.

Simple and Mild Dehalogenation Reactions Effected by Molybdenum Hexacarbonyl on Alumina

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One of the most active areas of research in organic chemistry involves the use of reagents supported on porous solids to effect various synthetic transformations. Such reactions often occur under gentle conditions, are simple to work up, and can be selective as well. Recent studies,

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