faces[7b,c] or through the ground-state enol.[20] The whole situation is illustrated in Scheme I.

In summary, the main features of the photochemistry of **1a** are (1) only one observable triplet state is produced with a unit quantum efficiency, (2) the steric effects are important in understanding both an unusually large activation energy for the intramolecular hydrogen-abstraction reaction and the high quantum yield for the formation of **2a**, and (3) the sterically promoted photoreaction such as **1a** → **2a** has potential for energy-storage applications.

Acknowledgments. We thank the Ministry of Education in Japan and the Kawakami Foundation for financial support. We are also grateful to Professor Peter J. Wagner for his valuable comments.

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(20) It is inferred experimentally[4c] and theoretically[7b] that a benzocyclobutenol is formed from the biradical and that a ground-state enol leads only to the starting ketone without going to the cyclobutenol. In the case of **1a**, we could not demonstrate the formation of the corresponding enol, since the irradiation of **1a** in CH_3OD or in the presence of dimethyl acetylenedicarboxylate gave no deuterium-incorporated starting ketone **1a** ($\Phi < 0.02$) or no Diels-Alder type adduct, respectively.

(21) The ratios of *cis*- to *trans*-piperylene at a photostationary state for **1a** and benzophenone as sensitizers were 0.77 ± 0.02 and 0.81 ± 0.04, respectively, identical within the experimental error. This result suggests that steric hindrance to energy transfer is not significant.[22]

(22) Herkstroeter, W. G.; Jones, L. B.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4777-4780.

(23) The phosphorescence spectra of **1a** and **1b** were structureless, and their intensities were much smaller than that of benzophenone (relative intensity **1a**/**1b**/benzophenone = 0.022:0.033:1.0).

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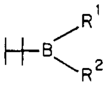
Thexylchloroborane. A Versatile Reagent for the Preparation of Mixed Thexyldiorganoboranes

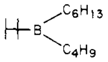
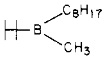
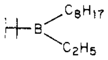
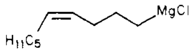
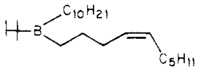
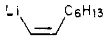
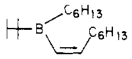
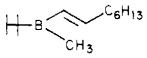
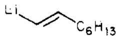
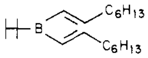
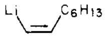
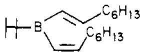
Sir:

As a consequence of the low migratory tendency of the thexyl group, thexyldialkylboranes play an important role in many organoboron-mediated carbon-carbon bond-forming reactions.[1] Although a variety of thexyldialkylboranes are available via sequential hydroboration of the appropriate olefins with thexylborane (**1**, 2,3-dimethyl-2-butylborane),[2] this procedure is not suitable for obtaining thexyldialkylboranes containing different, unbranched primary alkyl groups.[2] Also, certain thexylalkylalkenyl- and thexyldialkenylboranes may not be obtained by the procedure.

In connection with ongoing synthetic interests,[3] our need for ready access to a variety of thexylboron intermediates prompted us to explore other routes for their synthesis. We now report that the use of thexylchloroborane (**2**) obviates the synthetic limitations attendant upon thexylborane (**1**) and provides, via a hydroboration-alkylation sequence, an operationally simple approach for preparing hitherto inaccessible mixed thexylboranes. This novel procedure thus greatly enhances the synthetic utility of thexyl-substituted organoboranes as shown below by their use in the preparation of ketones via the cyanidation reaction.[4]

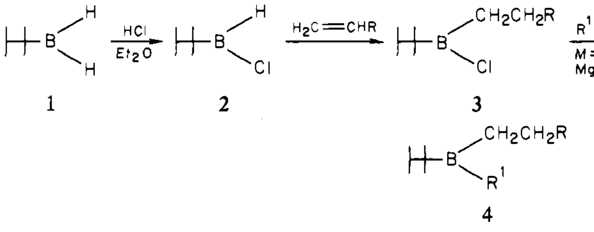
Table I. Preparation of Mixed Thexyldiorganoboranes and Their Conversion into Ketones via the Cyanidation Reaction[a]



entry	R^1 derived from	R^2 derived from	structure	% **6**[c]
1	1-hexene	BuLi		80
2	1-octene	CH_3Li		72
3		C_2H_5MgBr		74
4	1-decene			74[b]
5	1-hexene			
6	1-octyne	CH_3Li		
7				
8				

[a] The conversion of alkenylboranes (entries 5-8) into the corresponding α,β-unsaturated ketones via the cyanation reaction has not yet been reported. [b] The ketone contained a small percent of an unknown compound. [c] Isolated yield of ketone.

To a 2.55 M solution of $BH_3{\cdot}SMe_2$ (15 mmol)[5] in THF was added 2,3-dimethyl-2-butene (15 mmol), while maintaining the temperature during the addition below 10 °C (ice bath). After the solution was stirred for 1 h at 25 °C, the resulting thexylborane was treated at 0-5 °C with an ethereal solution containing an equimolar amount of dry hydrogen chloride (3.8 M) (eq 1). This



(1)

was accompanied by the rapid and quantitative evolution of hydrogen to give a solution whose IR spectrum exhibited a strong absorption at 2442 cm^{-1}, indicating the presence of a nonbridged boron hydride species. However, the spectrum was devoid of an absorption in the 1550-cm^{-1} region, which is characteristic for the BH_2B bridge in **1**.[6] These observations clearly point to the formation of thexylchloroborane.

As part of an investigation of the behavior of **2** for hydroboration of terminal olefins, 1-octene was treated with the reagent at 0-5 °C. After the mixture was maintained at room temperature for 2 h, oxidation of the resultant borane **3** with alkaline hydrogen peroxide afforded, besides thexylalcohol (95%), 1-octanol (97%) in at least 99% isomeric purity. In a similar manner but after 10-h reaction, 99% isomerically pure 2-phenylethanol was obtained from styrene in 83% yield. Therefore, thexylchloroborane is a highly regiospecific hydroborating agent for 1-alkenes, being comparable in its behavior to chloroboranes (BH_2Cl and $BHCl_2$)[7] and dialkylboranes.[1]

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(1) Brown, H. C. "Boranes in Organic Chemistry", Cornell University Press: Ithaca, New York, 1972. Pelter, A.; Smith, K. *Compr. Org. Chem.* **1979**, *3*, 689.

(2) Brown, H. C.; Negishi, E. *Synthesis* **1974**, 77. Brown, H. C.; Negishi, E.; Katz, J.-J. *J. Am. Chem. Soc.* **1975**, *97*, 2791. Brown, H. C.; Katz, J.-J.; Lane, C. F.; Negishi, E. *Ibid.* **1975**, *97*, 2799.

(3) Zweifel, G.; Backlund, S. J.; Leung, T. *J. Am. Chem. Soc.* **1978**, *100*, 5561.

(4) Pelter, A.; Smith, K.; Hutchings, M.; Rowe, K. *J. Chem. Soc., Perkin Trans. 2* **1975**, 129.

(5) Brown, H. C.; Mandel, A. K.; Kulkarni, S. U. *J. Org. Chem.* **1977**, *42*, 1392.

(6) Brown, H. C.; Negishi, E. *Synthesis* **1974**, 77.

(7) Brown, H. C.; Ravindran, N. *J. Org. Chem.* **1972**, *42*, 2533.

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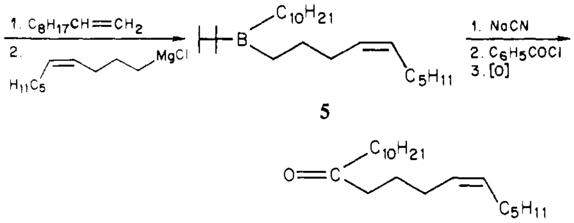
Treatment of the thexylalkylchloroboranes **3** with equimolar amounts of primary organolithium or Grignard reagents results in clean monoalkylations of boron to produce the corresponding thexyldialkylboranes **4** (Table I). They were converted into the corresponding unsymmetrically substituted ketones via the cyanidation reaction[4] to ascertain whether we were indeed dealing with mixed thexyldialkylboranes, and to demonstrate their utility in organic synthesis. This is exemplified by the preparation of (*Z*)-6-heneicosen-11-one (**6**), the sex pheromone of the Douglas fir tussock moth (eq 2).



5

(2)

6

To a solution of **2** (15 mmol) in THF at 0–5 °C was added 1-decene (15 mmol). After the reaction was maintained at 25 °C for 2 h, the resultant thexyldecylchloroborane was treated at −78 °C with a 1 M solution of (*Z*)-4-decen-1-magnesium chloride (15 mmol)[8] in ether. After the mixture was warmed to room temperature and diluted with pentane (20 mL), it was freed from precipitated magnesium chloride by transferring it directly into a second flask through a short column filled with anhydrous Na_2SO_4 (25 g).[10,11] The initial flask was washed with pentane (30 mL), the washings were also passed through the column into the second reaction flask, and the solvents were removed under reduced pressure (1 torr). The resultant organoborane **5** was diluted with THF (30 mL), treated with powdered, very dry sodium cyanide (16.5 mmol), and stirred at 45 °C for 1 h. After the addition of benzoyl chloride (18 mmol)[12] at 25 °C, the reaction mixture was stirred for 12 h at 45 °C before being oxidized with 3 N NaOH (13 mL) and 30% H_2O_2 (7.5 mL) at 40–45 °C. After the mixture was stirred at ambient temperature for 2 h, it was extracted with pentane. Distillation of the extract afforded 3.4 g (74%) of (*Z*)-6-heneicosen-11-one; bp 109–114 °C (10^{-4} torr), $n^{25}{}_D$ 1.4550.

A summary of the thexyldialkylboranes prepared in this study and the yields of ketones derived from them are shown in Table I. The small amounts of thexyl-substituted ketones produced in these reactions (<5%) confirm the previous report[4] that the thexyl moiety primarily serves as an anchor group. It is important to note here that less than 1% of any symmetrical ketones was formed in these reactions, implying that the mixed thexyldialkylboranes initially formed do not undergo symmetrization under the reaction conditions used.

Thexylchloroborane (**2**) may also serve as a precursor for the preparation of a variety of thexylalkylalkenyl- and thexyldialkenylboranes. These are of considerable synthetic interest. For example, sequential treatment of **2** with 1-hexene at 0 °C, followed by stirring at 25 °C for 2 h and addition of (*Z*)-1-lithio-1-octene (−78 → 0 °C), afforded the thexylalkylalkenylborane shown in entry 5 (Table I). The trans alkenyl moiety is conveniently introduced via monohydroboration of the appropriate 1-alkyne with thexylchloroborane (1 h at 25 °C). Subsequent alkylation produces the [(*E*)-alkenyl]alkylthexylborane (entry 6). The above hydroboration–alkylation sequence may also be extended to the preparation of thexyldialkenylboranes possessing trans–trans and cis–trans alkenyl moieties as shown in entries 7 and 8.

The structures of the alkenylthexylboranes (entries 5–8) are proposed on the basis of the olefins and thexyl alcohol formed when they are protonolyzed or oxidized, respectively. Furthermore, NMR examination of the vinyl proton regions of the unsaturated organoboranes has unambiguously established that the alkylations and alkenylations have proceeded to the tri- and not to the tetrasubstituted boron compounds.

In summary, the difunctional thexylchloroborane provides for transformations involving a combination of hydroboration with alkylation steps. This novel approach possesses great flexibility and opens up a convenient route to thexyl-substituted alkyl- and alkenylboranes and to the many synthetic applications for which they can be utilized. Thus, it is apparent that thexylchloroborane strongly compliments thexylborane (**1**) for the preparation of certain organoboranes containing the thexyl moiety.

Acknowledgments. We thank the National Science Foundation for support of this investigation.

Note Added in Proof. After submitting our manuscript, Professor Brown has informed us that thexylchloroborane may also be prepared from 2,3-dimethyl-2-butene and monochloroborane–methyl sulfide. Brown, H. C.; Sikorski, J. A.; Kulkarni, S. U.; Lee, H. D., manuscript submitted for publication.

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Structure of Goniomine, an Alkaloid of a New Type Biogenetically Related to Indole Alkaloid. X-Ray Analysis of Dihydrogoniomine[1]

Sir:

We have isolated goniomine (**4**) [mp 223 °C (methanol), $[\alpha]^{20}{}_D$ −270° (*c* 0.5, $CHCl_3$)] from *Gonioma malagasy* Mgf and P. Bt (Apocynaceae),[2] following classical alkaloid extraction and purification methods. Goniomine, $C_{19}H_{22}O_2N_2$, gave the following spectral data: mass spectrum (MS), *m/e* 310 ($M^{+\cdot}$, 80%), 200 (35), 172 (60), 158 (24), 144 (54), 143 (100), 130 (24), 124 (17), 123 (76), 95 (19); IR ($CHCl_3$) 1675, 1590 cm^{-1}; UV (ethanol, qualitative) 212, 233, 272, 305 nm; ^1H NMR ($CDCl_3$, Me_4Si $\delta = 0$) δ 1.42 (d, 3 H, $J = 6.5$ Hz), 5.18 (d, 1 H, $J \simeq 1$ Hz), 5.98 (d, 1 H, $J \simeq 1$ Hz); ^{13}C NMR ($CDCl_3$, 22.63 MHz, Me_4Si $\delta = 0$) δ 15.9 (q), 30.1 (t), 32.2 (t), 38.2 (d), 43.1 (t), 53.4 (t), 59.8 (s), 62 (d), 68 (s), 73.8 (d), 119.2 (t), 122.3 (d), 123.3 (d), 125.2 (d), 128 (d), 138.3 (s), 146.9 (2s), 201.7 (s).

$NaBH_4$ reduction of **4** in methanol yielded a dihydro derivative **6**, Scheme I: mp 228 °C (ethanol); exact mass *m/e* 312.1791 (calcd for $C_{19}H_{24}O_2N_2$, 312.1832); IR ($CHCl_3$) 1675, 1590 cm^{-1}; UV (ethanol, qualitative) 217, 249, 308 nm. In the ^1H NMR data ($CDCl_3$, Me_4Si $\delta = 0$), a new signal at 1.09 (d, 3 H, $J = 6.5$ Hz) appears while the two olefinic protons disappear. From these data, we could establish the presence of an *exo*-methylene group conjugated with a carbonyl function. Acetic anhydride/pyridine treatment of **4** gave easily an *O*-acetyl derivative **5**: MS *m/e* 352 ($M^{+\cdot}$); IR ($CHCl_3$) 1730, 1680, 1605 cm^{-1}.

It was not possible to assign a structure fitting with the chemical results and the spectral data although it was probable that goniomine was related to indole alkaloids such as the other known alkaloids found in the same plant. We will indeed see that goniomine has quite unexpected chemical reactivity. The complete structure and relative stereochemistry of goniomine were deduced from the single-crystal X-ray study of its 16,17-dihydro derivative[3]

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[8] Monohydroboration of 1-chloro-4-decyne with $BH_3{\cdot}SMe_2$ followed by protonolysis with acetic acid afforded (*Z*)-1-chloro-4-decene,[9] which was converted into the Grignard reagent in ether solvent.

(9) Kocienski, P. J.; Ostrow, R. W. *J. Org. Chem.* **1976**, *41*, 398.

(10) The cyanidation reaction does not proceed in the presence of magnesium or lithium salts.

(11) The filtration is conveniently effected with the aid of a double-ended Teflon tube (0.422-cm i.d.) under nitrogen pressure.

(12) Use of trifluoroacetic anhydride[4] instead of benzoyl chloride resulted in a lower ketone recovery.

(1) The first communication on the structure of goniomine was given at the International Symposium on Recent Advances in the Chemistry and Biology of Alkaloids, London, April 1979.

(2) Markgraf, F.; Boiteau, P. *Adansonia* **1972**, *12*, 223–229.

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