reported in full elsewhere. We wish, however, to mention that, as expected, in these cases stereoselectivity has also been observed.

These results demonstrate the usefulness of the chromatographic approach to the study of the complexation and stereoselectivity of biological molecules. The continuation of such studies should permit us to recognize the structural parameters and, possibly, the intermolecular interactions responsible for chiral recognition. Vice versa, these investigations should also lead to the design of novel synthetic molecules for the efficient resolution of optical isomers.

Acknowledgments. Y.H.K. thanks the Deutscher Akademischer Austauschdienst (DAAD) for financial support.

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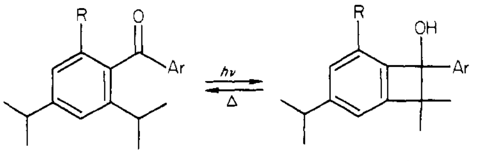
Received March 28, 1980

Sterically Promoted Benzocyclobutenol Formation from 2,4,6-Triisopropylbenzophenone Photolysis[1]

Sir:

Our persistent interest in high-energy compounds[2] urges us to search for a new system for the chemical storage of solar energy.[3] Benzocyclobutenols, which can be prepared by the photocyclization of particular 2-alkyl-substituted phenyl ketones,[4] are highly strained, and their thermal back reactions to the parent ketones are considerably exothermic.[5] Besides the practical interest in the benzocyclobutenol molecule as a potential for solar energy storage, its formation reaction is deeply related to the recent considerable controversy in the mechanism of photoenolization of 2-alkyl-substituted phenyl ketones.[4c,e,7] Previously, Matsuura and Kitaura found a quantitative reversible photocyclization of 2,4,6-triisopropylbenzophenone (**1a**) to the corresponding benzocyclobutenol **2a** (eq 1).[4a] We have undertaken a quantitative study of this reaction and found that steric effects are crucial for understanding this reaction.



(1)

1a, R = *i*-Pr,
Ar = Ph

2a, R = *i*-Pr,
Ar = Ph

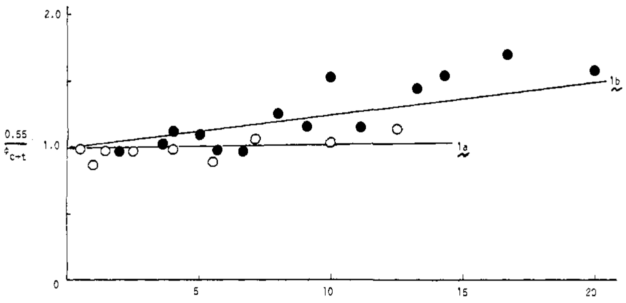


Figure 1. Photosensitized cis–trans isomerization of *cis*-piperylene in benzene by 0.05 M 2,4,6-triisopropylbenzophenone (**1a**) (○) and 0.05 M 2,4,6-trimethylbenzophenone (**1b**) (●).

Table I. Excited-State Properties of 2,4,6-Triisopropylbenzophenone (1a) and 2,4,6-Trimethylbenzophenone (1b)[a]

compd	Φ_{ST}	Φ_{CB}	$k_q\tau_T$, M^{-1}	τ_T, ns	E_S, kcal/mol	E_T, kcal/mol
1a	1.01 ± 0.04[b]	0.60	450 ± 30[d]	90 ± 6[e]	~75[f]	68.7[g]
1b	1.07 ± 0.15[b]	0.002[c]	35 ± 20[b]	7 ± 4[e]	~75[f]	~69[h]

[a] All the photokinetic data were obtained in benzene at 25 °C. [b] Determined from the photosensitized cis–trans isomerization of *cis*-piperylene (Figure 1).[21] [c] Reference 4a. [d] Slopes of linear Stern–Volmer plots with 2,5-dimethyl-2,4-hexadiene as quencher. [e] $k_q = 5 \times 10^9$ M^{-1} s^{-1} in benzene. [f] Estimated from the absorption spectra. [g] Reference 22. [h] Estimated from the phosphorescence spectrum in ethanol at 77 K.[23]

The quantum yield of the cyclobutenol formation (Φ_{CB}) for the reaction **1a** → **2a** was quite high and independent of the polarity or the hydrogen-bonding ability of the solvents employed, i.e., Φ_{CB} = 0.60 (benzene), 0.62 (*n*-hexane), 0.42 (cyclohexane), 0.60 (methanol), 0.77 (acetonitrile), 0.55 (Freon-11), and 0.52 (*n*-propyl bromide) at 25 °C.[8] This finding is remarkable, since Φ_{CB} is less than 0.1 in all the benzocyclobutenol formation reactions so far reported[4] with only one exception, γ-2,4,6-tetramethylvalerophenone (**3**), where Φ_{CB} is 0.21 in benzene containing 3 M dioxane.[4e]

Wagner and Scaiano have recently reported that 2-alkyl-substituted phenyl ketones such as 2-methylacetophenone (**4**),[7a,d] 2,4,6-triisopropylacetophenone (**5**),[4h] 2-methylbenzophenone (**6**),[4e] or **3**[4e] have two kinetically distinct triplets, i.e., a long-lived (>10 ns) and a short-lived (<1 ns) triplet, and that the overall triplet quantum yield was far less than unity in each ketone except **6**. In the cases of **3** and **5**, the short-lived triplets lead to the formation of the corresponding benzocyclobutenols, which are only inefficiently quenched by diene.[4e,h] In sharp contrast to these ketones (**3**–**6**), we estimated by the photosensitized cis–trans isomerization of *cis*-piperylene in benzene (Figure 1) that **1a** had only a long-lived triplet with the intersystem crossing yield $\Phi_{ST} = 1.01 \pm 0.04$.[9] Furthermore, the formation of **2a** was efficiently quenched by

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(1) Photoinduced Reactions, part 121.

(2) Ito, Y.; Matsuura, T.; Yokoya, H. *J. Am. Chem. Soc.* **1979**, *101*, 4010–4011. Ito, Y.; Matsuura, T.; Kondo, H. *Ibid.* **1979**, *101*, 7105–7107.

(3) Laird, T. *Chem. Ind.* (*London*) **1978**, 186–193. Wrighton, M. S. *Chem. Eng. News* **1979**, *57*, (Sept 3), 29–47.

(4) (a) Kitaura, Y.; Matsuura, T. *Tetrahedron* **1971**, *27*, 1597–1606. (b) Matsuura, T.; Kitaura, Y. *Ibid.* **1969**, *25*, 4487–4499. (c) Carrē, M. C.; Viriot-Villaume, M. L.; Caubēre, P. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2542–2549. (d) Viriot-Villaume, M. L.; Carrê, C.; Caubêre, P. *Ibid.* **1979**, 1395–1403. (e) Wagner, P. J. *Pure Appl. Chem.* **1977**, *49*, 259–270. (f) Arnold, B. J.; Mellows, S. M.; Sammes, P. G. *J. Chem. Soc., Perkin Trans. 1* **1974**, 401–409. (g) Heine, H. G. *Justus Liebigs Ann. Chem.* **1970**, *732*, 165–180. (h) Wagner, P. J., private communication.

(5) The following thermochemical and kinetic data were found for the thermal decomposition **2a** → **1a**: $\Delta H = -20.08$ kcal/mol (solid) (Inagaki, S.; Murata, S.; Sakiyama, M.; Ito, Y.; Umehara, Y.; Hijiya, T.; Matsuura, T. 15th Symposium on Thermochemical Measurement, Kanazawa, Oct. 1979; Abstr. p 150); $k = 3.52 \times 10^{-5}$ s^{-1} at 130.1 °C; $E_a = 28.6 \pm 1$ kcal/mol; log $A = 11.0 \pm 1$; $\Delta H^{\ddagger} = 27.8 \pm 1$ kcal/mol; $\Delta S^{\ddagger} = -10.7 \pm 4$ eu. The kinetic data were obtained in phenyl ether solvent (119–139 °C). Note that ΔH of quadricyclane to norbornadiene is exergonic only by 9.94 kcal/mol (gas).[6]

(6) Pedley, J. B.; Rylance, J. "Sussex—N. P. L. Computer Analyzed Thermochemical Data: Organic and Organometallic Compounds", University of Sussex: Brighton BN 19 Q, 1977.

(7) (a) Das, P. K.; Eneinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965–6970, and references cited therein. (b) Sevin, A.; Bigot, B.; Pfau, M. *Helv. Chim. Acta* **1979**, *62*, 699–710. (c) Haag, R.; Wirz, J.; Wagner, P. J. *Ibid.* **1977**, *60*, 2595–2607. (d) Wagner, P. J.; Chen, C.-P. *J. Am. Chem. Soc.* **1976**, *98*, 239–241. (e) Das, P. K.; Scaiano, J. C. *J. Photochem.* **1980**, *12*, 85.

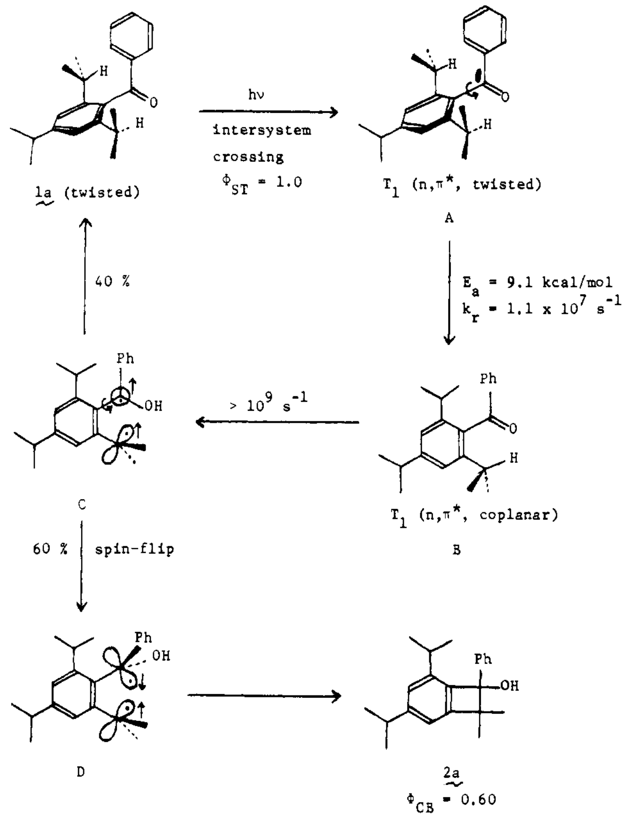
(8) In some of the good hydrogen-donating solvents, however, the quantum yield was significantly lower and as yet unidentified byproducts were formed probably as a result of a competitive intermolecular hydrogen abstraction, i.e., Φ_{CB} = 0.19 (ethyl ether), 0.19 (2-propanol), and 0.27 (ethanol). The type II elimination reaction of valerophenone in benzene was used as a standard for the quantum yield measurements. In all experiments throughout the present study, 0.1 M ketone solutions were degassed and irradiated on a merry-go-round apparatus by 313-nm light. The benzocyclobutenols were analyzed by high-pressure liquid chromatography (hexane–ethyl acetate, Jascosil SS-05).

(9) Because of the relatively long triplet lifetimes of **1a** and **1b** and of the experimental limitations in our VPC analysis, τ_T determined by this sensitization study was subject to large errors, and we cannot rule out the possibility that another longer lived triplet state of **1a** and **1b** might also be involved.[10]

(10) Wagner, P. J. *J. Photochem.* **1979**, *10*, 387–399.

0002-7863/80/1502-5917$01.00/0

Scheme I



2,5-dimethyl-2,4-hexadiene in benzene, $k_q\tau_T = 450\ M^{-1}$, $\tau_T = 90$ ns. The similar *cis*-piperylene sensitization study of 2,4,6-trimethylbenzophenone (**1b**) (Figure 1) revealed that $\Phi_{ST} = 1.07 \pm 0.15$ and $\tau_T = 7 \pm 4$ ns for **1b**.[9] It should be noted that Φ_{CB} is very small for **1b** (0.002). These results are summarized in Table I. The sharp difference between the behavior of 2,4,6-trialkylbenzophenones **1a** and **1b** and 2,4,6-trialkylphenyl alkyl ketones **3** and **5** is at present unexplainable, although it seems that a steric as well as an electronic effect of the unsubstituted phenyl ring in **1a** and **1b** must be considered.

As listed in Table I, the singlet (E_S) and triplet (E_T) energy levels of **1a** and **1b** are nearly the same as those of benzophenone ($E_S \sim 75$ kcal/mol, $E_T \sim 69$ kcal/mol). The small energy difference between E_S and E_T ($\sim$6 kcal/mol) as well as a blue shift ($\sim$15 nm) of the absorption spectra in ethanol relative to hexane observed with these three ketones indicates that the S_1 and T_1 states of **1a** and **1b** are of n,π* character, like those of benzophenone. The primary step of the cyclobutenol formation is apparently n,π* triplet-induced intramolecular abstraction of a benzylic hydrogen from the ortho position, since α-naphthyl 2,4,6-triisopropylphenyl ketone (**1g**) showed no photochemical reactivity. The T_1 state of **1g** was assigned to be of π,π* character on the basis of a large E_S–E_T separation ($\sim$19 kcal/mol).[11]

As shown by the crystal structure of **1a**,[12] the carbonyl group and the two benzene rings attached to it are severely twisted in the most strain-free conformation, which is unfavorable for the intramolecular hydrogen abstraction in view of its stereoelectronic requirement.[13] Therefore, during the lifetime of the triplet, the rotation of the C–C single bond between the triisopropylphenyl group and the carbonyl group must occur against a strong steric repulsion to approach a coplanar conformation, where the hydrogen abstraction is geometrically possible (A → B in Scheme I).[14] The requirement of the occurrence of the strongly hindered bond rotation prior to the hydrogen abstraction was reflected on an unusually large activation energy[16] for the hydrogen abstraction step ($E_a = 9.1 \pm 0.4$ kcal/mol, log $A = 13.7$), which was determined by 2,5-dimethyl-2,4-hexadiene quenching of the formation of **2a** in benzene at different temperatures (15–40 °C) on the assumption $k_r = \tau_T^{-1}$.[17] We believe that the triplet lifetime is controlled by the easiness of this hindered bond rotation, and once the coplanar structure is achieved the hydrogen abstraction will happen very rapidly with the rate $> 10^9\ s^{-1}$[7d] (B → C in Scheme I). The shorter triplet lifetime of **1b** than that of **1a** (Table I) may be ascribable to less steric hindrance to bond rotation in triplet **1b** than in triplet **1a** as a result of less bulkiness of the methyl group than the isopropyl group.

Table II. Quantum Yields of Benzocyclobutanol Formation from 2-Alkyl-Substituted Benzophenones 1a–f in Benzene at 25 °C[a]

compd	R	Ar	Φ_{CB}
1a	*i*-Pr	Ph	0.60
1b[d]			0.002[b]
1c	*i*-Pr	4-MePh	0.48[c]
1d	*i*-Pr	3,4-Me_2Ph	0.55
1e	*i*-Pr	4-CF_3Ph	0.35
1f	H	Ph	0.11

[a] Estimated errors ±10%. [b] Reference 4a. [c] 0.38 (in *n*-hexane), 0.32 (in methanol). [d] 2,4,6-Trimethylbenzophenone.

The quantum yields of cyclobutenol formation (Φ_{CB}) from several 2-alkyl-substituted benzophenones (**1a–f**) are summarized in Table II. The values of Φ_{CB} for **1a** and **1c–e** do not differ significantly, disclosing that Φ_{CB} is not correlated to the amount of n,π* character in the T_1 states of these ketones.[18] Moreover, as readily seen from Table I, the observed hydrogen-abstraction rate, $k_r = \tau_T^{-1}$, of **1a** was slower than that of **1b** whereas Φ_{CB} of **1a** was much larger than that of **1b**. By analogy to the Norrish type II reaction, the irrelevance of k_r and Φ_{CB} indicates that the biradical intermediate, e.g., C from **1a**, disproportionates back to the parent ketone in competition with the formation of the corresponding benzocyclobutenol.

The much larger Φ_{CB} of **1a** (0.60) than those of **1b** (0.002), **1f** (0.11), and 2,4,6-triethylbenzophenone (0.05)[4a] strongly suggests that the cyclobutenol formation from **1a** was enormously promoted by the bulky isopropyl groups substituted at the two ortho positions in the same benzene nucleus. Similarly, the benzocyclobutenol formation from benzocycloalkenones was accelerated by the steric effects of substituents at the ortho position.[4c] These results appear to be rationalized by consideration of the topology of the biradicals C and D. The large steric repulsion in the triplet biradical C between the C(OH)(Ph) group and the two ortho substituents (the isopropyl and CMe_2 groups) will result in a rotation of the C(OH)(Ph) group by 90° to relieve some of the steric repulsion, being accompanied by the simultaneous occurrence of a spin flip,[19] leading eventually to the singlet biradical D (Scheme I). Naturally, this bond rotation is assisted by the bulky substituents at the ortho positions for the steric reason. The singlet biradical D thus formed can spontaneously lead to the cyclobutenol **2a** without any activation energy as is usually the case for singlet biradical collapse in a favorable geometry.[7b] The triplet biradical C, which can also be described as the triplet state of the enol,[7a] will partly reketonize to the ground state of **1a** either through a rapid intersystem crossing caused by the crossing of the S_0 and T_1 sur-

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(11) $E_T \sim 56$ kcal/mol and $E_S \sim 75$ kcal/mol estimated from the absorption and phosphorescence spectra.

(12) Katsube, Y.; Fukuyama, K.; Ito, Y.; Matsuura, T.; Umehara, Y. 41th Annual Meeting of the Chemical Society of Japan, Osaka, April 1980.

(13) Turro, N. J. "Modern Molecular Photochemistry", Benjamin/Cummings: Menlo Park, Ca, 1978; pp 386.

(14) The rotation of two single C–C bonds between two benzene rings and the carbonyl group (C–CO–C) of **1a** is not so restricted in solution as expected from the molecular model. In fact, Maruyama found previously by the NMR measurement that the C–CO–C bondings of 2,6,2′,6′-tetramethylbenzophenones were freely rotating.[15] We have also found that the NMR signals of **1a**, including their temperature dependence (−60, 31, and 80 °C), are indicative of much more rotational freedom of bonds than expected from the molecular model. The details will be published elsewhere.

(15) Maruyama, K. *Bull. Chem. Soc. Jpn* **1966**, *39*, 2772–2773.

(16) Reference 13, p 237.

(17) Scaiano, J. C. *J. Chem. Soc., Chem. Commun.* **1972**, 390–391.

(18) Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604–5614.

(19) Reference 13, p 48.

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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Received February 28, 1980

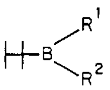
Thexylchloroborane. A Versatile Reagent for the Preparation of Mixed Thexyldiorganoboranes

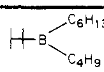
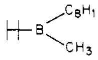
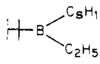
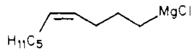
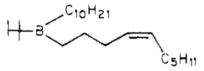
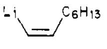
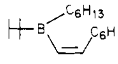
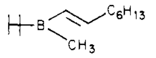
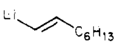
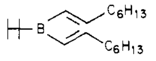
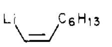
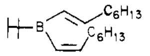
Sir:

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]

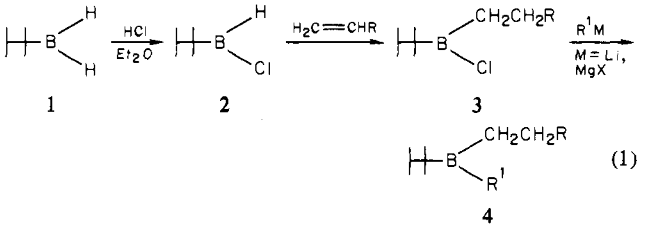
Table I. Preparation of Mixed Thexyldiorganoboranes and Their Conversion into Ketones via the Cyanidation Reaction[a]



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.

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