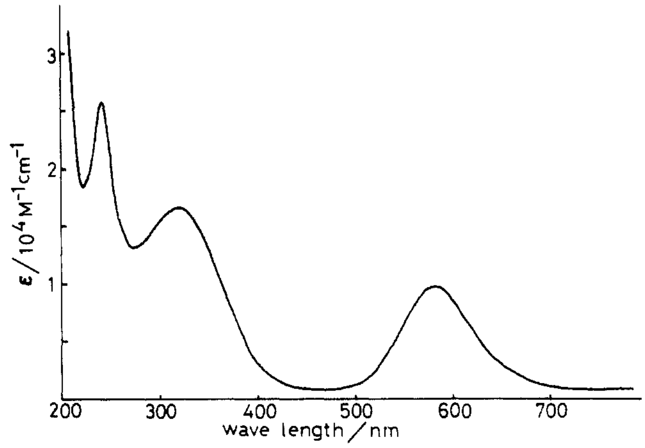

Figure 2. Absorption spectrum of $[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(py)_6](ClO_4)_2$ in CH_3CN.

deviates only slightly from a regular octahedron. The Ru–Ru distance (3.251 (2) Å) is considerably longer than that (2.572 Å) in $[Ru_2(\mu\text{-}OH)_2(\mu\text{-}CH_3COO)(tacn)_2]^{3+}$ (Ru–Ru single bond is suggested),[9] and a direct Ru–Ru bond is absent. The Ru–O(bridge) and Ru–O(acetate) distances as well as the Ru–Ru one are very close to the corresponding distances of the ruthenium(II,III,III) trimer, $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(PPh_3)_3]$,[14] and of the rhodium(III) trimer, $[Rh_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]^+$.[15] Thus the core structure $Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2$ is regarded as a partial structure of the trimeric core $Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6$. The two bridging acetates are twisted (torsion angles: O1–Ru1–Ru2–O2, 22.7°; O3–Ru1–Ru2–O4, 21.3°), and in fact the two octahedrons are twisted around the Ru–Ru axis to make the ion asymmetric. The twist could be the result of steric repulsion of coordinated pyridine molecules.

The new dimeric ion has a very strong absorption peak at 581 nm with $\epsilon = 9400\ M^{-1}\ cm^{-1}$ (Figure 2). The absorption should be due to the transitions between molecular orbitals composed of the Ru $d\pi$ and oxygen $p\pi$ orbitals basically similar to those of the $Ru_3(\mu_3\text{-}O)$ complex.[12] ^1H and ^{13}C NMR spectra indicate that the compound is essentially diamagnetic, spectral patterns being fully consistent with the solid-state structure.[16] Cyclic voltammetry in acetonitrile revealed two reversible one-electron oxidation processes at $E_{1/2} = +0.58$ and $+1.72$ V versus Ag/Ag^+, which should correspond to the reversible oxidation to the Ru_2(III,IV) and Ru_2(IV,IV) states, respectively. An irreversible reduction wave was observed at −0.88 V, which is assigned to the reduction to the Ru_2(II,III) state. The potential is more negative than the corresponding quasireversible wave at −0.374 V versus SCE of $[Fe_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(Me_3tacn)_2]^{2+}$.[4] The coordinated pyridines appear to be liberated at least partly in acidic aqueous solution, accompanied by a blue shift of the strong visible absorption band.

Attempts to isolate an aqua derivative of the dimeric core, which is expected to be a precursor to the pyridine complex, have been unsuccessful so far. Nevertheless, the dimeric ion (aqua derivative) can be important as a precursor to various mixed-metal trinuclear complexes of the type, $[Ru_2M(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6L_3]^{n+}$. In fact, the Ru_2Rh complex reported earlier[17] is likely to be formed via the dimeric state.

Acknowledgment. We are grateful to Dr. Akira Nagasawa for the measurement of ^1H and ^{13}C NMR spectra. This work was supported by the Joint Studies Program (1987–1988) of the Institute for Molecular Science.

Note Added in Proof. After the submission of this communication, Professor K. Wieghardt informed us about the preparation of a new complex, $[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(Me_3tacn)_2]^{3+}$ (*Angew. Chem.*, in press). We are grateful to Professor K. Wieghardt for providing us with this information.

Supplementary Material Available: Tables of atomic positional and thermal parameters and interatomic distances and bond angles for $[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(pyridine)_6](PF_6)_2$ (4 pages); table of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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(14) Cotton, F. A.; Norman, J. G., Jr. *Inorg. Chim. Acta* **1972**, *6*, 411–419.

(15) Glowiak, T.; Kubiak, M.; Szymanska-Buzar, T. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 1732–1737.

(16) ^1H NMR (270 MHz) data: δ 1.62 (s, 6 H, CH_3COO), 7.34 (t, 8 H, py-*m*-H), 7.58 (t, 4 H, py-*p*-H), 7.87 (d, 8 H, py-*o*-H), 8.33 (t, 4 H, py-*m*-H), 8.43 (t, 2 H, py-*p*-H), 9.41 (d, 4 H, py-*o*-H).

(17) Sasaki, Y.; Tokiwa, A.; Ito, T. *J. Am. Chem. Soc.* **1987**, *109*, 6341–6347.

Boratirane: Preparation and Characterization of *trans*-1,1,2,3-Tetraphenylboratirane

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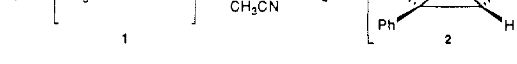
Received April 21, 1988

We report herein the preparation, structure, and characterization of the first example[1] of a new class of boron-containing compounds. Irradiation of tetramethylammonium triphenylstyrylborate (**1**) in an acetonitrile solution at 254 nm converts it to *trans*-1,1,2,3-tetraphenylboratirane (**2**), eq 1. Boratirane **2** is a stable, air and water sensitive, colorless crystalline solid.



(1)

The photochemistry of the tetraarylborates (Ar_4B^-) was first studied by Williams and co-workers[5] who concluded that irradiation in protic solvents leads to formation of unobserved bridged-boron intermediates. Later, Eisch and co-workers[6] suggested that photolysis of tetraphenylborate causes its direct fragmentation to biphenyl with concomitant formation of diphenylborate(I)—a hypovalent borene anion. Reinvestigation of this reaction revealed that direct irradiation of tetraphenylborate does not generate a borene anion but promotes intramolecular migration of a phenyl group.[7] We reasoned that this path might provide access to novel boron-containing structures. The photochemistry of **1** supports this hypothesis.

Borate **1** is prepared by reaction of *trans*-β-styryllithium with triphenylborane. As its tetramethylammonium salt, **1** is a colorless solid, unaffected by air or moisture. The ^{11}B NMR spectrum of

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(1) No compounds containing a tetravalent boron atom in a three-membered ring have been reported. There are previous examples of three-membered ring compounds containing trivalent boron atoms.[2–4]

(2) Wehrmann, R.; Klusik, H.; Berndt, A. *Angew. Chem.* **1984**, *96*, 369. Hildenbrand, M.; Pritzkow, H.; Zenneck, U.; Siebert, W. *Angew. Chem.* **1984**, *96*, 371. Klusik, H.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 877.

(3) Eisch, J. J.; Gonsior, L. J. *J. Organomet. Chem.* **1967**, *8*, 53. Eisch, J. J.; Becker, H. P. *J. Organomet. Chem.* **1979**, *171*, 141. Eisch, J. J.; Shen, F.; Tamao, K. *Heterocycles* **1982**, *18*, 245. van der Kerk, S. M.; Budzelaar, P. H. M.; Hoof, A.; van der Kerk, G. J. M.; Schleyer, P. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 48. Pachaly, B.; West, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 454.

(4) Eisch, J. J.; Shafii, B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 2526.

(5) (a) Williams, J. L. R.; Doty, J. C.; Grisdale, P. J.; Searle, R.; Regan, T. H.; Happ, G. P.; Maier, D. P. *J. Am. Chem. Soc.* **1967**, *89*, 5153. (b) Williams, J. L. R.; Doty, J. C.; Grisdale, P. J.; Regan, T. H.; Happ, G. P.; Maier, D. P. *J. Am. Chem. Soc.* **1968**, *90*, 53. (c) Williams, J. L. R.; Grisdale, P. J.; Doty, J. C.; Glogowski, M. E.; Babb, B. E.; Maier, D. P. *J. Organomet. Chem.* **1968**, *14*, 53–62. (d) Grisdale, P. J.; Babb, B. E.; Doty, J. C.; Regan, T. H.; Maier, D. P.; Williams, J. L. R. *J. Organomet. Chem.* **1968**, *14*, 63. (e) Grisdale, P. J.; Williams, J. L. R.; Glogowski, M. E.; Babb, B. E. *J. Org. Chem.* **1971**, *36*, 544.

(6) Eisch, J. J.; Tamao, K.; Wilcsek, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 895.

(7) Wilkey, J. D.; Schuster, G. B. *J. Org. Chem.* **1987**, *52*, 2117.

0002-7863/88/1510-6252$01.50/0

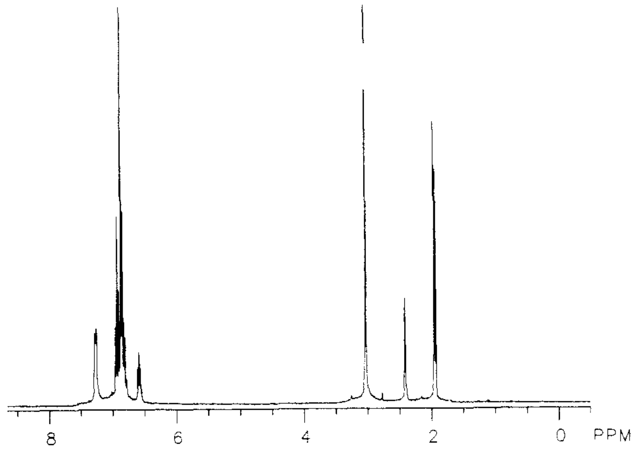


Figure 1. The ^1H NMR spectrum of tetramethylammonium 1,1,2,3-tetraphenylboratirane recorded at room temperature in CD_3CN solution. The peaks are as follows: δ 1.95 (CHD_2CN, from solvent), 2.39 (s, 2 H), 3.02 (s, 12 H, Me_4N^+), 6.56 (m, 2 H, J = 3.6), 6.78–6.95 (m, 14 H), 7.25 (d, 4 H, J = 6.4).

borate **1** (CD_3CN solution) shows a single peak at δ −9.1 ($BF_3{\cdot}OEt_2 = 0.00$). The UV absorption spectrum of borate **1** is characteristic of compounds containing a styryl chromophore: λ_{max} = 270 nm, ϵ_{max} = 23 000 M^{-1} cm^{-1}.

The irradiation of **1** in an oxygen-free acetonitrile solution (0.014 M, 254 nm, Rayonet Reactor) for 45 min converts it into a single product. As the reaction proceeds, the ^{11}B resonance characteristic of **1** decreases in intensity as a new peak at δ −9.4 grows into the spectrum. Revealing changes can also be observed in the ^1H NMR and UV spectra of the reaction mixture. In particular, the characteristic resonances of the vinyl protons of **1** decrease and are replaced by a single peak at δ 2.39; the ^1H NMR spectrum of the photoproduct is shown in Figure 1. Similarly, the optical absorption of **1** at 270 nm is converted to that of the photoproduct: λ_{max} = 280 nm; ϵ = 18 000 M^{-1} cm^{-1}.

The product from irradiation of **1** can be isolated by concentration of the photolysis solution and addition of ether (50% yield after recrystallization). Elemental analysis requires the empirical formula $C_{30}H_{34}BN$; the same as starting styryl borate **1**. The ^{13}C NMR spectrum of the photoproduct shows a weak, boron-coupled multiplet at δ 38.3 and eight unique carbons in phenyl rings; only one (δ 158) with one-bond boron coupling. These facts require the presence of a symmetry element in the photoproduct that leaves two unique phenyl groups and only one other unique, boron-coupled carbon atom.

The structure of the photolysis product was determined by X-ray crystallography as its tetraphenylarsonium salt, Figure 2.[8] The three-membered boron-containing ring is an isosceles triangle with C–B–C and C–C–B bond angles of 55 (1) and 62 (1)° and C–B and C–C bond lengths of 1.61 (3) and 1.49 (3) Å, respectively. The geometry at the boron atom is strongly distorted from tetrahedral symmetry, but this evidently has an almost negligible effect on the ^{11}B NMR chemical shift. The only other compound related to boratirane **2** whose structure has been determined is trimesitylborirene.[4] It, in contrast, is nearly an equilateral triangle.

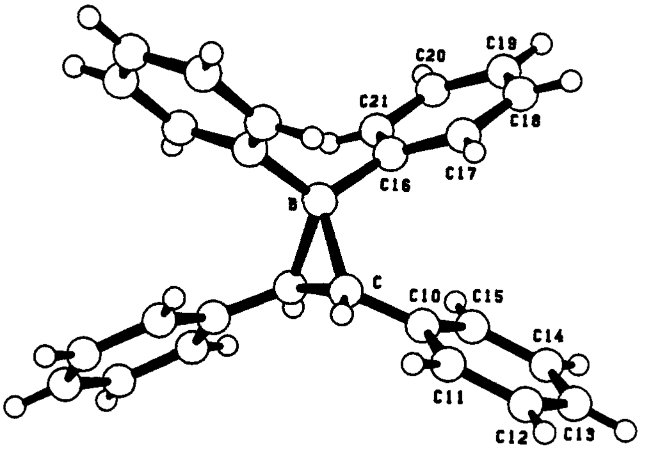
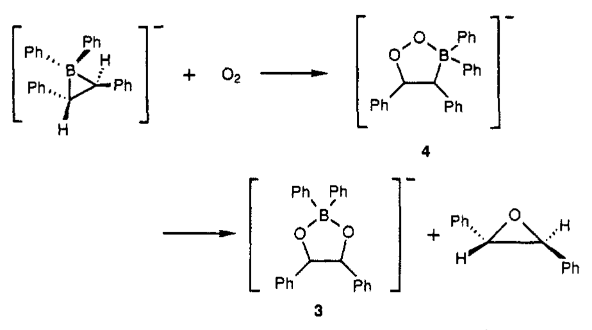


Figure 2. Structure of 1,1,2,3-tetraphenylboratirane determined by X-ray crystallography of its tetraphenylarsonium salt.

We have not yet examined the mechanism for the photorearrangement of **1** to **2**. However, it is apparent that there is a close parallel between the photochemistry of borate **1** and its all-carbon analogue, *trans*-1,3,3,3-tetraphenylpropene.[9] The mechanism in the hydrocarbon case has been studied in detail and is generally believed to involve phenyl group migration according to the di-π-methane paradigm.[10]

The electrochemical oxidation of borate **2** is quite remarkable.[11] Cyclic voltammetry in acetonitrile solution gives an irreversible oxidation wave with peak potential at ca. −0.8 V versus Ag/$AgNO_3$. For comparison, when analyzed under identical conditions, tetraphenylborate shows an oxidation wave at +0.82 V. Consistent with this exceptionally low oxidation potential is the observation that boratirane **2** spontaneously reduces methyl viologen to its radical cation. Ab initio calculations[12] on parent boratirane $[C_2H_6B]^-$ reproduce the geometry found experimentally for **2** and predict that the HOMO is a Walsh-like π-orbital[13] with a node between the carbon atoms and that the negative charge is concentrated primarily on the ring carbon atoms.

We have begun the exploration of the chemical properties of boratiranes. Addition of O_2 to an acetonitrile solution of **2** gives *trans*-stilbene oxide (45%), boratolane **3** (^{11}B NMR = δ 8.2, 20%), and *trans*-stilbene (5%), eq 2. The structure of **3** was confirmed



4

(2)

3

by its conversion to 2,4,5-triphenyl-1,3,2-borolane[14] with acid and by the conversion of the borolane to **3** with phenyllithium. The formation of these products signals the likely intermediacy of

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(8) Crystal data for $[C_{24}H_{20}As][C_{26}H_{22}B]{\cdot}(C_4H_{10}O)$: monoclinic, space group $C2/c$, a = 28.750 (12) Å, b = 13.228 (10) Å, c = 23.317 (5) Å, β = 105.35 (3)°, V = 8552 (12) Å^3, and Z = 8. Diffraction data: Enraf Nonius CAD4 automated κ-axis diffractometer, Mo radiation ($\lambda(K\bar{\alpha})$ = 0.71073 Å), range $3.0 < 2\theta < 46.0°$ ($-h-k\pm l$ for $h + k = 2n$), 6546 reflections (5940 unique, R_1 = 0.021, 1857 observed, $I > 2.58\sigma(I)$); corrected for anomalous dispersion, absorption, Lorentz and polarization effects but not corrected for a nonlinear crystal decay (less than 11%). Solution: Patterson methods (SHELXS-86); ether solvate molecule disordered about the 2-fold symmetry axis. Refinement: ether molecule and aromatic rings refined as rigid ideal groups, H atoms included as idealized contributors and remaining atoms independently refined (SHELX). Final: difference Fourier map (range $-0.55 < e/Å^3 < 0.81$) located maximum residual electron density in the vicinity of the As atom; variance between observed and calculated structure factors showed a slight dependence on amplitude and inverse sin (θ); agreement factors, R = 0.114, R_w = 0.135, and E = 2.50. The X-ray structure of the tetra-*n*-butylammonium salt was also determined and is consistent. A detailed report of the structure and its determination prepared by Dr. S. Wilson of the X-ray spectroscopy lab of the University of Illinois is included as Supplementary Material to this paper.

(9) Griffin, G. W.; Marcantonio, A. F.; Kristinsson, H.; Petterson, R. C.; Irving, C. S. *Tetrahedron Lett.* **1965**, 2951.

(10) Hixson, S. S. *Tetrahedron Lett.* **1972**, 1155. Zimmerman, H. E. *Rearrangements in Ground and Excited States*: de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 131XX.

(11) Chatterjee, S.; Gottschalk, P.; Davis, P. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 2326.

(12) The calculations were performed at the National Center for Super Computing at the University of Illinois on the GAUSSIAN 86 package with an STO321G basis set.

(13) Walsh, A. D. *Trans. Faraday Soc.* **1949**, 179.

(14) Letsinger, R. L.; Hamilton, S. B. *J. Org. Chem.* **1960**, *25*, 592.

peroxyboratolane **4** in the reaction of **2** with oxygen. When water or methanol is added to a solution of **2**, an unstable product is detected by ^{11}B NMR spectroscopy (δ −1.2, +1.5, respectively) that is presumed to be the diphenylalkylhydroxy (or methoxy) borate. Analysis of the product mixture containing these intermediates by gas chromatography reveals formation of bibenzyl.

In sum, the photochemical [1,2] shift of an aryl group is a useful route for formation of boratiranes. Boratiranes are reactive compounds characterized by unusually low oxidation potentials. We are continuing to explore their chemistry.

Acknowledgment. We thank David Hartsough of this department for his assistance with the molecular orbital calculations and Professor Larry Faulkner and Mark Burns for their assistance with the cyclic voltammetric measurements. This work was supported by a grant from the National Science Foundation.

Supplementary Material Available: Crystal data and tables of atomic coordinates, calculated positions, and thermal parameters for $[C_{24}H_{20}As][C_{26}H_{22}B]\cdot{}^1/_2(C_4H_{10}O)$ and crystal data for $N_4C_{168}B_4H_{232}$ (6 pages); table of observed and calculated structure factors for $[C_{24}H_{20}As][C_{26}H_{22}B]\cdot{}^1/_2(C_4H_{10}O)$ (8 pages). Ordering information is given on any current masthead page.

Acyloxyborane: An Activating Device for Carboxylic Acids[†]

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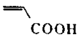
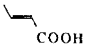
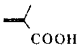
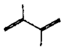
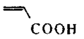
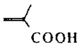
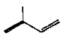
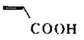
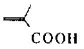
Received March 15, 1988

The synthetic power of borane reduction of carboxylic acids is well-documented, and the reaction is widely used as the peerless method in organic synthesis.[1] The remarkable reactivity of borane toward carboxylic acids over esters is one of the conspicuous characteristics of this element which is hardly seen in any other hydride reagents such as aluminum hydride.

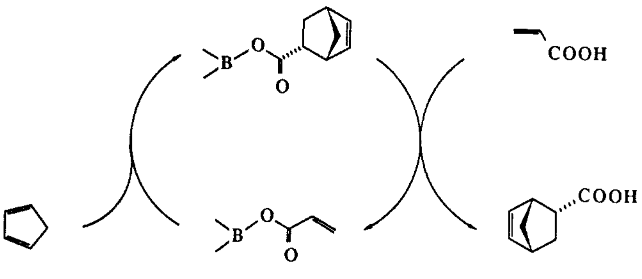
The rapid reaction between carboxylic acids and borane is related to the electrophilicity of borane. An acyloxyborane is recognized to be an initial intermediate.[1e] The carbonyl group in this molecule, which is essentially a mixed anhydride, is activated by the electronegative nature of the trivalent boron atom. This fact intrigued us greatly and then awoke our interest in whether the acyloxyborane can accept the attack of a molecule other than a simple hydride. Thus, if the acyloxyborane has enough reactivity to cause functionalization on its acid moiety, various applications should be anticipated, although such possibility has never been explored previously.[2] As an initial example, we chose α,β-unsaturated acids and investigated the reactivity of their borane adducts in Diels–Alder reactions. The reaction did proceed smoothly and has been found to be a useful method.

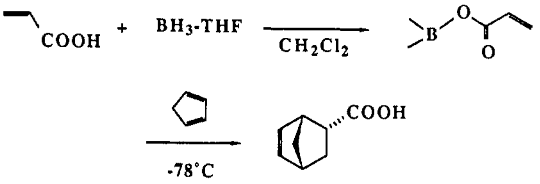
Addition of $^1/_3$ equiv of borane–THF complex to the acrylic acid dissolved in dichloromethane at 0 °C followed by the diene at low temperature resulted in the formation of the Diels–Alder adduct in good yield (eq 1). Further, the reaction could progress satisfactorily even with a catalytic amount of borane (10 mol% or less). The reaction could be applied to various types of acids and dienes, and some of the results are summarized in Table I.

Table I. Diels–Alder Reaction of Acyloxyboranes with Dienes[a]

dienes[b]	acids	temp (°C)	time (h)	yield[c] (%)
		−78	28	72
		0	40	52
		−20	16	71
		−20	48	60
		0	74	49
		0	30	75
		20	68	66

[a] Borane–THF complex (10 mol%) based on acid was used. [b] Diene (1.5 equiv) was used. [c] Isolated yield.


Scheme I

 (1)

We formulated the catalyzed reaction as shown in Scheme I. Thus, the fact that the reaction proceeded catalytically apparently indicates the facile exchange of the carboxylic acid moiety of acyloxyborane between Diels–Alder adduct and unreacted acid.

Addition of cyclohexanol (1 equiv to catalyst or more) to the reaction media remarkably reduced the reactivity of acyloxyborane, probably due to the irreversible exchange of acid with alcohol in borane complexes and also due to the reduced reactivity of the resulting alkoxy-substituted acyloxyborane.[3] Interestingly, however, monoalkoxy-substituted acyloxyborane still has sufficient reactivity to produce Diels–Alder product.

With the above experimental guidance, it became of interest to evaluate the inducing ability of appropriate chiral auxiliary by introducing them into the acyloxyborane intermediate both as a test of the mechanistic hypothesis and a step toward more powerful synthetic methodology. Although a number of asymmetric Diels–Alder systems have been reported and some of which could provide useful means for enantioselective synthesis, only limited methodology is available starting from simple dienophiles, i.e., aldehydes, acids, or simple esters.[4] Described below are results

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[†] Dedicated to Professor E. J. Corey on the occasion of his 60th birthday.

(1) (a) Brown, H. C.; Subba Rao, B. C. *J. Am. Chem. Soc.* **1960**, *82*, 681. (b) Brown, H. C.; Heim, P.; Yoon, N. M. *J. Am. Chem. Soc.* **1970**, *92*, 1637. (c) Yoon, N. M.; Pak, C. S.; Brown, H. C.; Krishnamurthy, S.; Stocky, T. P. *J. Org. Chem.* **1973**, *38*, 2786. (d) Lane, C. F. *Chem. Rev.* **1976**, *76*, 773. (e) Brown, H. C.; Stocky, T. P. *J. Am. Chem. Soc.* **1977**, *99*, 8218. See, also: (f) Choi, Y. M.; Emblidge, R. W.; Kucharczyk, N.; Sofia, R. D. *J. Org. Chem.* **1987**, *52*, 3925. (g) Cha, J. S.; Kim, J. E.; Lee, K. W. *J. Org. Chem.* **1987**, *52*, 5030. (h) Brown, H. C.; Cha, J. S.; Yoon, N. M.; Nazer, B. *J. Org. Chem.* **1987**, *52*, 5400.

(2) Ganem et al. reported the improved procedure for conversion of simple acyloxyboranes into amides by the use of catecholborane: Collum, D. B.; Chen, S.-C.; Ganem, B. *J. Org. Chem.* **1978**, *43*, 4393.

(3) Almost no Diels–Alder adduct was obtained by the addition of 2 equiv of alcohol. Alkoxyboron species derived directly from 2 equiv of alcohol and borane showed also no activity as Diels–Alder catalyst in the present case.

0002-7863/88/1510-6254$01.50/0