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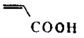
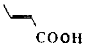
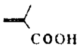
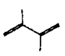
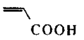
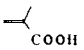
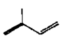
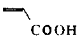
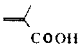
The synthetic power of borane reduction of carboxylic acids is well-documented, and the reaction is widely used as the peerless method in organic synthesis.[1] The remarkable reactivity of borane toward carboxylic acids over esters is one of the conspicuous characteristics of this element which is hardly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

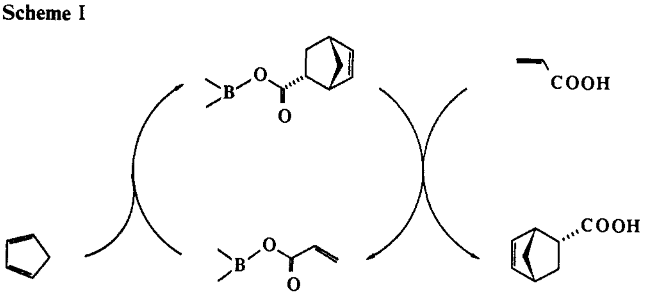
Addition of $^1/_3$ equiv of borane–THF complex to the acrylic acid dissolved in dichloromethane at 0 °C followed by the diene at low temperature resulted in the formation of the Diels–Alder adduct in good yield (eq 1). Further, the reaction could progress satisfactorily even with a catalytic amount 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.

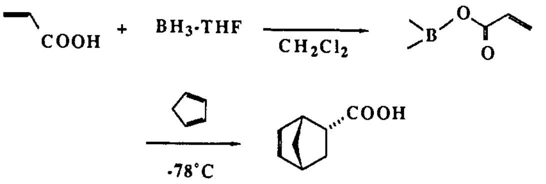
Table I. Diels–Alder Reaction of Acyloxyboranes with Dienes[a]

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.

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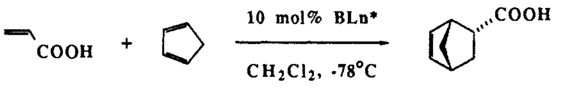
of our initial investigation that demonstrate for the first time the possibility of achieving useful enantioselectivities with a simple chiral controller ligand, easily obtainable in either enantiomeric form from inexpensive tartaric acid.

Reaction of the monoacylated tartaric acid (**1a–d**)[5] with 1 equiv of borane–THF complex in dichloromethane at 0 °C should result in the formation of a chiral acyloxyborane intermediate. Acrylic acid (10-fold excess) was added to this catalyst solution at 0 °C, and then the mixture was cooled to −78 °C. To this was added cyclopentadiene, and the resulting mixture was stirred at the same temperature for 24 h. After usual workup and chromatographic separation, Diels–Alder adduct was isolated in 93% yield (mixture of endo and exo isomers in the ratio of 96:4). The product mixture was subjected to iodolactonization, and the major endo isomer was separated as iodolactone.[6] The product showed a specific rotation ([α]$_D$) of −86°, which corresponded to 78% optical yield with *R*-configuration.[7] The use of the D-tartaric acid should afford the enantiomer of the adduct. In fact, *S*-isomer was obtained from the unnatural form of tartaric acid in 85% yield and 78% ee. The reaction seems to be general and applicable to other dienes and unsaturated acids.[8] The extent of asymmetric induction largely depended on the acyl moiety of tartaric acid derivatives, and **1d** revealed the highest asymmetric induction among the tartaric acid derivatives tested so far.[9]

1a: R = CH$_3$
b: R = t-Bu
c: R = Ph
d: R = 2,6-(MeO)$_2$Ph



	Yield(%)	ee(%)
2a:	66	34
b:	68	51
c:	88	35
d:	93	78

We believe that the experimental results gained in this work will stimulate further exciting advances in this important area of chemistry. At present, the mechanism of asymmetric induction is not clear, but it may be supposed that α-hydroxy acid and borane make the rigid cyclic structure to form effective asymmetric field.[10] Many applications of this new catalytic methodology in synthesis can be foreseen.

Acknowledgment. Support of this research by the Ministry of Education, Science and Culture, Japanese Government is gratefully acknowledged.

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[4] For the asymmetric Diels–Alder reaction of chiral ester or analogues, see: (a) Paquette, L. A. In *Asymmetric Synthesis, Vol. 3*; Morrison, J. D., Ed.; Academic Press: Orlando, FL, 1984. (b) Helmchen, G.; Karge, R.; Weetman, J. In *Modern Synthetic Methods, Vol. 4 · 1986*; Scheffold, R., Ed.; Springer-Verlag: Berlin, Heidelberg, 1986. (c) Oppolzer, W. *Tetrahedron* **1987**, *43*, 1969. Recently, some catalytic processes using chiral Lewis acid have been explored: (d) Hashimoto, S.; Komeshima, N.; Koga, K. *J. Chem. Soc., Chem. Commun.* **1979**, 437. (e) Bednarski, M.; Maring, C.; Danishefsky, S. *Tetrahedron Lett.* **1983**, *24*, 3451. (f) Kelly, T. R.; Whiting, A.; Chandrakumar, N. S. *J. Am. Chem. Soc.* **1986**, *108*, 3510. (g) Narasaka, K.; Inoue, M.; Okada, N. *Chem. Lett.* **1986**, 1109. (h) Maruoka, K.; Sakurai, M.; Fujiwara, J.; Yamamoto, H. *Tetrahedron Lett.* **1986**, *27*, 4895. (i) Narasaka, K.; Inoue, M.; Yamada, T. *Chem. Lett.* **1986**, 1967. (j) Bir, G.; Kaufmann, D. *Tetrahedron Lett.* **1987**, *28*, 777. (k) Quimpere, M.; Jankowski, K. *J. Chem. Soc., Chem. Commun.* **1987**, 676. (l) Chapuis, C.; Jurczak, J. *Helv. Chim. Acta* **1987**, *70*, 436. (m) Seebach, D.; Beck, A. K.; Imwinkelried, R.; Roggo, S.; Wonnacott, A. *Helv. Chim. Acta* **1987**, *70*, 954. (n) Takemura, H.; Komeshima, N.; Takahashi, I.; Hashimoto, S.; Ikota, N.; Tomioka, K.; Koga, K. *Tetrahedron Lett.* **1987**, *28*, 5687. (o) Narasaka, K.; Inoue, M.; Yamada, T.; Sugimori, J.; Iwasawa, N. *Chem. Lett.* **1987**, 2409. (p) Maruoka, K.; Itoh, T.; Shirasaka, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 310.

(5) These compounds were prepared by the monoacylation of dibenzyl tartrate followed by hydrogenolysis.

(6) Berson, J. A.; Ben-Efraim, D. A. *J. Am. Chem. Soc.* **1959**, *81*, 4083. No recrystallization of the product was conducted.

(7) Kirmse, W.; Siegfried, R. *J. Am. Chem. Soc.* **1983**, *105*, 950.

(8) For a preliminary experiment, the reaction of crotonic acid and cyclopentadiene with this catalyst at −20 °C gave the Diels–Alder adduct of 60% ee. Acrylic acid also reacted with 2,3-dimethyl-1,3-butadiene under the similar reaction conditions to afford the adduct of 55% optical purity. The detailed results will be published in full.

(9) The appropriate designing of the chiral tartaric acid ligands should reach to the satisfactory level of asymmetric synthesis.

(10) The possibility for the existence of oligomeric or polynuclear species cannot be ruled out. See: Pedersen, S. F.; Dewan, J. C.; Eckman, R. R.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 1279.

Syndiospecific Propylene Polymerizations with Group 4 Metallocenes

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Isotactic polypropylenes have been synthesized in stereospecific group 4 metallocene polymerizations. Stereochemical control by chiral growing chain ends and by enantiomorphic sites led to two different isotactic polymer configurational microstructures.[1,2]

Partially syndiotactic polypropylene has been obtained in vanadium-catalyzed polymerizations below −50 °C. The polymer ...rrrrrmrrrrr... stereosequences are in accord with chain end stereoregulation.[3]

In this contribution we describe new syndiospecific polymerizations with Hf and Zr metallocenes yielding crystalline polymer in high yields at conventional polymerization conditions. The polymer configurational microstructure is consistent with site control and with the active sites isomerizing with each monomer addition.

Metallocenes. The molecular structure and atom numbering scheme of isopropyl(cyclopentadienyl-1-fluorenyl)hafnium(IV) dichloride (i-PrCp-1-FluHfCl$_2$) is displayed in Figure 1. The crystal structure reveals a bent, sandwich complex with trihapto bonding of the fluorenyl ligand to hafnium. The complex is prochiral, C(2) and C(5) in the C5 fluorene ring are chiral and of opposite handedness, and the hydrocarbon ligand system is stereorigid.[4,5]

Polymerizations. Schering's methylalumoxane was used to alkylate and, possibly, produce brightly colored violet Zr and pink Hf active cations.[1] The catalysts were precipitated at 25 °C with liquid propylene and prepolymerized for 3 min while heating to the polymerization temperatures. This procedure resulted in uniformly sized, symmetrical, free flowing, granular polymer

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(1) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355–6364.

(2) Ewen, J. A.; Haspeslagh, L.; Atwood, J. L.; Zhang, H. *J. Am. Chem. Soc.* **1987**, *109*, 6544–6545.

(3) Zambelli, A.; Locatelli, P.; Provasoli, A.; Ferro, D. R. *Macromolecules* **1980**, *13*, 267.

(4) The ligand was synthesized from stoichiometric reaction of fluorenyllithium salt and 6,6-dimethylfulvene in THF. The bright yellow hafnium and the deep red zirconium complexes were isolated by crystallization at −20 °C after warming the ligand dianion and a slurry of MCl$_4$ in CH$_2$Cl$_2$ from −78 °C to 25 °C.

(5) The space group for i-PrCp-1FluHfCl$_2$ is $P2_1/c$ (no. 14) with a = 10.66 (1) Å, b = 8.878 (5) Å, c = 18.59 (2) Å, β = 100.51 (9)°, V = 1729 (3) Å^3, Z = 4, and D_{calcd} = 1.996 g/cm^3. Refinement on the 1614 data $I > 3.00(I)$ resulted in residuals R = 0.058 and R_w = 0.060.

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