radical cation of this structure ($4^{\bullet+}$) upon stabilization by hydrogen atom or hydride ion transfer[6c] would be the bicyclo[2.2.2]oct-2-ene radical cation, which has a very different ESR spectrum[9] from that of $3^{\bullet+}$.

A more intriguing possibility[15] is that the mechanism includes a skeletal rearrangement of the Wagner–Meerwein type[16] after endo vinyl addition from C-1 of the ene radical cation, in which case structure $4^{\bullet+}$ now needs to be reconsidered. Instead of a delocalized species with $C_2$ symmetry, it may conceivably adopt the distonic structure $4a^{\bullet+}$ (bicyclo[2.2.2]oct-2-yl-5-ylium radical cation), in which the charge and spin are localized separately[17] at the diyl centers. As shown in Scheme II, this species can rearrange to $5^{\bullet+}$ by a 1,2-alkyl carbonium ion shift, ample precedent being supplied by the transformation of the bicyclo[2.2.2]oct-2-ylium cation to the bicyclo[3.2.1]oct-2-ylium cation in solvolysis reactions,[18] and only a vicinal hydride shift would then be needed to complete the rearrangement to $3^{\bullet+}$.

**Acknowledgment**. We thank Mr. R. S. Pappas and Dr. J. T. Wang for their help with the AM1 calculations and experimental procedures, respectively. We are also indebted to Professor R. M. Pagni for useful discussions. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy (Grant No. DE-FG05-88ER13852).

**Supplementary Material Available:** ESR spectra taken after the radiolytic oxidation of **1** in $CFCl_3$ showing the conversion of $1^{\bullet+}$ to $3^{\bullet+}$ between 95 and 140 K and a matching spectrum of $3^{\bullet+}$ produced by the oxidation of **3** in $CFCl_3$ (1 page). Ordering information is given on any current masthead page.

---

(15) We thank one of the reviewers for this suggestion.

(16) Ingold, C. K. *Structure and Mechanism in Organic Chemistry*; Cornell University Press: Ithaca, New York, 1953; pp 482–486, 488–494, 513–524.

(17) (a) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5805; *Tetrahedron* **1986**, *42*, 6225. (b) Hammerum, S. *Mass Spectrom. Rev.* **1988**, *7*, 123–202.

(18) (a) Doering, W. von E.; Farber, M. *J. Am. Chem. Soc.* **1949**, *71*, 1514. (b) Goering, H. L.; Sloan, M. F. *J. Am. Chem. Soc.* **1961**, *83*, 1992. (c) Streitwieser, A., Jr. *Solvolytic Displacement Reactions*; McGraw-Hill: New York, 1962; pp 133–134, 184–185.

---

## Two-Point-Binding Asymmetric Diels–Alder Catalysts: Aromatic Alkyldichloroboranes

Joel M. Hawkins* and Stefan Loren

*Department of Chemistry*
*University of California, Berkeley*
*Berkeley, California 94720*

*Received June 21, 1991*

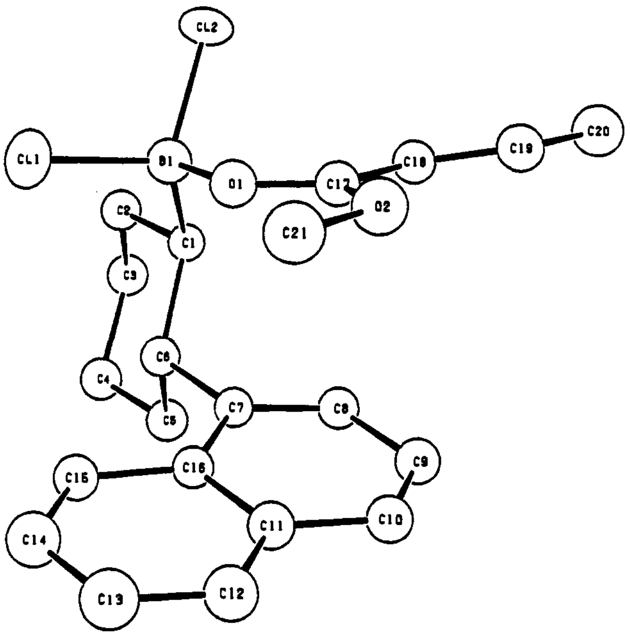
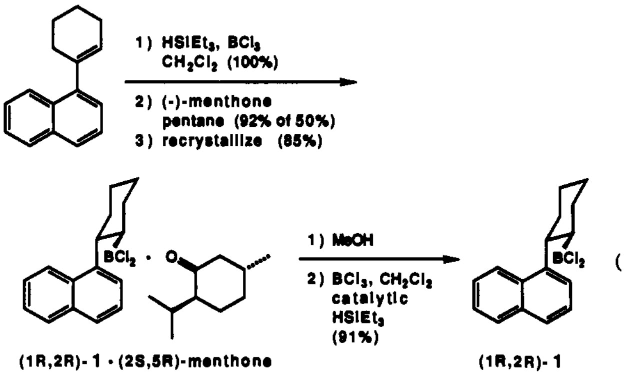


Figure 1. ORTEP view of (±)-**1**·methyl crotonate. Selected bond distances (Å) and angles (deg): B1–C1 = 1.609 (16); B1–Cl1 = 1.862 (12); B1–Cl2 = 1.876 (13); B1–O1 = 1.538 (15); O1–C17 = 1.266 (12); C17–C18 = 1.436 (15); C18–C19 = 1.340 (15); O1–B1–C1 = 115.1 (9); O1–B1–Cl1 = 101.0 (7); O1–B1–Cl2 = 105.2 (7); C17–O1–B1 = 130.3 (9).

The development of chiral Lewis acids can lead to useful asymmetric catalysts and to a better understanding of molecular recognition. We seek asymmetric Lewis acids for the Diels–Alder reaction[1] which individually correspond to catalytically active species of predictable geometry, and as a group provide the ability to vary structural elements in a controlled manner in order to probe weak attractive interactions in the transition state. Alkyldihaloboranes containing aromatic groups fit these characteristics.[2] They do not readily aggregate or disproportionate, bind only one donor ligand at a time, and allow attachment of the complexed metal directly to a stereocenter via a short bond between tetrahedral atoms, thus making complexes amenable to conformational analysis. The arene provides an electron-rich and polarizable group to attract electron-deficient and polarized boron-bound dienophiles, giving a second binding interaction with the catalyst. We report the synthesis and resolution of alkyldichloroborane **1**, the crystal structure of **1** complexed with methyl crotonate, NMR data indicating that this structure is maintained in solution, and asymmetric Diels–Alder reactions catalyzed by **1** with 86–97% ee corresponding to approach of the dienes to the predicted open face of the complexed dienophiles.

Racemic **1** was prepared by hydroboration[3] and resolved via its crystalline complex with menthone (eq 1). Greater than 99% de[4] menthone complex was obtained after a single recrystallization from dichloromethane/pentane in 78% yield from the olefin. This is the first borane resolution via a bimolecular complex.[5] The menthone-free catalyst was obtained in 91% yield by methanolysis and rechlorination with $BCl_3$.



(1)

Crystals of (±)-**1**·methyl crotonate suitable for X-ray diffraction were obtained from pentane (Figure 1).[6] The following features

---

(1) For leading references on asymmetric Diels–Alder catalysts, see: Furuta, K.; Shimizu, S.; Miwa, Y.; Yamamoto, H. *J. Org. Chem.* **1989**, *54*, 1481. Narasaka, K.; Iwasawa, N.; Inoue, M.; Yamada, T.; Nakashima, M.; Sugimori, J. *J. Am. Chem. Soc.* **1989**, *111*, 5340. Corey, E. J.; Imwinkelried, R.; Pikul, S.; Xiang, Y. B. *J. Am. Chem. Soc.* **1989**, *111*, 5493.

(2) Nonaromatic chiral alkyldihaloboranes have given up to 28% ee in asymmetric Diels–Alder reactions: Bir, G.; Kaufmann, D. *Tetrahedron Lett.* **1987**, *28*, 777.

(3) Soundararajan, R.; Matteson, D. S. *J. Org. Chem.* **1990**, *55*, 2274.

(4) Determined by the ee of the corresponding acetate obtained by oxidation and acetylation. Absolute configuration determined by the crystal structure of the analogous menthyl carbonate.

(5) For a resolution via an alkoxyborane, see: Masamune, S.; Kim, B. M.; Petersen, J. S.; Sato, T.; Veenstra, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 4549. For an in situ catalyst generation via diastereoselective complexation, see: Maruoka, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1989**, *111*, 789.

0002-7863/91/1513-7794$02.50/0

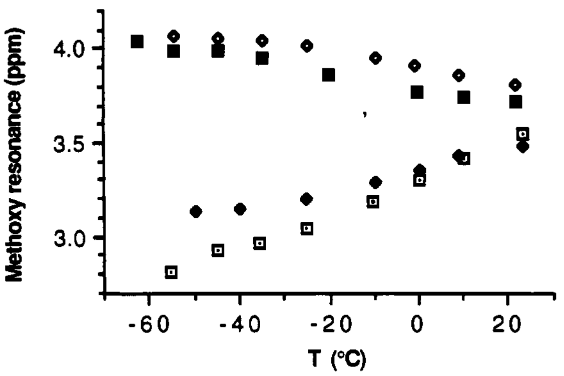
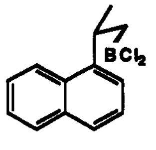


**Figure 2.** Methoxy resonance of methyl crotonate combined with borane 1 (⊡), 2 (◆), 3 (■), or 4 (◇) as a function of temperature.

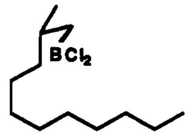
of the structure were predicted by conformational analysis: the conformation about the C7–C6 bond positions the smallest benzylic substituent (H) toward the naphthalene *peri*-H,[7] the naphthalene and boron are equatorial on the chair cyclohexane, the C1–B1 and B1–O1 bonds are staggered,[8] boron complexes the carbonyl oxygen anti to the C17–O2 bond of the ester,[9] the enone unit is s-trans,[9] and the carbonyl group is positioned over and approximately parallel to the naphthalene ring within van der Waals radii (C17···C8 = 3.172 (15) Å). Electrostatic and dipole-induced-dipole attractions between the Lewis acid activated carbalkoxy group and the electron-rich arene likely favor this conformation relative to other conformations with staggered C–B and B–O bonds (vide infra).[10,11] In this conformation, the edge of the naphthalene *blocks the bottom face of the dienophile*, leaving the top face open to approach by dienes.[12]

Spectroscopic evidence indicates that this structure is largely maintained in solution. Variable-temperature $^1$H NMR spectra of methyl crotonate combined with 1 equiv of borane **1**, **2**, **3**, or **4** were recorded in $CDCl_3$. As the temperature was lowered, the $\alpha$-, $\beta$-, and $\gamma$-protons of methyl crotonate moved downfield as a greater percentage of the ester coordinated to the Lewis acid. These protons behaved similarly with arene-containing boranes **1** and **2** and aliphatic models **3** and **4**. The *methoxy* signal, however, was shifted *upfield* with the arene-containing boranes, in contrast to downfield shifts observed with the references (Figure 2). At −55 °C, the methoxy resonance in the presence of **1** was 1.2 ppm upfield relative to the corresponding complex with **3**, indicating a time-averaged preferred geometry with the methoxy group oriented over the naphthalene ring, as observed in the solid state.[13] The similar behavior of methyl crotonate with boranes **1** and **2** suggests that the attraction between the boron-bound carbonyl group and the arene is sufficient to hold the methoxy over the naphthalene in a complex with **2**, even without the conformational restrictions imposed by the cyclohexane ring in **1**.



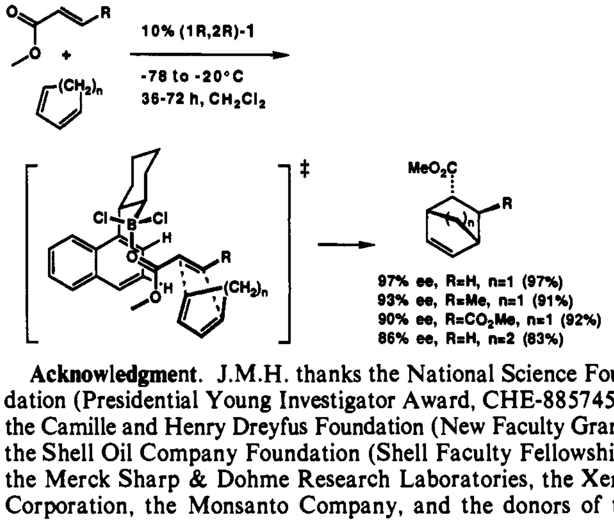
**2**

**3**



**4**

These structural studies involve the ground state of **1**·methyl crotonate. Since conformational equilibria within this complex (rapid on the NMR time scale) are much faster than Diels–Alder reactions with the coordinated dienophile (moderate rate on the laboratory time scale), the system is under Curtin–Hammett conditions. Accordingly, ground-state stabilization should not decrease the reactivity of a conformation but, rather, increase its reactivity if this stabilization is maintained in the transition state. Diels–Alder reactions with methyl acrylate, methyl crotonate, and dimethyl fumarate support this premise and demonstrate the enantioselectivity of this system. Using 10% **1** as a catalyst, these esters gave adducts with cyclopentadiene and cyclohexadiene with 86–97% ee (eq 2).[14] The absolute configurations are all consistent with *approach of the diene to the open face of the dienophile as predicted by conformational analysis and the* **1***·methyl crotonate structure*. The effect of varying the polarizability and dipole of the arene and the extension of this catalyst to other systems will be reported shortly.



(2)

**Acknowledgment.** J.M.H. thanks the National Science Foundation (Presidential Young Investigator Award, CHE-8857453), the Camille and Henry Dreyfus Foundation (New Faculty Grant), the Shell Oil Company Foundation (Shell Faculty Fellowship), the Merck Sharp & Dohme Research Laboratories, the Xerox Corporation, the Monsanto Company, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support. S.L. thanks the Regents of the University of California and the Syntex Corporation for fellowships. Crystal structure analyses were performed by Dr. F. J. Hollander and M. Scott at the UC Berkeley X-ray crystallographic facility.

**Supplementary Material Available:** Details of the structure determination for (±)-**1**·methyl crotonate, including tables of crystal and data parameters, positional parameters and their estimated standard deviations, anisotropic thermal parameters, and intramolecular distances and angles (3 pages). Ordering information is given on any current masthead page.

---

(6) One crystal structure of a bimolecular complex between a carbonyl and a boronic Lewis acid has been reported. (a) Reetz, M. T.; Hullmann, M.; Massa, W.; Berger, S.; Rademacher, P.; Heymanns, P. *J. Am. Chem. Soc.* **1986**, *108*, 2405. (b) Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Angew. Chem.* **1990**, *29*, 256.

(7) Pirkle, W. H.; Hoover, D. J. *Top. Stereochem.* **1982**, *13*, 263.

(8) The complex of benzaldehyde with $BF_3$ shows similar O–B bond staggering.[6a]

(9) The 2:1 complex of ethyl cinnamate with $SnCl_4$ also shows an s-trans enone conformation with the tin located anti to the ethoxy group: Lewis, F. D.; Quillen, S. L.; Hale, P. D.; Oxman, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 1261. $BF_3$ complexes of cinnamic esters display similar structures in solution: Lewis, F. D.; Oxman, J. D.; Gibson, L. L.; Hampsch, H. L.; Quillen, S. L. *J. Am. Chem. Soc.* **1986**, *108*, 3005.

(10) Morokuma, K. *Acc. Chem. Res.* **1977**, *10*, 294.

(11) A Lewis acid enhanced electronic interaction between an arene and a dicarbonyl has been observed in an ene system: Whitesell, J. K.; Younathan, J. N.; Hurst, J. R.; Fox, M. A. *J. Org. Chem.* **1985**, *50*, 5499.

(12) $\pi$–$\pi$ interactions between the *carbon–carbon* double bond of dienophiles and aromatic rings in covalently bound chiral auxiliaries have been proposed for several asymmetric Diels–Alder reactions: Evans, D. A.; Chapman, K. T.; Bisaha, J. *J. Am. Chem. Soc.* **1988**, *110*, 1238 and references therein.

(13) Upfield shifts as small as 0.2–0.5 ppm are associated with $\pi$-stacking between aromatic surfaces in host–guest complexes: Askew, B.; Ballester, P.; Buhr, C.; Jeong, K. S.; Jones, S.; Parris, K.; Williams, K.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 1082. Muehldorf, A. V.; Van Engen, D.; Warner, J. C.; Hamilton, A. D. *J. Am. Chem. Soc.* **1988**, *110*, 6561.

(14) Reactions 0.5 M in dienophile. Enantiomeric excesses determined with chiral shift reagent Eu(hfc)$_3$ in $CDCl_3$ (R = Me, $n$ = 1; R = $CO_2Me$, $n$ = 1) or by chiral stationary phase GC on a J&W Scientific Cyclodex-B column (R = H, $n$ = 1; R = H, $n$ = 2). Absolute configurations determined by comparison of optical rotations with literature values; R = H, $n$ = 1: Berson, J. A.; Walia, J. S.; Remanick, A.; Suzuki, S.; Reynolds-Warnhoff, P.; Willner, D. *J. Am. Chem. Soc.* **1961**, *83*, 3986. R = Me, $n$ = 1: Berson, J. A.; Hammons, J. H.; McRowe, A. W.; Bergman, R. G.; Remanick, A.; Houston, D. *J. Am. Chem. Soc.* **1967**, *89*, 2590. R = $CO_2Me$, $n$ = 1: Sauer, J.; Kredel, J. *Tetrahedron Lett.* **1966**, 6359. R = H, $n$ = 2: Cervinka, O.; Kriz, O. *Collect. Czech. Chem. Commun.* **1968**, *33*, 2342.