shorter than a calculated value (2.59 Å).[19] Three Si atoms form an imaginary three-membered ring with three phantom bonds[16] (Chart I). The average PBL is almost the same value as the Si–Si bond length of hexa-*tert*-butyltrisilane.[21]

The isolation of the trisilabicyclo[1.1.1]pentane **4** was very exciting (without any bulky groups), because 2,4,5-trisilabicyclo[1.1.1]pentane (strain energy 54.2 kcal/mol) is calculated to be more strained than pentasilabicyclo[1.1.1]pentane (strain energy 37.4 kcal/mol)[16e] whose derivative was isolated very recently.[24]

The cage C–Si bond of **4** showed a high reactivity to moisture. The compound **4a** reacted with H_2O in MeOH or EtOH at room temperature to give ring-opening products **7a** and **8a** (Scheme II),[25] although normal disilacyclobutanes do not show such a reactivity.[28]

The high reactivity of the cage Si–C bond to the nucleophile may be rationalized in terms of the polarization of the cage.[29] If Streitwieser's ionic model can apply to this system, the polarization can be accounted for by a model shown in Chart II.[16c,30] The bridgehead C–$SiMe_2R$ groups are represented by the point charge −3 and the bridge $SiMe_2$ groups as point charge +2. The net Coulomb interaction of this model acts as the attraction; it resulted in the shortening of the atomic distance (or the bond length). The energy minimum of Streitwieser's model is found at about $\theta = 80°$;[16c] this value is very close to the C–Si–C angle of **4b** (79.5°).[31] The NMR signal of the cage ^{29}Si was observed at the lower field (**4a**, −4.9 ppm; **4b**, 31.9 ppm), compared with that of the substituent (**4a**, −11.4 ppm; **4b**, −5.10 ppm). From these results we concluded that the bonds of 2,4,5-trisilabicyclo[1.1.1]pentane, **4**, have considerable ionic character.

Acknowledgment. This work was supported by the Grant-in-Aid for Scientific Research on Priority Area of Molecular Design by heteroatom and for General Scientific Research from the Ministry of Education, Science and Culture, Japan.

Supplementary Material Available: Complete spectral data of all new compounds and detailed information of the X-ray crystal analysis (32 pages); table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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(17) We use the term "a phantom bond" in imitation of Nagase's paper and to avoid a term "nonbonded distance". We do not think that there is chemical bonding between bridge silicon atoms. It is natural to postulate chemical bonding between spatially closing atom. It may be that there is some special bond which has considerable ionic character, otherwise σ-bridged-π bonding has been a very recently proposed alternative.[18]

(18) (a) Liang, C.; Allen, L. C. *J. Am. Chem. Soc.* **1991**, *113*, 1878. (b) Jackson, J. E.; Allen, L. C. *J. Am. Chem. Soc.* **1984**, *106*, 591.

(19) The value was calculated by trigonometry using the data of ref 16e.

(20) Michalczyk, M. J.; Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1986**, *5*, 531.

(21) Shäfer, A.; Weidenbruch, M.; Peters, K.; Schnering, H. G. v. *Angew. Chem.* **1984**, *96*, 311. The PBL is shorter than the Si–Si bond of 1,3-diiodotetra-*tert*-butyltrisilane (2.581, 2.644 Å)[23] and hexa-*tert*-butyldisilane (2.697 Å).[24]

(22) Weidenbruch, M.; Flintjer, B.; Schnering, H. G. v.; Peters, K. *Angew. Chem.* **1984**, *98*, 1090.

(23) Wiberg, N.; Schuster, H.; Simon, A.; Peters, K. *Angew. Chem.* **1986**, *98*, 100.

(24) Kabe, Y.; Kawase, T.; Okada, J.; Yamashita, O.; Goto, M.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 794.

(25) The isomers could be easily separated by TLC; it suggests the notable difference between their polarities. ^1H NMR signal of the methylene proton of **7a** is shifted to low field by δ 0.4 ppm, compared with **8a**. Both isomers showed the very sharp IR absorption of O–H stretching, and the absorption of **7a** was slightly shifted to low wave number. These results suggested that the difference of the polarity of these isomers could result in the intramolecular hydrogen bond type interaction shown in Scheme II. Glidewell calculated the carbon acidity of CH_4 and $(H_3Si)_3CH$, the silyl substitutions increased the acidity by 289 kJ/mol.[26] **7a**: MS *m/e* 347 (M − 15); ^1H NMR (C_6D_6) δ 0.463 (s, 6 H), 0.413 (s, 6 H), 0.207 (s, 6 H), 0.166 (s, 9 H), 0.085 (s, 9 H), 0.287 (s, 1 H); IR (CCl_4 solution) ν/cm^{-1} 3690 (Si–OH). **8a**: MS *m/e* 347 (M − 15); ^1H NMR (C_6D_6) δ 0.480 (s, 6 H), 0.393 (s, 6 H), 0.244 (s, 9 H), 0.168 (s, 6 H), 0.097 (s, 9 H), −0.115 (s, 1 H); IR (CCl_4 solution) ν/cm^{-1} 3694 (Si–OH). The compound **4b** also reacted with H_2O in EtOH to give the mixture of corresponding hydrolized products, which were detected by GC-MS and ^1H NMR spectroscopy (see supplementary material). The stereochemistry of these isomers was determined by NOESY NMR spectroscopy.[27]

(26) Glidewell, C.; Thompson, C. *J. Comput. Chem.* **1982**, *3*, 495.

(27) Macura, S.; Ernst, R. R. *Mol. Phys.* **1980**, *41*, 95. Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546.

(28) Devine, A. M.; Haszeldine, R. N.; Tipping, A. E. *J. Chem. Soc., Dalton Trans.* **1975**, 1832, 1837 and references cited therein.

(29) Allen, C. L. *J. Am. Chem. Soc.* **1989**, *111*, 9003, 9115, and private communication; Lewis–Langmuir atomic charges were calculated to be $CSiMe_3(O) = -0.4221$ and $SiMe_2(O) = +0.2818$.

(30) Nagase also reported the polarization. Reference 16a,b and Kudo, T.; Nagase, S. *J. Am. Chem. Soc.* **1985**, *107*, 2589.

(31) The replacement by point charges is a gross approximation; fractional not proportional charges would give an identical result.[16c]

Radical Cation Rearrangement of 4-Vinylcyclohexene to Bicyclo[3.2.1]oct-2-ene: A Matrix-Isolation ESR Study

Guo-Fei Chen and Ffrancon Williams*

Department of Chemistry, University of Tennessee
Knoxville, Tennessee 37996-1600

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Both mass spectrometric studies[1] and theoretical calculations[2] have concluded that the ion–molecule reaction of 1,3-butadiene proceeds through an acyclic intermediate to form the 4-vinylcyclohexene radical cation ($\mathbf{1}^{\bullet+}$), the overall transformation being regarded as the classical example of an indirect radical cation Diels–Alder reaction.[3] Here we report that when $\mathbf{1}^{\bullet+}$ is generated by radiolytic oxidation in Freon matrices at 77 K,[4] it undergoes a further rearrangement to the bicyclo[3.2.1]oct-2-ene radical cation ($\mathbf{3}^{\bullet+}$) on annealing to 140 K. The observation of this novel cycloaddition indicates that $\mathbf{3}^{\bullet+}$ is a more stable isomer than $\mathbf{1}^{\bullet+}$ on this important $C_8H_{12}^{\bullet+}$ potential energy surface.[1-3,5]

Evidence for the thermal rearrangement of $\mathbf{1}^{\bullet+}$ to $\mathbf{3}^{\bullet+}$ was obtained by ESR spectroscopy. After the radiolytic oxidation of **1** in $CFCl_3$ at 77 K, the initial spectrum observed with optimal resolution at 95 K can be assigned to $\mathbf{1}^{\bullet+}$ with the positive hole localized at the ene group. This assignment rests on the similarity of the spectrum to that of the cyclohexene radical cation,[6] their common features including the diagnostic ca. 8–9 G triplet splitting from the two cycloolefinic hydrogens in the wing lines and approximately the same total spectral width. A detailed analysis by simulation showed that the conformationally dependent β-hydrogen couplings for $\mathbf{1}^{\bullet+}$ (Table I) are not equivalent in pairs, presumably due to the absence of C_2 symmetry. On annealing of the sample to 140 K, a much narrower pattern grew in *irreversibly*, the spectrum obtained on recooling to 95 K having the same profile as that of the 140 K spectrum except for poorer resolution. This new signal carrier produced in $CFCl_3$ was identified as $\mathbf{3}^{\bullet+}$ from studies in other matrices (vide infra), and the assignment was then corroborated by finding that its spectrum matched precisely with that resulting from the direct oxidation of **3** in $CFCl_3$.[7]

A solution to the problem of identifying the species formed on annealing only became feasible when a spectrum of higher resolution was obtained following the oxidation of **1** in $CFCl_2CFCl_2$ (Figure 1a). This spectrum has precisely the same total width as that obtained in $CFCl_3$ but the much-improved resolution now allows all the coupling constants greater than ca. 5 G to be

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(1) Groenewold, G. S.; Gross, M. L. *J. Am. Chem. Soc.* **1984**, *106*, 6569.

(2) (a) Bauld, N. L.; Bellville, D. J.; Pabon, R. A.; Chelsky, R.; Green, G. *J. Am. Chem. Soc.* **1983**, *105*, 2378. (b) Bellville, D. J.; Bauld, N. L. *Tetrahedron* **1986**, *42*, 6167.

(3) Bauld, N. L. *Tetrahedron* **1989**, *45*, 5307.

(4) (a) Shida, T.; Kato, T. *Chem. Phys. Lett.* **1979**, *68*, 106. (b) Shida, T.; Haselbach, E.; Bally, T. *Acc. Chem. Res.* **1984**, *17*, 180.

(5) For neutral C_8H_{12} isomers: Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981; Chapter 8, Section IV, pp 271–286.

(6) (a) Shida, T.; Egawa, Y.; Kubodera, H.; Kato, T. *J. Chem. Phys.* **1980**, *73*, 5963. (b) Blackstock, S. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 2484. (c) Guo, Q.-X.; Qin, X.-Z.; Wang, J. T.; Williams, F. *J. Am. Chem. Soc.* **1988**, *110*, 1974. (d) Williams, F.; Guo, Q.-X.; Petillo, P. A.; Nelsen, S. F. *J. Am. Chem. Soc.* **1988**, *110*, 7887.

(7) Matching spectra from the oxidation of **1** and **3** were also observed in the $CF_2ClCFCl_2$ and CF_3CCl_3 matrices.

0002-7863/91/1513-7792$02.50/0

Table I. ESR Parameters and Calculated ΔH_f Values of **1**$^{\bullet+}$ and **3**$^{\bullet+}$

radical cation	matrix	T, K	g_{iso}	hyperfine couplings,[a,b] G	ΔH_f,[b] kcal mol^{-1}
1$^{\bullet+}$	$CFCl_3$	103	2.0033 (6)	8.7 ($2H_\alpha$), 16.4 ($1H_\beta$), 29.5 ($1H_\beta$), 51.4 ($1H_\beta$), 62.5 ($1H_\beta$)	
				−7.9[c] *($2H_\alpha$), 26.9 ($1H_\beta$), 29.1 ($1H_\beta$), 53.3 ($1H_\beta$), 54.4 ($1H_\beta$)*	*211.50*
3$^{\bullet+}$	$CFCl_3$	149	2.0034 (6)	5.8 ($2H_\alpha$), 9.6 ($1H_\gamma$), 24.3 ($1H_\beta$), 27.5 ($1H_\beta$), 54.6 ($1H_\beta$)	
	$CFCl_2CFCl_2$	135	2.0030 (3)	5.9 ($2H_\alpha$), 9.6 ($1H_\gamma$), 24.5 ($1H_\beta$), 27.6 ($1H_\beta$), 54.9 ($1H_\beta$)	
	$CF_2ClCFCl_2$	114	2.0030 (3)	5.8 ($2H_\alpha$), 9.7 ($1H_\gamma$), 24.5 ($1H_\beta$), 27.8 ($1H_\beta$), 55.0 ($1H_\beta$)	
				−9.4[d] *($2H_\alpha$), 7.0 ($1H_\gamma$),*[e] *3.9 ($1H_\beta$),*[f] *31.4 ($1H_\beta$), 52.1 ($1H_\beta$)*	*197.45*

[a] Experimental values were obtained by spectral simulation. [b] The results of AM1[10]–UHF calculations are given in italics; 1s spin densities after annihilation were multiplied by 1177 G (Clark, T.; Nelsen, S. F. *J. Am. Chem. Soc.* **1988**, *110*, 868) to obtain the coupling constants. [c] Average of −8.15 and −7.65 G for cycloolefinic hydrogens. [d] Average of −9.38 and −9.48 G. [e] Exo hydrogen at C-7. [f] Bridgehead hydrogen at C-1.[8]

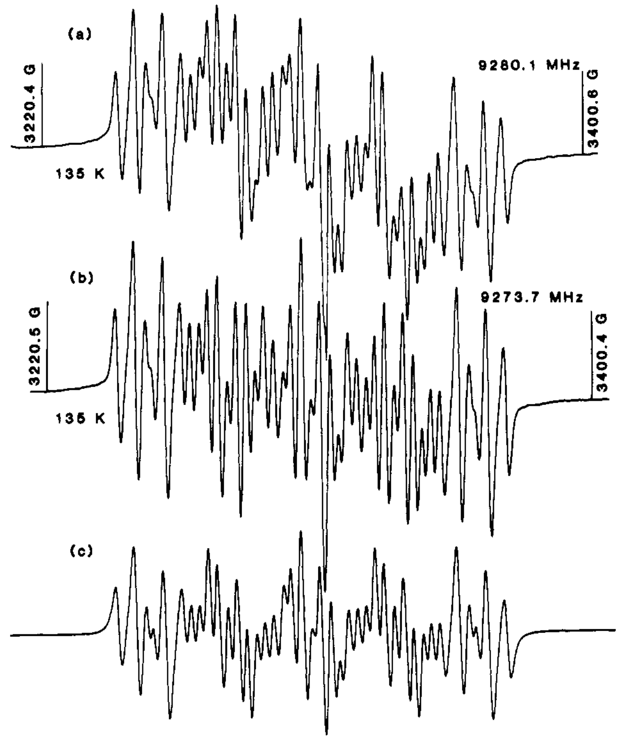
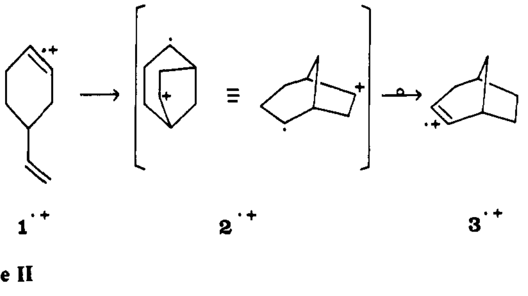


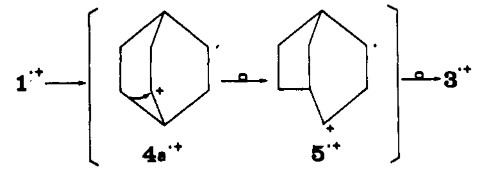
Figure 1. ESR spectra of γ-irradiated ca. 0.05 mol % solutions of 4-vinylcyclohexene (a) and bicyclo[3.2.1]oct-2-ene (b) in $CFCl_2CFCl_2$ (dose, 0.3 Mrad) at 135 K. Spectrum c was simulated using the coupling constants for **3**$^{\bullet+}$ in Table I and a line-width parameter (ΔH_{pp}) of 0.8 G.

evaluated unambiguously by inspection, and comparison with the simulated spectrum (c) shows the excellence of the fit. An examination of these coupling constants (Table I) suggested **3**$^{\bullet+}$ as a suitable candidate since the magnitudes of the hyperfine interactions are consistent with a structure possessing two nearly equivalent olefinic α-hydrogens, three nonequivalent β-hydrogens,[8] and one γ-hydrogen. The latter coupling provided an especially important clue to the correct structure since the required long-range interaction is well characterized in *bicyclic* systems.[9] As shown in Figure 1, the spectrum (b) generated upon the oxidation of **3** matches spectrum a in all its fine detail, leaving no doubt that **3**$^{\bullet+}$ is the thermal rearrangement product.

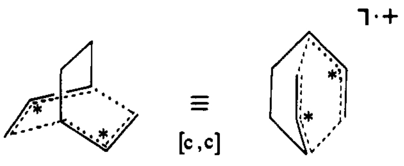
Scheme I



Scheme II



The most direct mechanism to explain this unusual cycloaddition is represented in Scheme I, where endo attack from C-2 of the ene radical cation on the pendant vinyl group forms the bicyclo[3.2.1]oct-2-yl-6-ylium (**2**$^{\bullet+}$) distonic species, which then undergoes a facile 1,5-hydride ion transfer from the 3-position to the carbocation center. AM1 calculations[10] predict that **2**$^{\bullet+}$ (ΔH_f = 213.00 kcal/mol) is of comparable energy to **1**$^{\bullet+}$ (ΔH_f = 211.50 kcal/mol) and that the rearrangement of **1**$^{\bullet+}$ to **3**$^{\bullet+}$ is 14.05 kcal/mol exothermic, corresponding to a significant thermodynamic driving force. Thus, the proposed mechanism is consistent with **2**$^{\bullet+}$ being of relatively low energy although a long-range hydride ion transfer is then required to form the more stable monoolefin radical cation.[11]



4$^{\bullet+}$

Other mechanisms must also be considered. Since 4-vinylcyclohexene formally corresponds to a 1,5-diene system, the delocalized bisallylic[12] or diyl[6c,13] radical cation intermediate represented by **4**$^{\bullet+}$ could, in principle, be formed in the first step of a Cope-like transformation.[6c,13] However, previous calculations show that an "acyclic" bisallylic intermediate of this [c,c] type[14] is ca. 20 kcal/mol higher in energy than **1**$^{\bullet+}$ along the retrogressive path of the Diels–Alder ion–molecule reaction for 1,3-butadiene.[2,3] Moreover, the expected product of a *delocalized* bicyclic diyl

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(8) The bridgehead β-hydrogen shows a larger coupling than the calculated value (Table I), indicating that its angular geometry is not properly optimized in the computation.

(9) Nunome, K.; Toriyama, K.; Iwasaki, M. *Tetrahedron* **1986**, *42*, 6315 and references therein.

(10) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(11) (a) The stabilization achieved in the conversion of a distonic diyl radical cation to an olefin radical cation is obviously similar to but less than that which accompanies the change from a neutral biradical to an olefin. (b) It should be noted that the widely employed ($^{\bullet+}$) notation (see ref 3, for example) is used in Scheme I to designate the site of the positive hole in **1**$^{\bullet+}$ and **3**$^{\bullet+}$. Strictly speaking, therefore, the structures drawn for **1**$^{\bullet+}$ and **3**$^{\bullet+}$ are not proper Lewis structures whereas those for **2**$^{\bullet+}$, **4a**$^{\bullet+}$, and **5**$^{\bullet+}$ are. It would, of course, be necessary to write two Lewis structures to represent **3**$^{\bullet+}$, for example, since charge and spin reside on *both* carbons of the olefin group. We thank one of the reviewers for giving us an opportunity to clarify this point.

(12) (a) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1985**, *107*, 716. (b) Roth, H. D.; Schilling, M. L. M.; Abelt, C. J. *Tetrahedron* **1986**, *42*, 6157. (c) Roth, H. D.; Abelt, C. J. *J. Am. Chem. Soc.* **1986**, *108*, 2013. (d) Momose, T.; Shida, T.; Kobayashi, T. *Tetrahedron* **1986**, *42*, 6337. (e) Dai, S.; Wang, J. T.; Williams, F. *J. Am. Chem. Soc.* **1990**, *112*, 2835.

(13) Williams, F.; Guo, Q.-X.; Bebout, D. C.; Carpenter, B. K. *J. Am. Chem. Soc.* **1989**, *111*, 4133.

(14) A [c,t] bisallylic intermediate for **4**$^{\bullet+}$ could adopt a strained chair conformation with a 4.2.0 frame but this is likely to be of higher energy than the 2.2.2 boat form of the [c,c] conformer discussed here and elsewhere.[2,3]

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 $3^{\bullet+}$.

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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.

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(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

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.

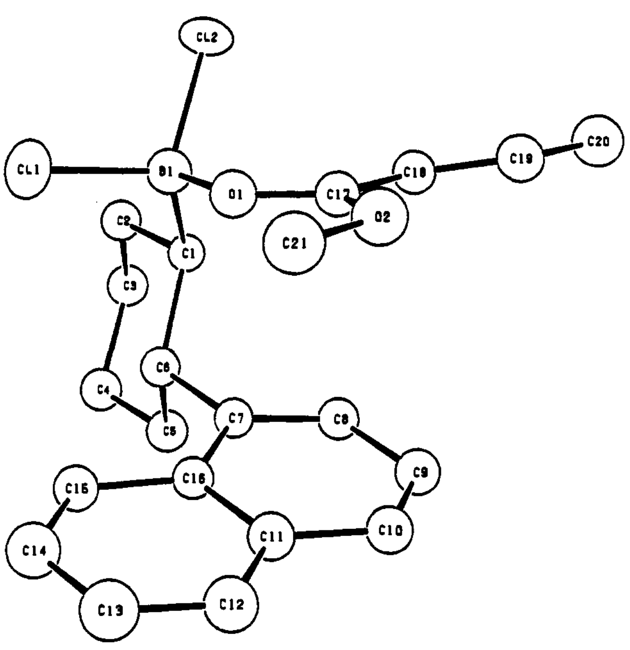
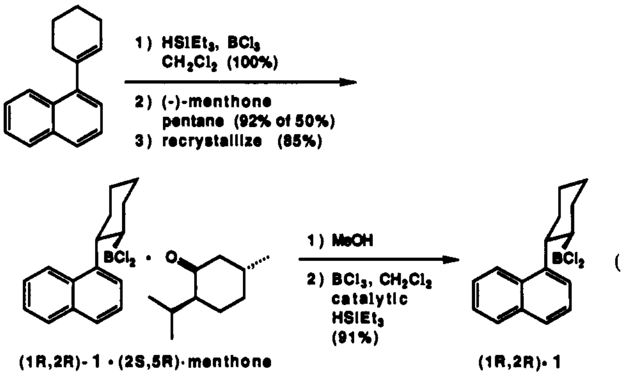


Figure 1. ORTEP view of (±)-**1**·methyl crotonate. Selected bond distances (Å) and angles (deg): B1–C1 = 1.609 (16); B1–Cl1 = 1.862 (12); B1–Cl2 = 1.876 (13); B1–O1 = 1.538 (15); O1–C17 = 1.266 (12); C17–C18 = 1.436 (15); C18–C19 = 1.340 (15); O1–B1–C1 = 115.1 (9); O1–B1–Cl1 = 101.0 (7); O1–B1–Cl2 =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

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

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(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.

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