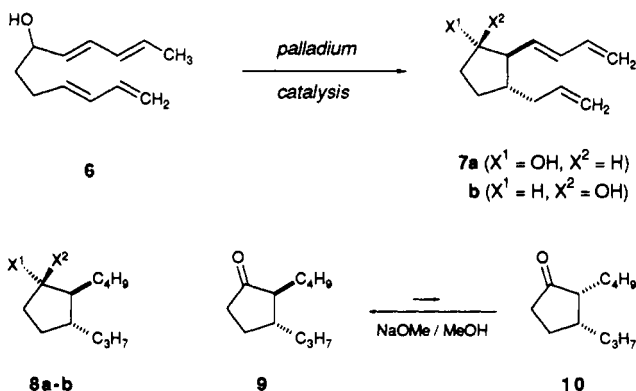


Table I. Six Membered Ring Forming Palladium-Catalyzed Carbocyclizations of Simple Tetraene Substrates^a

Substrate	Product	Yield
11a (R = H; E = CO ₂ Et)	12a (R = H; E = CO ₂ Et)	90 %
11b (R = C ₂ H ₅ ; E = CO ₂ Et)	12b (R = C ₂ H ₅ ; E = CO ₂ Et)	84 %
13a (R = H; Ar = p-MeC ₆ H ₄)	14a (R = H; Ar = p-MeC ₆ H ₄)	72 %
13b (R = C ₂ H ₅ ; Ar = p-MeC ₆ H ₄)	14b (R = C ₂ H ₅ ; Ar = p-MeC ₆ H ₄)	86 %
15 (X = OTBDMS)	16a/b (X = OTBDMS)	62 %
17 (X = OH)	18a/b (X = OH)	76 %

^a All reactions are carried out with approximately 1 mmol of substrate, 0.05 mmol of Pd(OAc)₂, 0.10–0.15 mmol of Ph₃P, and 5 mmol of triethylamine in 10 mL of refluxing THF unless otherwise noted. The reaction progress is monitored by TLC.

assignment of the hydroxyl stereochemistry for **7a,b** is made on the following basis. Hydrogenation of a mixture of **7a** and **7b** (1 atm of H₂/EtOH/5% Rh on Al₂O₃/24 h) gives the corresponding mixture of **8a** and **8b**. PCC oxidation affords predominantly cyclopentanone **9** (>95% trans). Base-catalyzed equilibration of **9** with its less favorable cis isomer **10** confirms the trans assignment of **7a,b** and, by analogy, **5a,b**. Reduction of **9** (Li-(*sec*-Bu)₃BH/THF/−78 °C) re-forms **8b**, enabling assignment of the stereochemistry shown in **7b** to the minor isomer formed in the palladium-catalyzed cyclization of **6**.



The results of several six membered ring forming cyclizations are summarized in Table I. Simple functionalized cyclohexanes (**12a,b**) and *N*-sulfonylpiperidines (**14a,b**) are generally formed in good yield (72–90%) and high isomeric purity (>95%). Silyl ether **15** is an exception. It reacts relatively slowly in refluxing THF/Et₃N and affords an unfavorable mixture (1.7:1) of the diastereomeric products **16a:16b** (62% yield). The corresponding alcohol **17** is both more reactive and more selective, affording a 5:1 ratio of diastereomeric alcohols **18a,b** (76%), with the all-equatorial isomer **18a** predominating.

In summary, the palladium-catalyzed reaction of tetraene substrates provides a promising new cyclization strategy in the case of substrates in which one of the 1,3-diene subunits is appropriately 1,4-disubstituted. Cyclization proceeds with high

diastereoselectivity, and the cyclized product contains functionality that should prove useful for further synthetic transformations.

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Supplementary Material Available: An experimental procedure for the palladium-catalyzed tetraene cyclization and characterization data for compounds **5a,b**, **7a,b**, **12a,b**, **14a,b**, and **18a,b** (8 pages). Ordering information is given on any current masthead page.

Generation and Chemical Trapping of a Bis(ethano) Derivative of Tricyclo[3.3.0.0^{3,7}]oct-1(5)-ene: The Consummate Member of a Series of Pyramidalized Alkenes

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Tricyclo[3.3.0.0^{3,7}]oct-1(5)-ene (**1**) is the consummate member of the homologous series¹ of pyramidalized olefins,² which one of our groups has been studying. The hydrogenation energy of **1** is calculated to be greater than that of the unbridged alkene, bicyclo[3.3.0]oct-1(5)-ene, by fully 70.6 kcal/mol,^{3,4} and to exceed even those of cubene³⁻⁵ and homocub-4(5)-ene^{4,6} by, respectively, 11.9 and 5.1 kcal/mol. The very high olefin strain energy^{3,7} (70.6 kcal/mol) computed for **1** is due largely to the weakness of the highly pyramidalized "π" bond in this olefin, which is calculated to have a dissociation energy of only 13.3 kcal/mol.⁸ This bond dissociation energy (BDE) is 52.9 kcal/mol less than the calculated π BDE of bicyclo[3.3.0]oct-1(5)-ene, 9.7 kcal/mol less than the "π" BDE of cubene, and 4.6 kcal/mol less than that of homocub-4(5)-ene.^{8,10} The calculated energy difference between the

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(4) Computed at the (TC)SCF/6-31G*//[(TC)SCF/3-21G level, using SCF for alkanes and two-configuration SCF (TCSCF) for alkenes.

(5) Synthesis: Eaton, P. E.; Maggini, M. *J. Am. Chem. Soc.* **1988**, *110*, 7230.

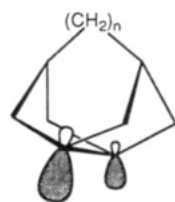
(6) Synthesis: Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 7229. Schäfer, J.; Szeimies, G. *Tetrahedron Lett.* **1988**, *29*, 5253.

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(8) Calculated,^{4,9} using the definition proposed by Benson (Benson, S. W. *J. Chem. Educ.* **1965**, *42*, 502), as the negative of the radical disproportionation energy, 2 alkene-H• → alkene + alkane.

(9) Energies of doublet and triplet states were calculated at the ROHF/6-31G*//UHF/3-21G level.

singlet⁴ and the lowest triplet state⁹ of **1** is only 14.8 kcal/mol. This energy separation is 11.3 kcal/mol smaller than that computed for cubene^{11b} and just 4.5 kcal/mol larger than that calculated^{11a,b} for 1,4-dehydrocubane.^{11a,c}



1, $n = 0$



- 2, X-Y = —
 3, X = Y = CO₂CH₃
 4, X = Y = Br
 5, X = Y = I
 6, X = Y = H
 7, X = (CH₃)₃C, Y = H

Alkene **2** may be regarded as a bis(ethano) derivative of **1**. Not surprisingly, therefore, calculations using the AM1 semiempirical method¹² predict very similar geometries for the double bonds in **1** and **2** and heats of hydrogenation that differ by only 1 kcal/mol.¹³ The ease of preparing diester **3** by a domino Diels–Alder reaction,¹⁴ followed by catalytic hydrogenation of the pair of double bonds in the adduct,^{14b} and the known conversion of **3** into dibromide **4** by hydrolysis and a double Hunsdiecker reaction on the diacid^{14b} make **2** a potentially more easily accessible synthetic target than **1**. Moreover, in addition to being a potentially readily preparable derivative of **1**, **2** can be regarded as a dehydro derivative of *syn*-sesquiorbornene,^{15a} in which the additional C–C bond in **2** enforces pyramidalization in the opposite sense to that found in the latter hydrocarbon.^{2,15b–d} In this communication we report the synthesis and chemical trapping of **2**.

Treatment of either dibromide **4**^{14b} or diiodide **5**^{16,17} with excess

tert-butyllithium afforded two volatile products, the reduced hydrocarbon (**6**)^{14b} and the *tert*-butyl adduct (**7**),¹⁷ in ratios that ranged from 1:20 from reaction of **5** in 1:1 ether/pentane at 0 °C to 2:1 from reaction of **5** in THF at –78 °C. The reduction product (**6**) was identified by comparison of its ¹H NMR spectrum with that reported in the literature [(CDCl₃, 220 MHz) δ 1.48 (s, 10 H), 2.15 (s, 6 H)],^{14b} and this structural assignment was confirmed by the appearance of only four peaks in the ¹³C NMR spectrum¹⁸ [(CDCl₃, 75 MHz) δ 52.93 (CH), 48.19 (CH), 46.35 (CH), 25.75 (CH₂)]. The ¹H NMR spectrum of **7** [(CDCl₃, 300 MHz) δ 2.15 (s, 4 H), 2.03 (d, *J* = 2 Hz, 2 H), 1.96–1.91 (m, 2 H), 1.54–1.52 (m, 1 H), 1.50–1.41 (m, 6 H), 1.03 (s, 9 H)] was less useful than the ¹³C NMR spectrum [(CDCl₃, 75 MHz) δ 57.47 (C), 57.36 (CH₂), 53.76 (CH₂), 48.72 (CH), 48.16 (CH), 33.31 (C), 28.95 (CH₃), 27.25 (CH₂), 23.06 (CH₃)] in establishing the structure. Selective ¹H decoupling showed that the unique proton in **7** at δ 1.54–1.52 is attached to the tertiary carbon that appears at δ 48.72.

When the reaction of **4** with *tert*-butyllithium was repeated and D₂O used to quench the reaction mixture, mass spectral analysis showed that only one deuterium was incorporated into both **6** (45% d₁) and **7** (35% d₁). In the ²H NMR spectrum of the **7**-d₁ thus formed, only one deuterium resonance (δ 1.54) was observed, and the proton-decoupled ¹³C NMR spectrum of this material showed the peak at δ 48.72 to be split into a triplet, *J* = 22 Hz, by this deuterium.

These spectral data establish that in **7**-d₁ deuterium is incorporated in the fashion expected from formation of **2**, followed by addition of excess *tert*-butyllithium across the pyramidalized double bond,¹⁹ and quenching of the resulting organolithium species by deuterium capture. Similarly, the observation that **6** incorporates just one deuterium suggests that this product may be formed by reduction of **2**, either by transfer of an electron into its very low-lying LUMO,⁴ followed by hydrogen atom abstraction, or simply by transfer of hydride. In either case, just one deuterium would be incorporated on workup, whereas two deuteriums would presumably be incorporated if **6** were formed by double lithium–bromine exchange of **4**,²⁰ instead of via the intermediacy of **2**.

The formation of **2** was confirmed by trapping of the olefin in a Diels–Alder reaction with diphenylisobenzofuran (DPIBF). Reaction of **5** with a 20% excess of *n*-butyllithium in THF at –78 °C in the presence of 1.2 equiv of DPIBF led, after workup and column chromatography on silica gel, to a quantitative yield of an adduct. Recrystallization from hexane/CH₂Cl₂ afforded an 80% yield of white needles, mp 222.5–223.5°. Both the ¹H and ¹³C NMR spectra of this material were wholly consistent with the formulation of its structure as that expected from a Diels–Alder reaction between DPIBF and **2**.

Our finding that, despite the very weak π bond expected in **2**, this highly pyramidalized alkene can be generated in solution and lives long enough to be intercepted chemically suggests that it may be possible to matrix isolate **2** and also to trap it as a (Ph₃P)₂Pt complex. The success of these two additional experiments, which are planned, would allow an assessment of how the additional pyramidalization in **2** causes its IR and UV spectra and the ¹³C NMR spectra of its (Ph₃P)₂Pt complex to differ from those measured for higher homologues of **1**.^{1,21,22}

(10) The more strained of the two isomers of prismene, in which the double bond is contained in two of the four-membered rings, is calculated to have a hydrogenation energy that is 6.3 kcal/mol higher than that of **1**, but a π BDE and a singlet–triplet splitting that differ insignificantly from those computed for **1**. The less strained prismene isomer is calculated to have a π BDE that is 10.4 kcal/mol higher and a singlet–triplet splitting that is 11.5 kcal/mol larger than the more strained isomer. These highly pyramidalized alkenes are as yet unknown, but Szeimies and co-workers have succeeded in generating two quadricyclene isomers,² which may be regarded as homologues of the two prismenes: Harnisch, J.; Baumgartel, O.; Szeimies, G.; Van Meerse, M.; Germain, G.; Declercq, J.-P. *J. Am. Chem. Soc.* **1979**, *101*, 3370. Baumgartel, O.; Szeimies, G. *Chem. Ber.* **1983**, *116*, 2180. Baumgartel, O.; Harnisch, J.; Szeimies, G.; Van Meerse, M.; Germain, G.; Declercq, J.-P. *Chem. Ber.* **1983**, *116*, 2205. Kenndorf, J.; Polborn, K.; Szeimies, G. *J. Am. Chem. Soc.* **1990**, *112*, 6117. Tricyclo[3.1.0.0^{2,6}]hex-1(6)-ene, which has also been generated and trapped by Szeimies and co-workers,² is computed² to have a hydrogenation energy that is about 6 kcal/mol less than that of **1**.

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(21) The IR spectrum of the matrix-isolated *n* = 1 olefin, formed by potassium vapor dehalogenation of the diiodide precursor,¹⁸ shows a weak band at 1496 cm^{–1}: Radziszewski, J. G.; Michl, J.; Yin, T.-K.; Renzoni, G. E.; Borden, W. T., unpublished results.

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Acknowledgment. We thank the National Science Foundation for support of this research. W.T.B. also thanks the National Science Foundation for providing funds that enabled the purchase of the Convex C-2 computer, on which some of the calculations reported here were performed, and the San Diego Supercomputer Center for a generous allocation of time on the Cray Y-MP8/864 computer at SDSC.

Supplementary Material Available: RHF, TCSCF, and ROHF/6-31G* energies used to calculate the hydrogenation energies, π BDEs, and singlet-triplet energy differences reported in the text and complete spectral and analytical data on **4**, **5**, **7**, and the Diels-Alder adduct of **2** with DPIBF (5 pages). Ordering information is given on any current masthead page.

Mobility-Ordered Two-Dimensional Nuclear Magnetic Resonance Spectroscopy

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Recent advances in high-resolution electrophoretic NMR (ENMR) permit the resolution of NMR spectra of mixtures on the basis of electrophoretic mobilities of contributing ions.^{1,2} However, these experiments observe a counterflow of ions and only the magnitudes of the mobilities can be detected. Also, for monodisperse ions, resolution is severely limited by truncation errors in the Fourier transformations with respect to the electric current amplitudes. Here we report an experiment that recovers the signs of mobilities through the use of a cylindrical electrophoresis chamber with appropriate modifications in pulse sequences and data handling. The truncation problem has been solved by means of linear prediction (LP) methods. We note that this experiment determines the electrophoretic mobilities of ions and identifies the ions by their NMR spectra. Furthermore, it does not require labeling of ions for detection, and it permits the use of short (<1-s) migration times.

Our 2D-ENMR experiments are usually performed with the LED pulse sequence shown in Figure 1a.³ This is a stimulated echo (STE) experiment^{4,5} in which two additional $\pi/2$ rf pulses are used to store and recover the stimulated echo so that magnetic field disturbances associated with the gradient pulse at Δ will have time (T_c) to decay. J -modulation effects can also be avoided since the transverse evolution period ($\tau - \delta$) can be as small as 600 μ s.³ For an ion with diffusion coefficient D and electrophoretic mobility μ , the magnetization immediately after the fifth $\pi/2$ rf pulse has the form

$$M(\Delta + \tau + T_c) = \exp[i\phi(I)]f(\tau, \Delta, T_c) \quad (1)$$

where $\phi(I) = K\mu\Delta I/(\kappa A)$, $f(\tau, \Delta, T_c) = (M_0/2) \exp[-2\tau/T_2 - (\Delta + T_c)/T_1 - DK^2(\Delta - \delta/3)]$, $K = \gamma g \delta$, γ is the magnetogyric ratio, and g and δ are the amplitude and duration of the magnetic field gradient pulses, respectively. The electric current I in the sample is given by $I = \kappa A E_{dc}$ where E_{dc} is the electric field, κ is the conductivity, and A is the cross-sectional area of the sample tube. 2D-ENMR spectra are usually obtained by a Fourier transformation with respect to the acquisition time t_2 and a transformation with respect to the current I .

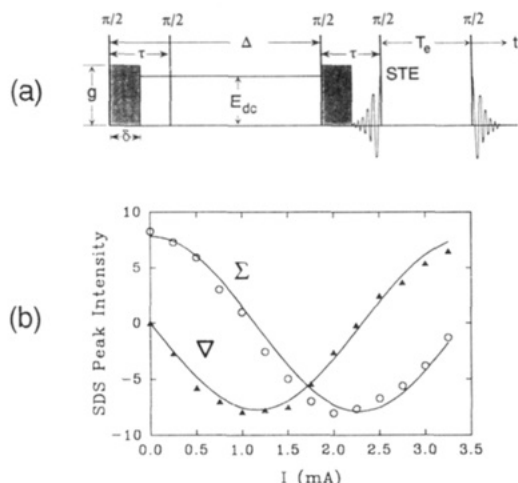


Figure 1. (a) The LED-ENMR pulse sequence. The gradient prepulses, homospoil pulses, and phases of the rf pulses are not shown. (b) A plot of Σ and ∇ for the SDS ^1H peak at 1.08 ppm (see text).

The electrodes must be arranged so that bubbles can escape. U-tube chambers satisfy this condition but yield low filling factors for receiver coils, difficult shimming for the magnetic field, spectral phasing problems, and a counterflow of ions. Since there are equal contributions from ions having positive and negative velocities, the phase factor in eq 1 must be replaced with $\cos [K\mu\Delta I/(\kappa A)]$ and information about the sign of the electrophoretic mobility is lost. As an alternative we have developed a chamber made up of two concentric tubes. The outer tube (10.0 mm o.d.) is sealed at the bottom, and the inner tube (3–5 mm o.d.) is open at both ends. The inner tube is held in place by a 1.0-cm-long Teflon spacer at the top and contains a 4-mm polyacrylamide gel plug at the bottom to separate the two chambers. A salt solution fills the annulus between the tubes, and the solution under study fills the inner tube. This arrangement, which permits Pt electrodes to be placed in the top of both chambers, is practical for commercial NMR probes.

When the STE version of the experiment is adequate, the last two rf pulses in Figure 1a are deleted and the acquired FID is just the second half of the stimulated echo. The reverse precession method can then be used to determine the sign of the mobility.⁶ For each value of the current, FIDs are collected with positive and negative polarities of the electric field. After Fourier transformation with respect to t_2 , the signals with positive and negative polarities can be represented by

$$S_{\pm}(\omega_2, I) = S_0 \exp[\pm i\phi(I)]f(\tau, \Delta, T_c)[a(\omega_2) + id(\omega_2)] \quad (2)$$

where $a(\omega_2)$ and $d(\omega_2)$ are Lorentzian absorption and dispersion components.⁷ The combinations $\Sigma = \text{Re}(S_+ + S_-)$ and $\nabla = \text{Im}(S_+ - S_-)$ give absorption spectra modulated by $\cos [K\mu\Delta I/(\kappa A)]$ and $\sin [K\mu\Delta I/(\kappa A)]$, respectively. These data sets can be analyzed to obtain the magnitude and sign of μ or transformed with respect to current to obtain a 2D-ENMR spectrum with positive and negative mobility values.

When the full LED sequence is used, the fourth $\pi/2$ pulse is directed along the $-x$ and $-y$ directions in the rotating frame in order to store the real and imaginary parts of the magnetization, respectively. Typically the polarity of the electric field is negative when the real component is stored and positive when the imaginary part is stored. This yields the correct signs for the mobilities and prevents mass polarization of the sample. Figure 1b shows LED-ENMR data for an anion in an aqueous solution containing 2.0 mM tetramethylammonium chloride (TMA) and 2.0 mM sodium dodecyl sulfate (SDS) stabilized by 0.5% agarose gel. The

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