on silica gel (elution with petroleum ether). There was isolated 110 mg (4.6%) of tetraene **37** and 546 mg of pentaene **8**: colorless oil; IR (CCl_4, cm^{-1}) 3025, 2895, 1428, 1175, 975, 910, 712, 688, 675, 648; UV (cyclohexane, λ_{max}) 250 nm (ϵ 10010); ^1H NMR (200 MHz, $CDCl_3$) δ 5.91 (dd, J = 7.5 and 2.9 Hz, 4 H), 5.84 (t, J = 1.4 Hz, 2 H), 5.48 (dd, J = 7.5 and 2.9 Hz, 4 H), 2.09 (d, J = 1.4 Hz, 4 H); ^{13}C NMR ($CDCl_3$) 134.56 (4 C), 128.66 (2 C), 123.96 (4 C), 38.07 (2 C), 35.61 ppm (2 C); m/z calcd (M^+) 182.1096, obsd 182.1093.

Shapiro Degradation of 45. A solution of **29** (780 mg, 3.94 mmol) and p-toluenesulfonylhydrazide (790 mg, 4.2 mmol) in methanol (50 mL) containing 2 drops of concentrated hydrochloric acid was stirred at room temperature for 24 h. The solvent was removed in vacuo at 20 °C to deliver **45** as a pale yellow solid. A suspension of the unpurified tosylhydrazone in ether (100 mL) was cooled to −60 °C under nitrogen and treated with methyllithium (13 mL of 1.6 M in ether, 20.8 mmol). The reaction mixture was stirred at −60 °C for 30 min, allowed to warm to room temperature, and stirred for an additional 7 h. Water (40 mL) was added and the products were extracted into ether (3×). The combined organic layers were dried and carefully evaporated to leave an oily residue that was subjected to MPLC on silica gel (petroleum ether elution). There was isolated 350 mg of **46**, 25 mg of **8**, and 15 mg of an unidentified hydrocarbon.

For **46**: ^1H NMR (300 MHz, $CDCl_3$) δ 6.63 (dd, J = 5.4 and 3.1 Hz, 1 H), 6.49 (d, J = 5.4 Hz, 1 H), 6.48 (m, 1 H), 5.76 (dt, J = 7.2 and 2.0 Hz, 1 H), 5.71 (d, J = 2.4 Hz, 2 H), 2.46–2.32 (m, 3 H), 2.03 (dt, J = 18.1 and 2.4 Hz, 1 H), 1.94–1.86 (m, 2 H), 1.74 (d, J = 18.9 Hz, 1 H), 1.48 (d, J = 6.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 147.08, 140.74, 127.73, 126.85 (2 C), 124.99, 59.77, 49.16, 41.62, 40.20, 36.59, 33.97, 29.54, 25.11 ppm; m/z calcd (M^+) 182.1084, obsd 182.1094.

Kinetic Measurements. In each case, the compound was dissolved in chlorobenzene-d_5 and sealed under vacuum in an NMR tube after several freeze–thaw cycles. The tubes were heated at 160 °C for **37** and at 95 °C for **8**. The rate of reaction was determined with a Bruker WP-300 instrument. The tetraene did not react measurably after being heated for 90 h. Assuming first-order decomposition and a detection limit of much less than 5% reaction, the actual rate constant must be less than the value shown below:

$$\ln (100/95) = kt;\ k < 1.58 \times 10^{-7}\ s$$

The pentaene underwent smooth retro-Diels–Alder reaction at 95 °C. No internal standard was used and the assumption was made that only the relative proportions of pentaene and naphthalene (+ butadiene) changed with time. The data adhere well to first-order kinetics with $k = 1.67 \times 10^{-4}$ s (r = 0.997).

Acknowledgment. This investigation was underwritten financially in large part by the National Science Foundation.

Dual Generation of the [4.4.4]Propella-2,4,7,9,11-pentaenyl Cation. Its Threefold Wagner–Meerwein Rearrangement Cascade Leading to 4a,7-Dihydropleiadiene

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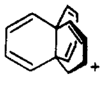
Contribution from Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210. Received November 20, 1985

Abstract: On treatment with diphenylbis(1,1,1,3,3,3-hexafluoro-2-phenyl-2-propoxy)sulfurane, tetracyclo[$4.4.4.0^{1,6}.0^{5,8}$]tetradeca-2,9,11,13-tetraen-4-ol (**5a**) is transformed via a deep-seated carbocation rearrangement cascade into 4a,7-dihydropleiadiene (**6a**). The structure of the hydrocarbon product was unraveled by a series of 2-D NMR experiments including the INADEQUATE technique. When the *4-d* derivative of **5a** was comparably dehydrated, the isotopic label was found uniquely at position 2. Because of the suspected intermediacy of the [4.4.4]propella-2,4,7,9,11-pentaenyl cation (**1**), [4.4.4]propella-2,4,7,9,11-pentaen-13-ol (**10**) was also prepared. When heated with the Burgess reagent, **10** also furnished **6a**. The relationship of these observations to the topography of polyunsaturated propellanes of this type is discussed. Most relevantly, the barrier to ring flipping within **1** is sufficiently high that enantiomerism cannot occur by this mechanism. As a result, **1** maintains its dissymmetry, only one of the flanking cyclohexadiene rings finds it stereoelectronically feasible to undertake Wagner–Meerwein migration, and the deuterium label is not dissipated to more than one site. These results provide unusual insight into a chemical phenomenon that has appealing future prospects.

As part of a study of cationic delocalization within polyunsaturated propellanes, we have presently examined two methods for generation of the [4.4.4]propella-2,4,7,9,11-pentaenyl cation (**1**), the largest such system currently known. The chemical properties of **1** have been found to contrast remarkably with those of its lower homologue **3**, which we have recently shown to arise from **2** with anchimeric assistance and to possess bishomotropylium ion character.[2] Relevantly, **3** is resistant to structural isomerization and gives rise only to unrearranged solvolysis products. This striking kinetic stability is quite uncharacteristic of longicyclic carbocations to which **1** is apparently more closely related.[3] Of complementary mechanistic significance is the cascade of migratory rearrangements to which **1** is subject that eventuates in formation of 4a,7-dihydropleiadiene (**6**). Most significantly, the propeller-shaped **1** has been found capable of maintaining its dissymmetry during the course of chemical events that lead to **6**.



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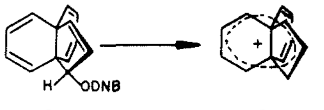

2

3

Results

The Cyclobuta[*d*]naphthalenol Approach. The preparation of ketone **4** has been previously described.[4] When this substance

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[1] Campus Chemical Instrumentation Center, The Ohio State University.

[2] Paquette, L. A.; Ohkata, K.; Jelich, K.; Kitching, W. *J. Am. Chem. Soc.* **1983**, *105*, 2800.

[3] Consider as an example the bicyclo[4.3.2]undecatetraenylium cation: (a) Goldstein, M. J.; Kline, S. A. *J. Am. Chem. Soc.* **1973**, *95*, 935. (b) Goldstein, M. J.; Tomoda, S.; Pressman, E. J.; Dodd, J. A. *Ibid.* **1981**, *103*, 6530.

[4] (a) Paquette, L. A.; Jendralla, H.; Jelich, K.; Korp, J. D.; Bernal, I. *J. Am. Chem. Soc.* **1984**, *106*, 433. (b) Jendralla, H.; Jelich, K.; DeLucca, G.; Paquette, L. A. *J. Am. Chem. Soc.*, preceding paper in this issue.

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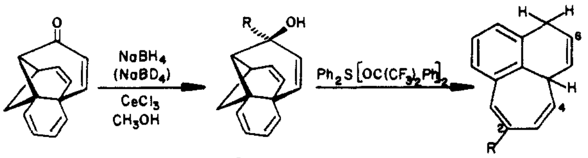
was reduced with sodium borohydride in the presence of cerium trichloride,[5] a stereochemically homogeneous allylic alcohol was isolated. The usual considerations of steric approach control best accommodate **5a** as the end product of this stereospecific process. Exploitation of its hydroxyl group stereochemistry by suitable chemical modification into a group having exceptional leaving characteristics was considered to be an appropriate way to foster cleavage of the antiperiplanar cyclobutane bond and conversion to the title cation (**1**). For this purpose, **5a** was treated with Martin's diphenylbis(1,1,1,3,3,3-hexafluoro-2-phenyl-2-propoxy)sulfurane reagent[6] in chloroform solution at room temperature. Immediate reaction occurred to deliver efficiently an oily $C_{14}H_{12}$ hydrocarbon whose ^{13}C NMR spectrum indicated it to lack any element of symmetry.



4

5a, R=H
b, R=D

6a, R=H
b, R=D

The 500-MHz proton spectrum of this hydrocarbon (Figure 1) is significantly complicated by extensive overlap of the group of four protons labeled F as well as the superimposed nature of the three protons labeled D. In addition, the protons in groups A and B are broadened as the result of couplings to other segments of the molecule. Initially, a 2-D COSY experiment[7] was performed in an effort to establish proton connectivities through J coupling. The 2-D spectrum (Figure 2) revealed the existence of the following spin–spin interactions:

A coupled to B, C, and D

B coupled to A and D

C coupled to A and D

D coupled to A, B, C, and E

E coupled to D and F

F coupled to E

Unfortunately, specific couplings within the groups D and F could not be interpreted unambiguously. As a consequence, the sequencing of protons by virtue of their vicinal coupling patterns could not be rigorously established. Furthermore, any interpretation of connectivities on this basis is apt to be seriously misleading, as a number of observed correlations turn out to be of allylic and homoallylic origin.

Subsequently, the ^{13}C shifts were correlated with the proton shifts with the aid of Bruker's XHCORRD program. This pulse sequence not only gives the desired polarization transfer from ^{1}H to ^{13}C but also contains a bilinear rotation pulse that removes J(H–H) couplings from the F_1 domain.[8,9] The 2-D spectrum was acquired with 32 transients of 128 t_1 increments in 2K data blocks. The t_1 data were zero-filled to 512 words and the data processed in both domains by a $\pi/10$ shifted sine-bell window function. The absolute value mode spectrum showed the correlations compiled in Table I.

At first glance, the ^{1}H NMR spectrum of the hydrocarbon (Figure 1) suggests that a disubstituted aromatic ring is present. However, the coupling noted between proton E and one of the F protons led us to consider that this may not be the case. At this point, further progress in achieving a solution to the structural assignment clearly demanded that the location of the three quaternary carbons be determined. To this end, two INADEQUATE experiments[10] were performed to define the carbon connectivities. The first experiment covered the entire carbon spectral window (15 151 Hz). With a recycle delay of 7.2 s and a delay of 5 ms for $1/(4J)$, 128 scans for each of 90 t_1 increments were acquired with 4096 t_2 data points. The data in t_1 were zero-filled to 512 points, the t_1 and t_2 data were multiplied by a $\pi/3$ shifted sine-bell, and Fourier-transformed data were displayed as a power spectrum. Ultimately, a contour plot of these data revealed a correlation between the methylene carbon B, the quaternary carbon Q3 (131.81 ppm), and the carbon at 128.09 ppm (E). In addition, the methine carbon A was seen to be connected to Q2 (132.81 ppm) and the olefinic carbons C and D1.

Table I. $^{13}C-^{1}H$ Correlation for **6a**

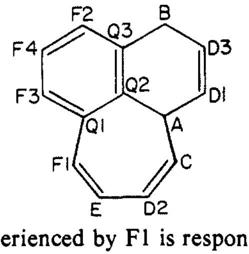
carbon no.	shift,[a] ppm	proton[b]	H[c]
1	134.44	C	5.59
2	133.80	F1	7.23
3	128.83	F2	7.29
4	128.09	E	6.63
5	127.71	D1	6.15
6	125.94	F3	7.32
7	125.18	F4	7.26
8	124.68	D2	6.16
9	124.38	D3	6.12
10	37.76	A	3.24
11	29.26	B	3.55

[a] In addition, there are three quaternary crbons (135.27, 132.81, 131.80 ppm) labeled Q1, Q2, and Q3, respectively. [b] Subsequently, this letter code will be used to identify either the proton in question or its attached carbon. [c] The chemical shifts for these protons were measured from slices of the 2-D data set for carbon–proton correlation with proton decoupling in the F1 domain.

Because data resolution in the F_1 domain was low (59 Hz/pt), it proved difficult to measure accurately the connectivities between the aromatic and olefinic carbons. As we were particularly interested in observing any possible interactions among the quaternary carbons, the INADEQUATE experiment was repeated with a 1748-Hz sweep width in F2 to observe the sp^2-hybridized carbons, and a small amount of $Cr(acac)_3$ was introduced to decrease the relaxation time of the quaternary carbons. The result of this experiment, illustrated in Figure 3, was to identify the following connectivities:

carbon	attached carbons	carbon	attached carbons
Q1	F1, F3, Q2	E	F1, D2
C	D2, A	D1	D3, A
F1	Q1, E	F3	F4 (J_{AB} pattern), Q_1
Q2	Q1, Q3 (J_{AB} pattern), A	F4	F3, F2
Q3	Q2, F2, B	D2	C, E
F2	Q3, F4	D3	B, D1

By interlinking the carbon atoms listed above, the structure of **6a** was unequivocally defined as 4a,7-dihydropleiadiene. The trisubstituted aromatic ring is clearly apparent as shown in the labeled structural representation that follows:



The deshielding experienced by F1 is responsible for the initial presumption that the dehydration product might actually have been a disubstituted aromatic.

With this structural clarification came an opportunity to confirm by chemical means the structural framework of **6a**. Brief treatment with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in benzene at the reflux temperature effected its smooth conversion to bright red, highly crystalline pleiadiene (**7**), a naphtholog of

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(5) Luche, J.-L. *J. Am. Chem. Soc.* **1978**, *100*, 2226.

(6) Martin, J. C.; Arhart, R. J. *J. Am. Chem. Soc.* **1971**, *93*, 2341, 4327. We thank Professor Martin for making a generous supply of the sulfurane available to us.

(7) Aue, W. P.; Bartholdi, E.; Ernst, R. R. *J. Chem. Phys.* **1976**, *64*, 2229.

(8) Bax, A. *J. Magn. Reson.* **1983**, *53*, 517.

(9) Wilde, J. A.; Bolton, P. H. *J. Magn. Reson.* **1984**, *59*, 343.

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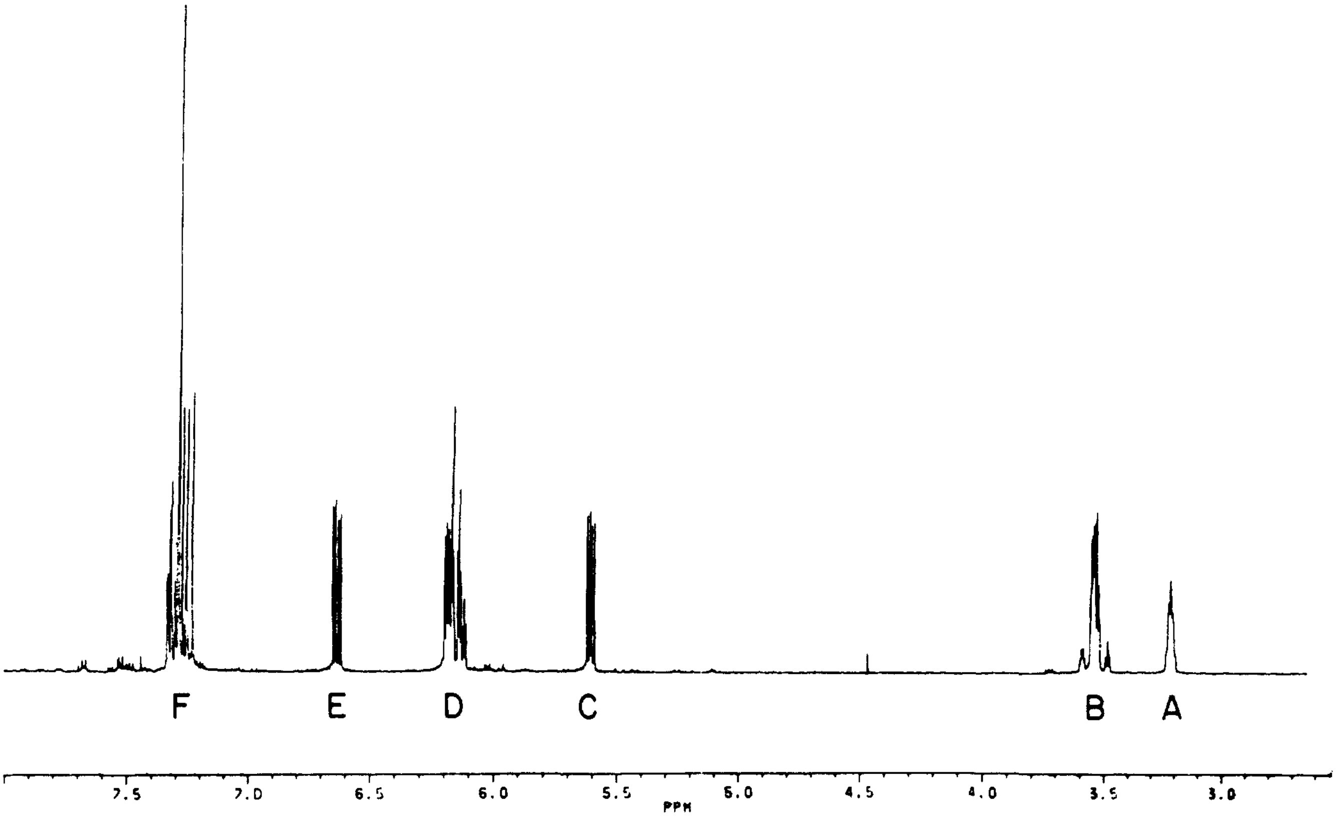

Figure 1. 500-MHz ^{1}H NMR spectrum of **6a** ($CDCl_3$ solution, 64K data points, sweep width 4273 Hz).

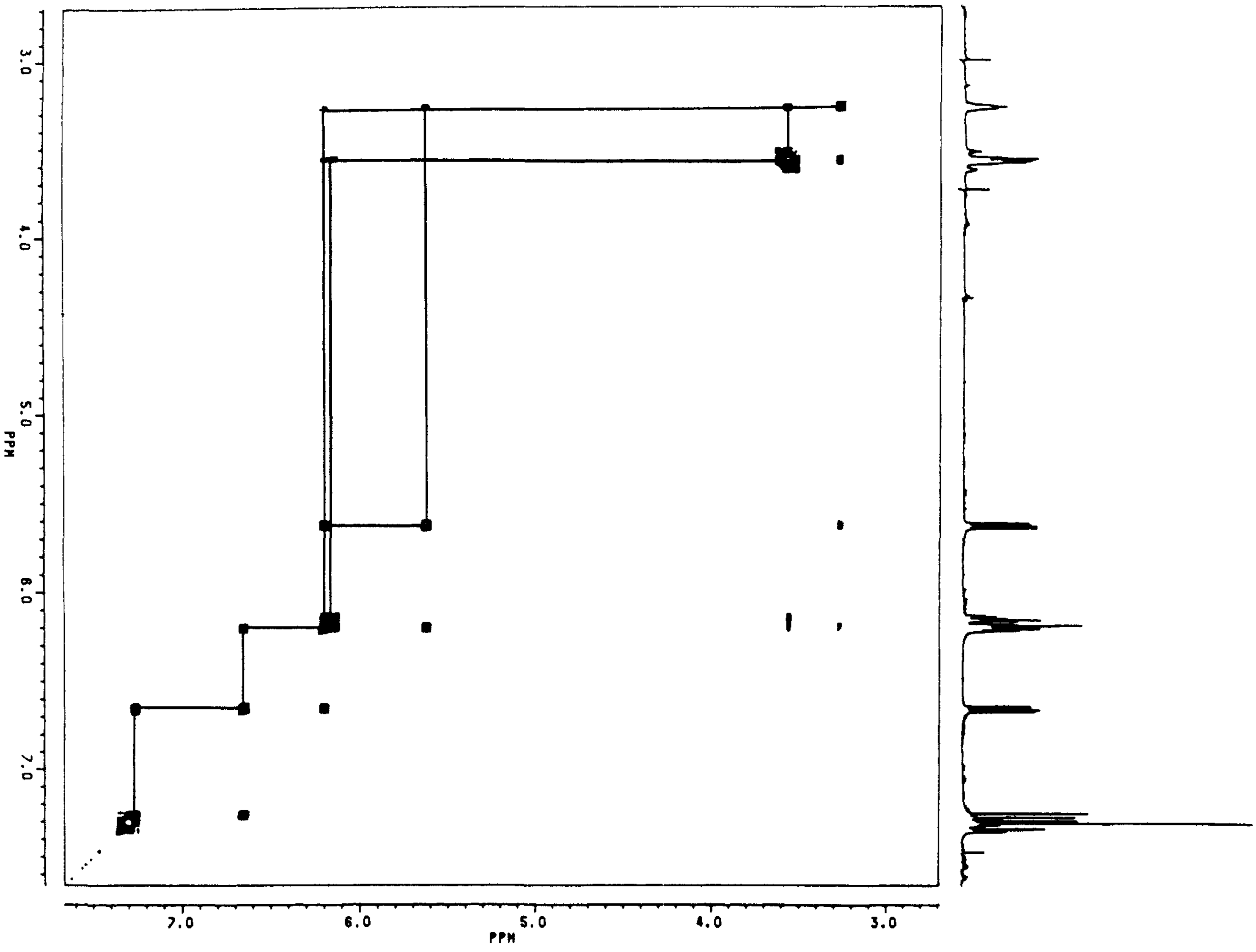

Figure 2. 500-MHz COSY spectrum of **6a**. Eight scans of 128 t_1 increments were acquired in 2K blocks. Data were processed with sine-bell window function in both t_1 and t_2 and displayed as an absolute value spectrum.

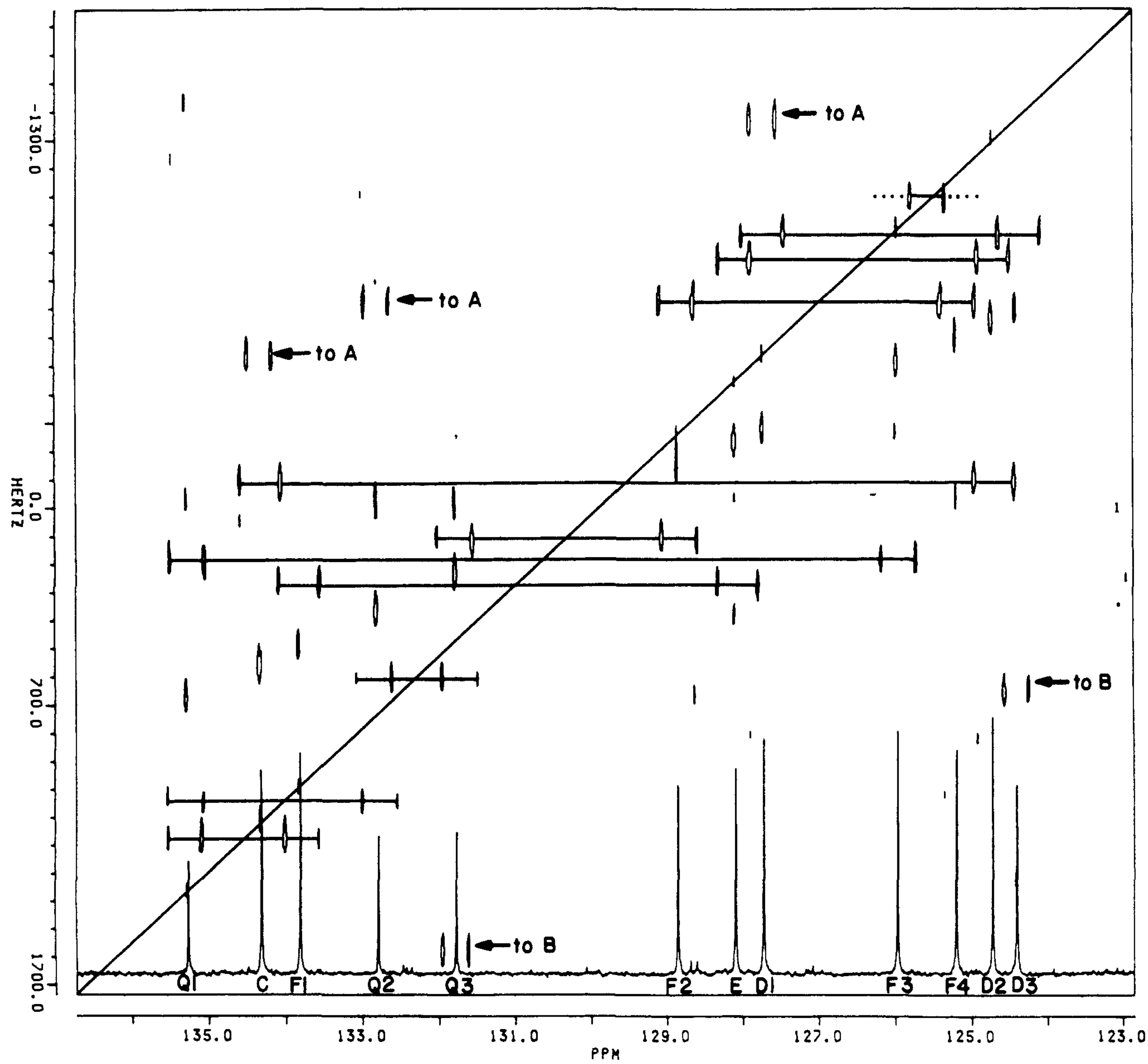

Figure 3. ^{13}C 2D-INADEQUATE spectrum of **6a** (125.7 MHz). 384 scans (2-s delay of 64 t_1 increments were acquired in 2K data blocks with $1(4J) = 5$ ms, and with a sweep width of 1748 Hz in F2 and twice that in F_1. The t_1 domain was zero-filled to 512 words and the data processed as a power spectrum after multiplying t_1 and t_2 by shifted sine-bell window functions ($\pi/5$ and $\pi/3$, respectively). The carbon-carbon J couplings are symmetrically displaced about the skew-diagonal ($\Omega_1 = 2^*\Omega_2$). The signals on the diagonal ($\Omega_1 = \Omega_2$) correspond to single quantum signals not completely converted to double quantum coherences.

azulene originally synthesized by Boekelheide and Vick in 1956.[11]

Quite unmistakably, a deep-seated rearrangement accompanies the conversion of **5a** into **6a**. In order to restrict the number of hypothetical intermediates and pathways, a deuterium label was introduced by $NaBD_4$–$CeCl_3$ reduction of **4** as before. When **5b** was exposed to the sulfurane reagent, the dihydropleiadiene was again observed to form rapidly. Since this d_1 product clearly lacks the proton signal at δ 6.63 attributed to E (see **6b**), it was made clear that a strictly constrained reaction channel which avoids multiple site options for the isotopic label was being followed.

Direct Probing from the [4.4.4]Propellapentaenyl Alcohol. The preceding mechanistic model contemplates an initial antiperiplanar cyclobutane bond cleavage leading to **1** and is not without certain questions of detail and nuance. To gain support for this original premise, the generation of **1** was probed in a more direct way.

The available [4.4.4]propellapentaene **8**[4,12] was regioselectively epoxidized, and resulting oxirane **9** was transformed into allylic alcohol **10** through the agency of lithium diisopropylamide in HMPA.[13] This cleavage process proceeds at an acceptable rate at 45 °C. Subsequently, **10** was exposed to the Burgess reagent[14] in benzene solvent at 60 °C. Under these conditions, **10** was found to rearrange completely to **6a**. No evidence was uncovered for simple dehydration to the highly elusive and still unknown hexaene **11**. The sulfurane reagent acts on **10** with entirely comparable consequences. Thus, carbocation **1** gives every indication of being generated readily from **10** and possibly to intersect at this point the reaction manifold followed by **5**.

Discussion

Conformational Characteristics of the [4.4.4]Propella-2,4,7,9,11-pentaenyl Cation. Any detailed mechanistic discussion involving **1** must give specific recognition to the fact that its constituent six-membered rings radiate as blades from a common rotation axis. As with any molecular propeller, each blade is

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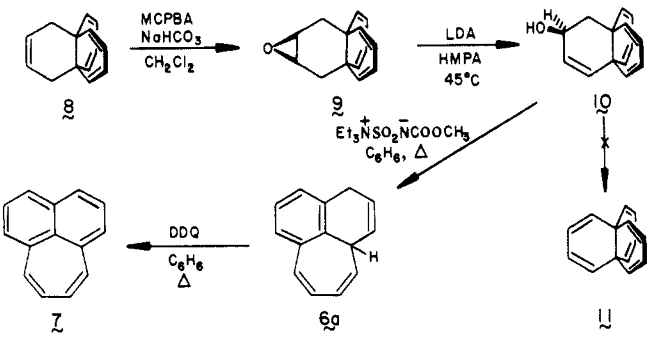
[11] Boekelheide, V.; Vick, G. K. *J. Am. Chem. Soc.* **1956**, *78*, 653.

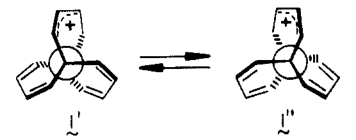
[12] Paquette, L. A.; Jendralla, H.; DeLucca, G. *J. Am. Chem. Soc.* **1984**, *106*, 1518.

[13] Crandall, J. K.; Apparu, M. *Org. React.* **1983**, *29*, 345.

[14] Burgess, E. M.; Penton, H. R., Jr.; Taylor, E. A. *J. Org. Chem.* **1973**, *38*, 26.

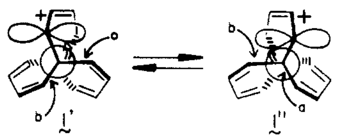


necessarily twisted in the same sense and a helical conformation is imparted to the molecule.[15,16] Dreiding molecular models reveal that the angle of twist enforces ca 25° of nonplanarity to the double bonds in each cyclohexadiene subunit, with the canting occurring in opposite directions. In contrast, the allyl cation moiety in the third ring is planar.



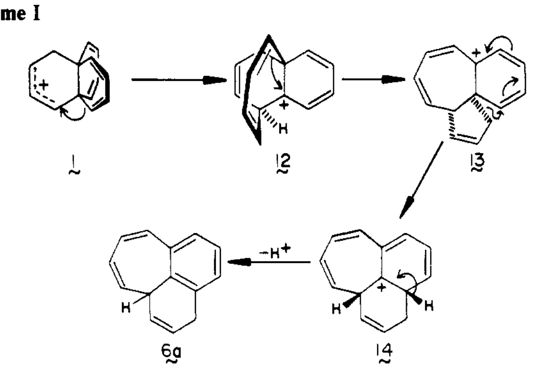
Enantiomer interconversion of the type **1'** ⇄ **1''** almost certainly requires synchronous three-ring flipping as a direct consequence of the trigonal nature of the great majority of the constituent carbon atoms. In accordance with several earlier NMR measurements on related systems, the ΔG^* for this conformational change can be reliably estimated at 16 ± 1 kcal/mol. Gilboa et al. have deduced the ΔG^* for dynamic interconversion of the D_3-symmetric [4.4.4]propella-3,8,12-triene to be 16.7 kcal/mol.[17,18] The value for 3,3-difluoro[4.4.4]propellane, a more flexible molecule, is 15.7 kcal/mol.[17] Two [4.4.4]propellatrienetriones have been shown to have activation energy barriers of comparable magnitude (15.8–16.5 kcal/mol).[19] The latter data disclose that incorporation of three –CH=CHCO– units does not measurably increase the energetic demands for enantiomerization. As a result, the isolation of such molecules in optically active condition is clearly precluded.

In the forthcoming discussion, explicit attention will be given to the stereoelectronic factors limiting Wagner–Meerwein rearrangement within **1'** and **1''**. In the illustrations that immediately follow, the proximal (to the viewer) p orbital of the allyl cation subunit is drawn in its proper orientation relative to the remaining molecular framework. As a direct result of rather rigid structural geometry, only bond a in **1'** is properly aligned stereoelectronically for 1,2-migration. Bond b is misaligned to an extent approximating 75°. The situation in conformer **1''** is, of course, precisely opposite. Consequently, the regioselectivity of Wagner–Meerwein rearrangement is intimately linked to the energetic demands of the **1'** ⇄ **1''** enantiomerization.

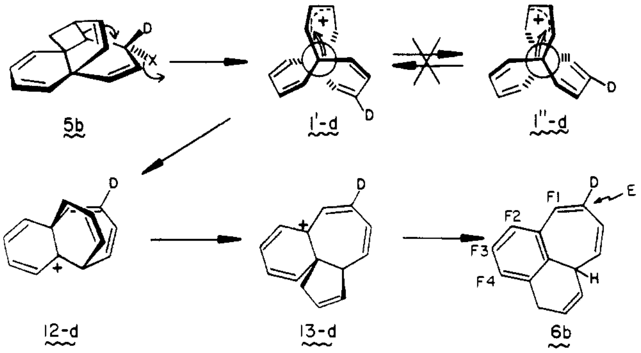


The Rearrangement Cascade. If one ignores for the moment the two conformational orientations that can be assumed by **1**, its ultimate conversion to **6** can be expediently accommodated by the three consecutive 1,2 carbon shifts shown in Scheme I. The initial conversion to **12**, a process presumably driven by the added stabilization accruing to pentadienyl cation formation, sets the stage for ring contraction by shifting of the methylene group. Once **13** is formed, a second 1,2-methylene shift reestablishes the second six-membered ring and permits aromatization by loss of an angular proton.

Scheme I



Scheme II



There are two important comments we wish to make about this mechanistic proposal. The first relates qualitatively to the ultimate fate of the three six-membered rings in **1**. The allylic cation segment eventuates as the non-benzenoid 1,4-cyclohexadienyl ring in **6** and it does so by experiencing a ring contraction–expansion cycle. In the process, one of its original sp^2 centers becomes incorporated into the seven-membered ring, thus accounting for this particular ring enlargement.

Of greater mechanistic interest and import is the question of the inherent dissymmetry of **1**. As drawn in Scheme I, **1** would appear to be symmetric and to offer an equal opportunity to either neighboring cyclohexadiene subunit to engage in Wagner–Meerwein rearrangement. However, as pointed out above, indiscriminate regioselectivity can arise only if the barrier to 1,2-shifting exceeds that for the **1'** ⇄ **1''** enantiomerization. Because it has not proved convenient to label **10** isotopically (due principally to the propensity of the derived ketone for intramolecular Diels–Alder cycloaddition), this particular point of entry onto the carbocation energy surface cannot offer suitable resolution of this question. The issue is, however, directly addressed by making entry from the direction of **5b**.

Entering the Manifold from the Cyclobuta[*d*]naphthalenol Direction. The configuration of **5b** is such that neighboring group involvement of the antiplanar cyclobutane σ bond can be expected to foster (and also likely accelerate) departure of the X group (Scheme II). One need only consult Dreiding models to appreciate that σ participation in this fashion necessarily leads initially to pentaenyl cation-**1'**-*d*. In large part, this eventuality can be traced directly to the rigid conformation that **5** must necessarily adopt in order to accommodate the strained cyclobutane ring. The relevant question at this point is whether **1'**-*d* equilibrates fully or in part with **1''**-*d* prior to its destined conversion to 4a,7-dihydropleiadiene (**6**). Any restriction of this conformationally dynamic option would serve to force the system to converge into the rearrangement manifold proceeding via **12**–*d* and **13**-*d* to **6b**. The extent to which **1''**-*d* is populated should in turn be directly reflected in leakage of protium into site E and

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(15) Mislow, K.; Gust, D.; Finocchiaro, P.; Boettcher, R. J. *Top. Curr. Chem.* **1974**, *47*, 1.

(16) Farina, M.; Morandi, C. *Tetrahedron* **1974**, *30*, 1819.

(17) Gilboa, H.; Altman, J.; Loewenstein, A. *J. Am. Chem. Soc.* **1969**, *91*, 6062.

(18) X-ray structural analysis: Ermer, O.; Gerdil, R.; Dunitz, J. D. *Helv. Chim. Acta* **1971**, *54*, 2476.

(19) Jendralla, H.; Doecke, C. W.; Paquette, L. A. *J. Chem. Soc., Chem. Commun.* **1984**, 942.

a corresponding influx of deuterium into position F4. Since expansion of 300-MHz ^{1}H NMR spectra of **6b** revealed no diminution in the intensity of the combined absorption of the four F protons and only 5–7% residual proton absorption at δ 6.63 (corresponding within experimental error to the level of deuterium substitution in **5b**), stereoisomerization of the propeller-shaped carbocation **1** can be discounted during the molecular rearrangement.

Summary

4a,7-Dihydropleiadiene (**6a**) has been produced from two different alcohols. Indirect evidence has been obtained for intervention of the [4.4.4]propella-2,4,7,9,11-pentaenyl cation (**1**) in both instances. The overall structural change is most economically rationalized in terms of a threefold Wagner–Meerwein cascade from **1** that eventuates in proton loss with concurrent aromatization. The companion investigation of deuterated alcohol **5b** has revealed that cation **1** must be a dissymmetric intermediate. Evidently, the barrier to enantiomeric ring flipping, estimated to be on the order of 16 kcal/mol, is adequately high to preclude symmetrization prior to competing 1,2-carbon migration. This distinctive characteristic of the maximally unsaturated propellanyl carbocation **1** is experimentally detectable because of its rigid topography which results in proper stereoelectronic alignment of only one cyclohexadienyl bridge relative to the proximate p orbital of the allylic cation moiety. We expect that the results described herein foreshadow a large area of interesting chemistry that has hardly been explored.

Experimental Section

Reduction–Dehydration of 4. A solution of somewhat impure **4** (392 mg, 2.0 mmol) in anhydrous methanol (freshly distilled from Mg powder, 90 mL) was treated with $CeCl_3$ (592 mg, 2.4 mmol) and stirred under nitrogen at room temperature for 20 min. Sodium borohydride (151.2 mg, 4.0 mmol) was next added in small portions and the mixture was stirred for an additional hour, poured into 1 N sodium hydroxide solution (100 mL), and allowed to hydrolyze for 1 h. Insolubles were separated by filtration through Celite, and the filter cake was washed with ether (100 mL). The aqueous layer was extracted with ether (3 × 30 mL), and the combined organic solutions were washed with water, dried, and evaporated. There was isolated 350 mg (90%) of **5a** as a colorless solid that was directly subjected to dehydration: ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.5–5.1 (series of m, 8 H), 3.8 (m, 1 H), 3.0–1.6 (series of m, 5 H).

When the same reaction was performed with $NaBD_4$ in CH_3OD, the same NMR spectrum was obtained except that the δ 3.8 signal was lacking: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.20 (dd, $J = 8.3$ and 5.6 Hz, 1 H), 6.0–5.65 (m, 4 H), 5.60 (t, $J = 8.5$ Hz, 2 H), 5.38 (d, $J = 8.3$ Hz, 1 H), 2.66 (q, $J = 5.6$ Hz, 1 H), 2.41 (d, $J = 5.6$ Hz, 1 H), 1.69–1.63 (m, 2 H), 1.25 (s, 1 H).

In a typical dehydration, **5a** (200 mg, 1.0 mmol) was dissolved in 1 mL of $CDCl_3$ that had been dried by passing through Merck activity I neutral alumina inside a glove box. This solution was added at once to a solution of the sulfurane (1.34 g, 2.0 mmol) in comparably dried $CDCl_3$ (2 mL). ^{1}H NMR analysis indicated that the alcohol reacted quickly. The yellow solution was washed with 10% sodium hydroxide solution (2 × 2 mL) and water (2 mL), dried, and filtered through a short alumina column (pentane elution). Further purification by MPLC on silica gel (elution with petroleum ether) afforded 108 mg of **6a** as a colorless oil: IR (CCl_4, cm^{-1}) 3022, 2890, 2820, 1445, 1210, 690, 670; UV (cyclohexane, λ_{max}) 374.5 nm (ϵ 140), 282.5 (7900), 208.5 (21,250); ^{1}H and ^{13}C NMR, see text; MS *m/z* calcd (M^+) 180.0939, obsd 180.1959.

Monodeuterated hydrocarbon **6b** lacked the proton signal at δ 6.63.

Dehydrogenation of 6a. Pleiadiene (7). A solution of DDQ (22.7 mg, 0.1 mmol) in anhydrous benzene-d_6 (0.4 mL) was treated with **6a** (18 mg, 0.1 mmol) under argon. The reaction mixture was heated at the reflux temperature for 90 min while progress of the reaction was monitored by ^{1}H NMR. The hydroquinone was separated by filtration and the filtrate was concentrated in vacuo. Chromatography of the residue on neutral alumina (elution with 2% ethyl acetate in pentane) yielded 8.9 mg (50%) of **7** as a bright red solid: mp 87–90 °C (lit.[11] mp 87–90 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (dd, $J = 8.26$, 1.3 Hz, 2 H), 6.96 (dd, $J = 8$, 7 Hz, 2 H), 6.61 (dd, $J = 6$, 1 Hz, 2 H), 6.0 (dd, $J = 9.5$, 3.7 Hz, 2 H), 5.35 (dd, $J = 9.5$, 3.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) 139.28, 138.61, 138.14, 134.41, 128.11, 127.97, 127.01, 126.36 ppm.

12,13-Epoxy[4.4.4]propella-2,4,7,9-tetraene (9). A cold (0 °C), magnetically stirred solution of **8** (182 mg, 1.0 mmol) in dry dichloromethane (10 mL) was treated sequentially with powdered sodium bicarbonate (252 mg, 3.0 mmol) and a solution of *m*-chloroperbenzoic acid (190 mg, 1.1 mmol, phosphate buffer washed) in the same solvent (5 mL). The reaction mixture was stirred at 25 °C for 3 h, at which point an additional 50 mg of oxidant was introduced. After a 4-h interlude, this treatment was repeated. Five hours later, water (5 mL) was added and the organic phase was shaken with saturated sodium sulfite solution (2 × 5 mL), saturated sodium bicarbonate solution (2 × 5 mL), and brine (5 mL) prior to drying. Solvent evaporation left a residue that was purified by medium-pressure liquid chromatography on silica gel (elution with 3% ether in petroleum ether). There was isolated 57.2 mg of unreacted **8** and 42.5 mg of **9**. The pure epoxide crystallized when stored overnight at −20 °C; it did not remelt at ambient temperature until the vial was held in the hand: IR ($CDCl_3$, cm^{-1}) 3030, 2990, 2910, 1565, 1442, 1425, 985, 968, 817, 802, 668; UV (cyclohexane, λ_{max}) 247.5 nm (ϵ 6650); ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.87 (dd, $J = 7.5$, 2.9 Hz, 2 H), 5.86 (dd, $J = 7.5$, 2.9 Hz, 2 H), 5.49 (dd, $J = 7.5$, 2.9 Hz, 2 H), 5.38 (dd, $J = 7.5$, 2.9 Hz, 2 H), 3.174 (dd, $J = 3.5$, 0.9 Hz, 2 H), 3.163 (dd, $J = 3.5$, 0.9 Hz, 1 H), 2.03 (dd, $J = 15.4$ 3.5 Hz, 2 H), 1.92 (dt, $J = 15.4$, 0.9 Hz, 2 H); ^{13}C NMR (20 MHz, $CDCl_3$) 133.74, 133.63, 124.12, 122.64, 50.80, 36.59, 34.07 ppm; MS *m/z* calcd (M^+) 198.1045 obsd 198.1092.

[4.4.4]Propella-2,4,7,9,11-pentaen-13-ol (10). A solution of *n*-butyllithium in hexane (0.5 mL of 1.6 M, 0.8 mmol) was injected into a dry flask under argon. Ether (750 mL) was added at 0 °C followed by 90 μL (0.7 mmol) of diisopropylamine. The reaction mixture was allowed to warm to room temperature with magnetic stirring, recooled to 0 °C, and treated with freshly distilled (from CaH_2) hexamethylphosphoramide (251 mg, 1.4 mmol). A yellow color developed immediately. The solution was heated to 100 °C for 5 min under a stream of argon to blow off the ether and hexane. The resulting deep brown reaction mixture was treated with a solution of **9** (33.7 mg, 0.17 mmol) in HMPA (2 mL) and heated at 45 °C for 26 h. After cooling, hydrolysis was achieved by addition of saturated ammonium chloride solution (15 mL) and the product was extracted into ether (5 × 10 mL). The combined organic extracts were washed with ice-cold 1 N hydrochloric acid (2×), saturated sodium bicarbonate solution, and brine. Following drying and solvent evaporation, the residue was purified by MPLC on silica gel (elution with 20% ethyl acetate in petroleum ether). There was isolated 5 mg of unreacted **9** and 24.4 mg (72%) of **10** as a colorless solid: IR (KBr, cm^{-1}) 3410, 3025, 2915, 1572, 1490, 1015, 742, 705, 688; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.90–5.80 (m, 5 H), 5.43 (d, $J = 9.4$ Hz, 1 H), 5.41 (d, $J = 9.3$ Hz, 1 H), 5.33 (d, $J = 9.3$ Hz, 1 H), 5.28 (d, $J = 8.9$ Hz, 1 H), 5.24 (d, $J = 8.9$ Hz, 1 H), 4.32 (br s, 1 H), 1.98 (dd, $J = 13.0$, 5.3 Hz, 1 H), 1.80 (dd, $J = 13.0$, 7.3 Hz, 1 H), 1.50 (br s, 1 H); MS *m/z* calcd (M^+) 198.1045, obsd 198.1058.

Dehydration of 10. A solution of **10** (23 mg) in dry benzene (5 mL) was added dropwise via syringe to a solution of the Burgess reagent (33.3 mg, 0.14 mmol) in 5 mL of the same solvent under argon. The reaction mixture was heated at 55–60 °C for 1 h. TLC analysis indicated the reaction to be complete with formation of a single nonpolar product. Water (3 mL) was added and the benzene layer was separated, dried, and concentrated to a volume of approximately 1 mL. This solution was directly submitted to MPLC on silica gel (elution with petroleum ether) to give **6a** as a colorless oil (12.9 mg). Its IR and ^{1}H NMR spectra were superimposable on those described.

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