Homoazulene[1]

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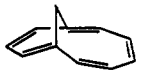
Received February 23, 1981

Abstract: The title compound (**1**) and its 5-methoxy derivative (**12**, azulene numbering) have both been prepared by synthetic sequences which begin with dihydrocinnamic acid. Oxidative cleavage of the central bond in propellane **6** by lead tetraacetate constitutes the key step in both syntheses. ^{1}H NMR spectroscopy reveals an induced diamagnetic ring current in homoazulene which is comparable to that in Vogel's 1,6-methano[10]annulene (**2**), despite the expected differences in π-bond torsion between the two isomeric hydrocarbons. Preliminary interpretation of visible absorption spectroscopic data suggests a similarity between the π system of **1** and that of azulene. The name given in the title has therefore been adopted for **1** in favor of alternatives (e.g., 1,5-methano[10]annulene).

Cyclic conjugation endows many organic compounds with special properties which are quite distinct from those of simple polyolefins.[2] These include, inter alia, thermodynamic, kinetic, geometric, magnetic, and electronic properties, each of which can be evaluated by several methods.[2] An understanding of the ways such properties depend on various factors has been the goal of much research during the past 25 years, and important advances have often resulted from the study of new systems containing unique structural features.[2] The title compound (**1**) appears ideally constituted to provide new insights into transannular and torsional effects in monocyclic Hückel π systems.

Transannular overlap between p orbitals on nonadjacent atoms in a simple annulene should significantly alter the properties of the monocyclic system. According to perturbation molecular orbital theory,[3] the consequences of such an additional interaction will depend a great deal on precisely which p orbitals overlap. In [10]annulene, for example, a larger perturbation is predicted for a 1,6-interaction than for a 1,5-interaction.[3] Comparisons between the properties of **1** and those of Vogel's hydrocarbon **2**[4] should be informative on this point. The importance of 1,6-overlap in **2** is now well established.[5a]



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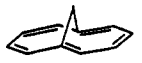

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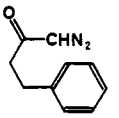
Torsional effects in annulenes arise whenever complete planarity of the π system cannot be achieved. Large distortions from planarity cause the dihedral angle (ϕ) between adjacent p orbitals to deviate substantially from the optimum value of 0°, and this reduced π overlap attenuates the consequences of cyclic conjugation. In the parent [10]annulenes (all-cis and mono-trans),[6] for example, conformational adjustments required to minimize angle strain completely destroy the cyclic conjugation. By contrast, X-ray data[5b] on a derivative of **2** reveal a surprisingly large ϕ_{max} of 34° in this bridged system, yet the molecule still exhibits properties attributable to cyclic conjugation,[4] e.g., an induced diamagnetic ring current. Molecular mechanics calculations reproduce the X-ray structure of **2** and predict a still larger ϕ_{max} of 54° in **1**[7]. It is, therefore, of interest to ascertain whether this compound will retain some degree of cyclic conjugation or will more closely resemble an acyclic polyolefin.

Considerable effort to prepare the title compound in many different laboratories since the middle 1960s[8-10] has recently culminated in two successful syntheses.[9,10] Herein we report the details of our route to **1** and to one of its methoxy derivatives.[10]

Synthesis of Homoazulene

Our synthesis begins with dihydrocinnamic acid, an inexpensive starting material available in unlimited quantities. By standard methods, this acid can be transformed first to the corresponding acid chloride and subsequently to diazo ketone **3** in essentially quantitative yield. Ring expansion of the β-phenyl group by intramolecular carbene addition then produces, after rearrangement of the initial intermediates, the nicely functionallized bicyclic trienone **4**.[11] We have previously developed this cyclization reaction into a short and versatile new azulene synthesis.[11]



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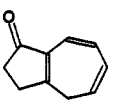

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Introduction of the one-carbon bridge was achieved by cyclopropanation of **4** with dimethylsulfoxonium methylide.[12] As expected, this nucleophilic reagent attacks only that double bond which is conjugated directly with the ketone to form the tricyclic

(1) IUPAC name for **1**: bicyclo[5.3.1]undeca-1,3,5,7,9-pentaene. Alternative name for **1**: 1,5-methano[10]annulene.

(2) Many books are available: (a) "Nonbenzenoid Aromatic Hydrocarbons"; Ginsburg, D., Ed.; Interscience: New York, 1959. (b) Lloyd, D. "Carbocyclic Nonbenzenoid Aromatic Compounds"; Elsevier: New York, 1966. (c) "Aromaticity"; The Chemical Society: London, 1967; Special Publication No. 21. (d) Badger, G. M. "Aromatic Character and Aromaticity"; Cambridge University Press: Cambridge, England, 1969. (e) "Nonbenzenoid Aromatics"; Snyder, J. P., Ed.; Academic Press: New York, 1969. (f) Garratt, P. J. "Aromaticity", McGraw-Hill: New York, 1971. (g) "Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity"; Bergmann, E. D.; Pullman, B., Eds.; Academic Press: New York, 1971. (h) "Topics in Nonbenzenoid Aromatic Chemistry"; Nozoe, T., Ed.; Wiley: New York, 1973. (i) Lewis, D.; Peters, D. "Facts and Theories of Aromaticity"; Macmillan Press: London, 1975.

(3) Dewar, M. J. S.; Dougherty, R. C. "The PMO Theory of Organic Chemistry"; Plenum: New York, 1975; Chapter 3.

(4) For a nice review of 1,6-methano[10]annulene and its chemistry, see: Vogel, E., in ref 2c.

(5) (a) Dewey, H. J.; Deger, H.; Frölich, W.; Dick, B.; Klingensmith, K. A.; Hohlneicher, G.; Vogel, E.; Michl, J. *J. Am. Chem. Soc.* **1980**, *102*, 6412-17, and references cited therein. (b) Dobler, M.; Dunitz, J. D. *Helv. Chim. Acta* **1965**, *48*, 1429-40.

(6) Masamune, S.; Darby, N. *Acc. Chem. Res.* **1972**, 272-81, and references cited therein.

(7) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973**, *95*, 3893-3907.

(8) (a) Ball, D. B. Ph.D. Dissertation, University of California, Santa Barbara, 1970. (b) Klem, R. Ph.D. Dissertation, University of California, Riverside, 1970. (c) Chong, B. Ph.D. Dissertation, University of Michigan, Ann Arbor, 1971. (d) Vogel, E.; Ippen, J.; Buch, V. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 566-7. (e) Unpublished work in other laboratories.

(9) (a) Masamune, S.; Brooks, D. W.; Morio, K.; Sobczak, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 8277-9. (b) Masamune, S.; Brooks, D. W. *Tetrahedron Lett.* **1977**, *3239*-40.

(10) Scott, L. T.; Brunsvold, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 4320-21.

(11) (a) Scott, L. T. *J. Chem. Soc., Chem. Commun.* **1973**, 882-3, and references cited therein. (b) Scott, L. T.; Minton, M. A.; Kirms, M. A. *J. Am. Chem. Soc.* **1980**, *102*, 6311-14.

(12) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353-64.

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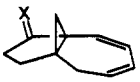
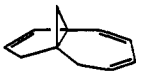
dienone **5a**. Under the usual conditions, however, cyclopropanation of this tetrasubstituted double bond proceeds rather slowly, and competitive deprotonation of **4** by the ylide becomes a serious problem. Fortunately, we were able to shift this latter equilibrium back toward the neutral trienone and the ylide, thus accelerating the desired reaction, simply by adding an excess of trimethylsulfoxonium iodide, the conjugate acid of the ylide.

In tricyclic dienone **5a**, all 11 carbon atoms of the homoazulene ring system have been assembled in their proper arrangement; only cleavage of the central C–C bond and functional group manipulations remain. Conversion of the ketone in **5a** to a double bond was accomplished in a straightforward manner via the corresponding tosylhydrazone **5b**.[13] The adjacent cyclopropane ring presented no complication during decomposition of **5b** with excess methyllithium, and the tricyclic hydrocarbon **6** was obtained in excellent yield.



5a X=O

b X=NNHTs



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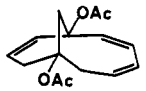
The success of any homoazulene synthesis based on tricyclo[5.3.1.0] intermediates hinges on selective cleavage of the propellane bond; however, much is known about the electrophilic opening of cyclopropanes,[14] even in other tricyclo[*m.n*.1.0] systems.[15] We examined a number of reagents and found that greatest selectivity for cleavage of the central bond in **6** could be achieved with lead tetraacetate, which gives the double bridgehead diacetate **7**, in 73% yield after purification.[16] This important transformation not only serves to excise the undesired C–C bond but also simultaneously raises the oxidation state of the molecule to that of the final target. Two elimination reactions are required to complete the 10-electron π system.

One molecule of acetic acid could be removed directly from **7** by a recently published method[17] using palladium acetate, triphenylphosphine, and sodium carbonate in hot heptane to give the tetraene monoacetate **8a**, presumably via an intermediate π-allylpalladium complex. Poor alignment of the remaining bridgehead acetate in **8a** with the adjacent π system prevents this reaction from continuing all the way to homoazulene, even under more forcing conditions. Further examination of molecular models, however, reveals a perfect anti-periplanar alignment of the bridgehead substituent in this system (**8**) with one of the allylic β-hydrogen atoms. Conversion of the acetate to a better leaving



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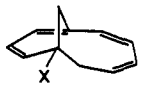


8a X=OAc

b X=OH

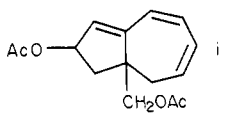
c X=OMs

(13) Shapiro, R. H. *Org. React.* **1976**, *23*, 405–507.

(14) For example, see (a) Moon, S. *J. Org. Chem.* **1964**, *29*, 3456–8. (b) Ouellette, R. J.; Miller, D.; South, A., Jr.; Robins, R. D. *J. Am. Chem. Soc.* **1969**, *91*, 971–5.

(15) For reviews of propellane chemistry, see (a) Ginsburg, D. *Int. Rev. Sci., Org. Chem., Ser. 2*, **1976**, *5*, 369–415. (b) Ginsburg, D. "Propellanes"; Verlag Chemie: New York, 1975.

(16) An isomeric diacetate, believed to have structure i, was obtained as a byproduct when the reaction was run in glacial acetic acid.



i

(17) (a) Tsuji, J.; Yamakawa, T.; Kaito, M.; Maudai, T. *Tetrahedron Lett.*, **1978**, 2075–8. (b) See also Trost, B. M., Verhoeven, T. R.; Fortunak, J. M. *Tetrahedron Lett.* **1979**, 2301–4.

Table I. ^{1}H NMR Chemical Shifts for Homoazulenes and Reference Compounds[a]

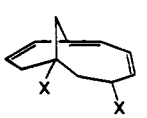
compd	bridge hydrogens	methine hydrogens
1[b]	−0.7 and −1.2	8.1 to 6.8
12[c]	−0.3 and −0.8	7.8 to 6.5
2[c,d]	−0.5	7.4 to 6.9
13[b,e]	+2.5 and +1.9	6.3 to 6.2

[a] In parts per million (δ) from internal Me_4Si. [b] $CDCl_3$. [c] CCl_4. [d] Reference 4. [e] Reference 25.

group would, therefore, set the stage for a classical β-elimination reaction to complete the synthesis. Accordingly, tetraene acetate **8a** was saponified to the bridgehead alcohol **8b**, from which mesylate **8c** could be prepared in high yield by standard methods.[18] The final elimination was achieved with potassium *tert*-butoxide in *tert*-butyl alcohol to give homoazulene **1**.

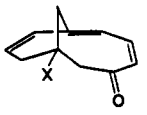
Synthesis of 5-Methoxyhomoazulene[10,19]

The discovery that diacetate **7** can be isomerized quantitatively in hot acetic acid to the more highly conjugated isomer **9a** suggested an alternative route to the homoazulene nucleus. Saponification of **9a** to the corresponding diol **9b** was achieved without difficulty; however, we were unable to eliminate HX cleanly from either **9a** or **9b**, or from any derivative thereof, under a variety of conditions. To facilitate elimination of the bridgehead substituent, therefore, we decided to oxidize the allylic oxygen function to a ketone. Thus, treatment of diol **9b** with manganese dioxide[20] gave ketol **10a**, which was converted to the corresponding mesylate **10b** with methanesulfonyl chloride and triethylamine.[18]



9a X=OAc

b X=OH



10a X=OH

b X=OMs

As anticipated, the second bridgehead double bond could then be introduced quite easily by brief treatment of **10b** with diazabicyclononene. The resulting tetraenone **11** was obtained in good yield. This highly unsaturated bicyclic ketone deserves special attention as a compound of interest in its own right. It can be viewed as a keto tautomer of 5-hydroxyhomoazulene, but it shows no tendency to tautomerize. Thus, there appears to be no overwhelming thermodynamic driving force for formation of the homoazulene π system.[21] However, tetraenone **11** can also be viewed as a 3,4-homotropone, constrained by an extra three-carbon bridge. In the parent tropone molecule, the remarkably low IR carbonyl stretching frequency (1582 cm^{-1}) and the planarity of the seven-membered ring, despite angle strain, attest to the importance of cyclic conjugation.[22] The similarly low IR carbonyl stretching frequency of tetraenone **11** (1590 cm^{-1}) would appear to be strong evidence for substantial overlap between bridgehead p orbitals in this system. Any special thermodynamic stability associated with the homotropone moiety would contribute to the reluctance of **11** to enolize.

Deprotonation of **11** with lithium diisopropylamide (LDA) in tetrahydrofuran provides a beautiful solution of the cherry red

(18) Crossland, R. K.; Servis, K. L. *J. Org. Chem.* **1970**, *35*, 3195–6.

(19) The numbering system for compound **1** depends on the nomenclature system chosen. For the name "homoazulene", we advocate use of the azulene numbering system as in **14**. The alternative name, "1,5-methano[10]-annulene", implies numbering around the small arm of the π system first, starting from one bridgehead. IUPAC numbering is unambiguous. Proper names for compound **12**, then, are 5-methoxyhomoazulene, or 7-methoxy-1,5-methano[10]annulene, or 3-methoxybicyclo[5.3.1]undeca-1,3,5,7,9-pentaene.

(20) Active manganese dioxide was prepared by the method of J. Attenburrow et al. as modified by Stork, G.; Tourasz, M. *J. Am. Chem. Soc.* **1964**, *86*, 471–8.

(21) Cf. 2-hydroxy-1,6-methano[10]annulene: Vogel, E. In ref 2c pp 129–30.

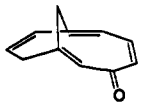
(22) Reference 2b, p 131.

Table II. Substituent Effects (nm) on the Absorption Maxima in the Visible Spectra of Azulene 14 and Homoazulene 1

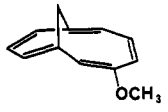
parent hydrocarbon (λ_{max})	substituent	position 1(3)	2	4(8)	5(7)	6
azulene 14	OCH_3	+105[b]	−55[c]	−35[d]	+35[d]	−49[e]
(579 nm)[a]	CH_3[a]	+29	−14	−10	+10	−13
homoazulene 1 (482 nm)	OCH_3	+23[f]			+8	

[a] Heilbronner, E. In ref 2a, Chapter 5. [b] Replogle, L. L. *J. Org. Chem.* **1964**, *29*, 2805–6. [c] Nozoe, T.; Seto, S.; Matsumura, S. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 1990–8. [d] Reid, D. H.; Stafford, W. H.; Ward, J. P. *J. Chem Soc.* **1958**, 1100–9. [e] Hafner, K.; Asmus, K.-D. *Justus Liebigs Ann. Chem.* **1964**, *671*, 31–40. [f] Reference 9a.

5-homoazulenolate anion. To our surprise, however, attempts to quench this "phenoxide" by O-methylation with methyl fluorosulfonate gave only recovered starting material and none of the desired 5-methoxyhomoazulene **12**. Obvious explanations for this



11



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negative result were checked one by one until we ultimately reached the conclusion that neutral diisopropylamine, the byproduct of enolate formation, must compete successfully for the methyl fluorosulfonate to give a quaternary ammonium salt which then protonates the enolate. This hypothesis, though implausible at first, now appears to be correct; removal of the offending proton solves the problem. Thus, all the diisopropylamine was converted back into LDA by the addition of 1 equiv of *n*-butyllithium to the enolate solution just prior to the methylation step. Excess methyl fluorosulfonate then gave the desired product **12** in good yield with no recovered starting material.

Properties

The ^1H NMR spectra of **1** and **12** both reveal a pronounced diamagnetic ring current[23] in the homoazulene system (Table I). Those hydrogens attached to the one-carbon bridge lie within the cavity of the cyclic π system and give rise to signals *upfield* of tetramethylsilane, whereas those attached to the outer periphery of the π system resonate at low field in the so-called "aromatic" region. Deshielding of the methoxy group in **12** is also evident (δ 3.86; cf. anisole, δ 3.73).

These NMR spectra should be compared with those of Vogel's methano-bridged annulenes **2** and **13** (Table I). Hydrocarbon **2** also supports a ring current,[4] but **13**, which has a more distorted Hückel π system (ϕ_{max} = 74°),[24] does not share this capability.[25] Clearly the homoazulene ring system enjoys a degree of cyclic conjugation comparable to that in **2**, as judged by ^1H NMR chemical shifts, despite the expected differences in π-bond torsion between the two systems.[7] The prediction[7] that **1** will exhibit bond alternation, as in **13**,[24] rather than bond convergence, as in **2**,[5b]

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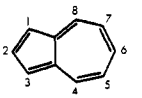
no longer appears reasonable, in light of the apparent correlation between bond convergence and ring current in these related compounds, but should still be tested by X-ray crystallography.

Homoazulene (**1**) absorbs visible light at λ_{max} 482 nm and thus appears orange in color. By contrast, the longest wavelength absorption maximum of **2** occurs below 400 nm.[4] In this respect, then, the two isomeric hydrocarbons differ dramatically.

Substituent effects on the visible absorption spectrum of **1** actually seem to parallel those of azulene **14** (Table II). This emerging pattern suggests a perturbation of the [10]annulene perimeter of **1** by overlap between transannular p orbitals, as in azulene, although more data are needed to strengthen the argument. The shorter wavelength maximum and the decreased magnitude of substituent effects in the visible absorption spectrum of **1**, relative to those of the nonalternant hydrocarbon **14**, are



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consistent with less effective transannular overlap in the methano-bridged system. Other factors which may also distinguish **1** from a true [10]annulene include (a) the effects of nonplanarity, (b) inductive effects of the bridge, and (c) hyperconjugative interaction of the bridge with the π system.[26] A more thorough analysis of these effects must await further study.

Finally, to emphasize the fact that **1** resembles azulene, and that it should not be regarded as a pure, Hückel [10]annulene, we advocate the name homoazulene.[1]

Experimental Section

General. Tetrahydrofuran (THF) and diethyl ether were purified by distillation under nitrogen from the sodium ketyl of benzophenone immediately prior to use. Dimethyl sulfoxide (Me_2SO) and hexamethylphosphoramide (HMPA) were dried by distillation from calcium hydride. All other solvents were distilled and, if necessary, dried by standard procedures. Woelm silica gel F and Merck alumina $PF_{254+366}$ were used for all preparative layer chromatography (TLC). Baker silica gel 60-200 was used for all column chromatography. ^1H and ^{13}C NMR spectra were recorded on a JOEL FX100 or a Hitachi Perkin-Elmer R24B spectrometer and are reported in ppm downfield from tetramethylsilane. Melting points are uncorrected.

Tricyclo[5.3.1.0]undeca-2,4-dien-10-one (5a).[12] This reaction was run in oven-dried glassware under a nitrogen atmosphere. To 600 mL of dry Me_2SO were added 1.92 g (50% in mineral oil, 40 mmol) of NaH and 24.4 g (111 mmol, threefold excess; see text) of trimethylsulfoxonium iodide (Aldrich, 98%). The mixture was stirred at room temperature until the solid suspension disappeared and the solution became clear (~20 min). A solution of 5.40 g (37.0 mmol) of trienone **4**[11] in 60 mL of dry Me_2SO was added dropwise over 30 min at room temperature to the ylide solution. The dark brown reaction mixture (enolate of **4**?) was then heated to 75 °C for 30–45 min, during which time the color lightened to a clear yellow. The light yellow reaction mixture was poured into 600 mL of ice water and extracted with four 200-mL portions of CH_2Cl_2. The combined CH_2Cl_2 layers were washed three times with 200-mL portions of saturated NaCl solution, dried over $MgSO_4$, and concentrated under reduced pressure to give 6.5 g of crude product. Chromatography on 200 g of silica gel with 15% EtOAc/petroleum ether afforded 4.49 g (76% yield) of **5a** as a pale yellow liquid: ^{13}C NMR ($CDCl_3$) 212.0, 128.8, 127.5, 127.3, 122.4, 58.2, 41.4, 32.6, 32.1, 28.3, 22.7; ^1H NMR (CCl_4) δ 1.15 (d, J = 4 Hz, 1 H, cyclopropyl), 2.0 (s, 4 H, $CH_2CH_2C{=}O$), 2.50 (d, J = 4 Hz, 1 H, cyclopropyl), 2.62 (d, J = 6 Hz, 2 H, $CH_2C{=}C$), 5.3–6.0 (mult, 3 H, vinyl H's), 6.35 (d, J = 11 Hz, 1 H, vinyl H); IR (neat) 3010 (s, sh), 2915 (s), 1710 (vs), 1595 (w), 1420 (m), 1285 (s), 1250 (m), 1080 (m), 1048 (s), 1012 (m), 920 (w), 848 (m), 775 (m), 702 (s, broad) cm^{-1}; MS M^+ 160.0889 (calcd 160.0889); UV (EtOH) λ_{max} = 251 nm.

Tosylhydrazone (5b). To a solution of 4.50 g (28.1 mmol) of tricyclic dienone **5a** in 7 mL of dry THF was added 5.55 g (29.8 mmol) of *p*-toluenesulfonohydrazide (Aldrich, 97%) with stirring at room temperature. The reaction mixture, which never became homogeneous, was stirred overnight and then filtered. It is important to avoid excess THF in the reaction mixture since the product is not completely insoluble. The white precipitate was washed with a minimum of ether and dried by suction for a few minutes. Further drying for 0.5 h with a vacuum pump afforded 7.67 g (83% yield) of **5b** as a white powder: mp 190–192 °C dec; ^{13}C NMR ($CDCl_3$) δ 167.8, 144.0, 135.5, 129.9, 129.5, 128.8, 128.2, 127.8, 121.8, 56.1, 37.2, 32.2, 31.1, 23.3, 21.6, 21.2; ^1H NMR ($CDCl_3$) δ 0.77 (d, J = 4 Hz, 1 H, cyclopropyl), 1.81–2.4 (mult, 5 H, 1 cyclopropyl and $CH_2CH_2C{=}N$), 2.36 (s, 3 H, CH_3), 2.55 (d, J = 6 Hz, 2 H,

(23) For a detailed discussion of ring currents in annulenes, see: Haddon, R. C. *Tetrahedron* **1972**, 3613–35, 3635–55, and references cited therein.

(24) Gramaccioli, C. M.; Mimun, A. S.; Mugnoli, A.; Simonetta, M. *J. Am. Chem. Soc.* **1973**, *95*, 3149–54.

(25) Vogel, E.; Haberland, U.; Günther, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 513–4.

(26) For a discussion of these effects in bridged [14]annulenes, see: Kolc, J.; Michl, J.; Vogel, E. *J. Am. Chem. Soc.* **1976**, *98*, 3935–48.

$CH_2C{=}C$), 5.3–6.0 (mult, 3 H, vinyl H's), 6.35 (d, J = 11 Hz, 1 H), 7.16 (d, J = 8 Hz, 2 H, aromatic H's), 7.34 (s, 1 H, NH), 7.73 (d, J = 8 Hz, 2 H, aromatic H's); IR (KBr) 3260 (m), 3050 (w), 2970 (w), 1650 (w), 1600 (w), 1400 (m), 1340 (s), 1305 (m), 1180 (s, sh), 1165 (s), 1075 (m), 1020 (s), 925 (m), 817 (m), 719 (s), 709 (s), 695 (s) cm^{-1}.

Anal. Calcd for $C_{18}H_{20}N_2SO_2$: C, 65.84; H, 6.14. Found: C, 65.78; H, 6.13.

Tricyclo[5.3.1.0]undeca-2,4,9-triene (6).[13] This reaction was run under a nitrogen atmosphere in flame-dried glassware. To a suspension of 5.0 g (15.2 mmol) of tosylhydrazone **5b** in 100 mL of dry ether at room temperature was added 16.0 mL (30.4 mmol) of 1.9 M methyllithium in ether (lithium bromide complex, Ventron) dropwise via syringe. After the first equivalent of MeLi was added, the mixture became homogeneous and pale yellow. After the second equivalent of MeLi was added, the solution became dark orange and gradually turned brown. After 4 h of continued stirring at room temperature, a few drops of water were added slowly to quench the reaction. The mixture was diluted with 100 mL of ether, washed with 50 mL of water, and dried over $MgSO_4$. The yellow solution was then concentrated at −10 °C, 15 Torr (**6** is volatile). The light orange oil thus obtained was chromatographed on 50 g of silica gel with pentane to give 2.0 g (92% yield) of **6** as a colorless liquid: ^{13}C NMR ($CDCl_3$) δ 138.6, 134.7, 128.6 (2C), 125.5, 121.9, 52.9, 43.6, 38.8, 32.6, 25.1; ^1H NMR (CCl_4) δ 0.30 (d, J = 3 Hz, 1 H, cyclopropyl), 2.26 (d, J = 3 Hz, 1 H, cyclopropyl), 2.4–2.8 (mult, 4 H, $CH_2C{=}C$), 5.1–5.9 (mult, 5 H, vinyl H's), 6.0 (d, J = 12 Hz, 1 vinyl H); IR (neat) 3050 (s), 2940 (s), 2860 (m), 1600 (m), 1425 (m), 948 (m), 937 (m), 900 (m), 848 (m), 738 (vs), 705 (m), 682 (s) cm^{-1}; UV (EtOH) λ_{max} 275 nm (ϵ 2900); MS, m/e (rel intensity) 144 (46), 143 (26), 141 (13), 130 (16), 129 (100), 128 (81), 127 (22), 117 (28), 116 (33), 115 (52), 103 (14), 91 (62), 79 (14), 78 (23), 77 (28), 65 (21).

1,7-Diacetoxybicyclo[5.3.1]undeca-2,4,9-triene (7). To 200 mL of dry benzene and 50 mL of glacial acetic acid at 15 °C were added 3.0 g (21 mmol) of triene **6** and 10.0 g (22 mmol) of lead tetraacetate (Aldrich). The reaction mixture was stirred at 15 °C until it became homogeneous (ca. 1 h). Stirring was continued for 3 h at room temperature, and 200 mL of water was then added. The benzene layer was separated, washed once with 200 mL of saturated NaCl and twice with 100-mL portions of saturated $NaHCO_3$, dried over $MgSO_4$, and concentrated under reduced pressure to give 6.0 g of crude product. Chromatography on 100 g of silica gel with 15% EtOAc/petroleum ether gave a colorless oil which slowly crystallized in the cold. The crystals were washed with cold pentane to give 4.0 g (73% yield) of **7** which could be stored indefinitely until needed. Recrystallization of a sample from petroleum ether gave colorless needles: mp 90–92 °C; ^{13}C NMR ($CDCl_3$) δ 169.6, 168.8, 130.2, 129.5 (2C), 127.9, 126.6, 124.7, 83.5, 83.3, 36.3 (2C), 33.0, 21.9 (2C); ^1H NMR (CCl_4) δ 1.93 (s, 6 H, two OAc), 2.0–3.0 (m, 5 H, aliphatic H's), 3.36 (d, J = 13 Hz, 1 bridging H), 5.3–5.9 (m, 5 H, vinyl H's), 6.10 (dd, J = 4 Hz, 10 Hz, 1 vinyl H); IR (KBr) 2950 (w), 1730 (vs), 1365 (m), 1255 (s, sh), 1225 (s), 1190 (m), 1020 (m), 1005 (m), 957 (s), 940 (m), 880 (m), 791 (m), 742 (m) cm^{-1}; UV (EtOH) λ_{max} 247 nm (ϵ 3500).

Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.69; H, 6.92. Found: C, 68.85; H, 6.93.

7-Acetoxybicyclo[5.3.1]undeca-2,4,8,10-tetraene (8a). The success of this reaction depends greatly on the purity of **7**. To a solution of 1.64 g (6.26 mmol) of *crystallized* diacetate **7** in 60 mL of heptane were added ca. 25 mg (0.1 mmol) of palladium acetate, 183 mg (0.68 mmol) of triphenylphosphine, and 610 mg (5.8 mmol) of sodium carbonate. The faint yellow, heterogeneous solution was stirred at 85 °C and gradually became darker with time. When TLC showed no more starting material (5–15 h), the reaction mixture was cooled and filtered through Celite which was then washed with ether. Concentration of the combined filtrates under reduced pressure gave a yellow oil which was purified by column chromatography on 30 g of silica gel with 15% EtOAc/petroleum ether. The first yellow band afforded 0.9–1.2 g (71–95% yield) of **8a** as an unstable, bright yellow oil: ^{13}C NMR ($CDCl_3$) δ 170.0, 138.7, 136.0, 130.9, 128.8, 127.6, 125.8, 124.7, 122.7, 84.3, 34.2 (2C), 31.5; ^1H NMR (CCl_4) δ 2.00 (s, 3 H, CH_3), 2.34 (dd, J = 8, 14 Hz, 1 H of $CH_2C{=}C$), 3.50 (br s, 2 bridging H's), 3.99 (dd, J = 8, 14 Hz, 1 H of $CH_2C{=}C$), 5.1–5.9 (mult, 6 vinyl H's), 6.01 (d, J = 10 Hz, 1 H, H_2); IR (neat) 3015 (m), 1735 (s), 1450 (m), 1370 (m), 1238 (s), 1050 (m), 1017 (m), 736 (m), 708 (m) cm^{-1}; UV (EtOH) λ_{max} 244, 276 (sh), 355 nm.

Bicyclo[5.3.1]undeca-2,4,8,10-tetraen-7-ol (8b). To a solution of 27 mg (0.13 mmol) of tetraene acetate **8a** in 3 mL of methanol were added 0.5 mL of water and 90 mg (1.16 mmol) of potassium hydroxide. The solution turned from yellow to brown within minutes at room temperature and was stirred for a total of 30 min at room temperature. Solvent was removed under reduced pressure. The residue was extracted with 20 mL of ether which was then dried over $MgSO_4$ and concentrated under reduced pressure to give 17 mg (80%) of **8b** as a yellow oil.

Alternatively, 10.0 mL (12 mmol) of 1.2 M methyllithium in ether was added dropwise via syringe to a solution of 1.2 g (5.9 mmol) of freshly prepared tetraene acetate **8a** in 25 mL of freshly distilled ether. The reaction mixture was stirred at room temperature for 0.5 h, after which time TLC showed only a single spot. Water was added to quench the reaction, and the aqueous layer was extracted twice with ether; the combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give 0.85–0.95 g (90–100% yield) of **8b** as an unstable, dark yellow oil which was used directly in the next reaction. Preparative TLC on silica gel with 15% EtOAc/petroleum ether afforded a pure sample of **8b** as a yellow oil (R_f 0.3): ^{13}C NMR ($CDCl_3$) δ 140.4, 104.4, 139.7, 131.2, 129.1, 128.4, 125.8, 125.6, 123.2, 76.8, 38.0, 35.2; ^1H NMR (CCl_4) δ 1.80 (dd, J = 7, 13 Hz, 1 methylene H superimposed on a 1 H singlet for OH), 2.95 (d of t, J = 12, 2 Hz, 1 bridging H), 3.52 (dd, J = 1, 12 Hz, 1 bridging H), 3.91 (dd, J = 7, 13 Hz, 1 methylene H), 5.2–5.8 (mult, 6 vinyl H's), 5.95 (d, J = 12 Hz, 1 vinyl H); IR (neat) 3500 (m), 3030 (m), 1380 (m), 1282 (m), 1088 (s), 1061 (m), 930 (m), 742 (s), 709 (s) cm^{-1}; UV (EtOH) λ_{max} 246, 282 (sh), 356 nm.

Bicyclo[5.3.1]undeca-2,4,8,10-tetraen-7-yl Methanesulfonate (8c). A solution of 850 mg (5.3 mmol) of freshly prepared tetraenol **8b** in 30 mL of dry methylene chloride was cooled to 0 °C. To this solution were added 2.15 g (21 mmol) of anhydrous triethylamine and 1.22 g (11 mmol) of methanesulfonyl chloride, in that order. The pale yellow solution was stirred at 0 °C for 30 min and then at room temperature for 45 min. No change in color occurred. The solution was then poured into 25 mL of 0.25 N HCl. The organic layer was separated, washed twice with 20-mL portions of saturated $NaHCO_3$ and then once with 20 mL of saturated NaCl, dried over $MgSO_4$, and concentrated under reduced pressure to afford 1.1–1.2 g (87–95% yield) of **8c** as an unstable, yellow oil which was used immediately without further purification: ^1H NMR (CCl_4) δ 2.45 (dd, J = 7, 14 Hz, 1 allylic H), 2.91 (s, 3 H, OMs), 3.39 (br d, J = 12 Hz, 1 bridging H), 3.70 (d, J = 12 Hz, 1 bridging H), 4.05 (dd, J = 7, 14 Hz, 1 allylic H), 5.2–6.0 (mult, 6 vinyl H's), 6.23 (d, J = 11 Hz, 1 vinyl H); IR (neat) 3000 (m), 2970 (m), 2920 (m), 1340 (s), 1165 (s), 1000 (s), 965 (s), 915 (s), 810 (s), 735 (m), 705 (m) cm^{-1}; UV (EtOH) λ_{max} 244, 280 (sh), 355 nm.

Homoazulene (1).[1] A solution of potassium *tert*-butoxide was prepared by dissolving 550 mg (14 mgatoms) of freshly cut potassium in 80 mL of dry *tert*-butyl alcohol under a nitrogen atmosphere. To this was added, via syringe, a solution of 434 mg (1.82 mmol) of freshly prepared mesylate **8c** in 25 mL of dry *tert*-butyl alcohol at room temperature. The reaction mixture became orange instantly. After 15 h, the UV spectrum of the reaction mixture ceased to change, and the product was isolated by adding 150 mL of pentane and washing repeatedly with 50-mL portions of saturated NaCl solution. The organic layer was dried over $MgSO_4$ and concentrated at 0–10 °C (**1** is volatile) under reduced pressure. The resulting dark orange oil was chromatographed on 20 g of alumina (not silica gel) with pentane. A bright orange fraction was collected and carefully concentrated (cold as above) to afford 78 mg (30% yield) of purified homoazulene as a bright orange oil: ^{13}C NMR (acetone-d_6) δ 160.4, 143.3, 132.8, 129.5, 128.1, 124.7, 34.5; 100 MHz ^1H NMR (acetone-d_6) δ 8.12 (d, J = 7 Hz, 2 H), 7.53 (d, J = 7 Hz, 2 H), 7.40–7.23 (m, 3 H), 6.85 (t, J = 7 Hz, 1 H), −0.74 (d, J = 9.5 Hz, 1 H), −1.23 (dt, J = 9.5, 1.6 Hz, 1 H); IR (neat) 3020 (m), 2960 (m, sh), 2920 (s), 2850 (m), 1455 (m), 1435 (m, sh), 760 (s), 655 (m) cm^{-1}; UV (hexane) λ_{max} 279 (ϵ 17800), 482 nm (220); mass spectrum, *m/e* (rel intensity) 142 (67, M^+), 141 (100), 129 (12), 128 (13), 115 (47), 86 (11), 84 (13), 71 (11), 63 (12), 57 (18), 51 (28), 49 (30); M^+ (calcd for $C_{11}H_{10}$) 142.0782 (found 142.0763).

Note Added in Proof: Homoazulene can be prepared in 50–60% yield by treatment of mesylate **8c** with DBN in refluxing Et_2O.

5,7-Diacetoxybicyclo[5.3.1]undeca-1,3,9-triene (9a). A colorless solution of 1.322 g (5.06 mmol) of recrystallized diacetate **7** in 30 mL of glacial acetic acid was heated at 75 °C with stirring for 6 h under nitrogen. The orange reaction mixture was then cooled, diluted with 30 mL of ether, washed twice with 30-mL portions of water and twice with 40-mL portions of saturated $NaHCO_3$, dried over $MgSO_4$, and concentrated under reduced pressure. Column chromatography of the crude product on 80 g of silica gel with 15% EtOAc/petroleum ether afforded 1.274 g (96% yield) of **9a** as a colorless oil.

Alternatively, diacetate **9a** can be prepared in higher overall yield directly from triene **6**. Thus, 630 mg (1.42 mmol) of lead tetraacetate was added with stirring to a 15 °C solution of 198 mg (90% pure, 1.23 mmol) of triene **6** in 7 mL of glacial acetic acid. The reaction mixture was stirred at 15 °C for 15 min and then at 75 °C for 6 h (or at 65–70 °C overnight). The crude product, obtained by the workup described above, was purified by preparative TLC on silica gel with 10% EtOAc/petroleum ether (two elutions). The lower band (R_f 0.40) gave 42 mg (13% yield) of a mixture of isomeric diacetates i.[16] The upper band (R_f 0.55) afforded 199 mg (61%) of **9a** as a colorless oil: ^{13}C NMR

($CDCl_3$) δ 169.7, 169.1, 139.6, 131.2, 128.8, 126.1, 125.8, 121.7, 81.9, 71.4, 38.3, 37.3, 35.0, 21.6, 20.7; ^1H NMR (CCl_4) δ 1.95 (3 singlets, 6 H, mixture of acetate methyls from 5-exo and 5-endo isomers), 2.1–3.1 (mult, 6 H, aliphatic H's), 5.2–6.3 (mult, 6 H, 5 vinyl and 1 methine H); IR (neat) 3030 (m), 2950 (m), 1735 (vs), 1535 (m), 1433 (m), 1372 (s), 1240 (vs, broad), 1060 (s), 1020 (s), 951 (m), 740 (m) cm^{-1}; UV (hexane) λ_{max} 265 nm (ε 6500).

5,7-Dihydroxybicyclo[5.3.1]undeca-1,3,9-triene (9b). To a solution of 225 mg (0.86 mmol) of diacetate **9a** in 5 mL of 10:1 CH_3OH:H_2O was added 150 mg (3.8 mmol) of potassium hydroxide, and the solution was stirred for 1 h at 25 °C. The light orange reaction mixture was then concentrated under reduced pressure and partitioned between 20 mL of ether and 2 mL of water. The organic layer was separated, dried over $MgSO_4$, and concentrated under reduced pressure to a yellow oil. Preparative TLC on silica gel with 40% EtOAc/petroleum ether gave a wide, colorless band centered at R_f 0.20 which afforded 123 mg (81% yield) of **9b** as a white solid. Recrystallization from $CHCl_3$ gave chunky, colorless crystals: mp 143–147 °C; ^{13}C NMR (Me_2SO-d_6) δ 141.2, 137.8, 129.2, 126.9, 122.1, 121.4, 71.7, 67.9, 43.3, 42.5, 39.4; ^1H NMR (Me_2SO-d_6) δ 1.00 (d, J = 10 Hz, 1 bridging H), 1.5–2.0 (mult, 4 H), 2.48 (d, J = 10 Hz, 1 bridging H), 3.07 (s, 2 H, 2 OH), 4.0–4.5 (mult, 1 H, *H*C–OH), 5.0–5.5 (mult, 4 vinyl H's), 5.93 (d, J = 10 Hz, 1 vinyl H); IR (KBr) 3290 (vs), 3020 (m), 2950 (m), 1410 (m), 1295 (m, sh), 1285 (m), 1257 (m), 1098 (m), 1075 (s), 1002 (s), 986 (s), 856 (m), 727 (s) cm^{-1}; UV (EtOH) λ_{max} 266 nm (ε 7300); MS, *m/e* (rel intensity) 178 (21), 160 (49), 159 (10), 145 (39), 142 (13), 141 (12), 132 (51), 131 (27), 121 (27), 120 (25), 118 (33), 117 (100), 115 (25), 107 (21), 105 (25), 92 (23), 91 (93), 79 (34), 77 (46).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.27; H, 7.90.

7-Hydroxybicyclo[5.3.1]undeca-1,3,9-trien-5-one (10a). To a solution of 51 mg (0.29 mmol) of diol **9b** in 20 mL of dry CH_2Cl_2 was added 250 mg (2.9 mmol, 10 equiv) of freshly prepared[20] MnO_2, and the reaction mixture was stirred at 25 °C until TLC showed no diol (ca. 10 h). Filtration through Celite and concentration of the filtrate under reduced pressure gave a yellow oil. Preparative TLC on silica gel with 35% EtOAc/petroleum ether afforded 49 mg (96% yield) of **10a** as a pale yellow solid (R_f 0.35): mp 109–12 °C; ^{13}C NMR ($CDCl_3$) δ 203.2, 151.0, 138.7, 133.2, 129.1 (2C), 121.3, 80.8, 51.1, 41.5, 41.1; ^1H NMR ($CDCl_3$) δ 2.14 (dt, J = 2, 12 Hz, 1 H), 2.3–2.6 (m, 3 H), 2.99 (d, J = 10 Hz, 1 H), 3.08 (s, 1 H, OH), 3.51 (d, J = 11 Hz, 1 H, bridging H), 5.67 (dt, J = 4, 10 Hz, H_9), 5.7–6.1 (two overlapping doublets, 2 H, H_2 and H_4), 6.35 (br d, J = 10 Hz, 1 H, H_{10}), 6.65 (dd, J = 4, 12 Hz, 1 H, H_3); IR (KBr) 3380 (s), 2950 (w), 1620 (vs), 1580 (m, sh), 1565 (m), 1280 (m), 1255 (m), 1190 (s), 1150 (s), 1066 (s), 932 (m), 863 (m), 850 (s), 762 (m), 727 (m) cm^{-1}; UV (hexane) λ_{max} 214 (ε 13 400), 323 nm (5100); MS, *m/e* (rel intensity) 176 (37), 160 (20), 158 (19), 148 (13), 145 (19), 134 (75), 133 (68), 132 (25), 131 (23), 129 (21), 119 (35), 117 (37), 115 (47), 114 (30), 108 (35), 107 (39), 106 (33), 105 (56), 104 (51), 103 (42), 95 (53), 94 (43), 93 (43), 92 (100), 91 (100), 82 (36), 79 (56), 78 (59), 77 (55).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.88; H, 6.87.

7-Methanesulfonatobicyclo[5.3.1]undeca-1,3,9-trien-5-one (10b). A faint yellow solution of 48 mg (0.27 mmol) of ketol **10b** in 5 mL of dry CH_2Cl_2 was cooled to 0 °C. With a syringe, 103 μL (0.70 mmol, 2.6 equiv) of dry triethylamine and 57 μL (0.54 mmol, 2.0 equiv) of methanesulfonyl chloride were added in that order. The reaction mixture was stirred at 0 °C for 20 min and at 25 °C for 30 min. Another 20 mL of CH_2Cl_2 was added, and the light yellow solution was washed successively with 5 mL of saturated NaCl solution and 10 mL of saturated $NaHCO_3$ solution. Drying over $MgSO_4$ and removal of the solvent under reduced pressure gave 68 mg (89% yield, 90% purity) of **10b** as pale yellow liquid which was used immediately: ^1H NMR ($CDCl_3$) δ 2.6–3.5 (br m, 6 H), 3.13 (s, 3 H, OMs), 5.67 (dt, J = 4, 10 Hz, 1 H, H_9), 5.8–6.2 (m, 2 H, H_2 and H_4), 6.40 (d, J = 10 Hz, H_{10}), 6.70 (dd, J = 5, 12 Hz, H_3); IR (neat) 3030 (w), 2960 (w), 1645 (s), 1335 (s, broad), 1165 (s), 1142 (s), 970 (m), 920 (s), 896 (s, br), 864 (m), 811 (m) cm^{-1}; UV (hexane) λ_{max} 318 nm (ε 4100).

Bicyclo[5.3.1]undeca-1,3,6,9-tetraen-5-one (11). To a pale yellow solution of 64 mg (0.23 mmol) of mesyloxy ketone **10b** (90% pure) in 2 mL of $CHCl_3$ was added, via syringe, 41 μL (0.33 mmol) of 1,5-diazabicyclo[4.3.0]nonene-5. After being stirred for 20 min at 25 °C, the solution became darker yellow, and TLC indicated that the reaction was complete. Ether (20 mL) was added, and the solution was washed successively with 5 mL each of saturated NaCl solution and saturated $NaHCO_3$ solution. The yellow ether layer was dried over $MgSO_4$ and concentrated under reduced pressure. Preparative TLC on silica gel with 30% EtOAc/petroleum ether afforded 24 mg (67% yield) of **11** as a pale yellow oil (R_f 0.25): ^1H NMR ($CDCl_3$) δ 2.70 (d, J = 9 Hz, 1 bridging H), 2.8–3.3 (m, 2 H, $CH_2C{=}C$), 3.43 (d, J = 9 Hz, 1 bridging H), 5.7–6.15 (m, 3 vinyl H), 6.3–6.8 (m, 3 vinyl H); IR (neat) 3070 (w), 2980 (w), 1645 (s), 1590 (vs), 1575 (s, sh), 1320 (m), 1220 (m), 1180 (m), 856 (s), 791 (m), 768 (m), 716 (m), 678 (m) cm^{-1}; UV (CH_2Cl_2) λ_{max} 336 nm (ε 5500).

5-Methoxyhomoazulene (12).[19] Solvents used in this procedure were degassed by the freeze–thaw method. All operations, including the workup, were conducted under a nitrogen atmosphere as much as possible. LDA was prepared at 0 °C by adding 0.12 mL (0.26 mmol) of *n*-BuLi/hexane (2.3 M, Ventron) to 2 mL of 3:1 THF:HMPA containing 37 μL (0.26 mmol) of diisopropylamine with magnetic stirring. After 10 min the LDA solution was cooled to −78 °C and 2 mL of THF containing 40 mg (0.25 mmol) of tetraenone **11** was added via cannula. The reaction mixture instantly became cherry red. After 2 min, an additional 0.12 mL (0.26 mmol) of the *n*-BuLi/hexane was injected to deprotonate the neutral amine present. The cherry red solution was stirred another 2 min at −78 °C before 60 μL (0.74 mmol, 3 equiv) of methyl fluorosulfonate (Aldrich) was injected. After being stirred for 5 min at −78 °C and 15 min at 0 °C, the reaction mixture was orange in color. THF was removed under reduced pressure, and the oily residue was partitioned between 20 mL of hexane and 5 mL of saturated $NaHCO_3$ solution. The organic layer was washed with two more 5-mL portions of saturated $NaHCO_3$ solution and was concentrated under reduced pressure to give a red oil. Attempted chromatography on silica gel was unsuccessful. Preparative TLC on alumina with 10% EtOAc/petroleum ether afforded 17 mg (40% yield) of **12** as a moderately air-sensitive red oil (R_f 0.90): ^1H NMR (CCl_4) δ −0.80 (dt, J = 10, 1.5 Hz, 1 bridging H), −0.27 (d, J = 10 Hz, 1 bridging H), 3.86 (s, 3 H, OMe), 6.45–7.29 (m, 5 H), 7.41 (br s, 1 H), 7.69 (d, J = 7 Hz, 1 H); IR (CCl_4) 2960 (m, sh), 2935 (m), 1460 (m), 1390 (m), 1196 (m), 1178 (m), 1137 (s) cm^{-1}; UV (hexane) λ_{max} 280 (ε 20 300), 490 nm (500).

Acknowledgment. We thank the National Science Foundation, the National Institutes of Health (Grant NCI-CA-23488), and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.