^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, J = 8.2 Hz, 2 H), 7.28 (d, J = 8.1 Hz, 1 H), 2.42 (s, 3 H), 2.31–2.06 (m, 3 H), 1.25–0.70 (series of m, 3 H), 0.97 (s, 3 H), 0.97 (d, J = 6.1 Hz, 3 H), 0.62 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 164.08, 143.67, 135.30, 129.15, 128.15, 36.14, 29.18, 27.83, 22.30, 21.52, 20.58, 19.48, 18.58, 16.22, 14.48; MS m/z (M^+) calcd 320.1559, obsd 320.1527; $[\alpha]^{20}_D$ +127° (c 1.27, CH_2Cl_2).

(+)-(1*R*,4*S*,6*R*)-3-Bromo-4,7,7-trimethylbicyclo[4.1.0]hept-2-ene (51). *n*-Butyllithium (1.32 mL of 1.5 M in hexane, 1.98 mmol) was added dropwise to a solution of **50** (141 mg, 0.44 mmol) in dry TMEDA (10 mL) at −55 °C. The reaction mixture was stirred at this temperature for 45 min and allowed to warm to 20 °C during 2 h. Following cooling to −60 °C, 1,2-dibromotetrafluoroethane (0.233 mL, 1.98 mmol) was introduced in one portion, and stirring was maintained at −60 °C for 1 h and at 20 °C for 1 h. The usual workup was applied (see **49**) to give 47 mg (50%) of **51** as a colorless liquid. Purification for analysis was accomplished by preparative GC as before: IR (neat, cm^{-1}) 3030, 3000, 2965, 2950, 2930, 2860, 1625, 1450, 1380, 1335, 1235, 1130, 1050, 1005, 990, 970, 950, 870, 835; ^{1}H NMR (300 MHz, C_6D_6) δ 6.14 (t, J = 3.1 Hz, 1 H), 2.46–2.30 (m, 1 H), 1.90–1.79 (m, 1 H), 1.25–1.05 (m, 1 H), 1.03 (d, J = 7.0 Hz, 3 H), 0.85 (s, 3 H), 0.83 (s, 3 H), 0.78–0.60 (m, 2 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 128.58, 127.47, 33.30, 30.48, 27.32, 26.58, 24.71, 22.30, 20.46, 15.35; MS m/z (M^+) calcd 216.0337, obsd 216.0349; $[\alpha]^{20}_D$ +80° (c 0.82, hexane).

Anal. Calcd for $C_{10}H_{15}Br$: C, 55.81; H, 7.03. Found: C, 55.93; H, 7.07.

Acknowledgment. This investigation was supported by NIH grant CA-12115.

Registry No. **4**, 498-15-7; **13**, 88390-11-8; **15**, 52153-58-9; **19**, 936-91-4; **20**, 4017-83-8; **21**, 5114-01-2; **21** (tosylhydrazone), 124719-01-3; **22**, 6909-01-9; **23**, 22327-37-3; **24**, 10309-64-5; **25**, 73582-90-8; **26**, 124719-02-4; **26** (tosylhydrazone), 124719-03-5; **27**, 124-73-2; **28**, 124719-04-6; (±)-**29**, 124719-05-7; **30**, 124719-06-8; **31**, 124817-19-2; **32**, 124719-07-9; **33**, 124719-08-0; **34**, 124719-09-1; **35**, 124817-20-5; **36**, 52153-58-9; **37**, 124719-10-4; **38**, 124719-11-5; **39**, 124719-13-7; **40**, 124719-14-8; **41**, 124719-12-6; **43**, 124719-15-9; **44**, 124719-16-0; (*E*)-**45**, 124719-17-1; (*Z*)-**45**, 124719-21-7; **46**, 124719-18-2; **47**, 124817-22-7; **48**, 124817-23-8; **49**, 124719-19-3; **50**, 124817-21-6; **51**, 124719-20-6; $ClCH_2SPh$, 7205-91-6; 2-cyclohexen-1-one, 930-68-7.

Supplementary Material Available: ^{1}H NMR and ^{13}C NMR spectra for compounds **15**, **21**, **26–35**, **38–41**, **43**, **46**, **47**, and **50** (31 pages). Ordering information is given on any current masthead page.

[4.4.4]Propellahexaene by Triple Shapiro Degradation. Structural and Electronic Properties of This Maximally Unsaturated Hydrocarbon and Consequences of O-Methylation of Its [4.4.4]Propellatrienetrione Precursors

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The trienetriones **6** and **7** were prepared and transformed into their tris(phenylsulfonyl)hydrazones to arrive at the title hydrocarbon (**5**). These derivatives were subjected in turn to triple Shapiro degradation. The D_3 symmetric nature of the resulting hexaene was suggested by its NMR spectra and corroborated by X-ray crystallographic analysis. When this molecule is viewed down its central C–C bond, its dramatic propeller-like shape is made evident. Thermochemical experiments established **5** to be a rather stable substance. Photoelectron spectroscopic studies involving **5** and its less unsaturated analogues **24** and **25** are also detailed. By this means, the electronic structure of **5** was shown to be such that there are no σ-MO's amid its high-lying π MO's. MNDO calculations for **5** predict the central bond to be 1.61 Å (experimental value = 1.57 Å). Also described are experiments detailing the fate of both **7** and its C_{3v} symmetric isomer **6** on attempted 3-fold O-methylation. In the first instance, the major product happens to be 3,6,9-trimethoxyphenanthrene (**42**). Skeletal rearrangement is not encountered with **6**. Rather, the major product is dimethoxy enone **39**, which is accompanied by lesser amounts of 2,7-dimethoxynaphthalene (**40**). On further processing of **39**, fragmentation to **40** occurs to a major extent, although it has proven possible to acquire limited amounts of the trimethoxy hexaene **41**. The interesting divergence in chemical response exhibited by **6** and **7** has no parallel. Finally, the relative rates and stereochemical course (where relevant) of the Diels–Alder reaction of *N*-methyltriazolinedione (MTAD) with **5**, **24**, and **25** are reported. The reactivity order is **5** > **24** > **25**, the hexaene being consumed instantaneously on mixing at room temperature. The facial selectivity exhibited by **24** during its initial capture by MTAD is best rationalized in terms of steric control. Like considerations apply to the pathways followed by **44**, **45** and **5** in their reactions with the same dienophile. Consequently, orbital symmetry considerations do not appear to play a major role in these processes.

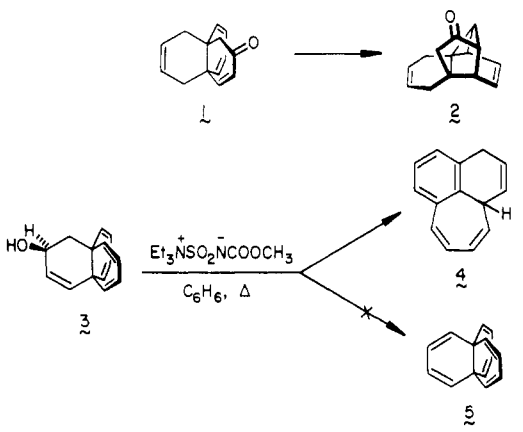
The larger fully unsaturated propellanes constitute a formidable challenge to those who would undertake their synthesis. At the purely chemical level, an increase in the extent of functionalization in any or all of the three constituent rings often results in the immediate onset of reactions seriously detrimental to acquisition of the particular target molecule. The intramolecular [4 + 2] capture of the cyclohexadiene subunit in **1**, a relatively rapid process at room temperature, is illustrative of the problem.[2]

(1) (a) Northern Illinois University. Author to whom inquiries regarding the X-ray crystallographic analysis should be directed. (b) Institut für Organische Chemie Heidelberg. Authors responsible for the photoelectron spectroscopy studies and associated calculations.

(2) (a) Paquette, L. A.; Jendralla, H.; DeLucca, G. *J. Am. Chem. Soc.* **1984**, *106*, 1518. (b) Jendralla, H.; Jelich, K.; DeLucca, G.; Paquette, L. A. *Ibid.* **1986**, *108*, 3731.

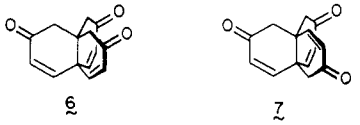
0022-3263/90/1955-1598$02.50/0

The remarkable ease with which alcohol **3** undergoes deep-seated Wagner–Meerwein rearrangement to 4a,7-dihydropleiadene (**4**) on attempted dehydration is equally exemplary.[3] As a consequence, the synthesis of [4.4.4]-propellahexaene (**5**) has proven very elusive despite an appreciable amount of activity in this area.[2-4]



Our efforts in this field have been directed toward several goals. Of course, it was hoped to achieve a convenient total synthesis of **5**.[5] In the process, reactions promising little or no risk of intramolecular bond formation had to be implemented; their efficiency and general usefulness warranted clarification. Also, functionalized derivatives of **5**, particularly methoxy-substituted examples, were desired in order to determine the effect of such groups on the thermal stability of this ring system.

The trienetriones **6** and **7** were selected as intermediary targets.[6] Such tricarbonyl compounds were believed to be capable of lending themselves to introduction of the remaining three double bonds. Riskier ventures would

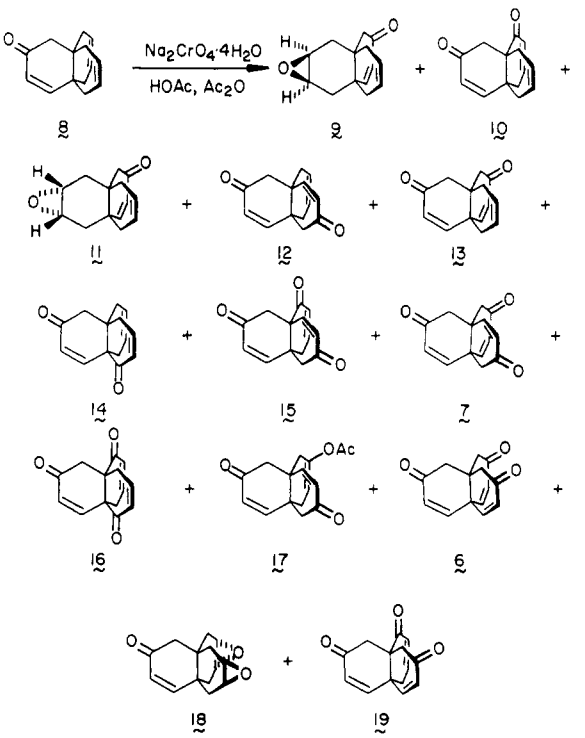


involve attempts to effect 3-fold O-methylation of the related enolate trianions. In what follows, these chemical issues are given specific attention, the structural and spectroscopic features of **5** are critically defined, the thermal stabilities of the hexaene and two trimethoxy derivatives are compared, and the Diels–Alder reactivities of **5** and related molecules are surveyed.

Results

Oxidation Chemistry of [4.4.4]Propella-3,6,10-trien-2-one. The known tricyclic ketone **8**[7] was oxidized with sodium chromate tetrahydrate (8 equiv) in a 5:3 mixture of acetic acid–acetic anhydride at ambient temperature.[8] This procedure led in moderate yield to a

Scheme I



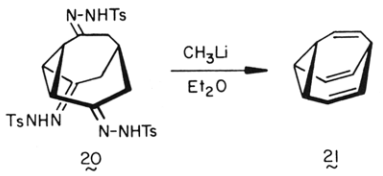
mixture of the monooxidation products **9–14** (27–31%), several 2-fold oxidation products **6**, **7**, and **15–19** (18–21%), as well as recovered starting ketone (4–7%). The product listing in Scheme I corresponds to increasing polarity on silica gel. By reoxidation of **9–14**, conversion to **6**, **7**, and **15–19** could be effected in 40% isolated yield. All of the compounds pictured in Scheme I were isolated in a pure state by medium-pressure liquid chromatography (MPLC) followed by crystallization, and structural assignments were made on the basis of the individual spectral parameters (see Experimental Section). When the oxidation of **8** was repeated with Collins reagent in dichloromethane, lower di- to monooxidation ratios were seen and inferior yields were realized. Pyridinium chlorochromate under comparable conditions gave no reaction.

The epoxides **9**, **11**, and **18** had previously been prepared by oxidation of **8** with *m*-chloroperbenzoic acid.[2b] For the highly symmetric **6**, only six carbon signals were seen. In the case of **7**, the 14 carbon signals established the molecule to be virtually frozen into one of the pair of available propeller conformations. Rapid equilibration would have reduced the number of signals to ten. The kinetic parameters for the antipodal ring inversion within **6** and **7** have been reported elsewhere.[6]

Adoption of those conditions most conducive to maximizing the conversion of **8** to **6** and **7** gave these important intermediates in yields adequate for further deployment in the synthetic scheme.

Synthesis and Crystal Structure of [4.4.4]Propellahexaene. Central to the scenario envisioned for gaining access to **5** is the Shapiro reaction.[9] The vinyl anions that result ultimately would not be in a position to undertake unwanted intramolecular condensations. In fact, a search of the literature revealed that numerous ditosylhydrazones have been subjected to this procedure without event.[9] More relevant to our objective is Serratosa's report of the degradation of tritosylhydrazone **20** to bullvalene (**21**) in 20% yield.[10]

(3) Paquette, L. A.; Waykole, L.; Jendralla, H.; Cottrell, C. E. *J. Am. Chem. Soc.* **1986**, *108*, 3739.
(4) Ginsburg, D. *Propellanes*; Verlag Chemie: Weinheim, West Germany, 1975; p 15.
(5) A preliminary communication on this subject has appeared: Waykole, L.; Paquette, L. A. *J. Am. Chem. Soc.* **1987**, *109*, 3174.
(6) Jendralla, H.; Doecke, C. W.; Paquette, L. A. *J. Chem. Soc., Chem. Commun.* **1984**, 942.
(7) Paquette, L. A.; Jendralla, H.; Jelich, K.; Korp, J. D.; Bernal, I. *J. Am. Chem. Soc.* **1984**, *106*, 443.
(8) (a) Marshall, J. A.; Johnson, P. C. *J. Org. Chem.* **1970**, *35*, 192. (b) Marshall, J. A.; Brady, S. F. *Ibid.* **1970**, *35*, 4068.
(9) Shapiro, R. H. *Org. React.* **1976**, *23*, 405.



20 21

Consequently, trienetrione **7** was transformed into its tris(phenylsulfonyl)hydrazone (**22**, Scheme II). Reaction of this pale yellow solid with a modest excess of ethereal methyllithium in TMEDA solution, initially at 0 °C and then at room temperature, was indeed successful in delivering the desired polyunsaturated hydrocarbon **5** (15%). A marginal improvement in yield (to 18%) was realized when starting from **6** and proceeding via **23**. The colorless crystalline hydrocarbon exhibits an AA′XX″ proton NMR spectrum (Figure 1)[11] and a simple three-line ^{13}C NMR spectrum, completely in agreement with its D_3 symmetry. The ultraviolet spectrum of **5** recorded in isooctane solution features maxima at 234, 242, 251, 271, 279, and 291 nm.

Slow sublimation of **5** at 0.1 Torr provided colorless needles of a quality adequate for X-ray crystallographic analysis. As seen in Tables I–III and Figure 2, the hexaene resides on a crystallographic 2-fold axis that bisects the C5–C5a and C7–C7a bonds. When **5** is viewed down the C5–C5a axis, the dramatic propeller-like shape of the molecule becomes obvious (Figure 2A). The bond between tetrahedral carbon atoms C5–C5a is the propeller shaft with each blade consisting of C5–C5a and a four-carbon diene unit (C1–C4, C1a–C4a, and C6, C7, C7a, C6a). The two unique torsion angles defining the twist of each blade from the shaft axis are C1–C5a–C5–C4 = 40.1° and C6a–C5a–C5–C6 = 41.3°. The relative orientation of each blade can be defined by the C1–C5a–C5–C1a (−79.9°), C4a–C5a–C5–C6 (−79.3°), C1–C5a–C5–C6 (160.7°), and C4a–C5a–C5–C4 (160.0°) torsion angles.

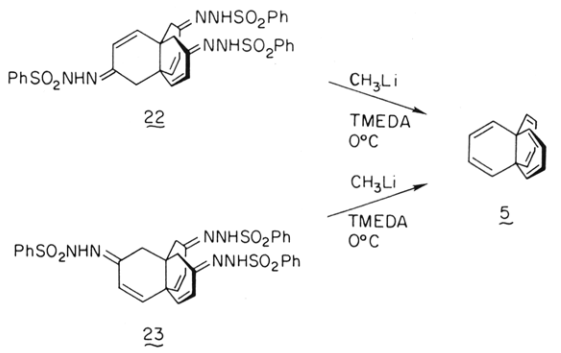
Each four-carbon diene unit is planar to within 0.04 Å. The double bonds are localized, the three unique values average 1.34 (1) Å. The C2–C3 and C7–C7a bond lengths average 1.46 (2) Å.

An alternate description of the molecular shape can be obtained by reviewing the dihedral angles between the planes defined by the diene units (Figure 2B). The three unique angles defined by the intersection of these planes average 72°. Each diene plane intersects the C1–C4a–C6a plane by an average angle of 69°.

The stage was now set for evaluation of the thermal stability of **5**. As expected,[2] the hydrocarbon is quite stable in air and solutions in bromobenzene-d_5 could be heated at 105 °C for 4.5 h without any noticeable change in the ^1H NMR spectrum when recorded at room temperature. The onset of degradation was apparent at 150 °C ($t_{1/2} \approx$ 5 h). The ill-defined products of this decomposition gave no evidence of being aromatic in nature (^1H NMR analysis).

Preparation of More Highly Saturated Analogues. In light of the very special topographical features of **5**, direct insight into the extent of through-space orbital interaction between its three 1,3-butadiene components was sought. This issue is capable of being addressed by photoelectron spectroscopy (PE). However, the set of compounds defined by hexaene **5**, tetraene **24**, and diene **25** was needed to provide the most rigorous test possible of the prevailing inter-ring electronic interactions. Accordingly, the synthesis of these simpler unknown polyolefins was first undertaken.

Scheme II



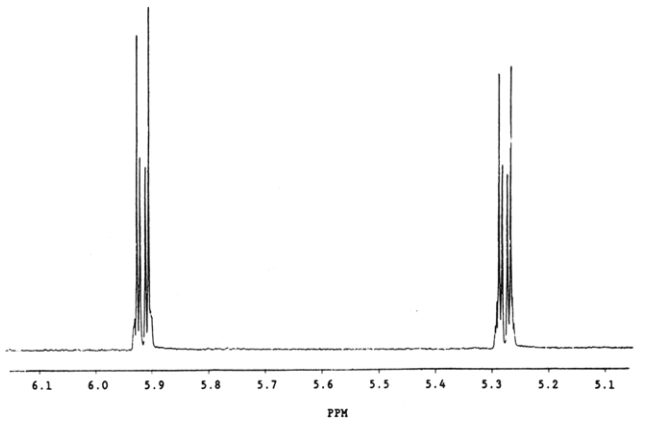


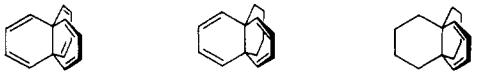
Figure 1. Expanded-scale 500-MHz ^1H NMR spectrum of **5** (in $CDCl_3$).

Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

cmpd	$C_{14}H_{12}$
color/shape	colorless fragment
M_r	180.25
space group	$P\bar{4}2_1c$
temp, °C	−150
cell constants[a]	
a, Å	8.280 (7)
c, Å	14.483 (9)
cell vol, Å^3	992.9
formula units/unit cell	4
D_{calcd}, g cm^{-3}	1.21
μ_{calcd}, cm^{-1}	0.13
diffractometer/scan	Enraf-Nonius CAD-4/ω–2θ
radiatn, graphite monochromator	Mo Kα (λ = 0.71073)
max crystal dimensions, mm	0.18 × 0.20 × 0.33
scan width	0.80 + 0.35 tan θ
standard reflctns	200; 020; 004
decay of standards	±2%
reflcts measd	578
2θ range, deg	$2 \le 2r \le 50$
range of h,k,l	+9, +9, +17 ($\lvert h\rvert \le \lvert k\rvert$ only)
reflctns obsd [$(F_o \ge 5\sigma(F_o)]$[b]	276
computer programs[c]	SHELX[33]
structure solution	SHELXS[35]
no. of parameters varied	64
weights	$[\sigma(F_o)^2 + 0.00004F_o^2]^{-1}$
GOF	4.1
$R = \sum\lvert\lvert F_3\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$	0.072
R_w	0.075
R inverse configrtn	0.072
largest feature final diff. map	0.3 e Å^{-3}

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 15 reflections $\theta > 20°$. [b] Corrections: Lorentz polarization. [c] Neutral scattering factors and anomalous dispersion corrections from ref 34.

(10) Font, J.; Lopez, F.; Serratosa, F. *Tetrahedron Lett.* **1972**, 2589.
(11) For a discussion of the classification of ^1H NMR spectra of the AA′XX′ and AA′BB′ type, see: Gunther, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 861.



5 24 25

Dicarboxylic acid **26**[12] was exhaustively esterified with diazomethane and partially saponified at the less sterically congested carbomethoxy group to produce **27b** (Scheme III). Conversion to methyl ketone **28** was accomplished through condensation of the acid chloride with lithium dimethylcuprate.[13] When it was discovered that the acid-catalyzed ketalization of **28** with ethylene glycol could not be driven at all close to completion,[14] recourse was made instead to protection of the ketone functionality with 2-methoxy-1,3-dioxolane[15] in the presence of a catalytic amount of *p*-toluenesulfonic acid. After 8 days *at room temperature* in dichloromethane solvent, the ketalization was judged to be essentially complete (>98.5% by capillary GC analysis). The resulting ketal **29** was then subjected to sequential lithium aluminum hydride reduction and pyridinium chlorochromate oxidation. Once the R group in **30b** had been adjusted to the aldehyde level, the ketone carbonyl was unmasked and **31** was cyclized under alkaline conditions. The overall yield of **32** from **30a** was 52%.

When **32** was oxidized with potassium chromate in acetic anhydride and acetic acid at 40 °C for 4 h and at room temperature for 4 days, the two desired dienediones **33a** (28%) and **34a** (11%) were obtained alongside two dienediones having unrearranged double bonds (8%), an epoxy enone (3%), and recovered starting material (25%). The **33a**:**34a** ratio was consistently 2.6:1. The separation of these isomers was readily accomplished by HPLC. Their spectral properties clearly showed **33a** to possess C_s symmetry and **34a** to ave a C_2 axis. Submission of either pure dienedione or the 2.6:1 mixture to the Shapiro sequence delivered **24** in 40–46% yield.

For the acquisition of **25**, ketal **29** was subjected to catalytic hydrogenation and the fully saturated **35** was processed in the manner just described (Scheme IV). Once enone **38a** was in hand, the conversion to **25** was realized in 67% yield.

Diene **25** is considerably more conformationally dynamic than either of its more unsaturated analogues **5** and **24**. The temperature-dependent ^{13}C NMR spectra of **25** (Figure 3) elicited interest because the constituent six-membered rings are forced to radiate as blades from a common axis. As already seen with **5** (Figure 2), the presence of a shared single bond causes each blade to be twisted in the *same* sense, with the result that the prevailing conformation is helical. When one of the isoenergetic forms is frozen out, the four pairs of methylene carbons in **25** have distinctively different chemical shifts, a feature clearly diagnostic of its propeller topography. Once conformational interconversion becomes sufficiently rapid, the number of signals for these atoms is reduced to two (Figure 3).

Table II. Bond Distances (Å) and Angles (deg) for 5

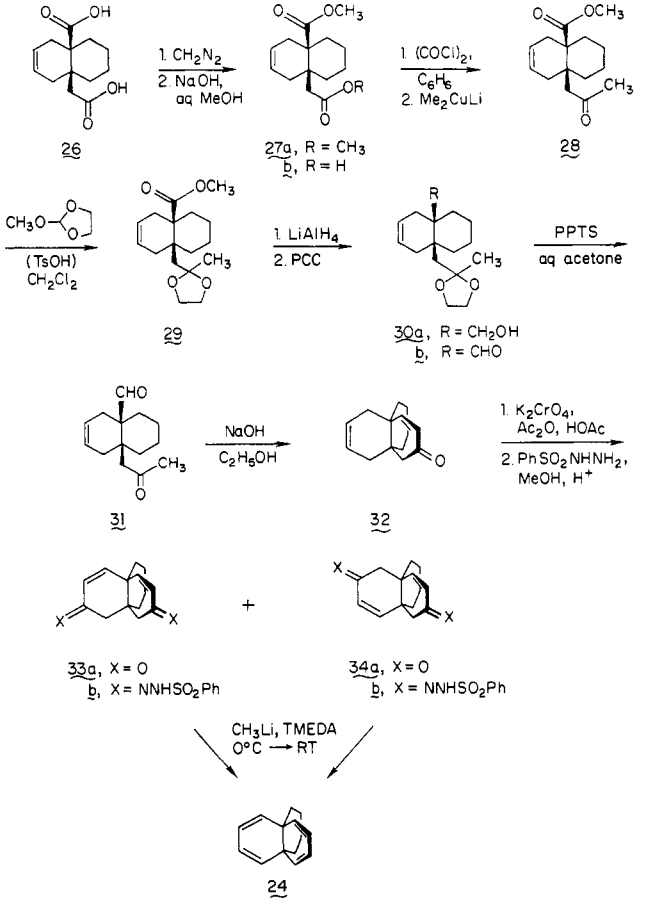
atoms	distance	atoms	distance
C(1)–C(2)	1.35 (1)	C(2)–C(3)	1.45 (2)
C(3)–C(4)	1.35 (1)	C(4)–C(5)	1.51 (1)
C(5)–C(6)	1.53 (1)	C(5)–C(1)a	1.54 (1)
C(5)–C(5)a	1.57 (2)	C(6)–C(7)	1.33 (1)
C(7)–C(7)a	1.46 (2)		
atoms	**angle**	**atoms**	**angle**
C(2)–C(1)–C(5)a	121.0 (1)	C(1)–C(2)–C(3)	121.8 (9)
C(2)–C(3)–C(4)	120.3 (9)	C(3)–C(4)–C(5)	121.6 (9)
C(4)–C(5)–C(6)	108.1 (8)	C(4)–C(5)–C(1)a	107.6 (8)
C(4)–C(5)–C(5)a	111.4 (9)	C(6)–C(5)–C(1)a	107.3 (8)
C(6)–C(5)–C(5)a	111.1 (6)	C(1)a–C(5)–C(5)a	111.1 (7)
C(5)–C(6)–C(7)	120.8 (9)	C(6)–C(7)–C(7)a	121.2 (5)

[a] Atoms related by the crystallographic 2-fold axis.

Table III. Torsion Angles (deg) for 5

atoms	angle
C(1)–C(5)a–C(5)–C(4)	40.1
C(1)–C(5)a–C(5)–C(6)	160.7
C(1)–C(5)a–C(5)–C(1)a	−79.9
C(4)a–C(5)a–C(5)–C(4)	160.0
C(4)a–C(5)a–C(5)–C(6)	−79.3
C(6)a–C(5)a–C(5)–C(6)	41.3

Scheme III



The equilibration of **25A** with **25B**, which likely occurs via synchronous three-ring flipping,[16] has been determined by dynamic ^{13}C NMR analysis to proceed with the following activation parameters: $\Delta H^{\ddagger}_{(298K)}$ = 14.3 ± 0.1 kcal/mol, $\Delta G^{\ddagger}_{(298K)}$ = 14.1 ± 1 kcal/mol, E_a = 14.9 ± 0.1 kcal/mol, and $\Delta S^{\ddagger}_{(298K)}$ = 0.58 eu. Comparison with the higher $\Delta G^{\ddagger}$ values previously recorded for **6** (16.2 kcal/

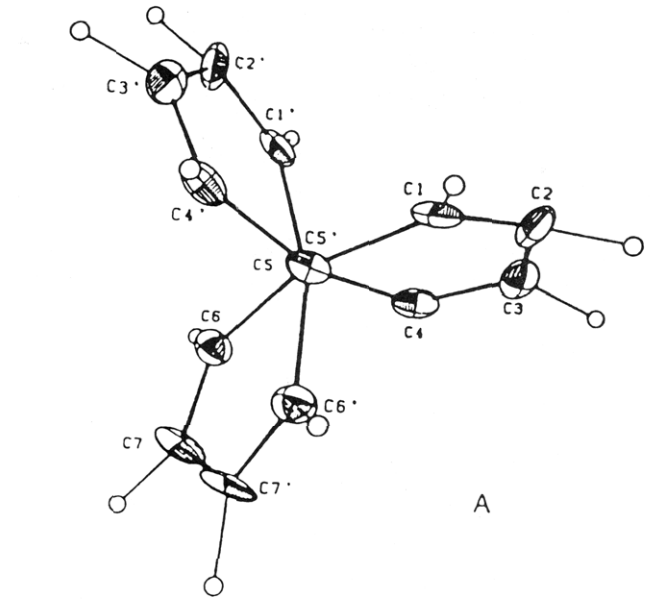
(12) Paquette, L. A.; Ohkata, K.; Jelich, K.; Kitching, W. *J. Am. Chem. Soc.* **1983**, *105*, 2800.

(13) (a) Posner, G. H.; Whitten, C. E. *Tetrahedron Lett.* **1970**, 4647. (b) Posner, G. H.; Whitten, C. E.; McFarland, P. E. *J. Am. Chem. Soc.* **1972**, *94*, 5106. (c) Fox, T.; Froborg, J.; Magnusson, G.; Thoren, S. *J. Org. Chem.* **1976**, *41*, 3518. (d) Paquette, L. A.; Snow, R. A.; Muthard, J. L.; Cynkowski, T. *J. Am. Chem. Soc.* **1979**, *101*, 6991.

(14) In a typical reaction conducted in refluxing benzene for 32 h, there was isolated 29% of **29**, 17% of the monoethyleneglycol ester of **28**, 9% of the monoethyleneglycol ester of **29**, and 26% of unreacted **28**.

(15) (a) Baganz, H.; Domaschke, L. *Chem. Ber.* **1958**, *91*, 650. (b) Glatz, B.; Helmchen, G.; Muxfeldt, H.; Porcher, H.; Prewo, R.; Senn, J.; Strezowski, J. J.; Stojda, R. J.; White, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 2171. (c) Ho, T.-L.; Hal, T. W. *Synth. Commun.* **1982**, *12*, 97.

(16) No insight has been gained into the more refined question of possible chair ⇄ boat processes concurrent with bridge flipping.



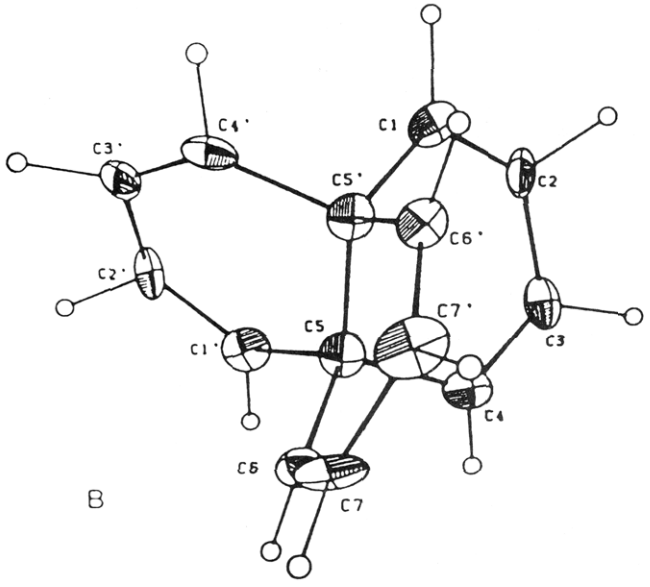
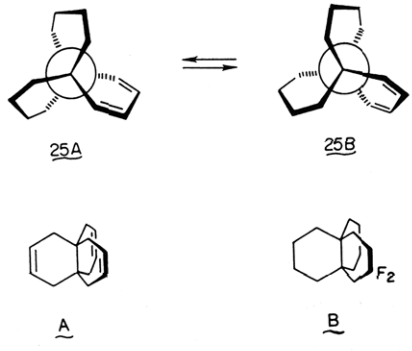


Figure 2. Two views of the crystallographically determined molecular structure of **5** as drawn with 50% probability ellipsoids.

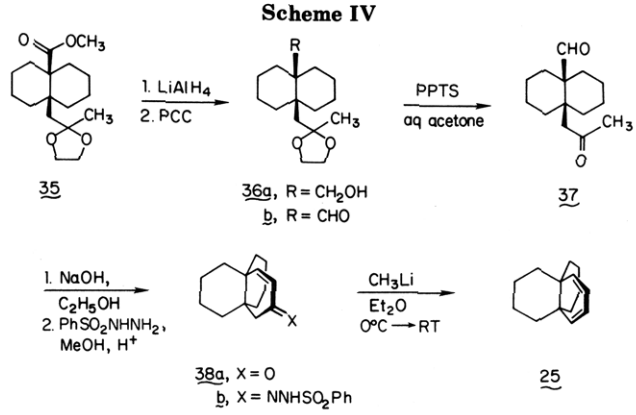
mol),[6] **7** (15.8 kcal/mol),[6] A (16.7 kcal/mol),[17] and B (15.7 kcal/mol)[17] is warranted.



Photoelectron Spectroscopic Studies. The photoelectron spectroscopic (PE) spectra recorded for **25**, **24**, and **5** are illustrated in Figure 4. The first band seen for **25** corresponds to π_2 of its butadiene unit. Its π_1 absorption

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

Scheme IV



Scheme V

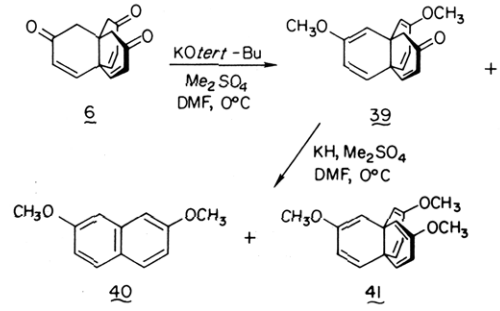


Table IV. Comparison between the Vertical Ionization Energies ($I_{v,j}$) and the Calculated Orbital Energies (ϵ_j) for the Unsaturated [4.4.4]Propellanes (All Values Are in eV)

compd	band	$I_{v,j}$	assignmnt	$-\epsilon$ (MNDO)
25	1	8.04	20a(π_2)	8.89
	2	9.8	18b(π_1)	11.12
24	1	7.94	19a	8.83
	2	8.40	17b	9.09
	3	10.2	16b	11.19
	4	10.6	18a	11.23
5	1	7.92	$1a_1''$	8.81
	2	8.42	5e″	9.09
	3	10.44	$1a_2'$	11.23
	4	10.7	6e′	11.24

is hidden under the broad second peak. The level of interaction realizable between the π-MO's in these [4.4.4]-propellanes is reflected in the PE spectrum of **24**. In this instance, a split of 0.5 eV (7.9, 8.4 eV) is evident. Although the effect is not large, the second 1,3-cyclohexadiene ring does exert an electronic influence on the first.

Assignments to the bands determined for **5** can be made in an equally straight-forward manner. The first peak can be attributed to ionization from $1a_1''$ and the second from 5e″ on the strength of two arguments: (1) the ratio of the areas of peaks 1 and 2 is approximately 1:2 and (ii) the first peak shows the expected vibrational fine structure, while the second reflects the anticipated Jahn–Teller broadening. A comparison between the experimental data and results from MNDO calculations is made in Table IV. The agreement is excellent in several respects. The sequence exhibited by **5** is correctly predicted (a_1'' above 5e″), with no σ-MO's appearing between the π-MO's. In addition, the central bond length is realistically estimated at 1.61 Å (experimental value = 1.57 Å). Most importantly, we see that the third 1,3-cyclohexadiene ring exerts no additional impact on the splitting of the two highest lying MO's. The split of 0.5 eV (7.9, 8.4 eV) is identical with that seen in **24**.

O-Methylation Studies. The extendability of earlier developments to the preparation of a pair of trimethoxy-

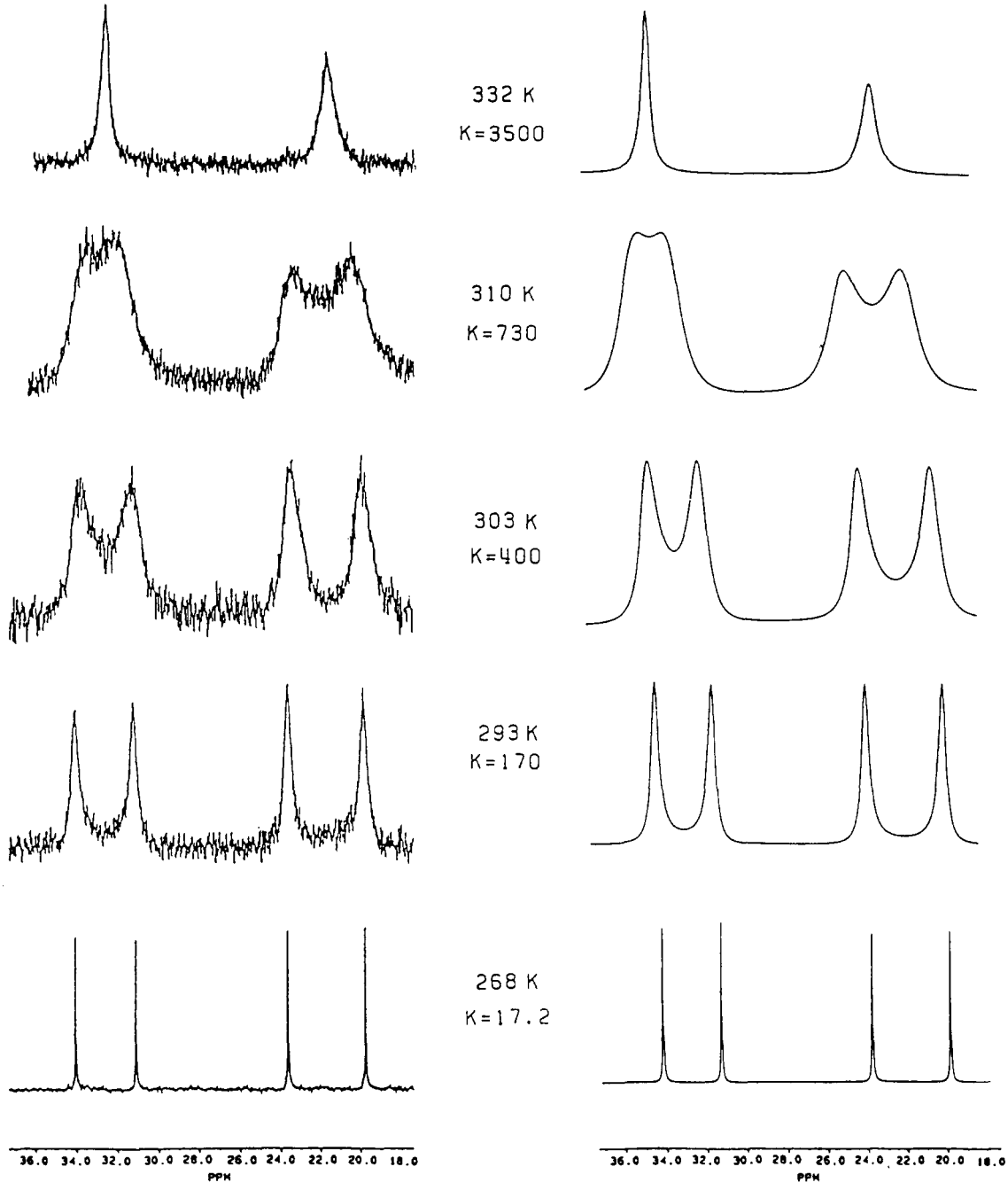


Figure 3. Representative variable-temperature 125-MHz ^{13}C NMR spectra of **25** in $CDCl_3$ solution (left) and computer-simulated spectra (right). Temperatures are considered accurate to ±1 K.

[4.4.4]propellahexaenes was next investigated. With the availability of conditions well suited to the O-methylation of enolate anions,[18] we set out initially to treat **6** at 0 °C with potassium *tert*-butoxide in anhydrous dimethylformamide and then dimethyl sulfate (Scheme V). Examination of the crude reaction mixture indicated the principal products to be the dimethoxy pentaenone **39** and 2,7-dimethoxynaphthalene (**40**). The ^1H NMR spectrum gave indication that traces of **41** were also present, but the substance could not be isolated. The structural assignment to **39** follows from its spectral features, which are especially diagnostic of the symmetry of this molecule and its lone remaining carbonyl group (see Experimental Section).

Quite surprisingly at first, all attempts to resubmit **39** to the original methylation conditions or to the action of $KN(SiMe_3)_2$/THF and then Me_2SO_4 gave rise to quite complex reaction mixtures. The outcome was somewhat more promising when recourse was made to potassium hydride as base in dry dimethylformamide as solvent, followed by the addition of dimethyl sulfate, all at 0 °C. Under these circumstances, **40** was unexpectedly found to predominate over **41** (by a factor of 17:1), a trend that was never reversed. Although the practicalities of acquiring reasonable quantities of **41** were not to be well served by this route, it proved possible to characterize this material spectroscopically. Furthermore, the issue of its sensitivity to heat could also be addressed. When warmed in benzene-d_6 solution at 80 °C for 4 h, **41** gave no evidence of decomposition. Consequently, it would appear that the 3,9,12-trimethoxy derivative possesses stability roughly comparable to that of the parent hexaene.

A mechanistically relevant fact is that **41** does not readily degrade to 2,7-dimethoxynaphthalene (**40**).

(18) Paquette, L. A.; Broadhurst, M. J. *J. Org. Chem.* **1973**, *38*, 1886.

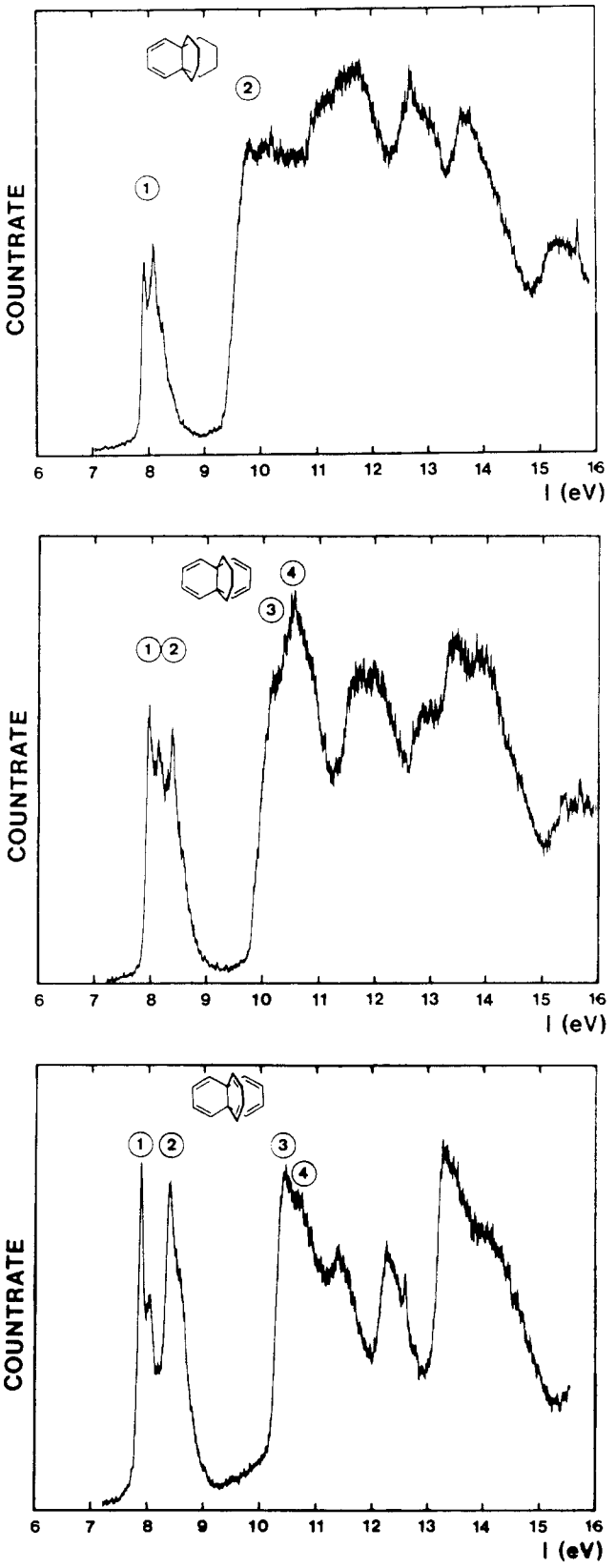
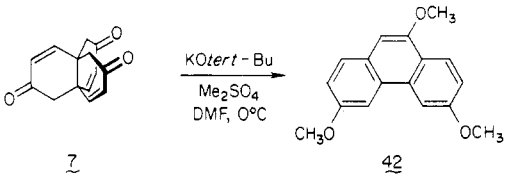


Figure 4. Photoelectron spectra of **25** (top), **24** (middle), and **5** (bottom).

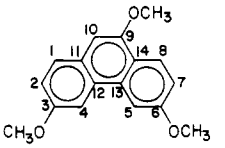
Therefore, it becomes implausible to argue that **40** is produced from **6** by a scheme that involved **41** in its late stages. Since **39** also proved to be a stable substance at room temperature, the most reasonable suggestion is that the fragmentation resulting in the loss of one six-membered ring occurs once **6** reacts with strong base. The precise pathway by which the 2-fold bond cleavage occurs is not known. Of course, we did seek to relate this observation to the response of **7** to comparable O-methylation conditions. The strikingly different chemical response now to be described holds particular interest.

Scheme VI



7 42

Table V. Detailed ^1H (500 MHz) and ^{13}C (125 MHz) Spectral Parameters for 42



proton	shift, ppm	mult (*J* in Hz)
H-8	8.21	d (9.0)
H-5	8.10	d (2.5)
H-4	8.05	d (2.5)
H-1	7.73	d (8.7)
H-7	7.25	d (8.7)
H-2	7.19	dd (9.0, 2.5)
H-10	6.98	dd (8.7, 2.5)
9-MeO	4.04	s
6-MeO	4.02	s
3-MeO	3.98	s

carbon	shift	carbon	shift
1	129.6	9	152.8
2	117.8	10	100.7
3	157.8	11	128.9
4	105.4	12	127.9
5	105.3	13	133.3
6	159.8	14	122.0
7	117.0	3-MeO	55.9
8	124.8	6-MeO	55.9
		9-MeO	55.8

Under essentially identical conditions, the isomeric triketone **7** was transformed predominantly into **42** (Scheme VI). Although smaller amounts (10–20%) of a second trimethoxyphenanthrene isomer was detectable by ^1H NMR, insufficient quantities were available to permit its purification and structure determination. However, there was no hint that **40** has been formed!

The structure of the major aromatic compound was deduced by using a combination of 1-D and 2-D NMR techniques. The proton spectral data are given in Table V. In particular, a 2-D COSY experiment[19] showed the following coupling patterns to be present:

J_{meta} J_{ortho}

H-5 ---------- H-7 ---------- H-8

H-4 ---------- H-2 ---------- H-1

These features are characteristic of 1,3,4-trisubstituted aryl rings. In addition, long-range couplings from H-10 to both H-2 and H-4 were observed in the contour plot of the COSY measurement.

A series of NOE difference spectra were then acquired where each of the three methoxy groups was irradiated in turn. These experiments revealed that H-10 is ortho to 9-MeO, protons H-5 and H-7 are ortho to 6-MeO, and

(19) (a) Aue, W. P.; Bartholdi, E.; Ernst, R. R. *J. Chem. Phys.* **1976**, *64*, 2229. (b) Nagayama, K.; Kumar, A.; Wuthrich, K.; Ernst, R. R. *J. Magn. Reson.* **1980**, *40*, 321.

protons H-2 and H-4 flank the 3-MeO substituent. At this stage of the analysis, only four possible structural isomers remained. Two additional NOE difference experiments were carried out in which H-10 and H-4 were separately irradiated to reduce the number of options still further. While the first of these gave evidence for a dipole–dipole interaction between H-10 and H-1, the latter showed an interaction to exist between H-4 and H-5. These combined data prove the compound to be 3,6,9-trimethoxyphenanthrene.

Following this, a 2-D carbon–proton chemical shift correlation[20] and a 2-D COLOC (long-range carbon–proton shift correlation)[21] were performed to make possible the assignment of all the carbon shifts in this molecule. The results are given in Table V.

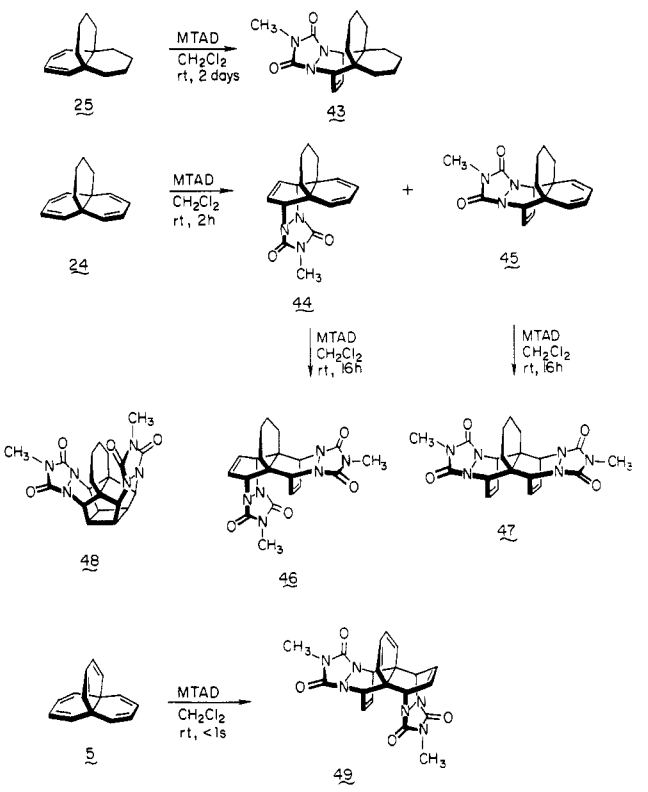
Cycloaddition Behavior. A comparative analysis of the reactivities of **5**, **24**, and **25** toward *N*-methyltriazolinedione (MTAD) was also undertaken for several reasons. Secondary orbital interactions have been cited as influencing the course of Diels–Alder reactions.[22] As established above, the multiply unsaturated [4.4.4]propellanes **24** and **5** are similar in this respect. Of course, steric considerations are quite disparate, with **5** offering the lowest level of nonbonded steric congestion to an approaching dienophile. Furthermore, stereochemical issues surface during the first stage of any [4 + 2] cycloaddition involving **24**. Of equal interest are the reaction trajectories that become kinetically dominant as **24** and **5** react with a second equivalent of dienophile. The choice of a triazolinedione was predicated on the exceptionally high reactivity of this compound class toward conjugated dienes, and prior experience gained by Jacobson in his examination of the preferred course of attack by the *N*-phenyl derivative on *cis*-dihydro, -tetrahydro, and -hexahydronaphthalenes.[23]

The two faces of the diene subunit contained in **25** are equivalent. Since exo/endo approach cannot be distinguished where MTAD is concerned, the major issue in this instance is rate. When **25** and MTAD were admixed in approximately equimolar amounts (CH_2Cl_2 solution) at room temperature, reaction occurred slowly. After 2 days, cycloaddition was still not complete as reflected in the isolation of **43** (63%) and recovery of **25** (19%) (Scheme VII).

In the case of **24**, comparable treatment resulted in the complete consumption of tetraene within approximately 2 h. The two chromatographically separable adducts **44** and **45** were produced in a 6.7:1 ratio. The indicated stereochemical assignments followed from simple steric considerations. To effect reaction along that channel which leads ultimately to **45** requires approach of the MTAD into an environment not dissimilar from that present in **25**. The alternative diene face is less sterically hindered and more amenable to dienophile capture. The implication here is that **5** should be quite reactive under these conditions, as was subsequently discovered (see below).

In separate reactions, **44** and **45** were admixed with a second equivalent of MTAD under otherwise identical conditions. In the first instance, overnight stirring furnished **46** in 71% yield alongside 14% recovery of unreacted **44**. Urazole **45** was entirely consumed during the same period and furnished **47** (88%). The C_{2v} symmetry of **47** was reflected in its simplified ^1H and seven-line ^{13}C NMR spectra. By comparison, the C_s symmetric **46** displays an 11-line carbon spectrum. The relative configuration assigned to **47** was substantiated by irradiation in acetone–dichloromethane solution with a 450-W Hanovia lamp. Since [2 + 2] cycloaddition giving rise to **48** (82% isolated) was complete in 3.5 h, the pair of double bonds in **47** need to reside in close spatial proximity. This transformation likewise confirmed the structural assignments earlier made to **44–46**.

Scheme VII



These findings reveal that the urazole subunit in **44** provides a greater steric (and electronic?) deterrent to dienophile capture than does the fused cyclohexane ring. Similarly, the isolated double bond in **45** is more encumbering than is the saturated six-membered ring. The absence of a second diastereomeric adduct from these product mixtures shows the magnitude of the energy gaps separating the pairs of Diels–Alder transition states to be sufficient to guarantee exclusive operation of a single reaction channel.

MTAD was found to consume **5** *instantaneously* at room temperature. In fact, the hexaene was so reactive that only bis-adduct **49** was isolated, even when an equimolar amount of the dienophile was added at −78 °C! Half of the hexaene was returned under these circumstances. Efforts to coax the diene part structure in **49** into a third [4 + 2] cycloaddition were made at 100,000 psi in a high pressure reactor at 25 °C for 7 days. No visible reaction took place under these circumstances.

The data just presented are inconsistent with the notion that orbital symmetry considerations play a dominant role in guiding the *stereochemistry* of these processes. The entire collection of data is instead explainable in terms of simple steric arguments. The relative kinetics of reaction are less easy to decipher. π orbitals do occupy a certain volume of space and are usually repulsive to the ap-

(20) (a) Bax, A. *J. Magn. Reson.* **1983**, *53*, 517. (b) Rutar, V. *Ibid.* **1984**, *58*, 306. (c) Wilde, J. A.; Bolton, P. H. *Ibid.* **1984**, *59*, 343.

(21) Kessler, H.; Griesinger, C.; Zarbock, J.; Loosli, H. R. *J. Magn. Reson.* **1984**, *57*, 331.

(22) (a) Gleiter, R.; Ginsburg, D. *Pure Appl. Chem.* **1979**, *51*, 1301. (b) Gleiter, R.; Paquette, L. A. *Acc. Chem. Res.* **1983**, *16*, 328 and references cited therein. (c) Agmon, I.; Kaftory, M.; Ashkenazi, P.; Müller, R.; von Philipsborn, W.; Ginsburg, D. *Heterocycles* **1989**, *28*, 33 and earlier papers in this series.

(23) Jacobson, B. M. *J. Am. Chem. Soc.* **1973**, *95*, 2579.

proaching dienophile prior to reaching the transition state. In the present instance, these effects appear to be less untoward than those brought on by added hydrogen atoms as the proximal six-membered ring becomes more saturated. In other words, methine units are more space-demanding than methylene groups in the present context. We cannot answer whether the appreciably increased reactivity of **5** stems only from its more favorable steric status or from some advantage residing in its capacity for intraring orbital interaction. Certainly, the superpositioning of secondary orbital effects is not mandatory to an appreciation of the π-facial selectivities demonstrated by these systems.

Discussion

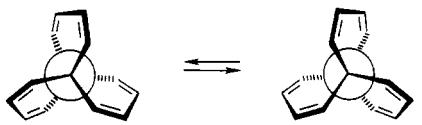
The title hydrocarbon (**5**) constitutes the largest member of a series of maximally unsaturated propellanes consisting of the lower homologues **50–52**. Triene **50** is not yet

50 **51** **52**

known. [4.2.2]Propella-2,4,7,9-tetraene (**51**) has been prepared by Tsuji and Nishida[24] and its photoisomerization to bicyclo[4.2.2]decapentaenes elucidated.[25] PE analysis of **51** revealed that its 1,3-butadiene moiety interacts only to a minute extent with the Dewar benzene part structure,[26] a consequence of the spatial overlap from both fragments being essentially zero.

In contrast, the pentaene **52** synthesized by Paquette and Philips[27] exhibits no tendency for thermally induced valence isomerization,[28,29] ejects acetylene to form naphthalene when irradiated,[30] and gives evidence of homoconjugative interaction between the π-systems of its two butadiene components that is of an order approaching the level present in norbornadiene.[31]

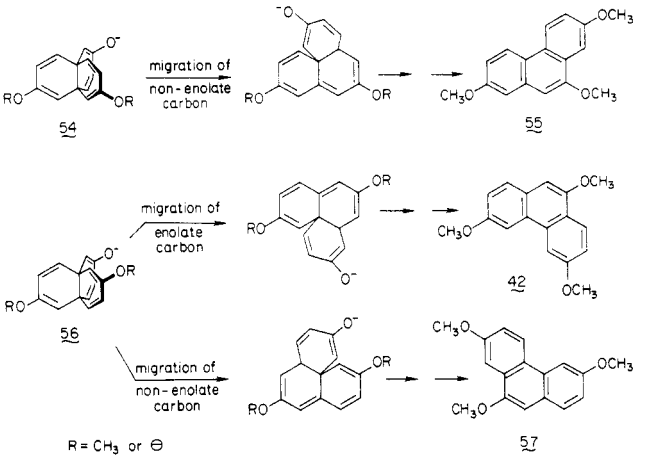
None of the smaller systems have the ability to attain a true propeller ground-state conformation as does **5** (and to a less symmetrical degree **24** and **25**). This sense of twist is important for chirality (see **5A** and **5B**). Although **5**



5A **5B**

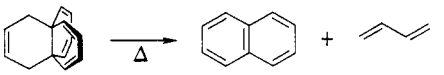
appears to be less conformationally flexible than **25**, no attempt has been made to resolve the hexaene. The relatively low $\Delta H^{\ddagger}$ values for **6**,[6] **7**,[6] and **25** suggested that retention of optical activity could only be accomplished with considerable experimental difficulty. Furthermore,

Scheme VIII



the conformational dynamics within **5** are surely controlled to a large extent by its angle of twist and the trigonal character of all the carbon atoms in each of the three bridges. Since each diene unit is virtually planar (Figure 2) and virtually none of this conjugation is lost in the transition state associated with enantiomeric interconversion, the contributions of peripheral substituents can be expected to do little to improve the possibilities for optical resolution. Support for our conclusions that the pitch-changing reaction **5A** $\rightleftarrows$ **5B** (from right-handed to left-handed propeller) may occur too readily to make separation of the two enantiomers conveniently possible comes from AM1, CNDO/S+CI, and QCFF/PI calculations performed by Zerbetto and Zgierski.[32] Their findings reveal the rate constant for the enantiomerization of **5** to be rather high, perhaps as a consequence of tunneling.

Our results also provide considerable insight into the divergence of reaction manifolds capable of being accessed by unsaturated [4.4.4]propellane derivatives. In an earlier report,[2] it was demonstrated that pentaene **53** undergoes smooth conversion to naphthalene and 1,3-butadiene at 95 °C with good first-order kinetics ($k = 1.67 \times 10^{-4}$ s^{-1}).



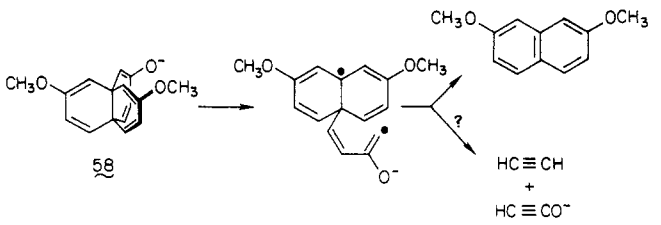
53

Hexaene **5** and its trimethoxy derivative **41** have no comparable capacity for retrograde Diels–Alder fragmentation and exhibit quite reasonable thermal stability. This appears to hold true for dimethoxy pentaenone **39**, although this compound has been less exhaustively studied. Significantly, no spectral evidence was uncovered in any of these cases for [1,5]-sigmatropic carbon migration or valence isomerization.

Given these facts, the response of **6**, **7**, and **39** to strong base is rather remarkable. The structurally related **6** and **39** experience ready loss of four constituent atoms at temperatures below 20 °C, despite the fact that no obvious Diels–Alder fragmentation pathway is available. If a

(24) Tsuji, T.; Nishida, S. *Tetrahedron Lett.* **1983**, *24*, 3361.
(25) Tsuji, T.; Nishida, S. *J. Am. Chem. Soc.* **1989**, *111*, 368.
(26) Gleiter, R.; Krennrich, G.; Bischof, P.; Tsuji, T.; Nishida, S. *Helv. Chim. Acta* **1986**, *69*, 962.
(27) Paquette, L. A.; Philips, J. C. *J. Am. Chem. Soc.* **1969**, *91*, 3973.
(28) Paquette, L. A.; Philips, J. C.; Wingard, R. E., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 4516.
(29) Heating of **52** to 470 °C in the gas phase induces intramolecular Diels–Alder reaction and eventual bond relocation to form benzocyclooctatetraene. The contact time is approximately 1 s.
(30) Paquette, L. A.; Wingard, R. E., Jr.; Photis, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 5801.
(31) Gleiter, R.; Heilbronner, E.; Paquette, L. A.; Thompson, G. L.; Wingard, R. E., Jr. *Tetrahedron* **1973**, *29*, 565.
(32) Zerbetto, F.; Zgierski, M. Z. Private communication from the National Research Council of Canada, Ottawa, Ontario.
(33) Sheldrick, G. M. SHELX76, a system of computer programs for X-ray structure determination as locally modified, University of Cambridge, England (1976).
(34) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 72, 99, 149. (Present distributor: Kluwer Academic Publishers, Dordrect).
(35) Sheldrick, G. M. SHELXS, in *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press, 1985; pp 175–189.

Scheme IX



carbanion intermediate is the species within which 2-fold bond scission occurs, as seems most probable in view of the limited evidence presently in hand, then it is the negatively charged fragment that is ultimately ejected from the tricyclic framework. The driving force for this unusually facile transformation appears to be intricately linked to the relative positioning of the oxygen atoms. Thus, exposure of isomer **7** to strong base does not bring about fragmentation, at least to a level detectable by ^{1}H NMR methods. Rather, [1,5] carbon sigmatropy prevails and operates efficiently at or below room temperature.

The number of mechanistic options available for transforming **7** into **42** is limited (Scheme VIII). With **54** as a base of reference, migration of the non-enolate carbon will uniquely eventuate in *direct* production of a phenanthrene, but it happens to be the 3,5,8-isomer **55**. For **56**, the situation is a great deal more promising. Sigmatropic migration of its enolate carbon does lead directly to **42**. Were [1,5]-shifting of the non-enolate carbon to occur, 2,6,8-trimethoxyphenanthrene (**57**) would result. It is entirely possible that **55** or **57** is the minor product that we observed spectroscopically.

To the extent that the preceding mechanistic proposals are indicative of the real world, it remains to explain why **58**, the conjugate base of **39**, is impelled to undergo fragmentation (Scheme IX). The answer must await further experimentation.

The feasibility of preparing [4.4.4]propellahexaene having now been demonstrated, we anticipate that this structurally intriguing hydrocarbon will see future service in a broad spectrum of synthetic applications.

Experimental Section

Sodium Chromate Oxidation of 8. A solution of **8** (1.00 g, 5 mmol) in a mixture of glacial acetic acid (25 mL) and acetic anhydride (15 mL) was treated with sodium chromate tetrahydrate (9.4 g, 40 mmol) under nitrogen at 0 °C. The mechanically stirred suspension was allowed to warm to room temperature. After 20 h, the original orange color had become a deep green. The suspension was transferred to a 1-L beaker with 20 mL of water. With stirring, solid sodium bicarbonate was added until carbon dioxide evolution ceased and ultimately until saturation was reached. The solids were removed by filtration and thoroughly washed (5×) with chloroform. In each instance, the rinse was used to extract the filtrate. The combined organic phases were dried and evaporated to leave 974 mg of a yellow oil. MPLC of this mixture on silica gel (elution with 65% ethyl acetate in petroleum ether) gave first 66 mg (6.6%) of recovered **8**. Subsequently, 286 mg (26.8%) of a mixture of the monooxidation products **9**–**14** were eluted. After this, the following six 2-fold oxidation products were obtained pure: **15** (28 mg), **7** (79 mg), **16** (26 mg), **17** (8 mg), **6** (52 mg), **18** (15 mg), and **19** (35 mg).

The collective monooxidation fraction could be separated into its constituents by repeating the process with a solvent system of lower polarity (36% ethyl acetate in petroleum ether). Under these conditions, there was obtained **9** (50 mg), **10** (55 mg), **11** (10 mg), **12** (51 mg), **13** (109 mg), and **14** (11 mg).

For **9**: white solid, mp 74 °C; identical with material obtained by epoxidation of **8**.[2b]

For **10**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.84 (dt, J = 10.1, 4.1 Hz, 2 H), 6.09 (d, J = 10.1 Hz, 2 H), 5.76 (m, 2 H), 3.0–2.0 (series of m, 8 H); MS m/z (M^+) calcd 214.0994, obsd 214.1016.

For **11**: white solid, mp 90–92 °C; identical with material obtained by epoxidation of **8**.

For **12**: white solid, mp 107–108 °C (from ether–pentane at −20 °C); IR (KBr, cm^{-1}) 3025, 2910, 2845, 1665, 1380, 1255, 1155, 690, 645; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.72 (d, J = 10.1 Hz, 2 H), 5.97 (d, J = 10.1 Hz, 2 H), 5.79 (br s, 2 H), 2.73 (d, J = 17.1 Hz, 2 H), 2.44 (d, J = 17.1 Hz, 2 H), 2.22 (br s, 4 H); MS m/z (M^+) calcd 214.0994, obsd 214.0951.

For **13**: white solid, mp 126–128 °C (from chloroform–ether at −20 °C): IR (KBr, cm^{-1}) 3030, 2900, 2880, 1680, 1670, 1380, 1255, 775, 760, 670; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.67 (d, J = 10.0 Hz, 2 H), 6.06 (d, J = 10.0 Hz, 2 H), 5.75 (AB with fine coupling, 2 H), 2.45 (br s, 4 H), 2.39 (m, 2 H), 2.01 (br s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 197.76, 151.84, 129.10, 126.42, 124.07, 46.21, 40.80, 38.72, 35.99, 34.79; MS m/z (M^+) calcd 214.0994, obsd 214.1023.

For **15**: white solid, mp 203–204 °C (from chloroform–pentane at −30 °C); IR (KBr, cm^{-1}) 3050, 3025, 2920, 2890, 1670, 1620, 1380, 1260, 1240, 780; UV $\lambda_{max}^{C_2H_5OH}$ 208 (ϵ 9690), 328 nm (61); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.01 (dt, J = 10.2, 4.2 Hz, 1 H), 6.92 (d, J = 10.2 Hz, 1 H), 6.65 (d, J = 10.2 Hz, 1 H), 6.33 (dt, J = 10.2, 1.9 Hz, 1 H), 6.29 (d, J = 10 Hz, 1 H), 6.19 (d, J = 10 Hz, 1 H), 2.97 (d, J = 15.8 Hz, 1 H), 2.70 (d, J = 15.8 Hz, 2 H), 2.3–2.0 (m, 3 H); MS m/z (M^+) calcd 228.0786, obsd 228.0778.

For **7**: colorless crystals, mp 187–188 °C (from chloroform–pentane at −30 °C); IR (KBr, cm^{-1}) 3050, 3020, 2900, 1670, 1615, 1380, 1295, 1265, 760; UV $\lambda_{max}^{C_2H_5OH}$ 212 (ϵ 19000) 332 nm (87); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.56 (d, J = 10.1 Hz, 2 H), 6.50 (d, J = 10.2 Hz, 1 H), 6.18 (d, J = 10.1 Hz, 1 H), 6.16 (d, J = 10.1 Hz, 1 H), 6.10 (d, J = 10.2 Hz, 1 H), 2.87 (d, J = 16.0 Hz, 1 H), 2.84 (d, J = 16.3 Hz, 1 H), 2.96 (d, J = 16.9 Hz, 1 H), 2.68 (d, J = 16.0 Hz, 1 H), 2.46 (d, J = 16.9 Hz, 1 H), 2.38 (d, J = 16.3 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 194.52 (2C), 193.65, 151.28, 148.27, 146.25, 131.87, 130.01, 127.50, 47.13, 45.27, 44.61, 43.36, 42.54; MS m/z (M^+) calcd 228.0786, obsd 228.0803.

For **16**: colorless solid, mp 176–177 °C (from chloroform–pentane at −30 °C); IR (KBr, cm^{-1}) 3050, 3030, 2920, 1690, 1675, 1665, 1625, 1610, 1430, 1390, 1270, 1255, 1210, 1150, 850, 760; UV $\lambda_{max}^{C_2H_5OH}$ 212.5 (ϵ 15865), 331 nm (91); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.91 (m, 1 H), 6.58 (d, J = 9.8 Hz, 1 H), 6.47 (m, 1 H), 6.23 (d, J = 9.9 Hz, 2 H), 6.09 (d, J = 10.0 Hz, 1 H), 3.5–2.2 (series of m, 6 H); MS m/z (M^+) calcd 228.0786, obsd 228.0834.

For **17**: colorless crystals, mp 200–215 °C dec (from chloroform–pentane at −30 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.91 (d, J = 10.0 Hz, 1 H), 6.58 (d, J = 10.2 Hz, 1 H), 6.36 (d, J = 10.2 Hz, 1 H), 6.14 (d, J = 10.0 Hz, 1 H), 5.22 (dd, J = 13.2, 6.1 Hz, 1 H), 2.81 (d, J = 14.1 Hz, 1 H), 2.71 (d, J = 16.9 Hz, 1 H), 2.61 (d, J = 17.4 Hz, 1 H), 2.51 (dd, J = 6.1, 13.7 Hz, 1 H), 2.29 (dd, J = 13.2, 13.7 Hz, 1 H), 2.24 (d, J = 17.4 Hz, 1 H), 2.21 (d, J = 14.1 Hz, 1 H), 2.18 (d, J = 16.9 Hz, 1 H), 2.17 (s, 3 H).

For **6**: colorless crystals, mp 225 °C (from chloroform–pentane at −30 °C); IR (KBr, cm^{-1}) 3055, 3020, 2915, 2840, 1680, 1390, 1250, 790, 785, 690; UV $\lambda_{max}^{C_2H_5OH}$ 225 (ϵ 2850) 330 nm (11); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.63 (d, J = 10.1 Hz, 3 H), 6.25 (d, J = 10.1 Hz, 3 H), 2.73 (d, J = 16.7 Hz, 3 H), 2.18 (d, J = 16.7 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 195.47, 144.13, 129.31, 45.50, 43.70, 41.95; MS m/z (M^+) calcd 228.0786, obsd 228.0765.

For **18**: white solid, mp 138–140 °C; identical with material obtained by epoxidation of **8**.[2b]

For **19**: white solid, mp 168–170 °C (from chloroform–pentane at −20 °C); IR (KBr, cm^{-1}) 2995, 2920, 1670, 1380, 1260, 790; UV $\lambda_{max}^{C_2H_5OH}$ 212.5 (ϵ 51437), 330 nm (82); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.91 (dt, J = 10.1, 4.2 Hz, 1 H), 6.67 (d, J = 10.1 Hz, 2 H), 6.16 (d, J = 10.1 Hz, 2 H), 5.94 (d, J = 10.1 Hz, 1 H), 3.3–1.8 (series of m, 8 H); MS m/z (M^+) calcd 228.0786, obsd 228.0804.

[4.4.4]Propellahexaene (5). A. Shapiro Degradation of 7. A mixture of **7** (45.6 mg, 0.2 mmol) and benzenesulfonohydrazide (103.2 mg, 0.6 mmol) in methanol (2 mL) was treated with 1 drop of concentrated hydrochloric acid and stirred at room temperature in the dark for 6 days. The solvent was removed in vacuo and the residue was triturated with anhydrous ether to give 138 mg (100%) of **22**. Recrystallization from ethanol to give a pale yellow solid having mp 195 °C: IR (KBr, cm^{-1}) 3450, 3200, 2920, 1600, 1405, 1380, 1340, 1170, 1090, 755, 720, 695; ^{1}H NMR (300 MHz, CD_3CN) δ 7.80 (br m, 6 H), 7.60 (m, 9 H), 6.10–5.60

(m, 6 H), 2.85–1.65 (series of m, 9 H); MS m/z ($M^+ + 1$) calcd 691.1489, obsd 691.1479.

To a cold (0 °C), magnetically stirred suspension of **22** (69 mg, 0.1 mmol) in TMEDA (3 mL, freshly distilled from barium oxide) was added methyllithium (0.6 mL of 1.5 M in ether, 2.2 equiv) over 2 min under a nitrogen atmosphere. The mixture was stirred at 0 °C for an hour and subsequently at room temperature for 16 h before 1 mL of water was introduced. Further dilution with water (5 mL) was followed by extraction with pentane (4 × 10 mL) and washing of the combined organic layers several times with brine. The pentane solution was dried and concentrated at room temperature under partial house vacuum. The resulting yellow oil was purified by filtration through a plug of TLC grade silica gel (elution with pentane). There was isolated 2.7 mg (15%) of **5** as colorless needles, mp 63 °C (after sublimation at 0.1 Torr and 30–40 °C); $\lambda_{max}^{isooctane}$ 234 (ε 25 730), 242 (24 100), 251 (27 780), 271 (9560), 279 (7615), 291 nm (6975); ^{1}H NMR (see Figure 1); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 129.19, 122.39, 39.84; MS m/z (M^+) calcd 180.0939, obsd 180.0870.

Anal. Calcd for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 92.92; H, 6.95.

B. Shapiro Degradation of 6. Reaction of **6** (1.199 g, 5.20 mmol) with benzenesulfonohydrazide (2.69 g, 15.6 mmol) in methanol (50 mL) containing 2 drops of concentrated hydrochloric acid (room temperature, 6 days) and workup as described above gave 3.60 g (100%) of **23** as a pale yellow solid, which was utilized without further purification.

Reaction of **23** (3.60 g, 5.20 mmol) in TMEDA (150 mL) with methyllithium (41.6 mL of 1.5 M in ether) as described in part A afforded 172 mg (18%) of **5**, spectroscopically identical with the hydrocarbon generated from **22**.

X-ray Crystallographic Analysis of 5. A transparent single crystal of **5** was mounted on a pin and transferred to the goniometer. The crystal was cooled to −150 °C during data collection using a stream of cold nitrogen gas. The space group was determined to be the acentric $P\bar{4}2_1c$ from the systematic absences. A summary of data collection parameters is given in Table I.

The hydrogen atoms were located from a difference Fourier map and included with fixed contributions (B = 3.95 Å^2). Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final values of R = 0.072 and R_w = 0.075. The final values of the positional parameters are given in the supplementary material.

Methyl *cis*-9-(Carbomethoxymethyl)-Δ^2-octalin-10-carboxylate (27a). A mechanically stirred solution of **26**[12] (111.04 g, 0.466 mol) in cold (0 °C), dry tetrahydrofuran (1300 mL) was treated with a thin stream of ethereal diazomethane solution (prepared from 260 g (2.52 mol) of *N*-methyl-*N*-nitrosourea). The reaction mixture was stirred at 0 °C for 3 h and then treated dropwise with acetic acid to destroy the excess CH_2N_2. After solvent evaporation, the residue was purified by flash chromatography on silica gel (elution with 5% ethyl acetate in petroleum ether). There was isolated 101.9 g (82%) of **27a** as a colorless oil; IR (neat, cm^{-1}) 3020, 2940, 2920, 2860, 1725, 1430, 1340, 1320, 1285, 1190, 1130, 1015, 665; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.59–5.57 (m, 2 H), 3.63 (s, 3 H), 3.61 (s, 3 H), 2.88 (d, J = 13.2 Hz, 1 H), 2.29 (d, J = 13.2 Hz, 1 H), 2.22 (br s, 4 H), 2.08–1.03 (series of m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 176.10, 172.74, 124.41, 122.82, 51.32, 51.05, 47.63, 39.34, 36.57, 32.75, 31.76, 30.32, 21.73, 20.80 (one carbon signal not observed); MS m/z (M^+) calcd 266.1518, obsd 266.1531.

Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.32. Found: C, 67.30; H, 8.37.

Methyl *cis*-9-(Carboxymethyl)-Δ^2-octalin-10-carboxylate (27b). A magnetically stirred mixture of **27a** (4.8 g, 18 mmol) and sodium hydroxide (830 mg, 20.8 mmol) in methanol (60 mL) and water (30 mL) was heated at reflux for 6 h under nitrogen. The cooled reaction mixture was freed of solvent under reduced pressure. The residue was partitioned between water (30 mL) and ether (2 × 25 mL). The aqueous layer was acidified to pH 3 with 6 N hydrochloric acid. The white crystalline precipitate was removed by filtration and air-dried. The filtrate was extracted with ether (2 × 25 mL) and the combined extracts were washed with brine, dried, and evaporated to leave additional solid **27b**. The combined weight of the two solid fractions was 4.0 g (88%), mp 99–100 °C (from dichloromethane–petroleum ether): IR (KBr, cm^{-1}) 3400–2700, 2940, 2920, 2860, 1720, 1705, 1630, 1465, 1440, 1385, 1290, 1235, 1190, 1150, 1140, 660, 635; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.60 (br s, 1 H), 5.61–5.59 (m, 2 H), 3.65 (s, 3 H), 2.94 (d, J = 13.2 Hz, 1 H), 2.34 (d, J = 13.2 Hz, 1 H), 2.26 (br s, 4 H), 2.18–1.38 (series of m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 178.66, 175.77, 124.00, 122.59, 51.15, 47.28, 39.09, 36.26, 31.47, 30.06, 29.90, 21.48, 20.62 (one carbon signal not observed); MS m/z ($M^+ - H_2O$) calcd 234.1256, obsd 234.1246.

Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.64; H, 7.93.

Methyl *cis*-9-Acetonyl-Δ^2-octalin-10-carboxylate (28). A magnetically stirred solution of **27b** (2.52 g, 10 mmol) in dry benzene (40 mL) was treated dropwise with oxalyl chloride (5.0 g, 39 mmol) under nitrogen. After 3 h, the volatiles were removed in vacuo and the pale yellow acid chloride (2.73 g, 100%) was utilized directly without purification.

Ethereal methyllithium (37.5 mL of 1.4 M, 52.5 mmol) was added to cold (−20 °C) copper(I) iodide (5 g, 26 mmol) under nitrogen. This mixture was cooled to −70 °C and treated with a solution of the crude acid chloride in dry ether (4 mL) via syringe. After 30 min at −70 °C, the mixture was quenched with 6 mL of absolute methanol, allowed to warm to room temperature, and poured into saturated ammonium chloride solution (40 mL). The product was extracted into ether (3 × 20 mL), and the combined organic solutions were washed with saturated ammonium chloride (2×) and brine solutions, dried, and evaporated. The residue was purified by flash chromatography (silica gel, elution with 15% ethyl acetate in petroleum ether) to give **28** as a pale yellow oil (1.91 g, 76% for the two steps): IR (neat, cm^{-1}) 3020, 2945, 2920, 2865, 1720, 1460, 1430, 1355, 1290, 1230, 1210, 1195, 1140, 1050, 1015, 680, 645; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.56 (br s, 2 H), 3.63 (s, 3 H), 3.04 (d, J = 14.5 Hz, 1 H), 2.37 (d, J = 14.5 Hz, 1 H), 2.26–2.18 (m, 4 H), 2.11 (s, 3 H), 2.10–1.20 (series of m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 209.25, 176.27, 124.49, 122.84, 51.31, 47.75, 46.46, 37.11, 33.08, 31.93, 30.38, 29.64, 21.92, 20.94 (one carbon signal not observed); MS m/z ($M^+ - OCH_3$) calcd 219.1385, obsd 219.1446.

Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 72.19; H, 8.94.

Ketalization of 28. A cold (0 °C), magnetically stirred solution of **28** (25 g, 0.1 mol) and 2-methoxy-1,3-dioxolane (20.8 g, 0.2 mol) in dry dichloromethane (100 mL) was treated with *p*-toluenesulfonic acid monohydrate (920 mg, 4.8 mmol), allowed to warm to room temperature under nitrogen, and stirred for 8 days. Sodium bicarbonate solution (40 mL) was introduced and the organic phase was separated after 10 min of stirring. The aqueous layer was extracted with dichloromethane (2 × 10 mL) and the combined organic solutions were dried and evaporated. After removal of the residual dioxolane at 0.1 Torr overnight, the residual ester was purified by flash chromatography on silica gel (elution with 10% ethyl acetate in petroleum ether) to give **29** as a colorless oil (28.2 g, 96%): IR (neat, cm^{-1}) 3020, 2950, 2870, 1725, 1460, 1430, 1380, 1285, 1230, 1190, 1140, 1085, 1065, 1050, 1020, 950, 660; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.70–5.50 (m, 2 H), 3.89 (s, 4 H), 3.62 (s, 3 H), 2.45–1.40 (series of m, 14 H), 1.36 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 176.24, 124.87, 122.34, 110.75, 63.62, 63.50, 50.95, 48.13, 40.65, 36.23, 31.76, 30.32, 29.99, 26.49, 21.68, 21.00 (one carbon signal not observed); MS m/z ($M^+ - CH_3$) calcd 279.1595, obsd 279.1617.

Anal. Calcd for $C_{17}H_{26}O_4$: C, 69.36; H, 8.90. Found: C, 69.23; H, 8.85.

Hydride Reduction of 29. To a stirred suspension of lithium aluminum hydride (1.5 g, 39.5 mmol) in dry ether (100 mL) was added a solution of **29** (5.53 g, 18.8 mmol) in dry ether (20 mL) via syringe over 30 min under nitrogen. The resulting mixture was stirred for an additional 30 min and then quenched with saturated sodium sulfate solution (70 mL). The aqueous phase was extracted with ether (3 × 10 mL) and the combined ethereal layers were washed twice with brine, dried, and evaporated. The residue was purified by flash chromatography (silica gel, elution with 40% ethyl acetate in petroleum ether) to give 4.87 g (97%) of **30a** as a colorless oil: IR (neat, cm^{-1}) 3640–3100, 3010, 2920, 2850, 1460, 1370, 1245, 1220, 1210, 1080, 1060, 1030, 985, 945, 900, 860, 800, 655; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.61 (br s, 2 H), 3.91 (s, 4 H), 3.80–3.60 (m, 2 H), 2.40–1.20 (series of m, 18 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 125.42, 123.51, 111.20, 66.92, 63.86, 63.73,

40.65, 39.45, 36.42, 30.83, 27.82, 26.72, 21.40, 20.83 (two carbon signals not observed); MS m/z ($M^+ - CH_3$) calcd 251.1647, obsd 251.1635.

Anal. Calcd for $C_{16}H_{26}O_3$: C, 72.14; H, 9.84. Found: C, 72.28; H, 9.97.

[4.4.4]Propella-3,6-dien-2-one (32). To a mechanically stirred suspension of pyridinium chlorochromate (6.06 g, 28.1 mmol, dried overnight under high vacuum) in dry dichloromethane (60 mL) was added a solution of **30a** (3.74 g, 14.06 mmol) in the same solvent (20 mL). After 25 min, ether (80 mL) was added, and the supernatant solution was decanted and washed with saturated sodium bicarbonate solution (3×), 10% hydrochloric acid (2×), saturated sodium bicarbonate solution (2×), and brine prior to drying. After solvent removal, 3.26 g of **30b** was obtained as a tan oil and used as is in the next step.

The unpurified **30b** was dissolved in a 9:1 acetone–water system (160 mL) and pyridinium *p*-toluenesulfonate (962 mg, 3.83 mmol) was added. The resulting mixture was heated at reflux for 1.5 h under nitrogen, cooled, and evaporated in vacuo. The residue was diluted with ether (35 mL) and this solution was washed in turn with saturated sodium bicarbonate solution (2×), 10% hydrochloric acid (2×), saturated sodium bicarbonate solution (2×), and brine. Drying and solvent evaporation left 2.34 g of crude **31** as a colorless oil, which was cyclized without delay.

The keto aldehyde was dissolved in absolute ethanol (200 mL), treated with sodium hydroxide (3.57 g, 89.3 mmol), and stirred at room temperature for 3 h. The solvent was evaporated, and the residue was diluted with ether (150 mL) and washed in turn with 10% hydrochloric acid (2×), sodium bicarbonate solution, and brine. After drying and solvent removal, the residue was subjected to flash chromatography (silica gel, elution with 10% ethyl acetate in petroleum ether) to give 1.48 g (52% overall) of **32** as white crystals, mp 54–55 °C: IR (KBr, cm^{-1}) 3010, 2920, 2910, 2850, 1660, 1440, 1380, 1265, 1235, 1140, 1080, 1005, 850, 760, 660; ^1H NMR (300 MHz, $CDCl_3$) δ 6.70 (d, J = 10.1 Hz, 1 H), 5.91 (d, J = 10.1 Hz, 1 H), 5.75–5.50 (m, 2 H), 2.60–1.10 (series of m, 14 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 200.54, 160.55, 127.58, 124.41, 124.27, 47.09, 39.04, 36.46, 36.01, 33.56, 32.31, 22.46, 21.44 (one carbon signal not observed); MS m/z (M^+) calcd 202.1357, obsd 202.1351.

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.11; H, 9.08.

Chromate Oxidation of 32. Potassium chromate (26.5 g, 136.4 mmol) was added to a solution of **32** (6.89 g, 34.1 mmol) in acetic anhydride (90 mL) and acetic acid (160 mL), and the resulting mixture was stirred at room temperature for 2 h and at 40 °C for 4 h. After being cooled to room temperature, the mixture was stirred for an additional 4 days, transferred to a beaker, and treated slowly with 500 mL of saturated sodium bicarbonate solution. Solid sodium bicarbonate was introduced in small portions until gas evolution ceased. The solids were removed by filtration and washed thoroughly with chloroform (5 × 100 mL). The filtrate was extracted with chloroform (3 × 100 mL) and the combined organic solutions were washed with saturated sodium bicarbonate solution and brine prior to drying and solvent evaporation. The residue was subjected to preparative HPLC on silica gel (elution with 25% ethyl acetate in petroleum ether). There was isolated 2.02 g (28%) of **33a**, 0.78 g (11%) of **34a**, 1.74 g (25%) of recoverd **32**, 231 mg (3%) of an epoxy enone, and 555 mg (8%) of two dienediones having unrearranged double bonds. The latter three compounds were not fully characterized.

For **33a**: colorless crystals, mp 133–134 °C (from ethyl acetate–pentane); IR (KBr, cm^{-1}) 3030, 2940, 2900, 2880, 2850, 1655, 1465, 1445, 1435, 1410, 1405, 1385, 1350, 1135, 1255, 1240, 1165, 1160, 1140, 1060, 915, 880, 790, 765; ^1H NMR (300 MHz, $CDCl_3$) δ 6.49 (d, J = 10.0 Hz, 2 H), 6.03 (d, J = 10.0 Hz, 2 H), 3.10–0.90 (series of m, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 198.09, 151.16, 131.04, 45.65, 42.78, 39.69, 34.49, 32.76, 21.35, 21.09; MS m/z (M^+) calcd 216.1151, obsd 216.1168.

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.76; H, 7.56.

For **34a**: colorless crystals, mp 191.5–192 °C (from ethyl acetate–petroleum ether); IR (KBr, cm^{-1}) 3030, 3010, 2920, 2850, 1665, 1440, 1425, 1405, 1380, 1300, 1275, 1260, 1135, 760; ^1H NMR (300 MHz, $CDCl_3$) δ 6.53 (d, J = 10.0 Hz, 2 H), 6.03 (d, J = 10.0 Hz, 2 H), 2.50 (br s, 4 H), 1.90–1.20 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 196.88, 155.75, 128.65, 45.17, 41.38, 33.39, 21.69; MS m/z (M^+) calcd 216.1150, obsd 216.1154.

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.57; H, 7.51.

[4.4.4]Propella-2,4,7,9-tetraene (24). A 380-mg (1.76 mmol) sample of **33a** was transformed into **33b** by reaction with benzenesulfonohydrazide (605 mg, 3.52 mmol) in absolute methanol (85 mL) as described above. The resulting yellow crystalline solid was triturated with ether, suspended in cold (0 °C) TMEDA (50 mL, freshly distilled from CaH_2), and treated with methyllithium (23.5 mL of 1.5 M in ether, 10 equiv) during 20 min. The predescribed reaction conditions and workup followed. Flash chromatography of the residue gave 146 mg (45% overall) of **24** as a colorless oil: IR (neat, cm^{-1}) 3040, 3020, 2980, 2920, 2840, 1440, 700, 680; ^1H NMR (300 MHz, $CDCl_3$) δ 5.87 (dd, J = 2.9, 7.6 Hz, 4 H), 5.34 (dd, J = 2.9, 7.6 Hz, 4 H), 1.70–1.20 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 133.21, 122.75, 39.78, 33.75, 20.34; MS m/z (M^+) calcd 184.1252, obsd 184.1254.

Anal. Calcd for $C_{14}H_{16}$: C, 91.25, H, 8.75. Found: C, 91.26; H, 8.76.

Catalytic Hydrogenation of 29. To a solution of **29** (2.50 g, 8.5 mmol) in ethyl acetate (300 mL) was added 200 mg of 5% palladium on carbon and 1 drop of triethylamine. Following hydrogenation under an atmosphere of hydrogen (supplied from a balloon), the mixture was filtered through Celite, evaporated, and subjected to column chromatography (silica gel, elution with 10% ethyl acetate in petroleum ether). There was isolated 2.41 g (96%) of **35** as a colorless oil: IR (neat, cm^{-1}) 2940, 2860, 1715, 1460, 1445, 1425, 1365, 1295, 1230, 1220, 1140, 1120, 1040, 1010, 950, 880, 850, 800, 760; ^1H NMR (300 MHz, $CDCl_3$) δ 3.91 (s, 4 H), 3.64 (s, 3 H), 2.35–1.20 (series of m, 18 H), 1.36 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 177.01, 111.14, 63.83, 63.70, 63.63, 50.96, 49.63, 41.49, 37.98, 26.76, 21.55, 21.47, 21.43, 21.39, 20.96, 14.15 (one carbon signal not observed); MS m/z ($M^+ - CH_3$) calcd 281.1753, obsd 281.1733.

Anal. Calcd for $C_{17}H_{28}O_4$: C, 68.89; H, 9.52. Found: C, 68.82; H, 9.54.

Hydride Reduction of 35. A 4.58-g (15.5 mmol) sample of **35** was treated with lithium aluminum hydride (1.18 g, 31 mmol) in anhydrous ether (90 mL) in the manner detailed above. After workup, solvent evaporation, and flash chromatography, there was isolated 4.01 g (97%) of alcohol **36a** as a colorless oil: IR (neat, cm^{-1}) 3600–3100, 2940, 2920, 2860, 1465, 1445, 1375, 1365, 1245, 1210, 1190, 1175, 1115, 1090, 1075, 1060, 1040, 965, 945; ^1H NMR (300 MHz, $CDCl_3$) δ 3.91 (s, 4 H), 3.48 (br s, 1 H), 2.23 (br d, 1 H), 2.00–1.20 (series of m, 18 H), 1.34 (s, 3 H), 1.14 (t, J = 6.1 Hz, O*H*); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 111.42, 66.36, 63.99, 63.57, 40.96, 40.14, 38.10, 33.71, 30.83, 27.88, 26.82, 26.19, 22.25, 21.70, 21.03 (one carbon signal not observed); MS m/z ($M^+ - CH_3$) calcd 253.1804, obsd 253.1801.

Anal. Calcd for $C_{16}H_{28}O_3$: C, 71.60; H, 10.51. Found: C, 71.28; H, 10.48.

[4.4.4]Propell-3-en-2-one (38a). To a suspension of pyridinium chlorochromate (6.65 g, 30.8 mmol) in dry dichloromethane (70 mL) was added a solution of **36a** (4.11 g, 15.3 mmol) in the same solvent (20 mL). The mixture was stirred for 25 min at room temperature and then processed as described above to give 4.14 g of crude aldehyde **36b** that was used without purification.

The unpurified **36b** (4.14 g) was dissolved in 9:1 acetone–water (200 mL), treated with pyridinium *p*-toluenesulfonate (1.22 g, 4.9 mmol), and heated at reflux for 1 h under nitrogen. The usual workup gave 3.62 g of **37** that was immediately dissolved in absolute ethanol (350 mL), treated with sodium hydroxide (5.52 g, 138 mmol), and stirred at room temperature for 3 h. Most of the solvent was then removed under reduced pressure. Following the described workup, there was obtained 1.85 g (59% overall) of **38a** as a white crystalline solid, mp 78 °C: IR (KBr, cm^{-1}) 3005, 2920, 2850, 1670, 1445, 1380, 1270, 1245, 1240, 1205, 1140, 865, 790, 755; ^1H NMR (300 MHz, $CDCl_3$) δ 6.52 (d, J = 10.1 Hz, 1 H), 5.93 (d, J = 10.1 Hz, 1 H), 3.00 (d, J = 16.8 Hz, 1 H), 1.76 (d, J = 16.8 Hz, 1 H), 2.15–0.80 (series of m, 16 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 201.00, 160.36, 127.26, 46.01, 40.36, 37.44, 34.52, 33.92, 32.01, 31.12, 23.34, 21.61, 21.29, 20.69; MS m/z (M^+) calcd 204.1514, obsd 204.1512.

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 81.96; H, 9.96.

[4.4.4]Propella-2,4-diene (25). To a solution of **38a** (102 mg, 0.5 mmol) and benzenesulfonohydrazide (86.1 mg, 0.5 mmol) in absolute methanol (10 mL) was added 1 drop of concentrated hydrochloric acid. The resulting solution was stirred overnight at room temperature, freed of solvent on a rotary evaporator. After being kept under high vacuum for 18 h, the crude sulfonylhydrazone was added to 10 mL of ether and cooled to 0 °C. Methyllithium (3.3 mL of 1.5 M, 10 equiv) was introduced over 5 min via syringe, and the reaction mixture was stirred under nitrogen for 1 h at 0 °C and 4 h at room temperature. After recooling to 0 °C, water (10 mL) was added and the predescribed workup followed. Flash chromatography on silica gel (elution with pentane) and sublimation (35–40 °C/0.1 Torr) delivered pure **25** (63 mg, 67% overall) as a colorless solid, mp 64–65 °C: IR (KBr, cm^{-1}) 3040, 3020, 2920, 2850, 1460, 1440, 1280, 1160, 845, 745, 690; ^1H NMR (300 MHz, $CDCl_3$) δ 5.83 (dd, J = 7.6, 3.0 Hz, 2 H), 5.43 (dd, J = 7.6, 3.0 Hz, 2 H), 2.4–0.5 (series of m, 16 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 138.46, 121.73, 38.66, 32.81, 21.76; MS m/z (M^+) calcd 188.1565, obsd 188.1559.

Anal. Calcd for $C_{14}H_{20}$: C, 89.30; H, 10.70. Found: C, 88.93; H, 10.71.

Attempted O-Methylation of 6. A magnetically stirred solution of freshly sublimed potassium *tert*-butoxide (1.218 g, 11 mmol) in 30 mL of dry dimethylformamide (distilled from CaH_2) was blanketed with nitrogen, cooled to 0 °C, and treated with **6** (213 mg, 0.94 mmol) in 4 mL of the same solvent via syringe. After 15 min of stirring at 0 °C, dimethyl sulfate (1.6 mL, 2.3 mmol) was introduced and stirring was maintained at 0 °C for 15 min and at room temperature for 30 min. The mixture was recooled to 0 °C, treated with 10% sodium hydroxide solution, and extracted with ether. The combined organic extracts were washed with 10% sodium hydroxide solution, water, and brine prior to drying and evaporation. The residue was triturated with 7% ethyl acetate in petroleum ether to leave **39** as a white solid. The soluble material was subjected to MPLC purification on silica gel to give additional **39** (total weight 74 mg, 31%) as well as 2,7-dimethoxynaphthalene (**40**) (6 mg, 3.4%)

For **39**: IR (CCl_4, cm^{-1}) 1690, 1665, 1655, 1470, 1460, 1445, 1400, 1270, 1250, 1240, 1225, 1215; ^1H NMR (300 MHz, $CDCl_3$) δ 6.27 (d, J = 10 Hz, 1 H), 6.02 (d, J = 10 Hz, 1 H), 5.92 (dd, J = 9.7, 2.1 Hz, 2 H), 5.51 (d, J = 9.7 Hz, 2 H), 4.29 (d, J = 2.1 Hz, 2 H), 3.51 (s, 6 H), 2.48 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 199.23, 152.33, 144.32, 128.85, 127.64, 124.50, 99.45, 54.38, 46.87, 42.13, 41.08; MS m/z (M^+) calcd 256.1099, obsd 256.1109.

For **40**: mp 137–139 °C; spectroscopically identical with a commercial sample (Aldrich).

Independent Methylation of 39. Into a preweighed, flame-dried 5-mL flask was introduced 50% potassium hydride suspension in oil. This material was washed three times with anhydrous benzene with intermittent settling. The residual solid was dried in vacuo and the flask reweighed. The residual amount of KH was 4 mg. Anhydrous dimethylformamide (1 mL) was introduced via syringe and the magnetically stirred suspension was cooled to 0 °C prior to addition of **39** (12.8 mg, 0.05 mmol) in 1 mL of the same solvent. After 1 h of stirring at 0 °C, dimethyl sulfate (0.1 mL) was injected into the mixture and reaction was allowed to proceed at 0 °C for 1 h and at room temperature for 1 h. The contents were poured into 10 mL of 2 N potassium hydroxide solution, stirred for 30 min, and extracted with ether (3 × 20 mL). The combined organic extracts were washed with brine (4 × 20 mL), dried, and concentrated to leave a yellow oil. This material was filtered through a small column of neutral alumina (elution with 7% ethyl acetate in petroleum ether) to give 2.5 mg of colorless solid, the ^1H NMR spectrum of which indicated it to be a 17:1 mixture of **40** and **41**.

For **40**: ^1H NMR (300 MHz, $CDCl_3$) δ 5.99 (dd, J = 9.8, 2.1 Hz, 3 H), 5.19 (d, J = 9.8 Hz, 3 H), 4.35 (d, J = 2.1 Hz, 3 H), 3.23 (s, 9 H); MS m/z (M^+) calcd 270.1256, obsd 270.1235.

Attempted O-Methylation of 7. A cold (0 °C), magnetically stirred slurry of freshly sublimed potassium *tert*-butoxide (800 mg, 7.1 mmol) in dry dimethylformamide (20 mL, distilled from CaH_2) was treated dropwise with a solution of **7** (124 mg, 0.54 mmol) in 4 mL of the same solvent. During 15 min of stirring at 0 °C, the reaction mixture became very darkly colored. Upon addition of dimethyl sulfate (0.80 mL, 9.0 mmol) via syringe, a burgundy red color developed. The reaction mixture was stirred at 0 °C for 15 min and at room temperature for 20 min. Workup as in the predescribed fashion gave a yellow oil, purification of which was effected by MPLC on silica gel (elution with 10% ethyl acetate in petroleum ether). There was isolated 25 mg (17%) of **42** as the major product. A second trimethoxyphenanthrene isomer, present in considerably lower amounts (2–4%), could also be observed spectroscopically, but was neither isolated pure nor characterized further.

For **42**: ^1H and ^{13}C NMR (see Table V); MS m/z (M^+) calcd 268.1085, obsd 268.1085.

MTAD Addition to 25. A solution of **25** (28.1 mg, 0.15 mmol) in dry dichloromethane (1.5 mL) was treated with MTAD (20.3 mg, 0.18 mmol) in the same solvent (1.5 mL) and stirred at room temperature for 2 days. Following the evaporation of solvent, the residue was purified by flash chromatography (silica gel, elution with 30% ethyl acetate in petroleum ether) to give 5.2 mg (19%) of unreacted **25** and 28.5 mg (63%) of **43** as colorless crystals, mp 176 °C (from ethyl acetate–petroleum ether): IR (KBr, cm^{-1}) 3030, 2990, 2940, 2900, 2860, 1760, 1680, 1455, 1390, 1260, 1230, 1010, 925, 775, 740, 730; ^1H NMR (300 MHz, $CDCl_3$) δ 6.39 (dd, J = 3.2, 4.0 Hz, 2 H), 4.17 (dd, J = 3.2, 4.0 Hz, 2 H), 2.99 (s, 3 H), 2.15–1.10 (series of m, 16 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 158.30, 129.43, 62.09, 37.79, 32.80, 32.78, 25.32, 19.43, 18.20; MS m/z (M^+) calcd 301.1790, obsd 301.1800.

Anal. Calcd for $C_{17}H_{23}N_3O_2$: C, 67.75; H, 7.69. Found: C, 67.76; H, 7.82.

MTAD Addition to 24. A solution of **24** (75 mg, 0.41 mmol) and MTAD (55 mg, 0.49 mmol) in dry dichloromethane (10 mL) was stirred at room temperature for 2 h. Sequential solvent evaporation and flash chromatography (silica gel, elution with 30% ethyl acetate in petroleum ether) afforded 60 mg (50%) of **44** and 9 mg (7%) of **45**.

For **44**: colorless crystals, mp 159 °C (from ethyl acetate–petroleum ether): IR (KBr, cm^{-1}) 3030, 2990, 2940, 2900, 2860, 1760, 1680, 1455, 1390, 1260, 1230, 1010, 925, 775, 740, 730; ^1H NMR (300 MHz, $CDCl_3$) δ 6.49 (dd, J = 3.3, 3.8 Hz, 2 H), 5.99 (dd, J = 2.8, 7.7 Hz, 2 H), 5.14 (dd, J = 2.8, 7.7 Hz, 2 H), 4.34 (dd, J = 3.3, 3.8 Hz, 2 H), 2.94 (s, 3 H), 1.60–1.10 (series of m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 157.31, 131.71, 129.61, 123.41, 58.22, 42.79, 30.61, 25.22, 16.60; MS m/z (M^+) calcd 297.1477, obsd 297.1436.

Anal. Calcd for $C_{17}H_{19}N_3O_2$: C, 68.67; H, 6.44. Found: C, 68.26; H, 6.57.

For **45**: colorless crystals, mp 220 °C dec (from dichloromethane–pentane); IR (KBr, cm^{-1}) 3040, 3020, 2940, 2930, 2860, 1760, 1695, 1455, 1430, 1390, 1205, 780; ^1H NMR (300 MHz, $CDCl_3$) δ 6.46 (dd, J = 3.3, 3.8 Hz, 2 H), 5.74 (dd, J = 2.8, 7.7 Hz, 2 H), 5.04 (dd, J = 2.8, 7.7 Hz, 2 H), 4.30 (dd, J = 3.3, 3.8 Hz, 2 H), 3.01 (s, 3 H), 2.23 (m, 2 H), 1.80–1.40 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 157.90, 130.58, 130.17, 123.48, 57.75, 43.19, 28.73, 25.40, 16.77; MS m/z ($M^+ - C_{10}H_{12}$) calcd 165.0578, obsd 165.0558; m/z ($M^+ - C_7H_7N_3O_2$) calcd 132.0939, obsd 132.0978.

Anal. Calcd for $C_{17}H_{19}N_3O_2$: C, 68.67; H, 6.44. Found: C, 68.30; H, 6.50.

MTAD Addition to 44. A solution containing 3 mg (0.01 mmol) of **44** and 1.4 mg (0.012 mmol) of MTAD in 1 mL of dry dichloromethane was stirred overnight at room temperature. Following the removal of solvent, the residue was chromatographed on silica gel [elution with ethyl acetate (50%)/dichloromethane (10%)/methanol (4%): petroleum ether (36%)] to give 2.9 mg (71%) of **46** and 0.6 mg of unreacted **44**.

For **46**: colorless crystals, mp > 300 °C (from ethyl acetate); IR (KBr, cm^{-1}) 3050, 3000, 2940, 2860, 1760, 1690, 1445, 1385, 1190, 1025, 770, 715; ^1H NMR (300 MHz, $CDCl_3$) δ 6.49 (dd, J = 3.3, 3.5 Hz, 2 H), 6.15 (dd, J = 3.5, 3.8 Hz, 2 H), 4.49 (dd, J = 3.5, 3.8 Hz, 2 H), 4.44 (dd, J = 3.3, 3.5 Hz, 2 H), 2.98 (s, 3 H), 2.90 (s, 3 H), 2.15–1.10 (series of m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 158.78, 156.40, 131.35, 124.40, 61.31, 57.05, 42.54, 32.51, 25.45, 25.27, 21.87; MS m/z (M^+) calcd 410.1702, obsd 410.1752.

Anal. Calcd for $C_{20}H_{22}N_6O_4$: C, 58.53; H, 5.40. Found: C, 58.77; H, 5.62.

MTAD Addition to 45. Cycloaddition to **45** (3 mg, 0.01 mmol) in the predescribed manner and comparable chromatographic purification furnished 3.6 mg (88%) of **47**: colorless crystals, mp > 300 °C (from dichloromethane–pentane); IR (KBr, cm^{-1}) 3050, 2980, 2940, 2930, 2850, 1760, 1695, 1445, 1385, 1260, 1195, 1180,

1080, 1030, 910, 790, 770, 750, 700; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.02 (dd, J = 3.5, 3.8 Hz, 4 H), 4.37 (dd, J = 3.5, 3.8 Hz, 4 H), 2.98 (s, 6 H), 2.19 (br s, 4 H), 1.61 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 158.43, 129.75, 61.07, 36.61, 33.29, 25.52, 23.33; MS m/z (M^+) calcd 410.1702, obsd 410.1754.

Anal. Calcd for $C_{20}H_{22}N_6O_4$: C, 58.53; H, 5.40. Found: C, 58.07; H, 5.49.

Photocyclization of 47. A solution of **47** (16 mg, 0.04 mmol) in acetone (16 mL) and dichloromethane (10 mL) was placed in a Pyrex text tube, stoppered with a rubber septum, and deoxygenated with argon for 3 min. Following irradiation with a 450-W Hanovia lamp housed in a Pyrex well for 3.5 h, TLC analysis showed no **47** remaining. The solvent was evaporated and the residue was purified by flash chromatography (silica gel, elution with the four-component solvent system used for **47**). There was isolated 13 mg (81%) of **48** as colorless crystals, mp > 300 °C (from dichloromethane–pentane): IR (KBr, cm^{-1}) 2950, 2920, 1745, 1680, 1460, 1390, 1255, 755, 740; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.05 (br s, 4 H), 3.11 (s, 6 H), 3.01 (br s, 4 H), 2.02–1.50 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 152.83, 56.41, 45.86, 35.14, 26.46, 25.40, 17.27; MS m/z (M^+) calcd 410.1702, obsd 410.1687.

Anal. Calcd for $C_{20}H_{22}H_6O_4$: C, 58.53; H, 5.40. Found: C, 57.92; H, 5.53.

MTAD Addition to 5. A solution of **5** (45 mg, 0.25 mmol) in dry dichloromethane (2.5 mL) was treated dropwise with a solution of MTAD (1.0 mmol) in the same solvent (2.5 mL). The red color of the dienophile was instantaneously consumed as it came into contact with the hexaene. The solvent was evaporated and the solid residue was recrystallized from ethyl acetate to give 48 mg of **49**. Chromatography of the mother liquor on silica gel returned an additional 22 mg of **49** (total yield of 69%), a colorless crystalline solid, mp 247 °C dec (from dichloromethane–pentane): IR (KBr, cm^{-1}) 3050, 3000, 2940, 2910, 1760, 1690, 1455, 1390, 1190, 1035, 775, 730; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.42 (dd, J = 3.3, 3.7 Hz, 2 H), 6.28 (dd, J = 3.4, 3.9 Hz, 2 H), 5.95 (dd, J = 2.8, 7.6 Hz, 2 H), 5.51 (dd, J = 2.8, 7.6 Hz, 2 H), 4.68 (dd, J = 3.4, 3.9 Hz, 2 H), 4.57 (dd, J = 3.3, 3.7 Hz, 2 H), 2.97 (s, 3 H), 2.95 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 158.04, 156.60, 129.53, 126.62, 125.19, 124.89, 56.96, 53.71, 46.52, 25.46; MS m/z (M^+ – $C_7H_7N_3O_2$) calcd 241.0851, obsd 241.0883.

Anal. Calcd for $C_{20}H_{18}N_6O_4 \cdot 0.3CH_2Cl_2$: C, 56.46; H, 4.21. Found: C, 56.53; H, 4.57.

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Supplementary Material Available: Tables of final fractional coordinates, thermal parameters, and least-squares planes (5 pages); observed/calculated structure factors for **5** (1 page). Ordering information is given on any current masthead page.

A Synthesis of Polycyclic Aromatic Compounds by the $Ca(OAc)_2$-Induced Aromatization of Polyoxoalkanedioates Generated from Diesters and Acetoacetate Dianion

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The dual-Claisen condensation of diesters with acetoacetate dianion generated tetraoxoalkanedioates, whose aromatization by $Ca(OAc)_2$-promoted intramolecular condensation constructed two carbocyclic rings containing phenol part. The reactions converted glutarates to bicyclic phenols and homophthalates to 1,9-dihydroxyanthracenes. The latters were air-oxidized to anthraquinones in the presence of K_2CO_3. The regiochemistry of the arene synthesis was studied. As the products of this synthesis also were glutarates, further extension of the aromatic ring system was carried out. Pentacenequinones were synthesized from anthracenes, while anthraquinones gave naphthacenequinones. The reactions are related to the biosynthesis of polycyclic aromatic compounds, and arenes obtained are useful intermediates in the natural products synthesis. A formal synthesis of aklavinone was achieved.

A variety of aromatic natural products are biosynthesized from simple acids such as acetic acid, propionic acid, and so on. It is considered that a series of Claisen condensations gives chain molecules with β-polyketone functionalities (polyketides), whose intramolecular condensation and enolization construct aromatic nuclei such as naphthalene, anthracene, naphthacene, and benz[a]anthracene.[1]

From the synthetic standpoint of view, the use of polyketides is quite attractive, since they give polyfunctionalized polycyclic aromatic compounds structurally related to the natural products. Generally, functionalization of polycyclic arenes at a particular position is not an easy

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