

Flattening of the Cyclooctatetraene Ring by Annulation

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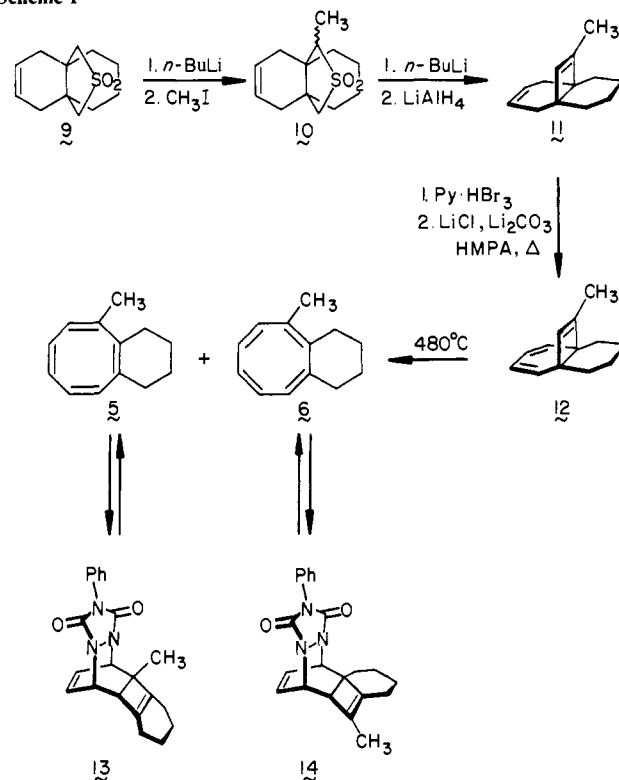
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Abstract: 1,2-Tetramethylene- (**5**) and 1,2-trimethylene-3-methylcyclooctatetraene (**4**) are prepared and shown by chemical methods to possess the specific arrangement of double bonds implied by the names. Despite the very close structural similarities of these hydrocarbons, their 500-MHz ¹H NMR spectra are not at all comparable, and while **5** enters into Diels-Alder cycloaddition with *N*-phenyltriazolinedione, **4** does not. Detailed ¹H NMR analyses and molecular mechanics calculations have revealed **4** to possess a less folded tub-shaped eight-membered ring than **5** and the cyclobutane-fused lower homologue to have a still more shallow low-energy conformation. The structural features of a number of crystalline cyclooctatetraenes are discussed and appropriate comparisons made.

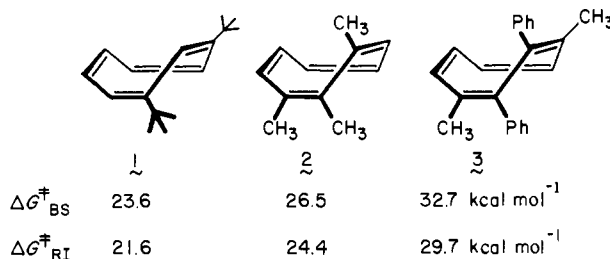
Following characterization of ground-state cyclooctatetraene as a *D*_{2d} tub-shaped molecule² came demonstration that dynamical ring inversion (RI) and bond shifting (BS) in this system can be quantified by NMR methods.³⁻⁵ The first of these processes corresponds directly to conformational mobility, presumably involves passage through a planar alternate *D*_{4h} transition state (localized double bonds), and requires approximately 10 kcal mol⁻¹ of activation energy.⁶ The barrier to bond shifting lies ca. 4 kcal mol⁻¹ higher. Because such factors as resonance destabilization (antiaromaticity),⁷ angle strain, van der Waals repulsions,⁸ and related phenomena⁹ require detailed consideration in the latter instance, the involvement of a planar *D*_{8h} species with equivalent CC bonds has yet to be proven and is presently viewed as speculative.^{9,10}

In earlier work, we have shown that judicious placement of alkyl and/or aryl groups on the cyclooctatetraene frame as in **1-3** introduces an element of chirality while simultaneously impeding both pathways adequately to allow for independent isolation of these hydrocarbons in optically active condition.¹¹⁻¹⁵ The onset of RI or BS now results conveniently in enantiomerization.

Scheme I

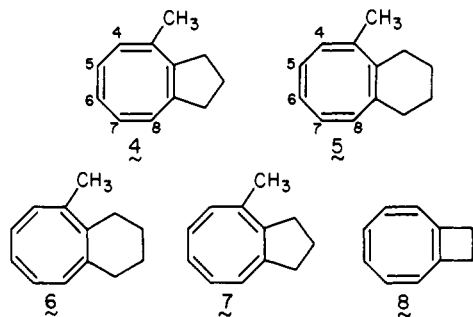


Dissection of the two racemization rate constants was realized by appropriate deuterium labeling where necessary.



Pursuant to our current goal of analyzing the consequences of ring-size effects on BS and RI,¹⁵ the annulated cyclooctatetraenes **4-6** were prepared in racemic form. The strikingly different ¹H NMR spectra of **4** and **5** signaled to us that appreciable modulation of the extent of flattening within the medium-sized ring was being directly observed. Described herein is a detailed spectroscopic analysis of **4** and **5**, together with supporting chemical and computational studies of the structures of these polyolefins as well as **6**. Comments relating to **7**, the bond-shift

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isomer of **4**, and to **8**, a known lower homologue in the series defined by **4** and **5**,¹⁶ are also included where pertinent for comparison purposes.

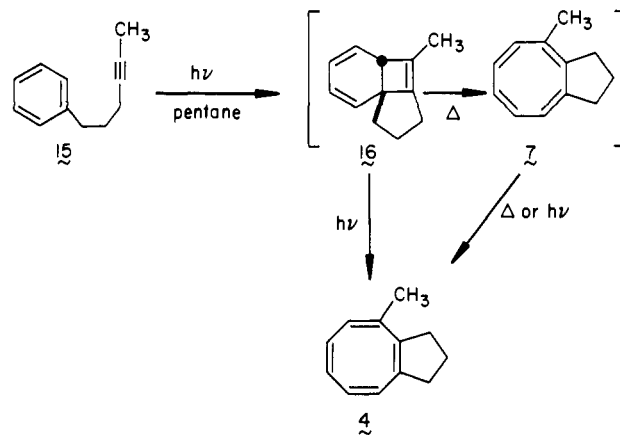
Chemistry

Synthetic access to **5** and **6** began by monomethylation of sulfone **9**.¹⁷ Generation of the anion by treatment with 1 equiv of *n*-butyllithium, addition of excess methyl iodide, and crystallization of the product gave **10**¹⁸ in almost quantitative yield (Scheme I). Reductive ring contraction-elimination of the corresponding α -sulfonyl carbanion with lithium aluminum hydride in refluxing dioxane¹⁹ afforded diene **11**. Oxidation of **11** to **12** by a regioselective bromination-dehydrobromination sequence was effected as before.¹⁸ Gas-phase pyrolysis²⁰ of **12** at 480 °C resulted in initial conversion to a mixture of **5** and **6**. On standing at room temperature, that component due to **6** was observed to isomerize gradually to **5**, thereby signaling the greater thermodynamic stability of the latter bond-shift isomer. To achieve the isolation of both **5** and **6** in isomerically pure condition, cycloaddition with *N*-phenyltriazolinedione was effected, and the resulting urazoles **13** and **14**¹⁸ were separated chromatographically. Subsequent hydrolysis-oxidation of the purified adducts readily returned the two cyclooctatetraenes as mutually uncontaminated valence isomers.

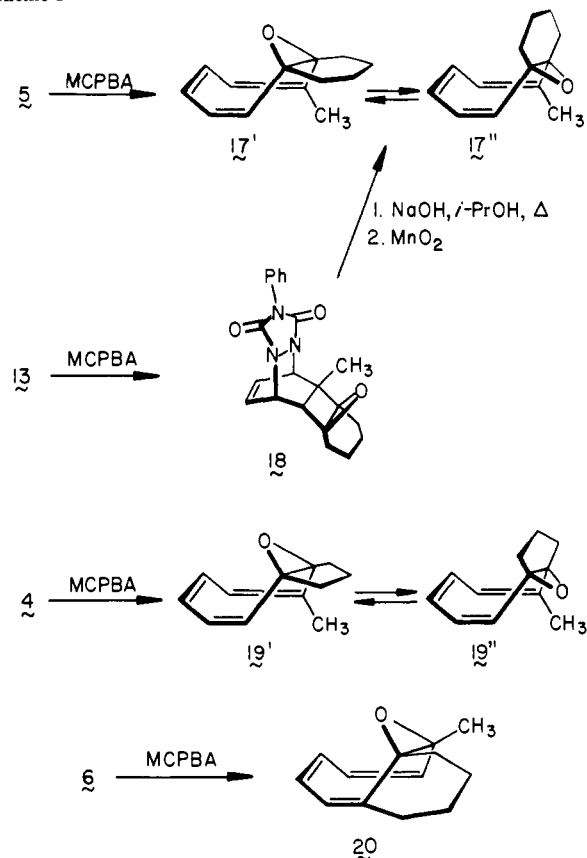
In an adaptation of the methodology developed by Lippke, Ferree, and Morrison,²¹ 6-phenyl-2-hexyne (**15**) was irradiated in deoxygenated hexane solution to produce **4** (Scheme II). Evidently, the initial intramolecular [2 + 2] photocycloaddition to give **16** is followed by rapid disrotatory (thermal) opening of its cyclohexadiene subunit. Although this process necessarily delivers **7**, this particular isomer is not observed. The ensuing bond shift to give ultimately **4** may occur thermally or perhaps as a consequence of further light absorption.¹¹⁻¹⁴ The possibility that **16** may experience direct excited-state conversion to **4** by disrotatory cyclobutene ring cleavage also cannot be discounted. The original authors were not able to make proper distinction between valence tautomers **4** and **7**.²¹ Proof that **4** does greatly dominate this equilibrium is given below.

The complications in structural assignment arise because the ¹H NMR spectra of these annulated cyclooctatetraenes are not unequivocally distinctive. As a consequence, a chemical protocol was developed to achieve unambiguous structural confirmation. In this connection, the peracid oxidation of **5** was found to give a single epoxide. That the oxygen atom had been inserted without prior bond shifting was established by ¹H and ¹³C NMR analyses (see Experimental Section) and by an independent synthetic route involving epoxidation of **13** to give **18** followed by hydrolytic removal of the urazole group (Scheme III).

Scheme II



Scheme III



When the cyclopentannulated cyclooctatetraene **4** was comparably epoxidized, a product was obtained whose ¹H NMR spectrum was very closely similar to that of **17**. Its assignment as **19** follows logically, especially in light of the fact that epoxide **20**, which arises exclusively upon analogous treatment of **6**, differs appreciably in its spectral properties. The question of the preferred conformation of epoxides **17** and **19** is deferred to a later section.

Spectroscopy

The downfield sector of the proton NMR spectrum of **5** proved readily amenable to interpretation, as this region is composed of two AB quartets along with a single broad resonance at δ 5.47. Noteworthy, the spectrum is complicated by long-range couplings between all of the vinylic protons as well as by couplings to the methyl group and at least one of the methylene groups of the cyclohexyl ring. A two-dimensional COSY spectrum²² and a 2-D *J*-resolved spectrum²³ were recorded to determine the proton

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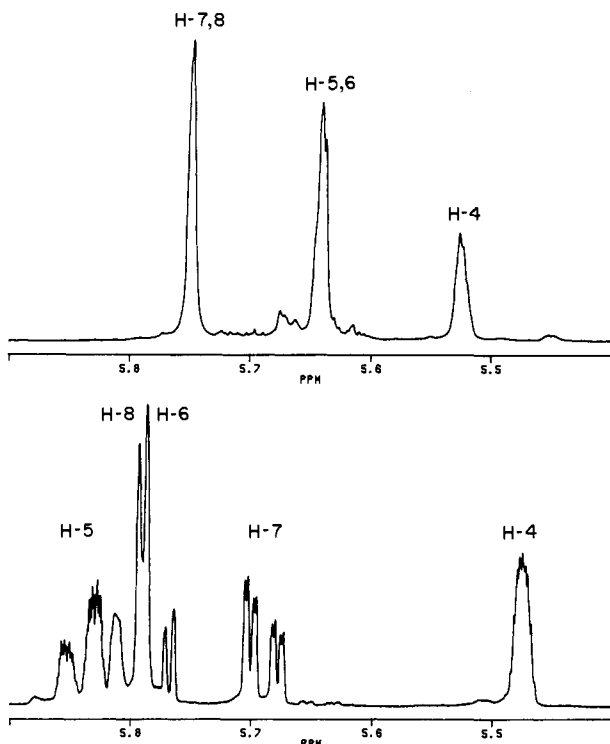
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Table I. Partial Listing of the Chemical Shifts (^1H and ^{13}C NMR; δ) and Coupling Constants (J) for **4** and **5** (CDCl_3 Solution)

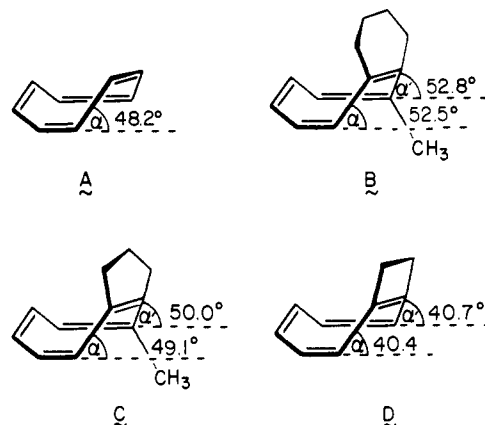
compd	atom	atom	atom	J , Hz ^a
4	C4	126.0	H4	5.52
	C5	131.0	H5	5.63
	C6	132.4	H6	5.64
	C7	130.4	H7	5.76
	C8	131.7	H8	5.76
				$J_{4,5} = 2.6$
				$J_{5,6} = 11.3$
5	C4	123.5	H4	5.47
	C5	136.2	H5	5.84
	C6	129.8	H6	5.78
	C7	127.7	H7	5.68
	C8	131.8	H8	5.80
				$J_{4,5} = 3.7$
				$J_{5,6} = 11.3$
			$J_{6,7} = 3.6$	
			$J_{7,8} = 11.8$	

^aOnly the coupling to the neighboring proton is reported. ^bProtons 7 and 8 differ by only 1 Hz (determined from the 2-D carbon-proton chemical shift correlation) and thus do not show any proton-proton coupling as they are almost equivalent. As a consequence, the assignments to C7 and C8 could be reversed in this instance.

**Figure 1.** Expanded scale 500-MHz ^1H NMR spectra of **4** (top) and **5** (bottom) recorded in CDCl_3 solution.

connectivities and the major coupling constants, respectively. In addition, an NOE difference experiment, performed by irradiating the methyl groups, established the methyl substituent to be vicinal to the highest field olefinic proton. It is important to note that the proton at δ 5.47 does not exhibit a large vicinal olefinic coupling; an interaction of this type would be observed if the compound were the bond-shift isomer **6**. To complete the analysis of this cyclooctatetraene, its ^{13}C shifts were correlated with the ^1H shifts by means of a 2-D carbon-proton chemical shift correlation experiment.²⁴ The results of these combined experiments are summarized in Table I.

Visual comparison of the spectra recorded for **4** and **5** (Figure 1) discloses a difference so great that these hydrocarbons hardly appear to be structurally related. The vinylic region of **4** is composed of three broad signals at δ 5.76 (2 H), 5.63 (2 H), and 5.52 (1 H). A decoupling experiment involving double irradiation of the methyl group in tandem with an NOE experiment in which the CH_3 was again irradiated established the proton at δ 5.52 to be vicinal to it. Again it is to be noted that no larger olefinic coupling was observed to this proton, thereby showing that we

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are not dealing with isomer **7**. As with **5**, COSY, 2-D J -resolved, and carbon-proton chemical shift correlation experiments were performed to enable definition of the coupling constants and chemical shifts (Table I). Usefully, it proved possible to resolve a 1-Hz shift difference between protons 7 and 8 during performance of the carbon-proton chemical shift correlation.

Thus, it can be seen that the downsize progression from cyclohexyl to cyclopentyl annulation serves to flatten the cyclooctatetraene ring in a manner that induces a reduction in the coupling constants between discrete pairs of olefinic protons (3.7 and 3.6 to 2.6 and 2.8 Hz) and causes the two sets of olefinic protons H5-H6 and H7-H8 to become almost equivalent. At least one caveat remains. The COT rings in **4** and **5** certainly are subject to dynamic twisting and other vibrational effects. The amplitudes of these vibrational motions are important and certainly affect the here discussed J values in an unpredictable way.

Molecular Mechanics. Comparison with Crystal Structure Data

The extent of puckering with a tub-shaped cyclooctatetraene can be defined by specifying the magnitude of the external dihedral angles. For simplicity, the present discussion will focus only on two angles as illustrated in Figure 2. In an effort to arrive at a more quantified definition of the geometry differences between **4** and **5**, molecular mechanics calculations were performed. Through use of Still's program MODEL²⁵ (an enhanced graphics interactive version of Allinger's MM2 program²⁶), multiple energy minimizations were made and refined. For the present unsubstituted cyclooctatetraene (A, Figure 2), the calculated α value is 48.2°.

Annulation with a six-membered ring as in **5** has the effect of increasing both α and α' by approximately 4° (see B in Figure 2). This enhancement in the extent of bending is likely the natural consequences of 1,2,3-trialkyl substitution and constitutes a useful reference point. Good agreement with the preceding spectroscopic analysis was realized for **4**, which was found to be somewhat flatter (ca. 3°) on both corners (see C, Figure 2).

The downfield segment of the 100-MHz NMR spectrum of **8**, a substance particularly prone to polymerization, has been described as a complex multiplet at δ 5.62-5.38.²⁸ The energy-minimized structure of this hydrocarbon (D, Figure 2) shows α and α' to drop to low values of 40.4° and 40.7°. Thus, it is clear that as the 1,2-annulated ring is reduced in size, the

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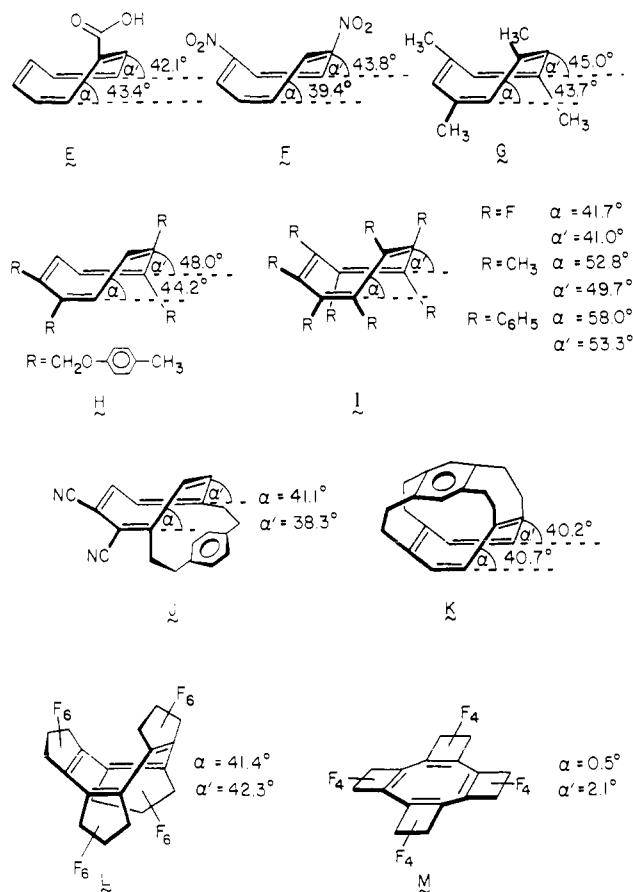


Figure 3. Conformational folding of several cyclooctatetraene derivatives as determined by X-ray analysis.²⁹⁻³⁹

eight-membered cyclooctatetraene ring becomes increasingly planarized.

Relevant to this point, several crystalline cyclooctatetraenes have, over the years, been submitted to X-ray analysis. The differing degrees of ring puckering observed for these molecules are illustrated graphically in Figure 3. Cyclooctatetraene-carboxylic acid (E),²⁹ the 1,4-dinitro derivative (F),³⁰ and the 1,3,5,7-tetramethyl example (G)³¹ exhibit dihedral angles between 39° and 45° . The 1,4,5,8-tetrasubstitution plan found in H³² expectedly increases the magnitudes of α and α' relative to G as a direct result of the paired enhanced proximity of the R groups. The data for the three octasubstituted derivatives I show a nicely defined trend. The small fluorine substituents³³ do not exert meaningful steric effects, and α (41.7°) and α' (41.0°) are small as a result. Considerable external angle widening (8.7 – 11.0°) occurs when the R groups become methyl.³⁴ A further increase in steric bulk as found in the octaphenyl example³⁵ leads to the greatest conformational folding of all with $\alpha = 58.0^\circ$ and $\alpha' = 53.3^\circ$.

The paracyclophane derivatives J³⁶ and K³⁷ show no unusual features. However, the contrast between the perfluorinated tetraannulated systems L³⁸ and M³⁹ is especially striking. While

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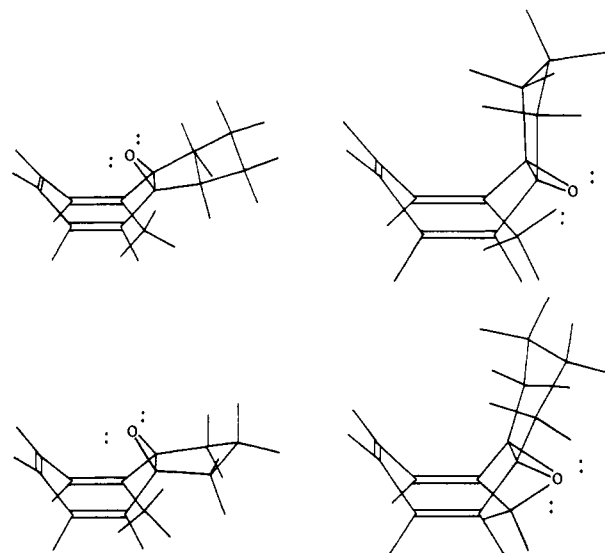
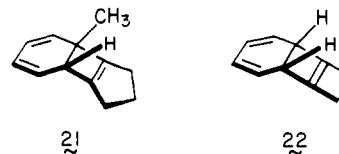


Figure 4. Energy-minimized conformations of 17' (top left), 17'' (top right), 19' (bottom left), and 19'' (bottom right).

the tetracyclopentane compound exhibits conformational properties quite similar to the other cyclooctatetraenes, its tetracyclobutane counterpart is hardly buckled at all and, in fact, has an essential planar eight-membered ring. The combined effect of four annulated cyclobutane rings is so dramatic that the possible consequences of two- to fourfold lateral cyclopropane fusion have recently been briefly commented on.⁹

Differing Cycloaddition Behavior. In addition to spectroscopic manifestations of the planarization phenomenon, reactivity differences between 4 and 5 have also been discerned. For example, whereas the cyclohexane-fused [8]annulene enters into Diels-Alder cycloaddition with *N*-phenyltriazolinedione to give 13, cyclopentannulation introduces considerable resistance to comparable [4 + 2] capture, even under reasonably forcing conditions. Evidently, the strain energy associated with gaining access to valence tautomer 21 is too large to overcome. The situation is, of course, further exacerbated in 22, the bicyclic isomer of 8.



Other differences in chemical reactivity are likely to surface as these systems are studied in greater detail.

Conformational Analysis of Epoxides 17 and 19. Molecular mechanics calculations show that the best structures for 17 and 19 have the medium-sized ring in a tub conformation (Figure 4). The question arises as to whether the torsional rigidity imposed by the propellane character of these molecules can best accommodate the oxirane oxygen in the concavity of the cyclooctatriene ring and the cycloalkyl unit on the convex surface as in 17' and 19' or vice-versa (see 17'' and 19''). From the bond angle patterns emanating from the oxirane carbon atoms, it can be seen at a glance that an "inside" oxygen in the primed conformational isomers is projected deeper into the confines of the flanking eight-membered tub than is the cyclohexane or cyclopentane part structure in the doubly primed series (Figure 4). With the respective energy minima reached, 17'' at $72.61 \text{ kcal mol}^{-1}$ is found to be approximately 10 kcal more stable than 17' ($82.79 \text{ kcal mol}^{-1}$). The energy difference associated with the conformers of 19 is smaller (7 kcal mol^{-1}), although also favoring 19'' ($92.51 \text{ kcal mol}^{-1}$) over 19' ($85.36 \text{ kcal mol}^{-1}$).

The preference of the smaller oxygen atom for the exocyclic orientation derives simply from the fact that the geometric con-

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straints enforced by the three-membered ring cause its constituent atoms (here especially the O) to adopt bonding angles appreciably different from groups appended thereto.

Experimental Section

11-Methyl-12-thia[4.4.3]propell-3-ene 12,12-Dioxide (10). To a cold (-78°C), magnetically stirred solution of **9**¹⁷ (5.11 g, 22.6 mmol) in 80 mL of anhydrous tetrahydrofuran was added a solution of *n*-butyllithium (22.6 mol) in hexane. The reaction mixture was stirred for 10 min and treated in one portion with methyl iodide (6.84 g, 48.2 mmol). Once the contents had warmed to room temperature, water was added and the product was extracted into dichloromethane. The organic phase was washed with water, dried, and evaporated to give **10** in quantitative yield. The sulfone was recrystallized from ethyl acetate–petroleum ether (mp $83\text{--}85^{\circ}\text{C}$ [lit.¹⁸ mp $83\text{--}85^{\circ}\text{C}$]) prior to use in the next step.

11-Methyl[4.4.2]propella-2,4,11-triene (12). A solution of **10** (10.0 g, 41.6 mmol) in 110 mL of dry dioxane was treated with 46.5 mmol of *n*-butyllithium in hexane, and this solution was transferred via cannula to a stirred and refluxing suspension of lithium aluminum hydride (208 mmol) in dry dioxane (600 mL) during 25 min. The reaction mixture was heated at reflux for 21 h and worked up as previously described.¹⁸ Chromatography of the product mixture on silica gel gave 1.42 g (19.5%) of **11** and 4.0 g (46.1%) of the sulfide, which was routinely reoxidized for resubmission to the reductive ring contraction–elimination.

The conversion of **11** to **12** was achieved in 94% overall yield by following the procedure earlier described.¹⁸

Thermal Isomerization of 12 and Conversion to Adducts 13 and 14. A 2.2-g sample of **12** was passed through a quartz tube packed with quartz chips that was heated to 480°C under a slow stream of nitrogen. The total elapsed reaction time was 2.5 h. The resulting dark brown oil was passed down a short column of silica gel (elution with petroleum ether), and the eluate was evaporated to give 2.0 g (91%) of **5** and **6** as a colorless oil.

This mixture of cyclooctatetraenes (1.89 g, 11.0 mmol) was dissolved in ethyl acetate (48 mL, distilled from CaH_2), treated with freshly sublimed *N*-phenyltriazolinedione (2.3 g, mmol), and heated at reflux for 2 h. The cooled solution was concentrated, and the residue was subjected to HPLC on silica gel involving six recycles (elution with 20% ethyl acetate in petroleum ether). There was isolated 560 mg (15%) of **13** and 128 mg (3.4%) of **14**. Both urazoles exhibited melting points identical with those reported earlier.¹⁸

For 13: ¹H NMR (300 MHz, CDCl_3) δ 7.48–7.31 (m, 5 H), 6.33–6.28 (m, 1 H), 6.14–6.08 (m, 1 H), 5.02–4.98 (m, 1 H), 4.65–4.62 (m, 1 H), 2.69 (br s, 1 H), 1.94–1.85 (br m, 2 H), 1.70–1.54 (br m, 6 H), 1.46 (s, 3 H).

For 14: ¹H NMR (300 MHz, CDCl_3) δ 7.47–7.26 (m, 5 H), 6.31–6.25 (m, 1 H), 6.17–6.12 (m, 1 H), 5.02–4.98 (m, 1 H), 4.74–4.71 (m, 1 H), 2.66 (br s, 1 H), 2.30–2.22 (br m, 2 H), 1.89–1.76 (br m, 2 H), 1.63–1.21 (series of m, 4 H), 1.53 (t, $J = 0.75$ Hz, 3 H).

Hydrolysis–Oxidation of Urazoles 13 and 14. A solution of **13** (46.6 mg, 0.13 mmol) and sodium hydroxide (59 mg, 1.5 mmol) in 5 mL of isopropyl alcohol was heated at reflux for 2.5 h. The cooled mixture was acidified to pH 1 with 3 N hydrochloric acid (ca. 5 mL) and then brought to pH 9 by addition of 3 N ammonium hydroxide (7 mL). Pentane (5 mL) and activated manganese dioxide (115 mg) were next introduced, and stirring was effected for 30 min. The hydrocarbon product was extracted into pentane, washed with water, dried, and carefully concentrated. Chromatography on silica gel (elution with pentane) afforded 16 mg (70%) of **5** as a pale-yellow oil (for ¹H NMR, see Figure 1): ¹³C NMR (75 MHz, CDCl_3) ppm 144.90, 136.30, 131.76, 131.67, 129.87, 127.79, 126.86, 123.45, 29.90, 28.67, 22.95, 22.75, 22.23.

A 30-mg (0.09-mmol) sample of **14** was treated comparably (38 mg of sodium hydroxide in 4 mL of isopropyl alcohol, reflux 2.5 h). Following acidification, rebaseification, and oxidation, there was isolated 15 mg (100%) of **6** as a pale-yellow oil after silica gel chromatography: ¹H NMR (300 MHz, CDCl_3) δ 5.89–5.75 (m, 3 H), 5.72–5.61 (m, 1 H), 5.51 (m, 1 H), 2.79–2.75 (m, 1 H), 2.42 (m, 1 H), 2.24–2.01 (m, 1 H), 1.69 (s, 3 H), 1.82–1.32 (series of m, 5 H).

Photocyclization of 6-Phenyl-2-hexyne.²¹ A solution of **15** (5.57 g) in hexane (1.5 L) was deoxygenated by bubbling argon through it for 1

h and irradiating it with a bank of 2537-Å lamps housed in a Rayonet reactor for 14 h. Evaporation of the solvent left a yellow brown oil, which was chromatographed on silica gel (elution with petroleum ether) to remove unreacted starting acetylene (ca. 4.5 g). The nonaromatic portion was purified by vapor-phase chromatography at 200°C to give 110 mg (2%) of **4** as a pale-yellow oil (for ¹H NMR, see Figure 1): ¹³C NMR (75 MHz, CDCl_3) ppm 142.74, 140.08, 139.02, 132.36, 131.60, 130.92, 130.38, 126.11, 37.08, 25.71, 22.68, 22.37.

Epoxidation of 5. A solution of **5** (20 mg, 0.12 mmol) in dichloromethane (2 mL) was cooled to 0°C and treated sequentially with 33 mg of sodium bicarbonate and 23 mg (0.13 mmol) of *m*-chloroperbenzoic acid dissolved in 2 mL of the same solvent. The mixture was stored overnight in a refrigerator, diluted with dichloromethane, and washed with saturated sodium bicarbonate solution and water prior to drying. Concentration left an oil (25 mg), which was subjected to MPLC on silica gel (elution with 4% ethyl acetate in petroleum ether). The colorless oily epoxide **17** was isolated: 13 mg, 59%; ¹H NMR (300 MHz, CDCl_3) δ 6.04 (d, $J = 11.4$ Hz, 1 H), 5.91 (m, 2 H), 5.71 (dd, $J = 11.5$, 2.7 Hz, 1 H), 5.55 (m, 1 H), 2.12–1.86 (m, 2 H), 1.90 (s, 3 H), 1.61–1.39 (m, 4 H), 1.25–1.17 (m, 2 H); ¹³C NMR (75 MHz, CDCl_3) ppm 141.59, 132.60, 127.10, 125.73, 125.09, 120.79, 66.88, 65.31, 30.88, 29.72, 20.47, 20.00, 19.27; MS, m/z (M^+) calcd 188.1201, obsd 188.1215.

Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{O}$: C, 82.94; H, 8.57. Found: C, 82.94; H, 8.61.

Epoxidation of 13. A solution of **13** (30 mg, 0.09 mmol) in 4 mL of dichloromethane was treated with 25 mg of sodium bicarbonate and cooled to 0°C . A solution of *m*-chloroperbenzoic acid (25 mg, 0.14 mmol) in 3 mL of the same solvent was added, and the reaction mixture was allowed to warm to room temperature where it was stirred for 18 h. Workup in the prescribed manner afforded 33 mg (99%) of **18** as a colorless solid: mp $218.5\text{--}219^{\circ}\text{C}$ (from ethyl acetate/hexane): ¹H NMR (300 MHz, CDCl_3) δ 7.46–7.23 (m, 5 H), 6.59–6.54 (m, 1 H), 6.48–6.44 (m, 1 H), 5.02–4.98 (m, 1 H), 4.72 (m, 1 H), 2.46 (d, $J = 4.9$ Hz, 1 H), 1.86 (m, 2 H), 1.59–1.18 (series of m, 6 H), 1.32 (s, 3 H); ¹³C NMR (75 MHz, CDCl_3) ppm 156.68, 156.66, 131.38, 129.47, 129.01, 128.19, 127.99, 125.42, 62.30, 58.89, 57.04, 52.00, 49.41, 21.27, 21.09, 19.17, 18.77, 16.17; MS, m/z (M^+) calcd 363.1583, obsd 363.1618.

Anal. Calcd for $\text{C}_{21}\text{H}_{21}\text{N}_3\text{O}_3$: C, 69.41; H, 5.82. Found: C, 69.32; H, 5.90.

Hydrolysis–Oxidation of 18. A solution of **18** (33 mg, 0.09 mmol) and sodium hydroxide (40 mg, 1.0 mmol) in 4 mL of isopropyl alcohol and 6 mL of tetrahydrofuran was heated at reflux for 2.5 h, cooled to room temperature, acidified with acetic acid, and finally neutralized with 3 N ammonium hydroxide. At this point, activated manganese dioxide (80 mg) and pentane (5 mL) were introduced, and the mixture was stirred at 25°C for 30 min. Workup in the manner described earlier afforded 5.0 mg (31%) of an epoxide identical in all respects with **17**.

Epoxidation of 4. A 48-mg sample of **4** was epoxidized in a manner paralleling that described for **5**. MPLC purification of the reaction mixture (silica gel, elution with 4% ethyl acetate in petroleum ether) furnished 23 mg (44%) of **19** as a colorless oil: ¹H NMR (300 MHz, CDCl_3) δ 6.02 (dd, $J = 11.2$, 0.6 Hz, 1 H), 5.84 (m, 1 H), 5.83 (m, 2 H), 5.69 (m, 1 H), 2.14–1.92 (m, 2 H), 1.94 (s, 3 H), 1.57–1.42 (m, 4 H); ¹³C NMR (75 MHz, CDCl_3) ppm 136.32, 127.71, 127.27, 127.16, 125.62, 122.97, 72.68, 70.92, 31.84, 30.75, 20.37, 19.44; MS, m/z (M^+) calcd 174.1045, obsd 174.1047.

Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{O}$: C, 82.72; H, 8.10. Found: C, 82.52; H, 8.19.

Epoxidation of 6. A 9-mg sample of **6** was epoxidized under the buffered conditions detailed for **5**. An identical workup afforded 4 mg (40%) of **20** as a colorless oil: ¹H NMR (300 MHz, CDCl_3) δ 6.03 (d, $J = 11.6$ Hz, 1 H), 5.90 (m, 2 H), 5.78 (m, 1 H), 5.66 (m, 1 H), 2.56 (m, 1 H), 2.26 (m, 1 H), 2.04–1.49 (m, 6 H), 1.27 (s, 3 H); MS, m/z (M^+) calcd 188.1201, obsd 188.1208.

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