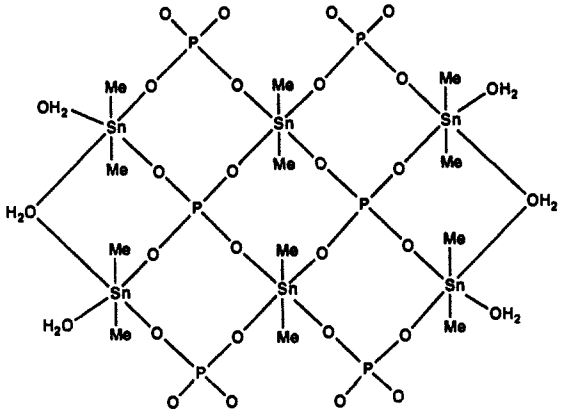
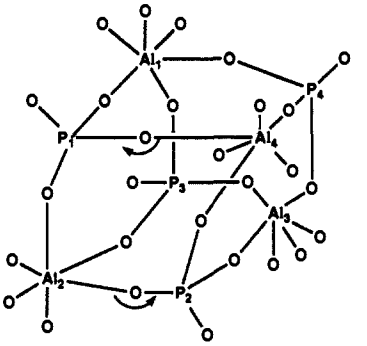
of **1** and **2** with other oxo- and hydroxo-bridged tin clusters[1b,6-9] does not assist in deciding between the two possibilities for **2**.

There is a close relationship between the apparently dissimilar frameworks indicated for **1** and **2**, which can be viewed, before assembly, as tautomers. The interconversion of the framework of **1** to the framework of **2** is illustrated in Chart III. On each side of the molecule of **1**, the hydrogen bond is broken followed by the formation of a bond between O42 and Sn1 with a simultaneous rupture of the bond between Sn1 and O31. The hydrogen atom of the bridging hydroxyl group could simultaneously be transferred to O31, leaving in **2** a bridging oxygen atom. However, it remains to uniquely establish the nature of these bridging positions in **2**.

Structural Analogies. Phosphate ligands appear in a unique arrangement in the cage cluster **1** coordinated to tin atoms in mono-, bi-, and tridentate fashion, whereas in **2** only bicoordination is observed. A complex, $(Me_2Sn)_3(PO_4)_2{\cdot}8H_2O$,[18] exhibiting hexacoordination around a Me_2Sn moiety, shows bi- and tetracoordination for phosphate ligands.



Structurally, more closely related to **1** is the aluminum phosphate, $[Al(PO_4)(HCl)(EtOH)_4]_4$,[19] made up of six eight-membered Al-O-P rings. The skeletal arrangement is shown:



Cleavage of the Al_4-O(P_1) and Al_2-O(P_2) bonds and formation of hydroxide bridges, Al_1-O(H)-Al_4 and Al_2-O(H)-Al_3, lead to a similar framework representation that is found for **1**.

Acknowledgment. The support of this research by the National Science Foundation (Grants CHE-8504737 and CHE-8819152), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and a Faculty Research Grant from the University of Massachusetts (to R.O.D.) is gratefully acknowledged.

Supplementary Material Available: Listings of atomic coordinates, anisotropic thermal parameters, additional bond lengths and angles, and hydrogen atom parameters (Tables S1-S4, respectively, for **1** and Tables S5-S8, respectively, for **2**) (22 pages); tables of calculated and observed structure factors (37 pages). Ordering information is given on any current masthead page.

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Synthesis and Dynamic Behavior of (1,5)Cyclooctatetraenophanes. Effect of Distal Atom Bridging on Racemization Rates and Electrochemical Reducibility

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Abstract: The [5]-, [6]-, [8]-, and [10](1,5)cyclooctatetraenophanes as well as non-C_2-symmetric methyl homologues of these 1,5-bridged [8]annulenes have been prepared conveniently via a route that holds promise of considerable generality. The scheme consists of applying the Cook-Weiss procedure to a cyclic α-diketone, transforming the carbonyl groups of the product into a pair of olefinic sites (with or without attachment of the methyl substituent), preparation of the bracketed semibullvalene via nickel carbonyl promoted cyclization of the doubly allylic dibromide, and finally flash vacuum pyrolysis of the semibullvalene. Cyclic voltammetric studies performed on the title compounds have quantified not only the standard electron-donating capacity of the pendant alkyl groups, but also the consequences of nonbonded steric interactions associated with maintaining a bridged structure as the cyclooctatetraene ring flattens. Microscale preparation of the dianion of **5d** permitted measurement of its ^{1}H NMR spectrum. Whereas **5b-d** reacted with (-)-*endo*-bornyltriazolinedione, the methyl congeners **15** and **21** did not. Chromatographic separation of the urazole diastereomers derived from **5c** and **5d** proved possible. Whereas hydrolysis-oxidation of individual adducts provided access to optically active **5c**, **5d** was invariably already racemized upon isolation. Thus, the latter experiences very rapid conversion to its enantiomer. The activation parameters for racemization within **5c** were determined, and it is argued that these reflect exclusively the energetic costs of bond shifting within its [8]annulene core.

Interest in the conformational dynamics of molecules carrying polymethylene chains has persisted for almost 50 years for many reasons.[1] The successful resolution of **1** by Lüttringhaus,[2] of **2** by Cram and Allinger[3] and by Blomquist,[4] and of **3** by Gerlach

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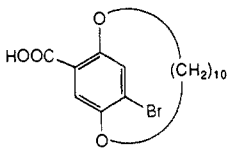
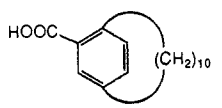
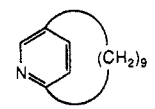


1



2

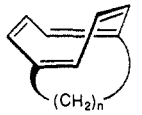


3

and Huber[5] set the stage for many ensuing studies of enantiomerism in the cyclophane area.[6,7] The structural properties of these molecules[8] hold fascination because of their relationship to bilayer systems, micelles, and synthetic polymers.[1] The advent of dynamic NMR spectroscopy has, in particular, facilitated the analysis of chain dynamics and allowed for direct observation of conformational processes along the loop.[9] Other investigations have been aimed at the systematic study of the effect of strained bridges on the properties of the annulated ring. The recent work dealing with the lower paracyclophanes by Bickelhaupt[10] and by Tobe,[11] the (2,7)troponophanes by Itô,[12] and the 3,6-annulated oxepins by Tochtermann[13] is exemplary.

In an earlier contribution,[14] we detailed the successful 1,4-bridging of an [8]annulene with a pentamethylene chain in a manner that delivered a chiral hydrocarbon and allowed for its resolution. Furthermore, **4** was shown to be the first cyclo-

4

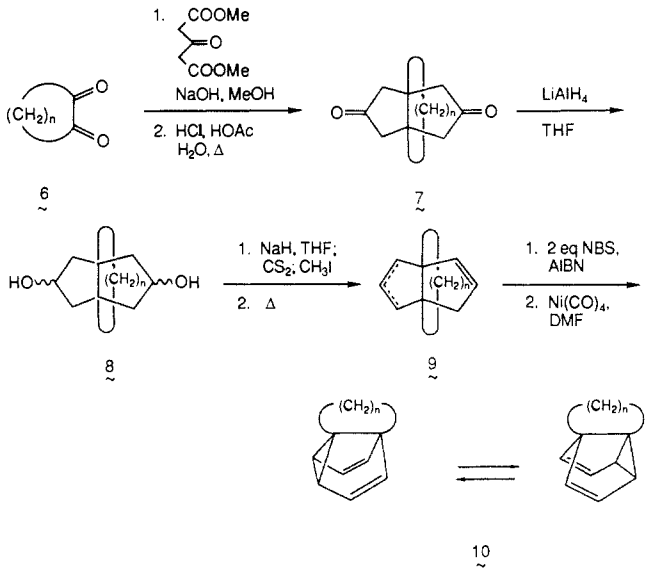


5

octatetraene incapable of dynamical conformational flexing in a way that would eventuate in the loss of optical activity. Defined by this extreme example of constrained belting is the important fact that bond shifting (BS) and ring inversion (RI) can indeed be simultaneously arrested.

A major long-range goal of our efforts in this area is clear-cut definition of the manner in which [8]annulenes undergo bond shifting. (1,4)Cyclooctatetraenophane **4** is too conformationally restricted to be useful for this purpose. At the other extreme, 1,2-annulated systems generally exhibit kinetic profiles so heavily dominated by accelerated ring-inversion rates that they also do not provide useful insight into this intriguing mechanistic issue.[15]

Scheme I



6 7 8 9

10

a, n = 5; b, n = 6; c, n = 8; d, n = 10

1,5-Bridged cyclooctatetraenes (**5**) can be expected to exhibit a strong interdependence between bridge size and bond-shifting energetics, in line with their close structural relationship to **1–3**. Since molecules of this class possess C_2 symmetry, they are intrinsically chiral and therefore resolvable in principle. The ease of racemization of **5** by means of ring inversion will be dictated by the ease with which either half of the cyclooctatetraene subunit can migrate from one surface of the polymethylene chain through the loop to the other. With chain lengths of modest size, this pathway will obviously be precluded for steric reasons. Since our expectation was that bond shifting within the [8]annulene core would hardly be subject to comparably high levels of steric congestion, we were convinced that k_{rac} would reflect pure k_{BS} at appropriate values of n in **5**.

Thus, we present here a detailed account[16] of the first synthetic entry to cyclooctatetraenes substituted at the most distant ring positions (C-1 and C-5) with hydrocarbon chains of varied length. This is followed by an analysis of the response of these molecules to electrochemical reduction. Reversible dianion generation under these conditions provides a direct, quantitative measure of the energy needed to flatten the polyunsaturated ring in each substrate. Finally, resolution of two of these hydrocarbons was accomplished and racemization rates have been measured in the octamethylene example. The weight of evidence provides for a convincing description of the transition-state geometry that intervenes during bond shifting, particularly when examined alongside findings derived from a detailed companion analysis of dynamic (1,3)-cyclooctatetraenophane behavior.[17]

Results

Synthesis of (1,5)Cyclooctatetraenophanes. Two of the most important preparative routes to cyclooctatetraenes are based on the principle of thermal structural reorganization within a $(CH)_8$ isomer.[18] Of these, the valence isomerization of bicyclo[4.2.0]octatrienes has been utilized the most extensively.[19] For the present purposes, however, the pyrolytic conversion of semibullvalenes[20] was considered more adaptable.[21] Application of

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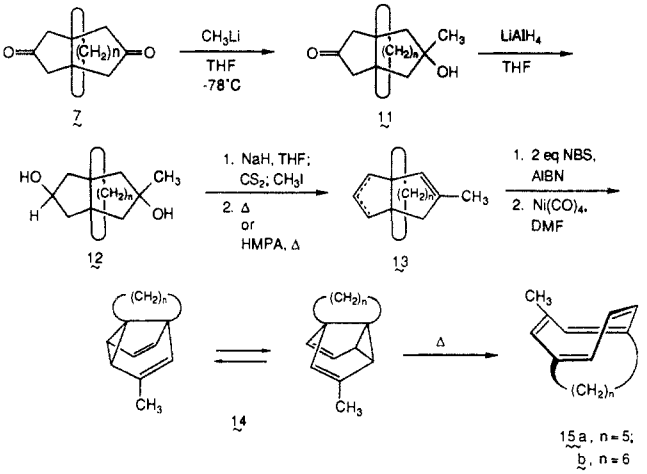
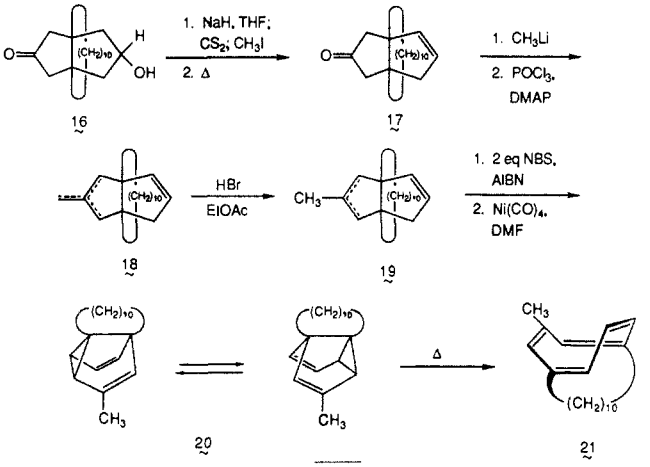
Scheme II



Scheme III



this strategy to the present needs reduces the problem to the synthesis of **10** and derivatives of this fluxional system. In view of existing reports dealing with the successful acquisition of semibullvalenes from precursor bicyclo[3.3.0]octadienes,[20c,22] this protocol was adapted to our purposes.

Condensation of cycloalkane-1,2-diones **6a–d**[23] with dimethyl 1,3-acetonedicarboxylate according to the Cook–Weiss procedure[23b] and subsequent hydrolysis in a refluxing mixture of hydrochloric and acetic acids afforded **7a**, **7c**, and the known diketones **7b**/**7d** (Scheme I).[23b] Lithium aluminum hydride reduction delivered the structurally related diols **8**, generally as a mixture of three diastereomers. Without separation, these intermediates were converted to the pair of regioisomeric dienes **9** by pyrolysis of the *neat* bis(xanthates) at *atmospheric* pressure.[24]

Although **9a–d** were responsive to 2-fold allylic bromination with *N*-bromosuccinimide in the presence of AIBN, subsequent attempts to effect intramolecular coupling with 0.4% lithium amalgam,[22,25] tri-*n*-butyltin hydride,[26] potassium or sodium iodide,[27] zinc,[28] zinc–copper couple,[29] and *tert*-butyllithium[30] were uniformly unsuccessful. Accordingly, recourse was made to extending the previously established[31] coupling of the regioisomeric allylic bromide mixtures with nickel tetracarbonyl. When these reactions were performed in dilute, dry, degassed dimethylformamide solution, semibullvalenes **10a–d** were produced very efficiently. The actual mechanism of this process is unclear. Since the initially colorless nickel carbonyl/dimethylformamide solutions gradually turn red as dibromide addition progresses, formation of a π-allylnickel complex is implicated.[31] Reductive elimination within these complexes could ultimately generate **10** and the observable green nickel bromide.

The high purity of **10a–d** following isolation indicated that subsequent structural isomerization had *not* occurred in the presence of the transition-metal catalyst.[32] As a consequence of the rapidity of Cope rearrangement within **10a–d** at room temperature, their ^1H and ^{13}C NMR spectra are fully time-averaged when determined under these conditions (see Experimental Section).[33]

When the flash-vacuum pyrolyses of these semibullvalenes were conducted at 500–521 °C and 0.1–0.01 Torr, the cyclooctatetraenophanes **5a–d** were formed cleanly (30% of **5a**; 71% of **5b**; 76% of **5c**; 82% of **5d**). The lower yield of **5a** is presumably a reflection of its high strain energy, air sensitivity, and polymerizability.

It will be recognized that placement of an R group at C-3 offsets the axial symmetry of **5**, makes available an internal NMR probe, and improves in principle the chances of optical resolution. Accordingly, our synthetic effort was expanded to include several 3-methyl derivatives as well. Scheme II illustrates the approach developed for acquiring **15a** and **15b**. Introduction of the substituent was accomplished early by reaction of **7a** and **7b** with methyllithium. Whereas keto alcohol **11a** was a single diastereomer, **11b** was a two-component mixture. All were subsequently reduced with lithium aluminum hydride and subjected directly to 2-fold dehydration. Whereas **12a** underwent Chugaev elimination without event, higher homologue **12b** did not respond at all well to this protocol. However, its smooth transformation into **13b** (88% yield) was accomplished by heating in HMPA to effect dehydration[34] and stirring with 48% hydrobromic acid in ethyl

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Table I. Reduction Potentials of Selected (1,5)Cyclooctatetraenophanes and Reference COT Derivatives in Anhydrous HMPA

compd	potential, V vs SCE[a] $E_{1/2}$ (1)	$E_{1/2}$ (2)
COT	−1.61	−1.92
1,5-Me_2COT	−1.94	−2.28
[10](1,5)COTphane (**5d**)	−2.01	−2.33
[8](1,5)COTphane (**5c**)	−2.08	−2.31
14-Me[10](1,5)COTphane (**21**)	−2.10	−2.39
[6](1,5)COTphane (**5b**)	−2.19[b]	
1,2,3-Me_3COT		−2.20[c]
1,2,3,4-Me_4COT		−2.54[c]

[a] The E values were obtained vs $Ag/AgClO_4$ and corrected to SCE by adding 0.36 V. The measurements were conducted in the presence of 0.1 M tetra-*n*-butylammonium perchlorate as the supporting electrolyte. [b] Irreversible one-electron reduction. [c] Both electrons are introduced concurrently at this potential.

acetate to induce double-bond isomerization. The remainder of the sequence parallels that earlier developed.

In order to accomplish the synthesis of **21** from **7d**, proper methylation had first to be realized. An alternative synthetic strategy was made necessary when it was recognized that direct reaction of this diketone with methyllithium or methylmagnesium bromide invariably gave rise to a statistical mixture of unreacted **7d**, **11** (n = 10), and dimethyl diol.[21] Eventually, it was determined that monoreduction to **16** could be accomplished expediently, as could conversion to enone **17** (Scheme III). In turn, this intermediate reacted cleanly with methyllithium. Heating the resulting tertiary alcohol in dimethyl sulfoxide,[35] acetic anhydride,[36] or phosphorus oxychloride resulted in the efficient formation of **18** as a regioisomeric mixture of three dienes (endocyclic:exocyclic ratio of 8.4:1). Because the exocyclic constituent was not serviceable to us, its isomerization to **19** was accomplished quantitatively by exposure of the mixture to a catalytic quantity of 48% hydrobromic acid in ethyl acetate solution at room temperature.[14]

Reaction of **19** with *N*-bromosuccinimide gave a complex mixture of regioisomeric allylic dibromides. Almost certainly, some bromination occurred at the methyl group; however, the actual extent is unknown. Without purification, the sensitive dibromide mixture was reacted with nickel carbonyl in dimethylformamide. Semibullvalene **20**, isolated in an overall yield of 51%, was transformed into **21** in 48% yield. In this instance, considerable charring was noted during the flash pyrolysis, presumably because of the reduced volatility of these molecules.

Reduction Studies. The electrochemical behavior of cyclooctatetraenes (COTs) is recognized to be dependent upon the level of alkyl substitution in the molecule. This is because the flattening of the nonplanar neutral molecule that accompanies reduction to the planar, dianionic species is inhibited by the nonbonded steric interactions of the substituents on the COT ring.[22a,37,38] As a consequence of this congestion, [8]annulenes that contain bulky or closely spaced groups tend to be more difficult to reduce than their less externally crowded counterparts.[22a,39-41]

When the substituents connect or bridge two of the COT ring carbons, as in the (1,5)cyclooctatetraenophanes, the effect of ordinary alkyl groups is compounded by the additional constraints of maintaining a bridged structure as the ring flattens during electron transfer. These effects can be quantified by determining reversible half-wave reduction potentials under standard conditions. As before, these data were measured in anhydrous HMPA solution in a vacuum-line cell designed to exclude moisture and oxygen completely.[42] In the presence of 0.1 M tetra-*n*-butylammonium perchlorate as background electrolyte,[43] three of the (1,5)-cyclooctatetraenophanes examined, viz. **5c**, **5d**, and **21**, underwent electrochemically reversible stepwise reduction to their dianions (Table I). A typical cyclic voltammogram is illustrated in Figure 1. Use is made of HMPA in order to extend the available reduction range since solvent breakdown in this case does not begin until approximately −3.2 V (vs Ag^0/Ag^+).[42]

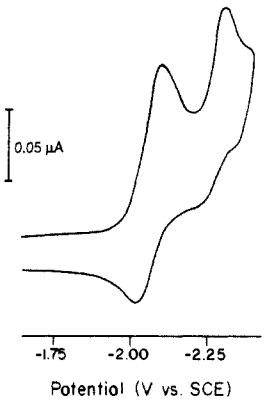


Figure 1. Cyclic voltammogram of [8](1,5)cyclooctatetraenophane (**5c**).

The electron-donating ability of a pair of methyl groups positioned 1,5 on the COT ring results in an approximate shift of 0.35 V to more negative potentials for both waves relative to the parent [8]annulene. The effect of 1,5-bridging by 10 and 8 methylene groups as in **5d** and **5c** is to displace the $E^{0\prime}$ values still further (Table I). Expectedly, the inductive and steric impact of yet a third alkyl group as in **21** is cumulative. Clearly, (1,5)cyclooctatetraenophanes bridged by $(CH_2)_8$ and $(CH_2)_{10}$ units have the capacity to experience flattening of their [8]annulene core when fully reduced. Furthermore, on the time frame of the electrochemical scans, the respective dianions are sufficiently stable that a substantial fraction of the radical anions and dianions undergo reoxidation to the neutral hydrocarbon.

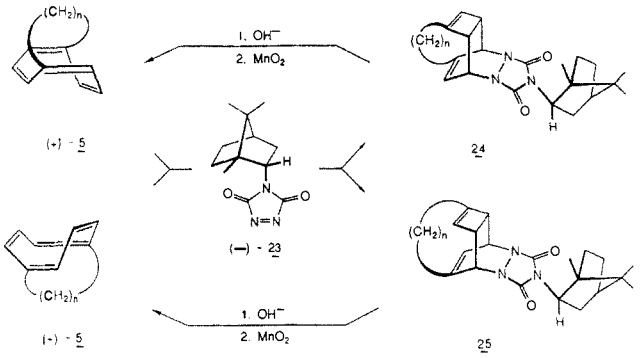
In no instance did the electrochemical response mirror that observed earlier for 1,2,3-Me_3COT and 1,2,3,4-Me_4COT. The substantial steric congestion present in these hydrocarbons causes both electrons to be introduced *simultaneously* at highly negative potentials and the electrochemical reactions to be irreversible.[40] As concerns **5b**, however, the addition of one electron produces a species sufficiently unstable that decomposition occurs rapidly. Cyclic voltammograms recorded at potentials much more negative than $E_1^{0\prime}$ show no additional reduction waves and the initial one-electron reduction is irreversible, even at scan rates approaching 450 mV s^{-1}.

The added shifts in the formal reduction potentials of **5c** and **5d** relative to those of 1,5-Me_2COT are attributed primarily to nonbonded steric interactions, both between segments of the bridge and between bridge atoms and the COT ring. These interactions increase in magnitude as the bridge length decreases because the constituent groups become more congested and the magnitude of the interactions is heightened. The [8]annulene ring experiences greater difficulty in becoming planar as a consequence.

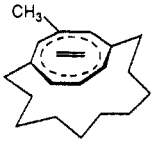
The success of the preceding experiments prompted macroscale reduction of **21** with potassium metal in freshly distilled ammonia and tetrahydrofuran. Once dianion formation was complete, the reaction mixture was transferred by cannula into an anhydrous mixture of iodine and pentane.[44] The cyclooctatetraenophane was recovered in 58% yield alongside some dihydro derivative, presumably the end product of proton transfer from adventitious moisture. Chemical reversibility was therefore also realized readily.

(35) Welch, S. C.; Prakasa Rao, A. S. C. *J. Org. Chem.* **1978**, *43*, 1957.
(36) Marshall, J. A.; Snyder, W. R. *J. Org. Chem.* **1975**, *40*, 1656.
(37) Paquette, L. A.; Russell, R. K.; Wingard, R. E., Jr. *Tetrahedron Lett.* **1973**, 1713.
(38) Paquette, L. A.; Gardlik, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 5033.
(39) Paquette, L. A.; Photis, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 4936.
(40) Paquette, L. A.; Gardlik, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 5016.
(41) Taggart, D. L.; Peppercorn, W.; Anderson, L. B. *J. Phys. Chem.* **1984**, *88*, 2875.
(42) Taggart, D. L. Ph.D. Dissertation, The Ohio State University, Columbus, OH, 1975.
(43) Mills, J. L.; Nelson, R.; Shore, S. G.; Anderson, L. B. *Anal. Chem.* **1971**, *43*, 157.
(44) Staley, S. W.; Cramer, G. M.; Orvedal, A. W. *J. Am. Chem. Soc.* **1974**, *96*, 7433.

Scheme IV



The actual structure of this dianion was suggested to be **22** by NMR spectroscopy. Reduction with potassium metal in tetrahydrofuran-d_8 at −78 °C during 1 h produced a red-brown species



22

(**22**). Its characteristic ^1H resonances include signals at δ 5.75–5.05 (olefinic), 2.86 (methyl), 1.60–0.95 (broad envelope), 0.44 (CH_2), and −0.72 (CH_2). The chemical shifts of the olefinic and methyl protons are consistent with literature precedent.[22a,37,45] The high-field resonances stem from methylene groups located directly under the doubly charged, planar ring, thereby providing convincing evidence that the conformation shown is most heavily populated.

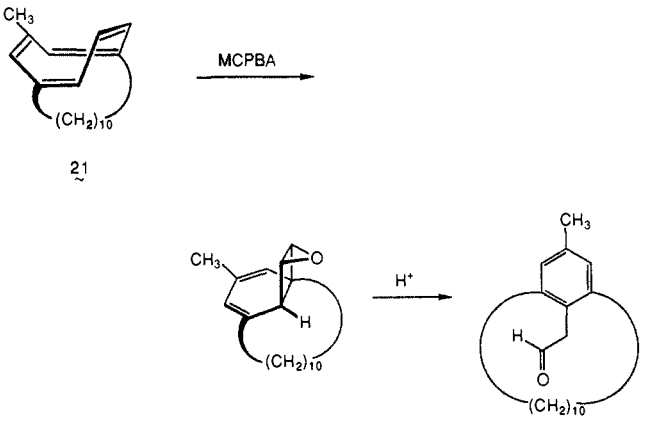
Direct Resolution of the Racemic Phanes. Recourse was made directly to Diels–Alder reaction of **5b–d** with (−)-*endo*-bornyltriazolinedione (**23**),[46] since past work has shown the diastereomeric urazoles generally to be chromatographically separable under high-pressure conditions.[14,15,17,38,40,47] Furthermore, the technique is nondestructive of the COT substrate, both adducts being capable of reconversion back to the respective optically active cyclic polyolefin via hydrolysis–oxidation. Hence, the three racemic (1,5)cyclooctatetraenophanes were heated with **23** in ethyl acetate solution to give mixtures of **24** and **25** (Scheme IV).

For the **c** and **d** series, the diastereomeric ratios could be conveniently monitored by simple examination of the upfield region of their 300-MHz ^1H NMR spectra. In these cases, the bridgehead methyl group in the two *endo*-bornyl moieties finds itself in sufficiently different chemical environments to appear as nonoverlapping singlets.[48] When $n = 6$, this was not the case. Furthermore, whereas **24c/25c** and **24d/25d** could be obtained in diastereomerically enriched condition, no techniques were found to separate **24b** from **25b** chromatographically, the use of Pirkle columns notwithstanding. Equally unsuccessful were attempts to resolve racemic [6](1,5)cyclooctatetraenophane (**5b**) by slow elution through swollen, microcrystalline triacetylcellulose.[49] On the other hand, hydrolysis–oxidation of suitably purified samples of **24c,d** and **25c,d** proved nicely workable. In this way, ample quantities of enantiomerically enriched **5c** were obtained for the kinetic studies to follow. The rate of racemization of **5d** was so accelerated, however, that rapid processing at low temperature was insufficient to deter total loss of optical activity upon isolation.

Our prior determination of the absolute stereochemistry of a number of alkyl-substituted COTs[19] permits tentative assignment of the stereostructures of the dextro- and levorotatory phanes, as shown in Scheme IV.

In contrast to the relative ease with which **5b–d** underwent cycloaddition with (−)-**23**, no comparable Diels–Alder reaction occurred when **15a**, **15b**, or **21** were heated with this triazolinedione. Either the valence isomeric bicyclo[4.2.0]octatrienes are now virtually absent from the respective equilibria or these necessary intermediates have become too sterically crowded with the added methyl group present to react at a reasonable rate. Consequently, partially destructive kinetic resolution techniques were applied to **21** in an attempt to obtain optically active material. However, reaction of racemic **21** with controlled amounts of diisopinocampheylborane[50] or *d*-peroxycamphoric acid[51] under a variety of conditions failed to accomplish the desired objective.[52]

In the course of examining the possible regioselectivity of epoxidation of **21**, the phane was treated with 1 equiv of *m*-chloroperbenzoic acid. The major product proved to be aldehyde **27**. Evidently, oxirane **26** is formed first and subsequently experiences acid-catalyzed isomerization to the acetaldehyde.



In light of these developments, racemization experiments were performed exclusively on **5c**.

Racemization Kinetics. The kinetic intricacies associated with ring inversion and bond shifting within an optically active cyclooctatetraene have been detailed elsewhere.[19,40,47] Usually, four isodynamical structures are required to define completely the mutual interconversion profile. However, for **5b** and **5c** in particular, ring inversion was anticipated to be sterically precluded in the modest temperature region of interest to us. A great deal of prior art forms the basis of this expectation (see **1–3**). In addition, the oxygen atom in **28**[53] and in **29**[53,54] but not the vinyl bridge is able to pass through the center of the macroring at reasonable rates at 25 °C. A complete line-shape analysis of **30** in acetone solution at −5 to +60 °C has established $\Delta G^{\ddagger}$ to equal 16.4 kcal/mol, corresponding to $\Delta H^{\ddagger} = 16.7$ kcal/mol and $\Delta S^{\ddagger} = 1.5$ eu.[55] The $\Delta G^{\ddagger}$ barriers for conformational ring flipping

(45) Russell, R. K.; Wingard, R. E., Jr.; Paquette, L. A. *J. Am. Chem. Soc.* **1974**, *96*, 7483.

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(50) (a) Brown, H. C.; Jadhav, P. K.; Mandal, A. K. *Tetrahedron* **1981**, *37*, 3547. (b) Brown, H. C.; Desai, M. C.; Jadhav, P. K. *J. Org. Chem.* **1982**, *47*, 5065.

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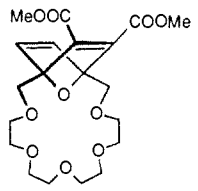
(52) For modestly successful application of this methodology in another cyclooctatetraene context, see: Reference 15.

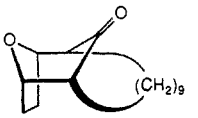
(53) Timko, J. M.; Moore, S. S.; Walba, D. M.; Hiberty, P. C.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 4207.

(54) Hoogeveen, H.; Husse, B. J. *Tetrahedron Lett.* **1976**, 699.

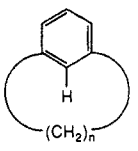


28

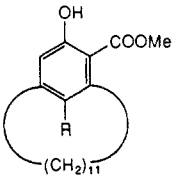
29a, R = CN
b, R = COOMe



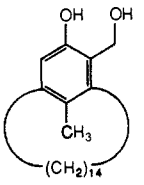
30



31a, n = 6
b, n = 7



32a, R = CH_2Ph
b, R = CH_3

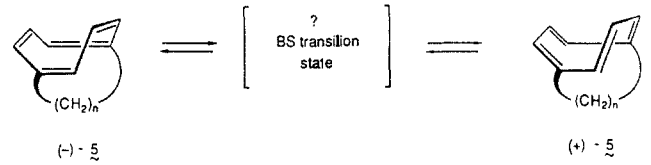


33

in **31a** and **31b** are 17.4 (T_c = 76.5 °C) and 11.5 kcal/mol (T_c = −28 °C), respectively.[56] Furthermore, refluxing (+)-**32a** or (−)-**32b** in benzene does not result in racemization.[7] Phenol **33** can be obtained in optically active condition, but completely loses its rotatory capability when heated in hexane for 5 min.[7]

For **5b–d**, three *contiguous* methine units need to be compressed through the polymethylene chain. When n = 6 or 8, steric restrictions to tub-to-tub inversion will surely apply.[57] The situation when n = 10 was considered less obvious and required comparative kinetic analysis before conclusions could be drawn.

If simple mechanical ring inversion is sufficiently inhibited, racemization can be attributed entirely to bond shifting, i.e., $k_{rac} \approx k_{BS}$. At the mechanistic level, the implication is that movement of the π bonds internal to the [8]annulene ring does not require passage of any of its constituent carbon atoms within the sphere of the pendant macrocycle. If this is so, what then is the actual geometry of the BS transition state?



(−)-5 (+)-5

For determination of the rate of racemization of **5c**, degassed solutions in purified diglyme were placed in a thermally equilibrated polarimeter cell at 20.0, 30.0, and 40.0 °C, and optical rotation readings were taken at appropriate time intervals. Plots of −ln α vs time gave straight lines, nicely reproduced in duplicate and triplicate experiments, whose slopes have been deemed equal to $2k_{BS}$[58] (see Discussion). A sample data set is provided in Table II. The finalized rate data, together with activation parameters, are collected in Table III.

Discussion

The ease with which **5d** experiences racemization parallels closely the behavior of simple alkyl and nonvicinal dialkyl substituted cyclooctatetraenes.[18,19,59] In such systems, ring inversion proceeds more rapidly than bond shifting, although the upper $\Delta G^{\ddagger}$ limit to both processes rarely exceeds 18 kcal/mol.[47h,60,61] The

Table II. Exemplary Rate Data for Racemization of (+)-**5c** (20.0 ± 0.1 °C)

time, s	α_{436}, deg	ln α_{436}	time, s	α_{436}, deg	ln α_{436}
0	+1.508	0.411	4200	+1.320	0.278
600	+1.480	0.392	4800	+1.295	0.259
1200	+1.453	0.374	5400	+1.270	0.239
1800	+1.425	0.354	6000	+1.247	0.221
2400	+1.398	0.335	6600	+1.223	0.201
3000	+1.372	0.316	7200	+1.201	0.183
3600	+1.346	0.297			
slope = 3.19 (±0.01) × 10^{-5} s^{-1}			y intercept = −0.410 (±0.01)		

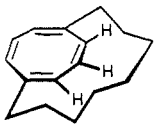
Table III. Data for Bond Shifting in **5c** and the Corresponding Activation Parameters

t, °C	slope = $2k_{BS}$, s^{-1}	rate constants for k_{BS} in **5c**, s^{-1}
20.0	3.19 × 10^{-5}	1.59 × 10^{-5}
	3.15 × 10^{-5}	
30.0	1.04 × 10^{-4}	5.18 × 10^{-5}
	1.03 × 10^{-4}	
40.0	3.37 × 10^{-4}	1.53 × 10^{-4}
	2.74 × 10^{-4}	
for bond shifting in **5c**:		
E_{act} = 20.2 kcal/mol		
ln A = 23.7		
$\Delta H^{\ddagger}$(25 °C) = 19.6 kcal/mol		
$\Delta S^{\ddagger}$(25 °C) = −13.4 eu		
$\Delta G^{\ddagger}$(25 °C) = 23.6 kcal/mol		

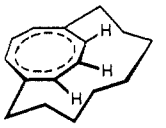
precise ordering of dynamic events within **5d** is, of course, not known. However, energy barriers of a comparably low order of magnitude are clearly at play.

The consequences of reducing the polymethylene chain size in **5** from 10 to 8 CH_2 units are substantial. Heightened barriers have been previously encountered when *tert*-butyl groups are present on the COT ring and when substituents are positioned on several contiguous carbons because of added peripheral steric factors, but such contributions are not at issue here.

The rate at which optical activity is lost in **5c** becomes conveniently measurable in the 20–40 °C range. Precedent has earlier been introduced to suggest that ring inversion within **5c** is not capable of operating at these rates within this temperature region. Were this conformational change to occur via the usual planar-alternate [8]annulene transition state (see **34**), the costs of slipping



34



35

the three contiguous methine centers through the midst of this relatively small loop would certainly be substantial. However, the $\Delta G^{\ddagger}$ for **5c** is identical with the $\Delta G^{\ddagger}_{BS}$ term for 1,3-di-*tert*-butylCOT (23.6 kcal/mol)[47b] and 3 kcal/mol less than the $\Delta G^{\ddagger}_{BS}$ for 1,2,3-trimethylCOT.[40,62] Without doubt, the added angular bending, van der Waals, and torsional energy terms that would accompany the passage of **5c** to **34** would be reflected in more substantial increases in total energy.

Consequently, **5c** must racemize by a more optimal pathway. For essentially identical reasons, the planar-alternate transition-state **35** can be dismissed as well from consideration. Nor is heavy-atom tunneling[63] a reasonable option in this instance because of the need to involve too many carbon atoms. However, the experimentally determined energy profile associated with the

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(56) Hirano, S.; Hara, H.; Hiyama, T.; Fujita, S.; Nozaki, H. *Tetrahedron* **1975**, *31*, 2219.
(57) The allylic methylene protons in **5c** appear as a narrow triplet ($w_{1/2}$ = 5.0 Hz) at room temperature in $CDCl_3$ at 500 MHz, and only minor broadening was observed as the temperature of this solution was slowly dropped to −95 °C.
(58) A detailed kinetic analysis of the complete array of isodynamical processes within cyclooctatetraenes is given in ref 40 and 47a.
(59) Oth, J. F. M. *Pure Appl. Chem.* **1971**, *25*, 573.
(60) Paquette, L. A.; Hefferon, G. J.; Samodral, R.; Hanzawa, Y. *J. Org. Chem.* **1983**, *48*, 1262.
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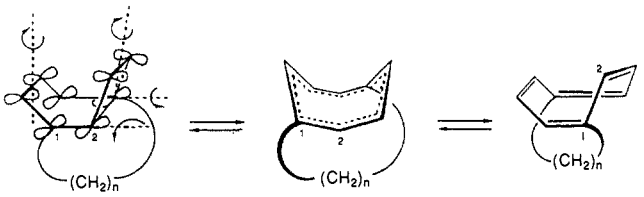
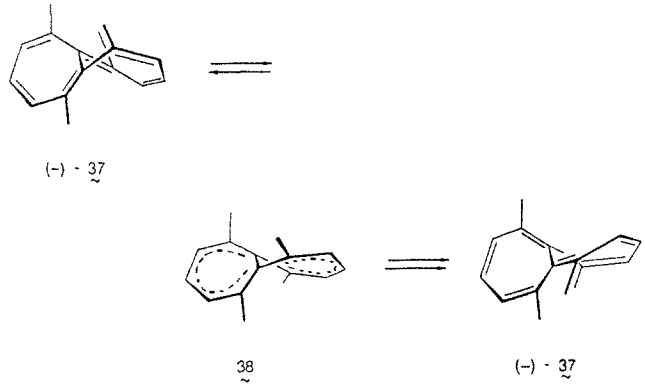
interconversion of (−)-**5c** with (+)-**5c** can be met by operating along a minimum energy path involving simultaneous pseudorotation at all eight trigonal centers (see **36**). As noted by Ermer,[64]



(−) - **36** **37** (+) - **36**

the transition state of this reaction pathway would resemble a somewhat flattened saddle. Thus, bond shifting is realized without ever attaining planarity within the [8]annulene. Dynamics relative to passage through the polymethylene loop are also not mandated. As pseudorotation begins, the energy costs are associated principally (though hardly exclusively) with the progressive dismantling of four C–C π bonds. However, these costs do not escalate because a twist of only 30° allows for incipient reconstruction of four new interconnective π bonds to the alternative nearest neighbor trigonal carbons. The net result of this tandem rebonding is to cause **37** to be positioned below **35** in total energy demand.

We point out here as well the strong likelihood that all cyclooctatetraenes may undergo the bond-shift process by the predescribed pseudorotation scheme. Planar-delocalized representations of the bond-shifting transition state (e.g., **35**) involve antiaromatic $4n$ species, and it has long been difficult to reconcile the small differences in BS and RI energetics in terms of potential energy surfaces involving such species.[62] Kinetic data recorded for substituted heptalenes are similarly incongruous with planar transition states for both processes. For these 12π systems, the energy barriers for ring inversion are invariably higher than those for bond shifting.[65-67] These facts have led Hafner to conclude that bond shifting in heptalenes must occur via nonplanar, helical, chiral transition states.[68] In support of this proposal is the capability of representative derivatives such as **37** to experience the bond-shift phenomenon with retention of configuration.



(−) - **37**

38 (−) - **37**

The adoption by the cyclooctatetraenes of saddle transition states for bond shifting has the effect of bringing peripheral substituents into closer proximity in the activated complex relative to the ground state. Consequently, the conclusions derived from the many investigations of simple steric and more complex buttressing effects still apply.[38] On the other hand, a very questionable practice is that of attempting to derive the delocalization energies of cyclooctatetraenes from the differences in energetics between the BS and RI processes.[69]

Finally, we note that the findings described in the companion study[17] are entirely reconcilable with adoption by cyclooctatetraenes of the pseudorotation pathway for bond shifting.

Experimental Section

Tetramethyl Hexahydro-2,10-dioxo-1*H*,4*H*-3a,8a-propanoazulene-1,3,9,11-tetracarboxylate. A mixture of dimethyl 1,3-acetonedicarboxylate (17.45 g, 0.1 mol), sodium hydroxide (4.05 g, 0.1 mol), and dry methanol (100 mL) was refluxed for 2 h. With continued heating, a solution of cycloheptane-1,2-dione[23a] (6.3 g, 0.05 mol) in dry methanol (10 mL) was added dropwise. After an additional 1.5 h of heating, the solution was cooled and evaporated. The residue was partitioned between dichloromethane (200 mL) and aqueous hydrochloric acid (100 mL of pH 3 solution). The separated aqueous phase was further extracted with dichloromethane (2 × 100 mL). The combined organic phases were washed with water (100 mL) and brine (100 mL), dried, and concentrated in vacuo. Recrystallization from hexane/dichloromethane afforded colorless prisms (15.32 g, 70%): mp 187–190 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.21 (br s, 2 H), 3.74 (s, 6 H), 3.63 (s, 6 H), 3.61 (s, 2 H), 2.23–1.98 (m, 4 H), 1.43 (br s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 171.23, 170.86, 170.26, 170.24, 169.80, 169.54, 169.20, 107.26, 105.79, 105.11, 61.11, 60.71, 59.97, 59.68, 57.07, 51.99, 51.93, 51.51, 51.28, 51.24, 37.72, 34.73, 32.16, 30.69, 30.51, 24.87, 24.50, 23.89; MS m/z calcd (M^+) 438.1526, obsd 438.1566. Anal. Calcd for $C_{21}H_{26}O_{10}$: C, 57.53; H, 5.98. Found: C, 57.75; H, 5.98.

Tetrahydro-1*H*,4*H*-3a,8a-propanoazulene-2(3*H*)-10-dione (7a). A mixture of preceding tetraester diketone (6.45 g, 0.015 mol), 2 M hydrochloric acid (50 mL), and concentrated acetic acid (18 mL) was heated at reflux for 4 h. The cooled solution was neutralized with dilute sodium hydroxide and extracted with dichloromethane (4 × 70 mL). The combined organic phases were washed with water (2 × 100 mL), saturated sodium bicarbonate solution (50 mL), and brine (100 mL) prior to drying and concentration under reduced pressure. The residue was recrystallized from hexane/dichloromethane to give colorless prisms (1.89 g, 62%): mp 106–107 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.50 (d, J = 19.5 Hz, 4 H), 2.27 (d, J = 19.5 Hz, 4 H), 1.72–1.57 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 216.44, 51.38, 48.99, 36.13, 28.50, 21.67; MS m/z calcd (M^+) 206.1307, obsd 206.1305. Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.70; H, 8.75.

Hexahydro-1*H*,4*H*-3a,8a-propanoazulene-2,10-diol (8a). To a slurry of lithium aluminum hydride (0.7 g, 0.018 mol) in dry tetrahydrofuran (75 mL) was added a solution of **7a** (2.49 g, 0.012 mol) in dry tetrahydrofuran (10 mL) via syringe during 1 h. After being stirred for 3 h, the reaction mixture was quenched by the careful addition of a saturated aqueous sodium sulfate solution. The inorganic salts were separated by filtration and the filtrate was evaporated in vacuo. Recrystallization of the residue from hexane/dichloromethane afforded colorless prisms as a mixture of three diastereomers (2.31 g, 92%): mp 154–155 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.53–4.20 (m, 2 H), 1.99–1.40 (m, 20 H); ^{13}C NMR (75 MHz, DMSO-d_6) ppm 71.64, 69.64, 68.82, 68.29, 52.82, 51.87, 51.33, 50.96, 50.17, 50.04, 40.74, 40.32, 40.15, 39.66, 38.66, 31.82, 31.30, 24.80, 24.70, 24.51; MS m/z calcd ($M^+ - H_2O$) 192.1514, obsd 192.1518. Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.06; H, 10.52.

5,6,7,8-Tetrahydro-3*H*,4*H*-8a,3a-propenoazulene and 5,6,7,8-Tetrahydro-1*H*,4*H*-8a,3a-propenoazulene (9a). A slurry of freshly washed (pentane) sodium hydride (0.1 g of a 60% mixture in oil, 2.5 mmol), dry tetrahydrofuran (25 mL), and **8a** (0.06 g, 0.29 mmol) was heated at reflux for 2 h. After cooling, carbon disulfide (0.1 mL, 1.66 mmol) was added to the mixture and heating was resumed for 1 h. To the cooled yellow solution was added methyl iodide (0.5 mL) and heating was resumed for 1 h. The cooled brick-red mixture was poured into water (80 mL) and extracted with dichloromethane (4 × 25 mL). The combined organic phases were washed with water (25 mL) and brine (25 mL) and dried. Upon evaporation of the solvent, the residue was deposited into a round-bottomed flask (10 mL) and immersed into a preheated oil

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bath at 200 °C for 30 min. The resulting residue was chromatographed on silica gel (elution with petroleum ether) to afford a colorless oil as a mixture of two regioisomers (0.0261 g, 53%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.57–5.30 (m, 4 H), 2.49–2.20 (m, 4 H), 1.70–1.46 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 141.31, 138.27, 126.90, 125.46, 69.95, 60.89, 52.85, 50.20, 44.73, 40.62, 37.21, 35.04, 32.08, 31.86, 25.28, 24.62; MS m/z calcd (M^+) 174.1409, obsd 174.1412. Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.55; H, 10.49.

1,1a,5,6,7,8-Hexahydro-4*H*-1,3a-ethenocyclopropa[*c*]azulene (10a). A solution of **9a** (0.291 g, 1.67 mmol), *N*-bromosuccinimide (0.596 g, 3.35 mmol), AIBN (10 mg), and dry carbon tetrachloride (10 mL) was heated at reflux for 10 min. The cooled mixture was filtered, and the filtrate was evaporated in vacuo. The residue was dissolved in dry, degassed dimethylformamide (10 mL) and added by syringe during 2 h to a solution of nickel carbonyl (3 mL, excess) in the same solvent (10 mL). After 18 h of stirring at room temperature, excess nickel carbonyl was removed by evacuation under reduced pressure. The solution was poured into water (80 mL) containing 10% aqueous hydrochloric acid (10 drops) and exhaustively extracted with petroleum ether (4 × 80 mL). The combined organic phases were washed with water (50 mL) and brine (50 mL) prior to drying. After removal of the solvent under reduced pressure, the resulting oil was chromatographed on silica gel (elution with petroleum ether) to afford a colorless oil (0.260 g, 89%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.13 (t, J = 2.7 Hz, 2 H), 4.19 (dd, J = 2.7, 1.2 Hz, 4 H), 1.56–1.53 (m, 4 H), 1.39 (br s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 119.62, 92.48, 65.43, 32.73, 32.08, 27.27; MS m/z calcd (M^+) 172.1252, obsd 172.1252.

[5](1,5)Cyclooctatetraenophane. Bicyclo[5.3.3]trideca-1(11),7,9,12-tetraene (5a). Semibullvalene **10a** (0.010 g, 0.058 mmol) was deposited in a round-bottomed flask (5 mL), which was connected to the pyrolysis apparatus and evacuated to 0.1 Torr. The sample was vaporized slowly by means of a Büchi Kugelrohr oven (T = 50–120 °C) into the hot (521 °C) pyrolysis tube. The trapped (−78 °C) pyrolysate was purified by chromatography on silica gel (elution with petroleum ether) to leave **5a** as a yellow oil (0.003 g, 30%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.77 (br s, 4 H), 5.59 (br s, 2 H), 2.46–2.22 (m, 4 H), 1.63–1.42 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 148.01, 132.28, 130.64, 125.97, 36.28, 31.48, 29.15; MS m/z calcd (M^+) 172.1250, obsd 172.1251.

Octahydro-3a,9a-propano-1*H*-cyclopentacyclooctene-2,11-diol (8b). To a slurry of lithium aluminum hydride (0.16 g, 4.2 mmol) in dry tetrahydrofuran (10 mL) was added a solution of **7b**[23b] (0.40 g, 1.81 mmol) in dry tetrahydrofuran (10 mL) via syringe during 5 min. After 3 h, the usual workup afforded a residual solid, which was recrystallized from hexane/dichloromethane to afford a mixture of three diastereomers as colorless needles (0.38 g, 93%): mp 112–113 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.65–4.18 (m, 2 H), 3.76 (br s, 2 H), 2.15–1.43 (m, 20 H); ^{13}C NMR (75 MHz, DMSO-d_6) ppm 70.75, 68.92, 68.88, 68.29, 52.83, 52.61, 51.25, 50.74, 50.47, 49.40, 49.28, 36.65, 36.39, 35.68, 26.53, 26.33, 25.84, 23.99, 23.41, 22.56; MS m/z calcd ($M^+ - H_2O$) 206.1716, obsd 206.1673. Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.60; H, 10.75.

4,5,6,7,8,9-Hexahydro-3a,9a-propeno-1*H*-cyclopentacyclooctene and 4,5,6,7,8,9-Hexahydro-3a,9a-propeno-3*H*-cyclopentacyclooctene (9b). A slurry of freshly washed (pentane) sodium hydride (8.28 g, of a 60% mixture in oil, 0.207 mol), dry tetrahydrofuran (375 mL), and **8b** (15.32 g, 0.069 mol) was heated at reflux for 2 h. After cooling, carbon disulfide (15.73 g, 0.207 mol) was added to the mixture and heating was resumed for 1.5 h. To the cooled yellow solution was added methyl iodide (34.3 g, 0.242 mol) and reflux was resumed for 1.5 h. The cooled brick-red mixture was poured into water (1 L) and extracted with dichloromethane (3 × 250 mL). The combined organic phases were washed with water and brine prior to drying. Upon evaporation of the solvent, the residue was deposited into a round-bottomed flask and immersed in a preheated oil bath at 205 °C for 30 min. The resulting residue was chromatographed on silica gel (elution with petroleum ether) to afford a mixture of two regioisomers as a colorless oil (11.06 g, 85%): bp 63–65 °C (0.06 Torr); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.58–5.32 (m, 4 H), 2.58–2.40 (m, 2 H), 2.28–2.14 (m, 2 H), 1.76–1.44 (m, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 141.88, 137.93, 126.89, 125.03, 66.51, 58.68, 52.85, 47.76, 43.43, 34.59, 32.71, 32.46, 26.64, 26.41, 25.39, 25.31, 25.12, 23.97; MS m/z calcd (M^+) 188.1565, obsd 188.1554. Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.26; H, 10.79.

1,1a,4,5,6,7,8,9-Octahydro-1,3a-etheno-3a*H*-cyclopropa[1,5]cyclopenta[1,2-*a*]cyclooctene (10b). A solution of **9b** (11.06 g, 58.8 mmol), *N*-bromosuccinimide (20.94 g, 117.6 mmol), AIBN (0.46 g), and dry carbon tetrachloride (175 mL) was heated at reflux for 45 min. The cooled mixture was filtered, and the filtrate was evaporated in vacuo. The residue was dissolved in dry, degassed dimethylformamide (150 mL) and added via syringe during 10 h to a solution of nickel tetracarbonyl (65.36 g, 0.382 mol) in the same solvent (375 mL). After 18 h of stirring at room temperature, excess nickel carbonyl was removed by evacuation under reduced pressure. The solution was poured into water (1400 mL) containing 10% hydrochloric acid (70 mL) and exhaustively extracted with petroleum ether (7 × 300 mL). The combined organic phases were washed with water (2 × 300 mL) and brine (300 mL) prior to drying. After removal of the solvent under reduced pressure, the resulting oil was chromatographed on silica gel (elution with petroleum ether) to give a colorless oil (7.68 g, 70%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.08 (t, J = 2.8 Hz, 2 H), 4.25 (dd, J = 2.8, 1.0 Hz, 4 H), 1.63 (t, J = 6.0 Hz, 4 H), 1.41–1.24 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 118.52, 92.77, 64.07, 28.66, 27.36, 25.58; MS m/z calcd (M^+) 186.1409, obsd 186.1431.

[6](1,5)Cyclooctatetraenophane. Bicyclo[6.3.3]tetradeca-1-(12),8,10,13-tetraene (5b). Semibullvalene **10b** (0.080 g, 0.43 mmol) was deposited in a round-bottomed flask (5 mL), which was connected to the pyrolysis apparatus and evacuated to 0.1 Torr. The sample was vaporized slowly by means of a Büchi Kugelrohr oven (T = 50–130 °C) into the hot (500 °C) pyrolysis tube. The trapped (−78 °C) pyrolysate was initially purified by chromatography on silica gel (elution with petroleum ether) to give a yellow oil (0.057 g, 71%). Final purification by GC (5% SE-30 on Chromosorb W; 1.1 m; 100 °C) afforded **5b** as a yellow oil (0.016 g, 20%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95–5.59 (m, 6 H), 2.29–2.00 (m, 4 H), 1.77–1.45 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 137.08, 136.86, 131.81, 128.69, 31.97, 29.18, 26.77; MS m/z calcd (M^+) 186.1409, obsd 186.1403.

Cook–Weiss Condensation of 1,2-Cyclodecanedione. A solution of sodium hydroxide (2.36 g, 58.9 mmol) in methanol (50 mL) was added dropwise to a solution of dimethyl 1,3-acetonedicarboxylate (9.32 g, 53.6 mmol) in the same solvent (12 mL) for 40 min. The resultant slurry was stirred and heated at the reflux temperature, during which time the salt dissolved. This hot solution was treated dropwise with a solution of **6c**[23c] (4.50 g, 26.8 mmol) in methanol (20 mL). After the addition was complete (1 h), the reaction mixture was allowed to cool to room temperature, stirred for 60 h, poured into cold, dilute hydrochloric acid (8 mL of concentrated HCl in 300 mL of water), and extracted with chloroform (3 × 100 mL). The combined organic phases were washed with water (1 × 100 mL) and brine (1 × 100 mL), dried, and concentrated in vacuo. Crystallization of the brownish oil from methanol afforded 3.86 g (30%) of colorless prisms: mp 178–180 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.67 (s, 2 H), 3.85 (s, 6 H), 3.76 (s, 6 H), 3.75 (s, 2 H), 2.16–2.07 (m, 2 H), 1.94–1.83 (m, 2 H), 1.78–1.65 (m, 2 H), 1.49 (br s, 6 H), 1.48–1.26 (m, 4 H); MS m/z calcd (M^+) 480.1995, obsd 480.1985. Anal. Calcd for $C_{24}H_{32}O_{10}$: C, 59.99; H, 6.71. Found: C, 60.02; H, 6.82.

[8.3.3]Propellane-12,15-dione (7c). A suspension of the preceding tetraester (2.40 g, 5.0 mmol) in acetic acid (4 mL) and 1 N hydrochloric aicd (25 mL) was stirred vigorously at the reflux temperature for 6 h. The cooled reaction mixture was extracted with chloroform (3 × 30 mL), and the combined organic layers were washed with saturated sodium bicarbonate solution (40 mL) and brine (50 mL), dried, and concentrated. The residue was purified by silica gel chromatography (elution with 25% ethyl acetate in petroleum ether) and recrystallization from ligroin; colorless prisms: mp 76–77.5 °C; 1.04 g (84%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.50 (d, J = 19.5 Hz, 4 H), 2.28 (d, J = 19.5 Hz, 4 H), 1.79 (m, 4 H), 1.53 (br s, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 216.50, 50.42, 49.08, 34.09, 27.70, 23.37, 21.50; MS m/z calcd (M^+) 248.1776, obsd 248.1744. Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.35; H, 9.74. Found: C, 77.38; H, 9.86.

[8.3.3]Propellane-12,15-diol (8c). A slurry of lithium aluminum hydride (0.36 g, 9.52 mmol) in dry tetrahydrofuran (25 mL) was blanketed with nitrogen and treated dropwise with a solution of **7c** (1.18 g, 4.76 mmol) in the same solvent (15 mL) during 30 min. After 3 h at room temperature, saturated sodium sulfate solution was introduced carefully, the inorganic salts were separated by filtration, and this solid was washed with tetrahydrofuran (20 mL). The filtrate was dried and concentrated in vacuo to leave **8c** as a colorless, solid mixture of diastereomers: mp 166.5–168 °C; 1.15 g (96%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.53–4.17 (m, 2 H), 2.05–1.37 (series of m, 24 H); ^{13}C NMR (75 MHz, DMSO-d_6) ppm 71.17, 68.98, 68.61, 67.47, 52.09, 51.89, 50.92, 49.83, 49.47, 35.13, 34.59, 33.61, 27.06, 26.99, 26.88, 20.91, 20.50, 20.43, 20.15, 20.03; MS m/z calcd (M^+) 252.2090, obsd 252.2103.

[8.3.3]Propellane-11,14- and 11,15-dienes (9c). A 1.03-g (4.09 mmol) sample of **8c** was subjected to Chugaev elimination in the manner described above. Following silica gel chromatography of the pyrolysate (elution with petroleum ether), a colorless oil was isolated (0.70 g, 79.5%) as a 58:42 mixture of two isomers. For the minor isomer: ^{13}C NMR (75 MHz, $CDCl_3$) ppm 136.91, 127.00, 67.45, 53.84, 47.84, 33.64, 30.12, 27.68, 27.49, 21.55, 20.68 (2 C not observed). For the major isomer: ^{13}C NMR (75 MHz, $CDCl_3$) ppm 141.77, 125.37, 59.67, 43.40, 31.48, 27.60, 21.31 (1 C not observed); MS m/z calcd (M^+) 216.1878, obsd 216.1879.

Anal. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18. Found: C, 88.73; H, 11.13.

1,1a,4,5,6,7,8,9,10,11-Decahydro-1,3a-etheno-3a*H*-cyclopropa[1,5]-cyclopenta[1,2-*a*]cyclodecane (10c). A 6.86-g (31.76 mmol) sample of **9c** was brominated allylically with *N*-bromosuccinimide (11.31 g, 63.5 mmol) and AIBN (0.25 g) in carbon tetrachloride in the predescribed manner. This product was taken up in dimethylformamide (125 mL) and added dropwise to a solution of nickel carbonyl (27 mL, 0.208 mol) in dry dimethylformamide (250 mL). After 18 h and the usual workup, there was isolated 3.69 g (54%) of **10c** as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.11 (t, J = 2.6 Hz, 2 H), 4.15 (dd, J = 2.6, 1.3 Hz, 4 H), 1.68 (t, J = 7.6 Hz, 4 H), 1.58–1.40 (m, 8 H), 1.30 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 119.07, 92.50, 64.09, 28.19, 27.15, 22.42, 21.96; MS m/z calcd (M^+) 214.1721, obsd 214.1734.

[8](1,5)Cyclooctatetraenophane (5c). Pyrolysis of **10c** (2.71 g, 12.7 mmol) at 500 °C and 0.01 Torr in the usual manner furnished 2.06 g (76%) of **5c** as a yellow oil: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 5.87 (dd, J = 11.2, 3.3 Hz, 2 H), 5.66 (d, J = 11.2 Hz, 2 H), 5.62 (d, J = 3.3 Hz, 2 H), 2.02 (m, 4 H), 1.67 (m, 2 H), 1.59 (m, 2 H), 1.52–1.33 (m, 6 H), 1.25 (m, 2 H); ^{13}C NMR (75 MHz, CD_2Cl_2) ppm 143.96, 135.27, 130.94, 128.79, 36.62, 26.43, 25.99, 25.80; MS m/z calcd (M^+) 214.1721, obsd 214.1707.

Dodecahydro-3a,13a-propano-1*H*-cyclopentacyclododecene-2,15-diol (8d). To a slurry of lithium aluminum hydride (0.07 g, 1.84 mmol) in dry tetrahydrofuran (10 mL) was added by syringe a solution of **7d**[23b] (0.1877 g, 0.68 mmol) dissolved in dry tetrahydrofuran (2 mL) during 5 min. After being stirred for 2 h, the reaction mixture was quenched by the careful addition of a saturated aqueous sodium sulfate solution. The inorganic salts were separated by filtration and the filtrate was evaporated in vacuo. Recrystallization of the residue from hexane/dichloromethane afforded a mixture of three diastereomers as colorless needles (0.19 g, 99%): mp 121–121.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.78–4.21 (m, 2 H), 2.16–1.83 (m, 28 H); ^{13}C NMR (75 MHz, DMSO-d_6) ppm 71.04, 69.70, 69.61, 68.69, 66.85, 53.99, 51.26, 50.81, 49.22, 48.93, 48.48, 48.31, 37.37, 36.75, 35.67, 27.06, 26.92, 25.50, 25.33, 24.98, 23.60, 23.39, 23.32, 23.18, 23.01, 22.73; MS m/z calcd (M^+) 280.2402, obsd 280.2415. Anal. Calcd for $C_{18}H_{32}O_2$: C, 77.09; H, 11.50. Found: C, 76.72; H, 11.47.

4,5,6,7,8,9,10,11,12,13-Decahydro-13a,3a-propeno-1*H*-cyclopenta-cyclododecene and 4,5,6,7,8,9,10,11,12,13-Decahydro-13a,3a-propeno-3*H*-cyclopentacyclododecene (9d). A slurry of freshly washed (pentane) sodium hydride (12.14 g of a 60% mixture in oil, 0.30 mol), dry tetrahydrofuran (500 mL), and **8d** (28.32 g, 0.101 mol) was refluxed under nitrogen for 2 h. After cooling, carbon disulfide (14.8 mL, 0.25 mol) was added to the mixture and heating was continued for 1.5 h. To the cooled yellow solution was added methyl iodide (55.4 g, 0.39 mol) and reflux was resumed for 1.5 h. The cooled brick-red mixture was poured into water (1400 mL) and extracted with dichloromethane (6 × 200 mL). The combined organic phases were washed with water and brine prior to drying. Upon evaporation of the solvent, the residue was deposited into a round-bottomed flask (50 mL) and immersed in a preheated oil bath at 200–210 °C for 30 min. The resulting residue was chromatographed on silica gel (elution with petroleum ether) to afford a mixture of regioisomers as a colorless oil (18.56 g, 75%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.61–5.42 (m, 4 H), 2.37–2.11 (m, 4 H), 1.56–1.41 (m, 20 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 140.60, 136.25, 127.78, 126.20, 67.18, 59.71, 54.16, 45.36, 43.26, 34.07, 33.96, 31.70, 27.80, 27.72, 27.69, 27.37, 26.95, 26.57, 25.23, 24.34, 23.85, 23.63, 23.42, 21.88; MS m/z calcd (M^+) 244.2191, obsd 244.2186. Anal. Calcd for $C_{18}H_{28}$: C, 88.45; H, 11.55. Found: C, 88.15; H, 11.57.

1,1a,4,5,6,7,8,9,10,11,12,13-Dodecahydro-1,3a-etheno-3a*H*-cyclopropa[1,5]cyclopenta[1,2-*a*]cyclododecene (10d). A solution of **9d** (0.316 g, 1.3 mmol), *N*-bromosuccinimide (0.462 g, 2.59 mmol), AIBN (10 mg), and dry carbon tetrachloride (3 mL) was heated at reflux for 10 min. The cooled mixture was filtered and the filtrate was evaporated in vacuo. The residue was dissolved in dry, degassed dimethylformamide (10 mL) and added via syringe during 2 h to a solution of nickel carbonyl (1.8 mL, excess) in the same solvent (10 mL). After 18 h of stirring at room temperature, excess nickel carbonyl was removed by evacuation under reduced pressure. The solution was poured into water (200 mL) containing 10% hydrochloric acid (10 drops) and exhaustively extracted with petroleum ether (5 × 50 mL). The combined organic phases were washed with water (50 mL) and brine (50 mL) prior to drying. After removal of the solvent under reduced pressure, the resulting oil was chromatographed on silica gel (elution with petroleum ether) to give a colorless oil (0.1992 g, 64%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.11–5.10 (m, 2 H), 4.22–4.21 (m, 4 H), 1.57–1.38 (m, 20 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 118.91, 92.35, 64.40, 29.50, 27.72, 27.06, 24.81, 24.02; MS m/z calcd (M^+) 242.2035, obsd 242.2051.

[10](1,5)Cyclooctatetraenophane (5d). Semibullvalene **10d** (3.36 g, 13.88 mmol) was pyrolyzed in the gas phase at 500 °C and 0.1 Torr as before. The trapped (−78 °C) pyrolysate was initially purified by chromatography on silica gel (elution with petroleum ether) to give a yellow oil (2.75 g, 82%). Final purification was accomplished by GC (5% SE-30 on Chromosorb W; 1.1 m; 170 °C): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.81 (dd, J = 11.5, 3.7 Hz, 2 H), 5.62 (d, J = 11.5 Hz, 2 H), 5.54 (d, J = 3.7 Hz, 2 H), 2.06 (d, J = 6.7 Hz, 4 H), 1.39 (br s, 16 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 144.07, 133.53, 132.13, 127.48, 37.23, 27.62, 27.20, 26.25, 26.10; MS m/z calcd (M^+) 242.2035, obsd 242.2024.

Tetrahydro-10-hydroxy-10-methyl-1*H*,4*H*-3a,8a-propanoazulen-2-(3*H*)-one (11a). To a cold (−78 °C) solution of **7a** (0.13 g, 0.63 mmol) and dry tetrahydrofuran (10 mL) was added methyllithium (1.8 mL of a 1.6 M solution, 2.88 mmol) over 3 min. After being stirred at −78 °C for 1.75 h, the reaction mixture was quenched with 10% hydrochloric acid (30 mL) and diluted with dichloromethane (50 mL). The separated aqueous phase was extracted with dichloromethane (3 × 50 mL). The combined organic phases were dried and evaporated in vacuo. The resulting solid was chromatographed on silica gel (elution with 40% ethyl acetate in petroleum ether) to give colorless prisms (0.09 g, 64%): mp 127–129 °C; IR (CH_2Cl_2) cm^{-1} 3600, 3420, 1738; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.11 (s, 1 H), 2.44 (br s, 4 H), 1.77 (br s, 4 H), 1.69–1.32 (m, 10 H), 1.26 (s, 3 H); ^{13}C NMR (20 MHz, $CDCl_3$) ppm 220.52, 78.76, 58.24, 53.98, 52.46, 39.73, 31.56, 27.71, 24.73; MS m/z calcd (M^+) 222.1620, obsd 222.1618. Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.60; H, 9.94.

Hexahydro-2-methyl-1*H*,4*H*-3a,8a-propanoazulene-2,10-diol (12a). To a slurry of lithium aluminum hydride (0.21 g, 5.53 mmol) in tetrahydrofuran (20 mL) was added **11a** (0.5 g, 2.25 mmol) dissolved in the same solvent (5 mL). After being stirred at room temperature for 4 h, the reaction mixture was quenched by the careful addition of a saturated aqueous sodium sulfate solution. After filtration of the inorganic salts, the filtrate was evaporated in vacuo to leave a crystalline residue. Recrystallization from heptane/ethyl acetate afforded **12a** as colorless rectangular prisms (0.48 g, 95%): mp 119–121 °C; IR (CH_2Cl_2) cm^{-1} 3680, 3600; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.76 (quintet, J = 7.0 Hz, 0.5 H), 4.33 (quintet, J = 5.5 Hz, 0.5 H), 2.91 (br s, 2 H), 2.17–1.47 (series of m, 18 H), 1.35 and 1.33 (2 s, 3 H); ^{13}C NMR (20 MHz, $CDCl_3$) ppm 80.11, 73.34, 71.55, 57.37, 55.90, 54.69, 52.33, 51.81, 41.21, 40.89, 31.95, 30.73, 30.16, 24.98, 24.67; MS m/z calcd (M^+) 224.1776, obsd 224.1787. Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.83; H, 10.60.

5,6,7,8-Tetrahydro-2-methyl-1*H*,4*H*-8a,3a-propenoazulene and 5,6,7,8-Tetrahydro-2-methyl-3*H*,4*H*-8a,3a-propenoazulene (13a). A slurry of freshly washed sodium hydride (0.23 g, of a 50% oil mixture, 4.65 mmol) in dry tetrahydrofuran (25 mL) and diol **12a** (0.48 g, 2.14 mmol) was refluxed for 24 h. After cooling, carbon disulfide (0.4 g, 5.3 mmol) was added to the mixture and heating was resumed for 1 h. To the cooled yellow solution was added excess methyl iodide and reflux was resumed for 1 h. The cooled brick-red mixture was poured into water (50 mL) and extracted with dichloromethane (5 × 50 mL). The combined organic phases were washed with water (1 × 50 mL) and brine (2 × 50 mL) prior to drying. Following solvent evaporation, the residue was deposited into a round-bottomed flask (15 mL) and immersed into a preheated oil bath at 205 °C for 30 min. The resulting residue was chromatographed on silica gel (elution with petroleum ether) to afford a colorless oil as a mixture of two regioisomers (0.30 g, 75%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.63–4.93 (m, 3 H), 2.47–2.07 (m, 4 H), 1.69–1.34 (m, 13 H); ^{13}C NMR (20 MHz, $CDCl_3$) ppm 141.50, 139.01, 136.65, 135.50, 134.92, 132.50, 126.36, 125.66, 61.72, 60.95, 54.69, 53.60, 50.15, 49.07, 44.92, 40.83, 37.63, 37.38, 35.33, 32.14, 31.95, 29.78, 25.37, 24.73, 16.62; MS m/z calcd (M^+) 188.1565, obsd 188.1551. Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.06; H, 10.72.

1,1a,5,6,7,8-Hexahydro-2-methyl-4*H*-1,3a-ethenocyclopropa[*c*]azulene (14a). A solution of **13a** (0.0924 g, 0.49 mmol), *N*-bromosuccinimide (0.175 g, 0.98 mmol), AIBN (5 mg), and dry carbon tetrachloride (2 mL) was heated at reflux for 10 min. The cooled mixture was filtered and the filtrate was evaporated in vacuo. The residue was dissolved in dry, degassed dimethylformamide (5 mL) and added by syringe during 2 h to a solution of dry, degassed dimethylformamide solution (10 mL) of nickel carbonyl (0.45 mL, 3.48 mmol). After 18 h of stirring at room temperature, the excess nickel carbonyl was removed by evacuation or under reduced pressure. The solution was poured into water (80 mL) containing 10% hydrochloric acid (3 drops) and exhaustively extracted with petroleum ether (4 × 80 mL). The combined organic phases were washed with water (50 mL) and brine (50 mL) prior to drying. After removal of the solvent under reduced pressure, the resulting oil was chromatographed on silica gel (elution with petroleum ether) to leave a colorless oil (0.0632 g, 69%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.18 (t, J = 3.8 Hz, 1 H), 4.10 (t, J = 3.8 Hz, 2 H), 3.83 (d, J = 2.9 Hz, 2 H), 1.63 (s, 3 H), 1.51–1.32 (m, 10 H); ^{13}C NMR (75 MHz $CDCl_3$) ppm 129.51, 118.72, 91.98, 90.62, 65.05, 32.73, 32.05, 27.29, 16.58; MS m/z

calcd (M^+) 186.1409, obsd 186.1403.

9-Methyl[5](1,5)Cyclooctatetraenophane. 9-Methylbicyclo[5.3.3]-trideca-1(11),7,9,12-tetraene (15a). Semibullvalene **14a** (0.115 g, 0.62 mmol) was deposited in a round-bottomed flask (5 mL), which was connected to the pyrolysis apparatus and evacuated to 0.1 Torr, and the compound vaporized slowly into the hot (519 °C) tube. The trapped (−78 °C) pyrolysate was purified by chromatography on silica gel (elution with petroleum ether) to leave a yellow oil (0.042 g, 36%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.72–5.53 (m, 5 H), 2.46–1.42 (series of m, 10 H), 1.74 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 147.69, 146.04, 140.51, 131.17, 131.07, 129.16, 125.70, 125.35, 36.26, 36.14, 31.49, 29.58, 28.77, 23.83; MS m/z calcd (M^+) 186.1409, obsd 186.1394.

Octahydro-11-hydroxy-11-methyl-3a,9a-propano-1*H*-cyclopentacyclooctan-2(3*H*)-one (11b). To a cold (−78 °C) solution of **7b** (0.198 g, 0.9 mmol) in dry tetrahydrofuran (3 mL) was added methyllithium (2.4 mL of a 1.5 M solution, 3.6 mmol) over 5 min. After being stirred at −78 °C for 1 h, the reaction mixture was quenched with 10% hydrochloric acid (50 mL) and extracted with dichloromethane (3 × 30 mL). The combined organic phases were dried and evaporated. The resulting residue was chromatographed on silica gel (elution with 35% ethyl acetate in petroleum ether) to afford colorless needles (0.145 g, 68%): mp 141–143 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.56, 2.23 (AB quartet, J_{AB} = 17.8 Hz, 4 H), 1.85–1.34 (m, 12 H), 1.32 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 219.22, 216.57, 77.97, 67.86, 57.20, 52.53, 51.43, 51.06, 48.69, 34.42, 33.95, 32.14, 26.11, 26.04, 25.55, 25.20, 23.09, 22.52; MS m/z calcd (M^+) 236.1776, obsd 236.1786.

Octahydro-2-methyl-3a,9a-propano-1*H*-cyclopentacyclooctene-2,10-diol (12b). To a slurry of lithium aluminum hydride (0.45 g, 12 mmol) in dry tetrahydrofuran (15 mL) was added a solution of **11b** (1.59 g, 6.7 mmol) in the same solvent (5 mL) via syringe during 30 min. After being stirred at ambient temperature for 18 h, the reaction mixture was quenched by the careful addition of a saturated aqueous sodium sulfate solution. Following removal of the inorganic salts by filtration, the filtrate was concentrated in vacuo. The residue was chromatographed on silica gel (elution with 40% ethyl acetate in petroleum ether) to give a mixture of diastereomeric diols **12b** as colorless needles (1.6 g, 100%): mp 100–103 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.86–4.32 (series of m, 1 H), 2.24–1.51 (m, 20 H), 1.39–1.21 (series of m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 79.19, 78.97, 78.31, 73.30, 73.10, 72.61, 70.96, 61.49, 58.39, 57.14, 55.46, 55.39, 54.43, 53.22, 52.22, 51.93, 51.03, 48.90, 46.75, 37.70, 37.37, 36.87, 35.77, 31.88, 30.49, 29.14, 26.76, 26.70, 26.53, 26.02, 25.30, 25.18, 23.62, 22.92, 22.81; MS m/z calcd (M^+) 238.1933, obsd 238.1979.

Twofold Dehydration of 12b. A solution of **12b** (9.90 g, 0.042 mol) in freshly distilled hexamethylphosphoramide (150 mL) was heated at the reflux temperature for 70 min. The cooled reaction mixture was poured into water (1 L) and extracted with petroleum ether (4 × 400 mL). The combined organic phases were washed with water (2 × 1 L) and brine (3 × 1 L) prior to drying. After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel (elution with petroleum ether) to afford 7.4 g (88%) of a mixture of three diene regioisomers: bp 36–38 °C (0.04 Torr); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.61–4.65 (m, 3.1 H), 2.69–1.99 (m, 5.3 H), 1.67 (br s, 2.5 H), 1.71–1.23 (m, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 142.06, 141.94, 138.70, 137.98, 135.85, 134.43, 131.78, 126.95, 126.05, 125.11, 125.07, 104.11, 59.43, 58.85, 58.69, 51.22, 47.77, 47.71, 43.65, 43.43, 34.65, 33.05, 32.83, 32.75, 32.69, 29.71, 26.59, 26.50, 26.41, 25.45, 25.30, 25.13, 24.04, 16.64.

4,5,6,7,8,9-Hexahydro-2-methyl-3a,9a-propeno-1*H*-cyclopentacyclooctene and 4,5,6,7,8,9-Hexahydro-2-methyl-3a,9a-propeno-3*H*-cyclopentacyclooctene (13b). A solution of the above diene mixture (5.31 g, 4.54:1 endo/exo ratio, 0.026 mol) in ethyl acetate (75 mL) containing 5 drops of a 48% aqueous hydrobromic acid solution was stirred at room temperature for 5 h. The reaction mixture was washed with water (2 × 50 mL) and brine (50 mL) prior to drying. After solvent evaporation, the residue was chromatographed on silica gel (elution with petroleum ether) to afford a colorless oil (5.27 g, 99%): bp 36–28 °C (0.04 Torr); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.55–4.94 (m, 3 H)), 2.54–2.00 (m, 4 H), 1.68 (t, J = 1.1 Hz, 3 H), 1.64–1.45 (m, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 141.99, 138.66, 136.72, 135.83, 134.36, 131.76, 126.00, 125.09, 66.61, 59.38, 58.80, 53.41, 52.07, 47.70, 43.63, 34.61, 33.03, 32.80, 32.74, 26.56, 26.47, 25.42, 25.32, 25.15, 24.04, 16.65; MS m/z calcd (M^+) 202.1722, obsd 202.1725. Anal. Calcd for $C_{15}H_{22}$: C, 89.04; H, 10.96. Found: C, 88.97; H, 11.04.

1,1a,4,5,6,7,8,9-Octahydro-2-methyl-1,3a-etheno-3a*H*-cyclopropa[1,5]cyclopenta[1,2-*a*]cyclooctene (14b). A solution of **13b** (1.02 g, 5.1 mmol), *N*-bromosuccinimide (1.79 g, 10 mmol), AIBN (30 mg), and dry carbon tetrachloride (5 mL) was heated at vigorous reflux for 20 min. The cooled mixture was filtered and the filtrate was evaporated in vacuo. The residue was dissolved in dry, degassed dimethylformamide (12 mL) and added by syringe during 1 h to a solution of nickel carbonyl (4.5 mL, excess) in the same solvent (12 mL). After 18 h of stirring at room temperature, the usual workup followed to give a colorless oil (0.531 g, 52%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.13 (t, J = 3.8 Hz, 1 H), 4.17–4.14 (m, 2 H), 3.86–3.85 (m, 2 H), 1.61 (t, J = 0.8 Hz, 3 H), 1.60–1.57 (m, 4 H), 1.37–1.26 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 128.32, 117.63, 92.13, 91.17, 63.74, 28.76, 27.42, 25.64, 16.51; MS m/z calcd (M^+) 200.1565, obsd 200.1550.

10-Methyl[6](1,5)Cyclooctatetraenophane. 10-Methylbicyclo[5.3.3]-tetradeca-1(12),8,10,13-tetraene (15b). Semibullvalene **14b** (17 mg, 0.1 mmol) was pyrolyzed at 0.1 Torr and 510 °C as previously described. The trapped pyrolysate was purified by chromatography on neutral alumina (elution with petroleum ether) to afford a light yellow oil (4 mg, 24%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.85–5.60 (series of m, 5 H), 2.30–1.30 (series of m, 12 H), 1.73 (s, 3 H); MS m/z calcd (M^+) 200.1565, obsd 200.1554.

Decahydro-15-hydroxy-3a,13a-propano-1*H*-cyclopentacyclododecen-2(3*H*)-one (16). To a cold (−78 °C) solution of **7d** (0.240 g, 0.87 mmol) in tetrahydrofuran (5 mL) was added Dibal-H (0.9 mL of a 1 M solution, 0.09 mmol) over 5 min. After being stirred at −78 °C for 2 h, the reaction mixture was poured into 10% hydrochloric acid (25 mL) and extracted with dichloromethane (3 × 50 mL). The combined organic extracts were washed with water (50 mL) and brine (50 mL) prior to drying and solvent evaporation. The residue was chromatographed on silica gel (elution with 30% ethyl acetate in petroleum ether) to leave a colorless oil (0.132 g, 55% or 94% based on recovered starting material): IR (CH_2Cl_2) cm^{-1} 3615, 2940, 2870, 1738; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.51–4.35 (m, 1 H), 2.49–2.00 (m, 8 H), 1.82–1.50 (m, 4 H), 1.44–1.22 (br s, 16 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 219.63, 219.19, 71.88, 71.16, 52.45, 51.85, 50.55, 50.27, 48.45, 48.32, 35.35, 34.68, 27.07, 25.67, 23.44, 23.28, 23.16, 22.85; MS m/z calcd (M^+) 278.2246, obsd 278.2239.

4,5,6,7,8,9,10,11,12,13-Decahydro-3a,13a-propano-1*H*-cyclopentacyclododecen-15-one (17). A slurry of freshly washed sodium hydride (0.058 g of a 60% oil mixture, 1.45 mmol), dry tetrahydrofuran (3 mL), and **16** (0.393 g, 1.42 mmol) was refluxed for 1.5 h. After cooling, carbon disulfide (0.1 mL, 1.66 mmol) was added and heating was resumed for 1.5 h. To the cooled solution was added methyl iodide (1 mL) and reflux was resumed for 1.5 h. The cooled solution was poured into water (30 mL) and extracted with dichloromethane (3 × 30 mL). The combined organic phases were washed with water (30 mL) and brine (30 mL), dried, and evaporated. The residue was deposited into a round-bottomed flask (10 mL) and immersed in a preheated oil bath at 205 °C for 12 min. The residue was chromatographed on silica gel (elution with 5% ethyl acetate in petroleum ether) to give a light yellow oil (0.263 g, 71%): bp 114–120 °C (0.05 Torr); IR ($CHCl_2$) cm^{-1} 2940, 2870, 1745; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.68–5.50 (m, 2 H), 2.50–2.15 (m, 6 H), 1.71–1.26 (m, 20 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 218.80, 139.77, 128.60, 58.10, 52.49, 51.21, 47.92, 44.50, 33.41, 27.29, 27.16, 26.55, 25.38, 23.59, 23.45, 23.42, 21.99; MS m/z calcd (M^+) 260.2140, obsd 260.2145.

4,5,6,7,8,9,10,11,12,13-Decahydro-15-methyl-3a,13a-propano-1*H*-cyclopentacyclododecen-15-ol. To a cold (−78 °C) solution of **17** (0.085 g, 0.33 mmol) in dry tetrahydrofuran (3 mL) was added methyllithium (0.35 mL of a 1.5 M solution, 0.53 mmol) during 1 min. After being stirred at −78 °C for 20 min, the solution was warmed to ambient temperature during 20 min. Stirring was continued for 30 min. Following quenching of the reaction mixture with 10% hydrochloric acid (30 mL), the aqueous phase was extracted with dichloromethane (3 × 50 mL). The combined organic phases were dried and concentrated and the residue was chromatographed on silica gel (elution with 2% ethyl acetate in petroleum ether) to give a thick, colorless oil (0.079 g, 88%): bp 130–134 °C (0.05 Torr); IR (CH_2Cl_2) cm^{-1} 2940, 2855; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.77–5.41 (m, 2 H), 2.52–2.30 (m, 2 H), 2.09–1.75 (m, 4 H), 1.72–1.32 (m, 20 H), 1.29 and 1.24 (two s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 141.73, 140.97, 129.25, 126.66, 78.87, 78.46, 63.00, 62.31, 59.29, 56.04, 54.20, 53.44, 52.91, 52.39, 47.39, 44.99, 37.15, 34.57, 34.11, 33.90, 31.11, 28.03, 27.80, 27.77, 27.25, 26.80, 26.60, 25.69, 25.30, 24.13, 24.00, 23.84, 23.74, 23.61, 22.57, 22.13; MS m/z calcd (M^+) 276.2453, obsd 276.2449. Anal. Calcd for $C_{19}H_{32}O$: C, 82.55; H, 11.67. Found: C, 82.42; H, 11.66.

4,5,6,7,8,9,10,11,12,13-Decahydro-2-methyl-13a,3a-propeno-1*H*-cyclopentacyclododecene and 4,5,6,7,8,9,10,11,12,13-Decahydro-2-methyl-13a,3a-propeno-3*H*-cyclopentacyclododecene (19). To a solution of the preceding alcohol (0.12 g, 0.44 mmol) and 4-(*N*,*N*-dimethylamino)pyridine (0.065 g, 0.53 mmol) in dry pyridine (1.5 mL), was added phosphorus oxychloride (0.065 mL, 0.69 mmol) during 15 s. After being stirred for 1.3 h, the reaction mixture was poured into 10% hydrochloric acid (90 mL) and extracted with dichloromethane (3 × 40 mL). The combined organic phases were washed with 10% hydrochloric acid (50 mL), water (50 mL), and brine (50 mL) prior to drying and

solvent evaporation. The residue was chromatographed on silica gel (elution with petroleum ether) to afford a colorless oil as an 8.4:1 mixture of endo/exo olefins (0.09 g, 82%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.59–4.70 (m, 3.1 H), 2.35–2.03 (m, 4.2 H), 1.68 (s, 2.7 H), 1.57–1.30 (m, 20 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 151.96, 140.72, 140.45, 137.59, 136.82, 135.62, 134.36, 130.15, 127.42, 127.01, 126.20, 104.38, 67.27, 61.32, 60.41, 59.87, 54.65, 49.89, 48.16, 47.54, 45.25, 44.79, 44.17, 43.37, 34.48, 34.18, 34.13, 34.03, 33.62, 32.00, 27.80, 27.75, 27.72, 27.66, 27.62, 27.39, 27.35, 26.95, 26.68, 26.55, 26.50, 25.51, 25.25, 24.31, 23.82, 23.73, 23.67, 23.57, 23.34, 22.20, 21.92, 16.83, 16.70; MS m/z calcd (M^+) 258.2348, obsd 258.2367.

A solution of these dienes (0.0379 g, 0.15 mmol) in ethyl acetate (1 mL) containing 1 drop of 48% hydrobromic acid was stirred at ambient temperature for 6 h. The reaction mixture was partitioned between half-saturated brine (40 mL) and dichloromethane (40 mL). The separated organic layer was washed with water (40 mL) and brine (40 mL), dried, and evaporated. The residue was chromatographed on silica gel (elution with petroleum ether) to give a colorless oil (0.037 g, 100%): bp 75–80 °C (0.03 Torr); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.59–5.42 (m, 2 H), 5.11–5.03 (m, H), 2.34–2.03 (m, 4 H), 1.67 (s, 3 H), 1.57–1.30 (m, 20 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 140.74, 137.63, 136.81, 135.64, 132.32, 130.10, 127.00, 126.15, 67.28, 60.42, 59.88, 54.65, 49.90, 47.53, 45.27, 43.37, 34.48, 34.18, 32.02, 27.81, 27.72, 27.66, 27.39, 26.95, 26.56, 25.26, 24.32, 23.84, 23.67, 23.57, 23.33, 21.94, 16.84, 16.70. Anal. Calcd for $C_{19}H_{30}$: C, 88.30; H, 11.70. Found: C, 88.20; H, 11.72.

1,1a,4,5,6,7,8,9,10,11,12,13-Dodecahydro-2-methyl-1,3a-etheno-3a*H*-cyclopropa[1,5]cyclopenta[1,2-*a*]cyclododecene (20). A solution of **19** (0.61 g, 2.36 mmol), *N*-bromosuccinimide (0.84 g, 4.72 mmol), AIBN (10 mg), and dry carbon tetrachloride (3 mL) was heated at reflux for 15 min. The cooled mixture was filtered, and the filtrate was evaporated in vacuo. The residue was dissolved in dry, degassed dimethylformamide (10 mL) and added by syringe during 0.5 h to a solution of nickel carbonyl (3.5 mL, excess) in the same solvent 10 mL). After 18 h of stirring at room temperature, excess nickel carbonyl was removed in vacuo. The solution was poured into water (80 mL) containing 10% hydrochloric acid (10 drops) and extracted with petroleum ether (4 × 80 mL). The combined organic phases were washed with water (50 mL) and brine (50 mL), dried, and evaporated. The residue was chromatographed on neutral alumina (elution with petroleum ether) to leave a colorless oil (0.31 g, 51%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.15 (t, J = 3.9 Hz, 1 H), 4.12 (t, J = 3.6 Hz, 2 H), 3.84 (d, J = 2.8 Hz, 2 H), 1.61 (s, 3 H), 1.54–1.51 (m, 4 H), 1.37 (br s, 16 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 128.78, 118,06, 91.83, 90.67, 64.05, 29.69, 27.77, 27.09, 24.87, 24.11, 16.59; MS m/z calcd (M^+) 256.2191, obsd, 256.2187.

14-Methyl[10](1,5)cyclooctatetraenophane. 14-Methylbicyclo-[10.3.3]octadeca-1(16),12,14,17-tetraene (21). A solution of semibullvalene **20** (0.28 g, 1.1 mmol) dissolved in distilled pentane (15 mL) was added via syringe to a hot (540 °C) vertical pyrolysis oven. The pyrolysate was collected under a positive argon flow (three bubbles/s). The crude product was purified by chromatography on neutral alumina (elution with petroleum ether) to afford a light yellow oil (0.136 g, 48%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80 (dd, J = 11.4, 3.7 Hz, 1 H), 5.62 (d, J = 11 Hz, 1 H), 5.50 (s, 2 H), 5.41 (s, 1 H), 2.07–2.01 (m, 4 H), 1.76 (s, 3 H), 1.37 (br s, 16 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 144.65, 141.85, 140.22, 133.34, 132.06, 130.61, 128.12, 126.37, 37.61, 37.10, 27.70, 27.57, 27.15, 26.44, 26.31, 26.09, 25.99, 24.55; MS m/z calcd (M^+) 256.2191, obsd 256.2206.

Electrochemical Reduction Studies. The procedures for the cyclic voltammetric studies performed herein, including techniques used for drying and purifying background electrolytes and solvents, are described elsewhere.[42] A vacuum-line electrochemical cell[43] was employed throughout to maintain anhydrous conditions.

Reduction–Oxidation of 21. To freshly distilled ammonia (5 mL) at −78 °C was added a solution of **21** (37 mg, 0.15 mmol) in anhydrous tetrahydrofuran (2 mL). Potassium metal (20 mg, excess) was added in one portion and the reaction mixture was stirred at −78 °C for 1.5 h before being transferred via cannula to a cold (−78 °C) mixture of iodine (100 mg, 0.39 mmol) in pentane (10 mL). Water (2 mL) was added followed by sodium thiosulfate (200 mg). The aqueous layer was separated and extracted with petroleum ether (3 × 20 mL). The combined organic phases were dried over anhydrous sodium sulfate and evaporated. The residue was chromatographed on neutral alumina (elution with petroleum ether) to afford **21** (21.5 mg, 58%), the spectroscopic properties of which were superimposable on those recorded earlier.

Cycloaddition of (−)-*endo*-Bornyltriazolinedione to 5b. To a refluxing solution of **5b** (2.28 g, 12.3 mmol) in ethyl acetate (40 mL) under nitrogen was slowly added dropwise a solution of freshly sublimed (−)-**23** (2.88 g, 12.3 mmol) in 12 mL of ethyl acetate for a period of 6 h. After cooling, the precipitate was separated by filtration, washed with a small amount of 20% ethyl acetate in petroleum ether, and dried (2.52 g). The filtrate was concentrated in vacuo and the residue was chromatographed on silica gel (elution with 7% ethyl acetate in petroleum ether) to give 0.365 g of recovered **5b** and 0.52 g of additional urazole as a colorless solid. The combined weight of adduct (3.02 g) represents a yield of 58%, or 70% based on consumed **5b**: mp 245–247 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.11 (t, J = 3.65 Hz, 2 H), 4.84 (dd, J = 2.87, 1.35 Hz, 2 H), 4.22 (m, 1 H), 2.93 (br s, 2 H), 2.41 (dd, J = 5.3, 12.9 Hz, 1 H), 2.11–2.03 (m, 2 H), 1.94–1.83 (m, 3 H), 1.80–1.66 (m, 3 H), 1.61–1.50 (m, 9 H), 1.34–1.25 (m, 1 H), 0.95 (s, 3 H), 0.87 (s, 3 H), 0.78 (s, 3 H); MS m/z calcd (M^+) 421.2729, obsd 421.2726. Anal. Calcd for $C_{26}H_{35}N_3O_2$: C, 74.07; H, 8.37. Found: C, 74.12; H, 8.41.

It was not found possible to separate the diastereomers of **24b** and **25b** on a variety of chromatographic absorbents at different pressure ratings. For example, recourse to HPLC on silica gel (as described below) with full deployment of recycling and peak-shaving techniques afforded leading and trailing edge materials that proved identical in their spectra optical rotation: $[\alpha]_D$ −4.8°. Hydrolysis of these urazoles gave only optically inactive **5b**. Alternative recourse to a Pirkle covalent phenylglycine column was equally unsatisfactory.

Cycloaddition of (−)-*endo*-Bornyltriazolinedione to 5c. A refluxing solution of **5c** (1.98 g, 9.25 mmol) in ethyl acetate (4 mL) under nitrogen was slowly treated dropwise with a solution of freshly sublimed (−)-**23** (2.17 g, 0.25 mmol) in 10 mL of ethyl acetate for a period of 6 h. The cooled reaction mixture was concentrated in vacuo. Column chromatography of the residue on silica gel (elution with 8% ethyl acetate in petroleum ether) gave first 0.61 g of recovered **5c** and 1.73 g (42%; 61% based on consumed **5c**) of the adducts as a white solid: mp 193–195 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.77 (br s, 2 H), 4.87 (t, J = 6.0 Hz, 1 H), 4.62 (dd, J = 1.8, 4.1 Hz, 1 H), 4.20 (m, 1 H), 3.10 (m, 1 H), 3.03 (m, 1 H), 2.40 (dd, J = 5.2, 12.9 Hz, 1 H), 2.29 (m, 1 H), 2.08 (m, 1 H), 1.90 (m, 2 H), 1.72 (m, 4 H), 1.57–1.38 (m, 8 H), 1.27–1.16 (m, 6 H), 0.94 (s, 3 H), 0.86 (s, 3 H), 0.77 (s, 1.5 H), 0.75 (s, 1.5 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 159.62, 159.49, 159.10, 153.50, 140.28, 140.15, 129.28, 129.23, 116.23, 116.05, 59.90, 58.80, 54.55, 54.47, 51.53, 51.48, 47.54, 45.25, 42.43, 42.37, 36.19, 33.37, 29.30, 26.92, 26.87, 26.77, 26.53, 26.29, 22.89, 22.36, 19.48, 18.57, 13.57; MS m/z calcd (M^+) 449.3042, obsd 449.3047. Anal. Calcd for $C_{28}H_{39}N_3O_2$: C, 74.80; H, 8.74. Found: C, 74.77; H, 8.91.

Urazoles **24c** and **25c** were partially separated on silica gel (elution with 5% ethyl acetate in petroleum ether) with a Waters Prep 500A HPLC chromatograph operating in the recycling mode. The mixture was dissolved in the minimum quantity of dichloromethane and injected onto the HPLC. The leading and trailing edges were independently collected after five recycles. The diastereomeric excess of each fraction was established by ^{1}H NMR integration of the δ 0.77 and 0.75 singlets.

Hydrolysis–Oxidation of 25c. A sample of **25c** (31 mg, 0.069 mmol, trailing edge, 20% diastereomeric excess, $[\alpha]^{23}_D$ = −12.93°, $[\alpha]^{23}_{436}$ = −27.13°) in isopropyl alcohol (3 mL) and sodium hydroxide (83 mg, 2.08 mmol) was heated at reflux for 2.5 h under nitrogen. The cooled solution was acidified with 2 N hydrochloric acid to pH 1 and neutralized with 3 N ammonium hydroxide solution to pH 9. Pentane (8 mL) and activated manganese dioxide (100 mg) were added. After 30 min of stirring at room temperature, the reaction mixture was treated with additional pentane (8 mL). After filtration, the pentane layer of the filtrate was separated. The aqueous phase was extracted with pentane (2 × 10 mL), and the combined organic layers were washed with water, dried, and concentrated in the absence of heat. The residue was immediately chromatographed at −30 °C on Florisil. Elution with pentane gave 3.8 mg (26%) of (−)-**5c**, the spectra of which were identical with those reported earlier. The following rotations were recorded: $[\alpha]^{20}_D$ −22.63°, $[\alpha]^{20}_{578}$ −24.21°, $[\alpha]^{20}_{546}$ −29.47°, $[\alpha]^{20}_{436}$ −73.16°, $[\alpha]^{20}_{365}$ −218.42° (c 0.19, $CHCl_3$).

Cycloaddition of (−)-*endo*-Bornyltriazolinedione to 5d. A refluxing solution of **5d** (2.34 g, 9.69 mmol) in ethyl acetate (4 mL) under nitrogen was slowly treated dropwise with a solution of freshly sublimed (−)-**23** (2.13 g, 9.07 mmol) in 7 mL of ethyl acetate for a period of 6 h. The cooled mixture was concentrated in vacuo. Column chromatography of the residue on silica gel (elution with 7% ethyl acetate in petroleum ether) gave 0.966 g of recovered **5d** and 1.878 g (41%; 69% based on consumed **5d**) of **24d/25d** as a white solid: mp 154.5–156.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.70 (br s, 2 H), 4.85 (t, J = 4.5 Hz, 1 H), 4.61 (dd, J = 1.8, 3.9 Hz, 1 H), 4.20 (m, 1 H), 3.06 (m, 1 H), 2.40 (dd, J = 5.2, 12.9 Hz, 1 H), 2.25 (m, 1 H), 2.04 (m, 2 H), 1.88 (m, 1 H), 1.75–1.65 (m, 4 H), 1.58–1.27 (m, 18 H), 0.95 (s, 3 H), 0.77 (s, 1.5 H), 0.76 (s, 1.5 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 159.57, 159.48, 159.25, 153.74, 140.40, 140.31, 128.01, 115.32, 115.03, 114.83, 59.07, 59.00, 58.84, 54.63, 54.58, 51.58, 51.53, 47.59, 45.30, 42.17, 36.22, 32.47, 29.34, 28.57, 27.41, 26.94, 26.27, 26.06, 25.90, 25.44, 25.21, 23.83, 23.22, 19.51, 18.59, 14.08, 13.86; MS m/z calcd (M^+) 477.3355, obsd 477.3369. Anal. Calcd for $C_{30}H_{43}N_3O_2$: C, 75.43; H, 9.07. Found: C, 75.43; H, 9.13.

Urazoles **24d** and **2kd** were partially separated on silica gel (elution with 5% ethyl acetate in petroleum ether) with a Waters Prep 500A HPLC chromatograph operating in the recycling mode. The urazole mixture was dissolved in the minimum quantity of dichloromethane and injected onto the HPLC. The leading and trailing edges were independently collected after six recycles. The diastereomeric excess of each fraction was determined by ^{1}H NMR integration of the δ 0.77 and 0.76 singlets.

Hydrolysis–Oxidation of 24d. A sample of **24d** (38 mg, 0.08 mmol, leading edge with 23% diastereomeric excess) in isopropyl alcohol (3 mL) and sodium hydroxide (82 mg, 2.05 mmol) was heated at reflux for 2 h under nitrogen. The cooled reaction mixture was acidified with 2 N hydrochloric acid to pH 1 and neutralized with 3 N ammonium hydroxide to pH 9. Pentane (6 mL) and activated manganese dioxide (60 mg) were added. After being stirred at room temperature for 30 min, the reaction mixture was diluted with more pentane (8 mL). After filtration, the pentane layer in the filtrate was separated. The aqueous phase was extracted with pentane (2 × 8 mL), and the combined organic layers were washed with water, dried, and concentrated. The residue was immediately chromatographed at −30 °C on silica gel. Elution with pentane gave 78 mg (40%) of **5d**, which had no optical rotation.

A similar reaction was performed using the trailing edge urazole (60.4 mg, 0.127 mmol, $[\alpha]_D$ −7.1° (*c* 6.0, $CHCl_3$), 14% diastereomeric excess) and furnished 8.0 mg (26%) of **5d**, which likewise was totally racemic.

Peracid Oxidation of 21. To a mixture of **21** (15.2 mg, 0.06 mmol) and anhydrous sodium bicarbonate (13 mg, 0.16 mmol) in anhydrous dichloromethane (3 mL) was added *m*-chloroperbenzoic acid (18.5 mg of 56% purity, 0.06 mmol) in one portion. The reaction mixture was stirred at ambient temperature for 3 h, diluted with dichloromethane (50 mL), and washed with water (50 mL), saturated sodium bicarbonate solution (50 mL), water (50 mL), and brine (50 mL) prior to drying. After removal of the solvent in vacuo, the residue was chromatographed on silica gel (elution with 2% ethyl acetate in petroleum ether) to give **27** as a colorless oil (4.9 mg, 31%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.53 (t, J = 2.2 Hz, 1 H), 6.91 (s, 2 H), 3.99 (d, J = 2.2 Hz, 2 H), 2.82–2.54 (m, 4 H), 2.30 (s, 3 H), 1.94–0.43 (m, 16 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 199.99, 141.92, 136.85, 129.57, 125.77, 44.68, 33.31, 28.30, 26.99, 26.48, 26.43, 21.03.

Procedure for Determining Rates of Racemization for 5c. The sample of **5c** used for the kinetic studies was characterized by $[\alpha]^{20}_D$ +125.3°, $[\alpha]^{20}_{578}$ +132.3°, and $[\alpha]^{20}_{546}$ +160.0° (*c* 0.37, diglyme) and was obtained by oxidation–hydrolysis of a urazole sample that was 33% diastereomerically enriched, $[\alpha]^{20}_D$ +12.04° (*c* 0.49, $CHCl_3$). A 7.5-mg quantity of (+)-**5c** was dissolved in a polarimeter cell thermally equilibrated by means of a circulating constant-temperature bath. The solution was allowed to equilibrate for 4 min at 20.0 °C, an accurate timer was started, and readings were taken at appropriate time intervals. After adequate data were recorded, the solution temperature was then increased to 30.0 and 40.0 °C, respectively, where additional readings were again taken at appropriate time intervals. The resulting −ln α data were plotted vs time and slopes of the straight lines were determined by least-squares methods.

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Is Pseudorotation the Operational Pathway for Bond Shifting within [8]Annulenes? Probe of Planarization Requirements by 1,3-Annulation of the Cyclooctatetraene Ring. Kinetic Analysis of Racemization and 2-D NMR Quantitation of π-Bond Alternation and Ring Inversion as a Function of Polymethylene Chain Length

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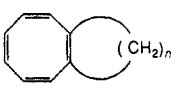
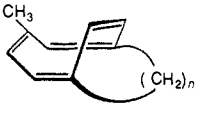
Abstract: The chiral 1,3-bridged cyclooctatetraenes **9a–c** have been prepared in nine steps from the appropriate 2-cycloalkenone precursors. Following annulation with ethyl acetoacetate to give **15**, *trans*-1,2-dichloroethylene was cycloadded photochemically in a [2 + 2] reaction and a cyclobutene ring was ultimately formed. Once reduction to alcohol **19** was accomplished, dehydration was effected and the bicyclo[4.2.0]octatrienes so generated underwent disrotatory ring opening to deliver the [8]annulenes. The rates of this electrocyclic ring opening were determined in two examples. Polarimetric studies provided quantitative measure of the readiness with which planar dianion formation occurs as a function of loop size. Unexpectedly, attempts to resolve these molecules failed to deliver them in optically active condition because of too rapid enantiomerization via ring inversion and/or bond shifting. The rates of these processes were determined by 2-D dynamic NMR methods, the data revealing that both processes are accelerated relative to nonbridged models. These and related findings are interpreted in terms of a pseudorotation scheme leading to flattened saddle and not planar-alternate transition states. The unique features associated with this mechanistic phenomenon are discussed.

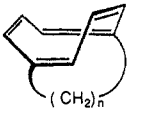
As extensive as studies of the dynamic properties of cyclooctatetraenes have been,[1] only recently has attention been paid to bracketing the [8]annulene core for the purpose of probing mechanistic detail. 1,2-Bridging as in **1** is now recognized to accelerate ring inversion rates relative to those of bond shifting.[2]



1



2



3

In contrast, (1,4)cyclooctatetraenophanes such as **2** that carry a short polymethylene chain (e.g., n = 5) are totally impeded from undergoing either process.[3] In the preceding paper,[4a] it was shown

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