Through-Bond Interaction via Cyclobutane Relay Orbitals. Evaluation of the Question of Extended Conjugation in Belted [4,5]Dihomotropones

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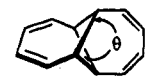
The preparation of tricyclo[6.5.0.0^{2,9}]trideca-3,6,10,12-tetraen-5-one (**3**), its dihydro derivative **16**, and the structurally related carbinol **17** has been successfully realized. In a companion synthesis of the lower homolog **4**, an inability to effect the desulfonylative ring contraction either of **26** or **29** was encountered. Although introduction of the ethylene bridge could be accomplished first as in **23**, the ease with which this ketal isomerized to **24** precluded its further use in the pursuit of **4**. Molecular mechanics calculations showed the dienone subunit in **4** to deviate significantly from planarity. This behavior is in striking contrast to the planar minimum energy conformations computed for [4,5]dihomotropone (**2**) and its higher vinylog **3**. An evaluation of the spectral properties of **3** reveal this ketone not to be polarized. No evidence that could be construed to be a reflection of ground-state through-bond interaction was uncovered.

The ability of perpendicularly oriented butadiene subunits to interact significantly[2] across the 1,3- and 2,4-positions of a cyclobutane ring as in **1** has been recognized for some time.[3] The symmetrical features of **1** and its 4*n* nature are particularly conducive to charge dispersal in the radical cation.[4] We have now investigated the feasibility of preparing the structurally related ketones **3** and **4** for the purpose of elucidating the interplay of



1

2

3

4

electronic interactions in these aesthetically appealing systems. In the preceding paper,[5] the parent unbelted [4,5]dihomotropone (**2**) has been described and shown to be a classical cross-conjugated cyclic ketone. As a consequence, this bridged cyclooctadienone network qualified as a suitable structural component for **3** and **4**.

The present effort seeks as its goal an experimental resolution to the question of whether the geometry, strain, and orbital constructs in **3** and **4** are conducive to through-bond interaction. If so, a respectable permanent dipole should be discernible, although understandably not to the level present in tropone[6] or its ten-π-electron homologue **5**.[7] Carbonyl base strength should consequently be suitably enhanced.[8]

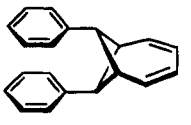
The ketone **6** was prepared several years ago and found to isomerize to **7** simply by chromatography on neutral alumina.[9] Obviously the strained nature of **6** lends itself to facile homolytic rupture of a cyclobutane bond adjacent to the carbonyl functionality. 1,5-Radical recombination delivers the more thermodynamically stable tricyclo-[5.3.0.0^{2,9}]decadienone framework.

5

6 **7**

Results

Anticipated Conformational Characteristics of 3 and 4. Among the several orientations that can be assumed by the diene bridge in **3**, it was expected that an essentially planar arrangement would be adopted. This assertion stems from X-ray crystallographic studies performed on **8**.[10] The conjugated diene component of



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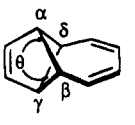

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this hydrocarbon was shown to be an essentially planar belt about the cyclobutane ring (<1.4° deviation at any point) despite the steric compression exerted across the

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(1) Abbott Fellow, 1993–1994.

(2) Bischof, P.; Gleiter, R.; Haider, R. *J. Am. Chem. Soc.* **1978**, *100*, 1036.

(3) (a) Dressel, J.; Chasey, K. L.; Paquette, L. A. *J. Am. Chem. Soc.* **1988**, *110*, 5479. (b) Gleiter, R.; Toyota, A.; Bischof, P.; Krennrich, G.; Dressel, J.; Pansegrau, P. D.; Paquette, L. A. *J. Am. Chem. Soc.* **1988**, *110*, 5490. (c) Paquette, L. A.; Dressel, J. In *Strain and its Implications*, de Meijere, A., Blechert, S., Eds.; Kluwer Academic Publishing: 1989; pp 77–107.

(4) For the UV and PE spectroscopy of related hydrocarbons, see: Gleiter, R.; Schäfer, W. *Acc. Chem. Res.* **1990**, *23*, 369.

(5) Paquette, L. A.; Watson, T. J.; Friedrich, D.; Bishop, R.; Bacqué, E. *J. Org. Chem.*, preceding paper in this issue.

(6) (a) Bertelli, D. J.; Andrews, T. G., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 5280. (b) Bertelli, D. J.; Andrews, T. G., Jr.; Crews, P. O. *J. Am. Chem. Soc.* **1969**, *91*, 5286.

(7) Grimme, W.; Reisdorff, J.; Jünemann, W.; Vogel, E. *J. Am. Chem. Soc.* **1970**, *92*, 6335.

(8) (a) Kende, A. *Adv. Chem. Phys.* **1965**, *8*, 133. (b) Hosoya, H.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1414.

(9) Gleiter, R.; Zimmermann, H.; Sander, W.; Hauck, M. *J. Org. Chem.* **1987**, *52*, 2644.

(10) Chasey, K. L.; Paquette, L. A.; Blount, J. F. *J. Org. Chem.* **1982**, *47*, 5262.

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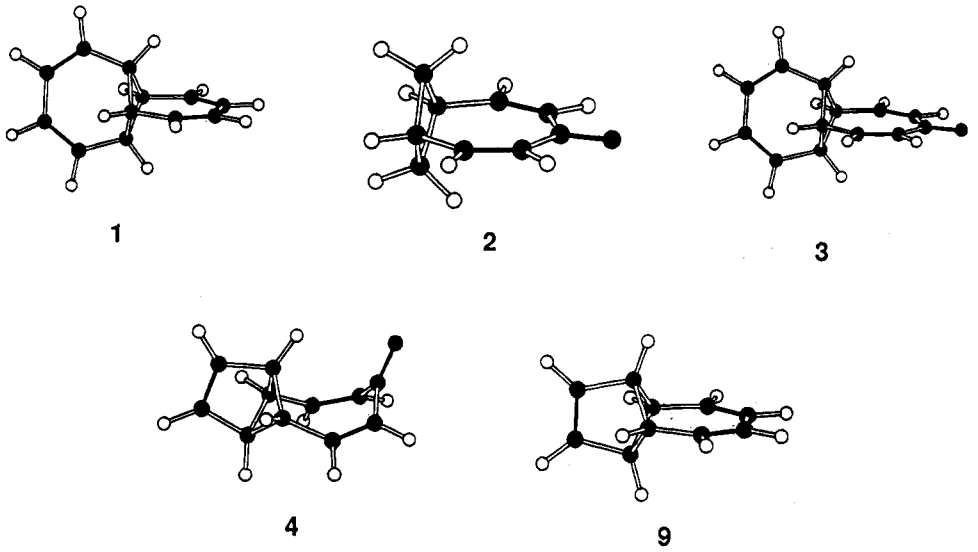


Figure 1. Global minimum energy conformations of **1**–**4** and **9** (Chem 3D output).

Table 1. Calculated Internal Angles (θ), Nonbonded α–γ Distances, and Cyclobutane Bond Lengths for 1-4 and 9[a]

compd	θ (deg)	α–γ distance, Å	β–δ length, Å
1	87.90	2.15	2.15
2	90.86	2.20	2.15
3	88.81	2.16	2.16
4	79.69	2.00	2.21
9	80.00	2.01	2.18

[a] The specific angle θ being defined is illustrated in the formulas. The α–γ distance and β–δ length are defined in **9**.

inner face of the two benzene rings. The spectral features of **1** and **9** are also consistent with high levels of planarity in their π-networks. Computational examination of the latter two polyolefins was carried out by means of the MODEL KS 2.99 program.[11] With use of the Grid Search function within this software package, multiconformer runs were performed simultaneously over each of the unsaturated rings but not the cyclobutane core. Following preliminary energy minimization analysis of the more than 25 conformers so generated, MMX was utilized to optimize the geometry of the global energy minimum. As seen in Figure 1, the dienyl bridges in **1** and **9** are completely planar. At 80.00°, the internal cyclopentenyl angles θ in **9** are approximately 8° more constrained than the cycloheptadienyl θ values in **1**. These data have been compiled in Table 1 alongside the calculated cyclobutane bond lengths.

Extension of these calculations to **2** revealed that incorporation of a carbonyl group at the midpoint of the diene functionality did not alter the preference of the π segment for adoption of a planar arrangement (Figure 1). Although the value of θ increases to 90.86° and the nonbonded α–γ distance is extended to 2.20 Å in order to accommodate this structural modification, the cyclobutane σ bond lengths remain normal.

The consequences of assimilating a dienone segment into **1** as in **3** on conformational planarity likewise appear to be negligible. The progression from **2** to **3** does give rise to a 2° compression in θ, equivalent to 0.4 Å in the α–γ distance, but exerts no discernible structural distortion in either bridge.

(11) We thank Prof. W. C. Still (Columbia) for making his program available for use and Prof. K. Steliou (Boston University) for providing us with updates of his software package.

This is not the case in **4**. Strikingly, the end result of constraining the nonketonic bridge to a single double bond is to fold the cyclooctadienone into a rather acute saddle-like geometry (Figure 1). This deviation from planarity is so remarkable and presents such a substantial departure from the norm that **4** was considered to be too strictly constrained to partake of through-bond interaction. Notwithstanding, our pursuit of the synthesis of this dienone was not interrupted.

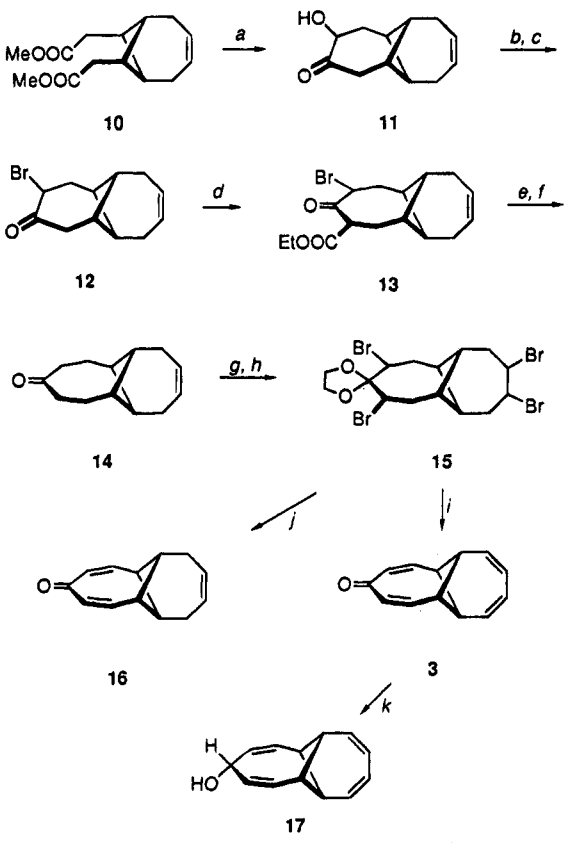
Synthesis of 3. The preparation of **3** began by acyloin cyclization of the bicyclo[4.1.1]octene diester **10** earlier utilized for the construction of tetraene **1**.[3a] Through use of 1:1 sodium–potassium alloy in benzene solution containing chlorotrimethylsilane, high dilution conditions for the desired ring closure could be conveniently skirted. Direct hydrolysis of the reaction mixture with 5% HCl in THF delivered **11** in 60% yield (Scheme 1). Conversion of this α-hydroxy ketone to **12** via the mesylate was accomplished according to standard protocol. With this intermediate in hand, the regioselective one-carbon homologation via reaction with ethyl diazoacetate under conditions of boron trifluoride etherate catalysis[12] was addressed as before.[5] Inductive control of bond migration operated splendidly in the desired direction and enabled the isolation of **13** in 80% yield. Although **13** was produced as a single diastereomer, it was unnecessary to specify the relative stereochemistry of the α and α' substituents since their removal was to ensue immediately. Treatment with powdered zinc and acetic acid in ether provided the α-keto ester, which underwent hydrolysis and decarboxylation when heated with 5 M hydrochloric acid in acetone.

The C_{2v} symmetry of **14** produced efficiently (80% overall) by this means was made readily apparent on spectroscopic grounds. Its 300 MHz ^{1}H NMR spectrum (in $CDCl_3$) consists only of a downfield singlet (δ 5.52, 2 H), midfield triplet (δ 2.58, J = 6 Hz, 4 H), and upfield multiplet (δ 2.18, 12 H). The seven-line ^{13}C NMR spectrum is consistent only with the indicated structural assignment.

The conversion of **14** to **15** was expeditiously accomplished by exhaustive bromination of the ethylene ketal. The conditions used were adequate to achieve

(12) Dave, V.; Warnhoff, E. W. *J. Org. Chem.* **1983**, *48*, 2590.

Scheme 1



[a] Na-K (1:1), Me_3SiCl, C_6H_6, Δ; 5% HCl, THF. [b] CH_3SO_2Cl, py, CH_2Cl_2. [c] LiBr, acetone, Δ. [d] $N_2CHCOOEt$, $BF_3{\cdot}OEt_2$, CH_2Cl_2, 0 °C. [e] Zn dust, HOAc, ether. [f] 5 M HCl, acetone, Δ. [g] Ethylene glycol, TsOH, C_6H_6, Δ (-H_2O). [h] Br_2 (9 eq), $HOCH_2CH_2OH$, ether. [i] 1.0 M KO*t*-Bu, THF, 0 °C → rt (3 h); 8% H_2SO_4. [j] LiBr, Li_2CO_3, CH_3CONMe_2, 120 °C, 10 min. [k] $NaBH_4$, $CeCl_3$, MeOH, 0 °C.

concurrent electrophilic attack at the olefinic π-bond as well as the sites positioned α and α′ to the ketal.[13] The latter sequence of events is made possible by acid-catalyzed opening of the ketal to an enol ether and brominative attack at these reactive centers. Once one bromine is introduced in this way, further halogen incorporation becomes kinetically impeded.

When the multiple dehydrobromination of **15** with potassium *tert*-butoxide, performed in THF at 0 °C to room temperature, was quenched after 3 h, and the resulting tetraene ketal directly hydrolyzed in 8% sulfuric acid, the target ketone **3** was obtained in 30% yield. The drop in yield incurred at the final step is not due to the inefficiency of the hydrolysis reaction but to the sensitivity of **3** to the acidic conditions required for the deprotection. Tricyclo[6.5.0.$0^{2,9}$]trideca-3,6,10,12-tetraen-5-one (**3**), a white solid of mp 92–93 °C, was easily identified by its ^1H and ^{13}C NMR spectra, the features of which are discussed below.

The need to have reference compounds in hand for direct comparison with **3** was met in two ways. In the course of a survey of reactions for effecting removal of the bromine atoms in **15**, brief heating with lithium bromide and lithium carbonate in dimethylacetamide at 120 °C was noted to promote 2-fold dehydrobromination α to the ketal as usual. For the nonoxygenated ring, however, reductive debromination was uniquely observed. As a consequence, subsequent mild acid hydrolysis afforded trienone **16**. Rather modest yields were realized, due in part again to the appreciable lability of this trienone.

Alcohol **17** is the sole product of the Luche reduction[14] of **3**. The heightened sensitivity of this alcohol required operation at 0 °C throughout its formation and spectral analysis. High field ^1H NMR data for **17** were recorded both in $CDCl_3$, to enable direct comparison with **3**, and in C_6D_6 since in this solvent system the vinyl protons were particularly well separated. As seen in Figure 2, the reduction of symmetry from C_{2v} to the C_2 level is reflected most clearly in the magnetic equivalence of the lateral cyclobutane protons labeled H_d and the wide disparity in the chemical shifts of their apical counterparts H_b and H_c.

Synthetic Plan for 4. The operational equivalent selected for the ethylene bridge in **4** was the -CH(Cl)-SO_2CH_2- array, in anticipation of successful ring contraction by means of the Ramberg–Bäcklund rearrangement.[15] Projected incorporation of this methodology led us back retrosynthetically to **22** where concurrent 1,2-elimination of HBr and 1,3-elimination of HCl would be required to operate. To this end, the known hydroxy ketone **18**[3a] was mesylated and subjected to S_N2 displacement with tetrabutylammonium bromide in refluxing benzene. Without purification of the α-bromo ketone, its tetrahydropyranyloxy groups were replaced directly by bromine following exposure to triphenylphosphine–dibromide in CH_2Cl_2 at 0 °C.[16] This three-step sequence afforded **19** in 75% yield (Scheme 2). As expected, regiocontrolled ring expansion by way of the Warnhoff procedure,[12] followed by reductive decarboxylation, made dibromo ketone **20** available with good overall efficiency (66%).

The effectiveness of this C_{2v} symmetric intermediate in the synthetic scheme required its controlled conversion to **21**. This transformation was realized without complication provided that ketalization preceded heating with sodium sulfide in anhydrous HMPA at 110 °C.[17] ^1H NMR spectroscopic analysis of this intermediate showed the four dioxolane protons to appear as a singlet and the remaining methylene groups to be displayed as three narrow multiplets. The ^{13}C NMR spectrum of **21** consisted of 7 lines.

Due to the constraints brought on by the nucleophilicity of divalent sulfur, it proved necessary to introduce the α-chloro sulfone functionality first. This conversion was achieved conventionally by heating **21** with 1 equiv of *N*-chlorosuccinimide in CCl_4[18] followed by peracid oxidation. Once this assemblage process was complete, α,α′-dibromination of the ketal proceeded well to give **22** (73% for the three steps). The two bromine atoms are depicted as having a trans relationship. Although this stereochemical feature could not be proven directly because of the spectroscopic complexities brought on by the configurational randomness at the chlorine-substi-

(13) Garbisch, E. *J. Org. Chem.* **1965**, *30*, 2109.

(14) Gemal, A. L.; Luche, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 5454.

(15) (a) Paquette, L. A. *Org. React.* **1977**, *25*, 1. (b) Clough, J. M. In *Comprehensive Organic Synthesis;* Trost, B. M., Ed.; Pergamon Press: 1991; Volume 3, Chapter 3.8.

(16) (a) Schwartz, M.; Oliver, J. E.; Sonnet, P. E. *J. Org. Chem.* **1975**, *40*, 2410. (b) Sonnet, P. E. *Synth. Commun.* **1976**, *6*, 21.

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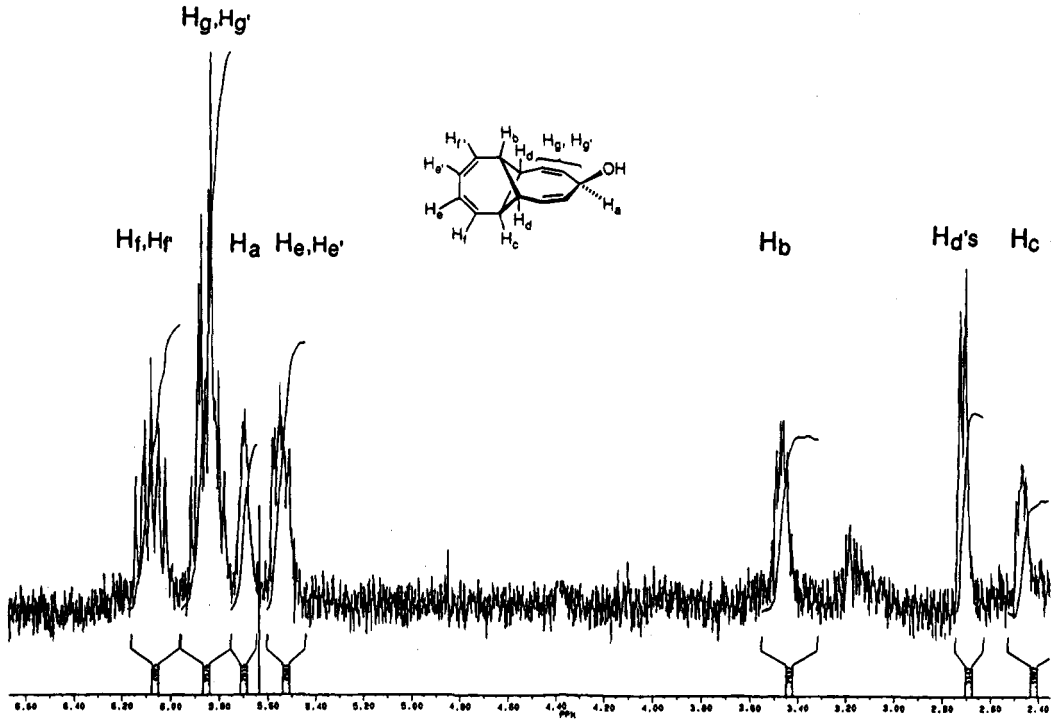


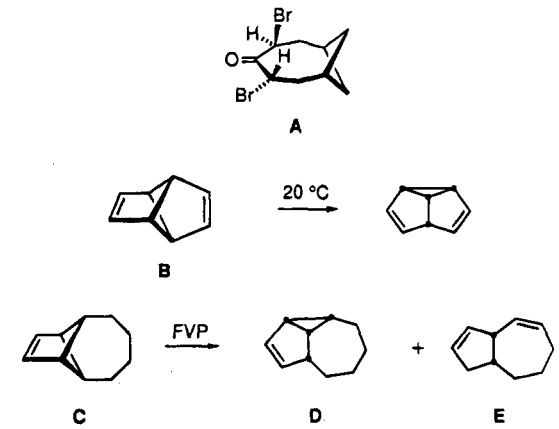
Figure 2. Expanded scale 300 MHz ^{1}H NMR spectrum of **17** recorded in C_6D_6 near 0 °C.

tuted carbon, a number of phenomena indirectly support this conclusion. The subsequent conversion of **22** to **23** (see below) is in agreement but is not confirmatory because of possible epimerization in the alkaline environment conducive to the Ramberg–Bäcklund process. More to the point, bromination of the ethylene ketal of bicyclo[5.1.1]nonan-4-one gives rise uniquely to **A**[5] and the sulfone of **21** affords only **27**. Consequently, following introduction of the first bromine, steric factors manifest themselves to direct the second bromine to the opposite surface of the transient enol.

With ample quantities of **22** available, it was possible to gain insight into the means for effecting the regiocontrolled dehydrohalogenation of this key intermediate. Our initial plan to utilize sodium methoxide in methanol at 0 → 25 °C surprisingly gave no observable reaction. When heating such solutions led to decomposition, certain boundary limitations were established early. At the high basicity end of the scale, potassium *tert*-butoxide in DMSO at rt similarly induced polymerization. Utilizing commercially available 1 M solutions of potassium *tert*-butoxide in THF and operating at −78 °C for short reaction times (10 min), we observed operation of the Ramberg–Bäcklund reaction with loss of sulfur dioxide to give **23**. As a consequence of the thermal instability of **23** (estimated $t_{1/2}$(0 °C) ≈ 45 min), one must process the material rapidly in order to record its NMR spectra. The seven-line carbon spectrum displayed by **23** requires that the bromine atoms have a trans relationship.

On standing for several hours, **23** was completely isomerized to **24**. The stereochemical assignment to **24** is based on the trans disposition of the bromine atoms established in the precursor ketal **23** and the observation of an NOE effect between the -C*H*Br- proton at δ 5.15 and the very characteristic cyclopropyl proton having a chemical shift of δ 0.66. As shown in the illustrated formula, this interaction requires that the two indicated protons be positioned cis on the topologically folded framework in order to achieve adequate proximity.

Analogous 1,3 shifts have been observed for **B**, which rearranges to semibull-valene with an estimated $t_{1/2}$(20 °C) of 10 min,[19] and for **C**, which is transformed into a



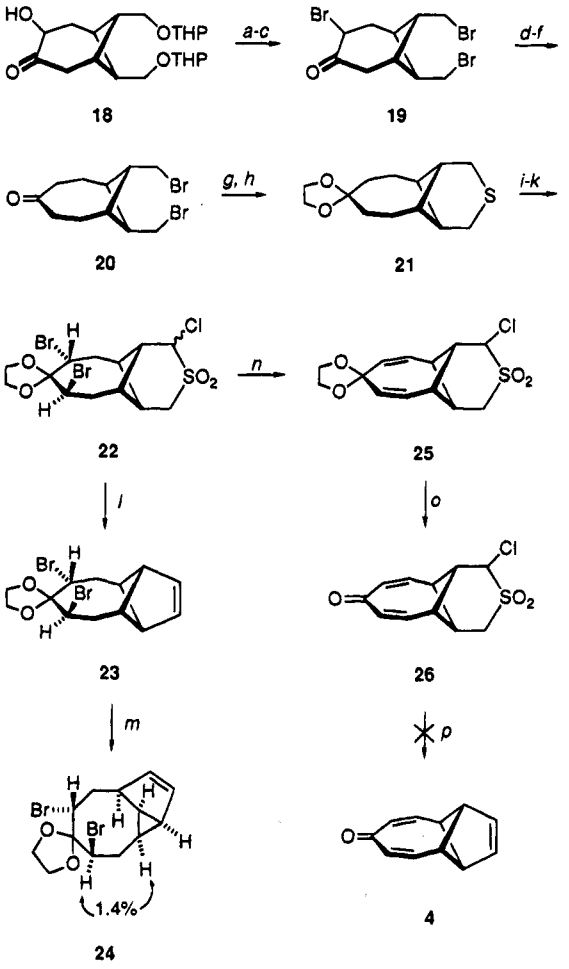
1:1 mixture of **D** and **E** at 500 °C and 10^{-5} Torr under flash vacuum pyrolysis conditions.[20] The reactivity of **23** is much more closely aligned to that of diene **B**, although it is related more closely in a structural sense to **C**. This unexpected turn of events prompted us to seek an alternative means for approaching **4**.

Brief heating of **22** with lithium bromide and lithium carbonate in dimethylacetamide permitted controlled conversion to **25** in 94% yield. Hydrolysis of this ketal by methodology developed earlier for the acquisition of **3** provided **26**. The heat- and light-sensitive nature of this dienone was soon recognized, and its expeditious handling was, of course, undertaken. All attempts to bring about the desulfonylative ring contraction of **26** failed to deliver **4**. From among the many bases exam-

(19) (a) Zimmerman, H. E.; Robbins, J. D.; Schantl, J. *J. Am. Chem. Soc.* **1969**, *91*, 5878. (b) Frey, H. M.; Hopkins, R. G. *J. Chem. Soc. B* **1970**, 1410.

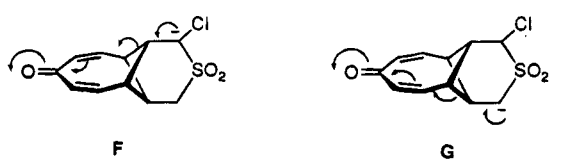
(20) Gleiter, R.; Steuerle, U. *Chem. Ber.* **1989**, *22*, 2193.

Scheme 2



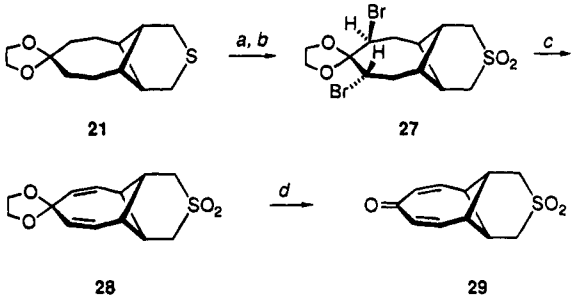
[a] CH_3SO_2Cl, Et_3N, CH_2Cl_2. [b] $Bu_4N^+Br^-$, C_6H_6, Δ. [c] $Ph_3P{\cdot}Br_2$, CH_2Cl_2, 0 °C. [d] $N_2CHCOOEt$, $BF_3{\cdot}OEt_2$, CH_2Cl_2, 0 °C. [e] Zn, HOAc, Et_2O. [f] 25% HBr, acetone, Δ. [g] Ethylene glycol, TsOH, C_6H_6, Δ (-H_2O). [h] Na_2S, HMPA, 110 °C. [i] NCS (1 eq), CCl_4, Δ. [j] MCPBA, $NaHCO_3$, Et_2O. [k] Br_2, Et_2O. [l] 1.0 M KO*t*-Bu, THF, -78 °C, 10 min. [m] $CDCl_3$, rt. [n] LiBr, Li_2CO_3, CH_3CONMe_2, 140 °C. [o] 8% H_2SO_4, THF, 0 °C, 2 min. [p] See text.

ined, including potassium *tert*-butoxide, potassium hydride, and lithium 2,2,6,6-tetramethylpiperidide at low temperatures, all were found to promote *immediate* formation of a heavy black tar. These observations, not normally associated with Ramberg–Bäcklund rearrangements, could be signaling the operation of an alternative mode of fragmentation arising after generation of the α-sulfonyl carbanions **F** or **G**.



Independent support for this conclusion was gained by preparation of dienone sulfone **29** as outlined in Scheme 3. Noteworthy as to stereochemical detail is the finding that the dibromination of the sulfone related to **21** provides in 99% yield the trans product exclusively. Point group considerations allow for proper distinction between the C_{2v}-symmetric **27** (seven ^{13}C lines) from the cis isomer of lower (C_2) symmetry (eight carbon signals)

Scheme 3



[a] MCPBA, CH_2Cl_2. [b] Br_2, Et_2O. [c] LiBr, Li_2CO_3, CH_3CONMe_2, 140 °C. [d] 8% H_2SO_4, THF, 0 °C, 2 min.

which was not seen. All attempts to generate the anion of **29** resulted in an entirely similar rapid production of black tar. The base sensitivity exhibited by **26** and **29** proved adequate to thwart this approach to **4** and further work was discontinued.

Assessment of the Electronic Nature of 3. Any elucidation of prevailing through-bond interaction in **3**, if operative at all, is dependent upon appropriate comparison of physically measurable properties with those of suitable model systems. Since the focus of our attention is on the neutral ketone, the methods of choice available for establishing an emerging polarization are primarily spectroscopic in nature. While dipole moment measurements often provide a quantitative measure of charge separation in the ground state and allow correlation with theoretically calculated electron distribution, the lability of **3** was not conducive to analysis in this manner.

The carbonyl stretching frequency of **3** in the infrared, as determined in CCl_4 solution, appears at 1654 cm^{-1}. The location of this absorption is identical within experimental error to that measured for the parent dihomotropone **2** (1653 cm^{-1}).[5] Both of these values reside at a somewhat higher wavenumber than that reported for 2,6-cyclooctadienone (1640 cm^{-1})[13] and very distant from the well-known tropone (1597 cm^{-1}) band. A much greater level of similarity is evident when comparison is made with 2,6-cycloheptadienone (1647 cm^{-1})[13] and 4,5-homotropone (1650 cm^{-1}, neat).[21] The latter dienone is recognized to experience essentially no delocalization through its cyclopropane ring.

NMR investigations of unsaturated 1,3-bridged cyclobutanes and their doubly annulated homologs abound.[22] The high level of interest in these systems has its origin in the unusually large ^{13}C shifts evident for the homoallylic carbons, while the allylic carbons are only slightly perturbed. Moreover, the direction of the shift increment relative to reference compounds is highly dependent on whether a monoene or diene bridge is involved.

As seen in Figure 3, the ^{13}C sequencing in **3** correlates very well with the data previously recorded for **1** and **2**. The carbon atoms labeled *d* in **1** and **3** exhibit virtually identical shifts. The internal carbon *c* in **3** appears 2.3 ppm downfield than its counterpart in **1**. This small difference can be reliably attributed to the small change in θ (Table 1) and to the obvious variation in the local paramagnetic anisotropy[22d] brought on by the presence

(21) Chapman, O. L.; Fugiel, R. A. *J. Am Chem. Soc.* **1969**, *91*, 215.
(22) (a) Christl, M.; Herbert, R. *Org. Magn. Reson.* **1979**, *12*, 150. (b) Sander, W.; Gleiter, R. *Chem. Ber.* **1985**, *118*, 2548. (c) Christl, M.; Herzog, C. *Chem. Ber.* **1986**, *119*, 3067. (d) Wilcox, C. F., Jr.; Gleiter, R. *J. Org. Chem.* **1989**, *54*, 2688.

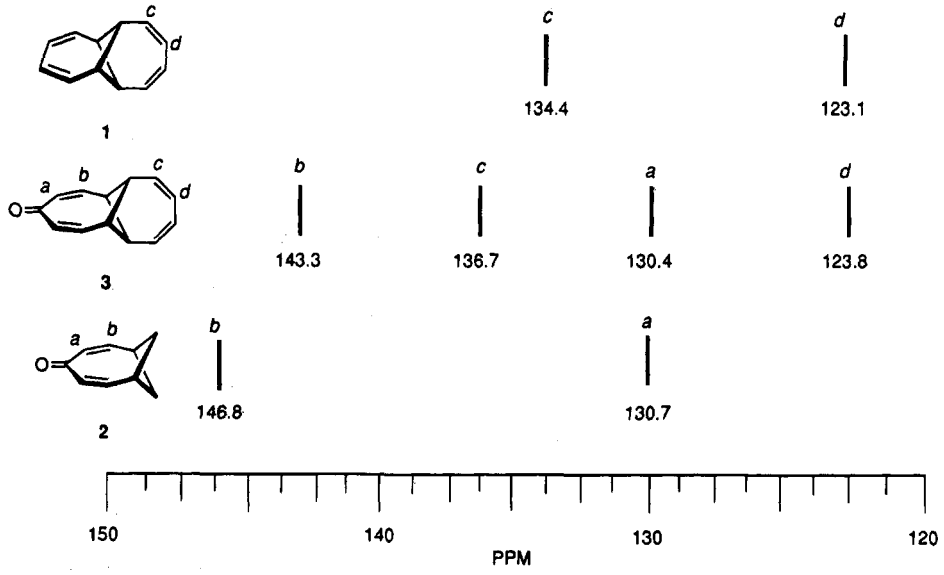


Figure 3. Comparison of the ^{13}C chemical shifts of the olefinic carbons in **1**–**3**.

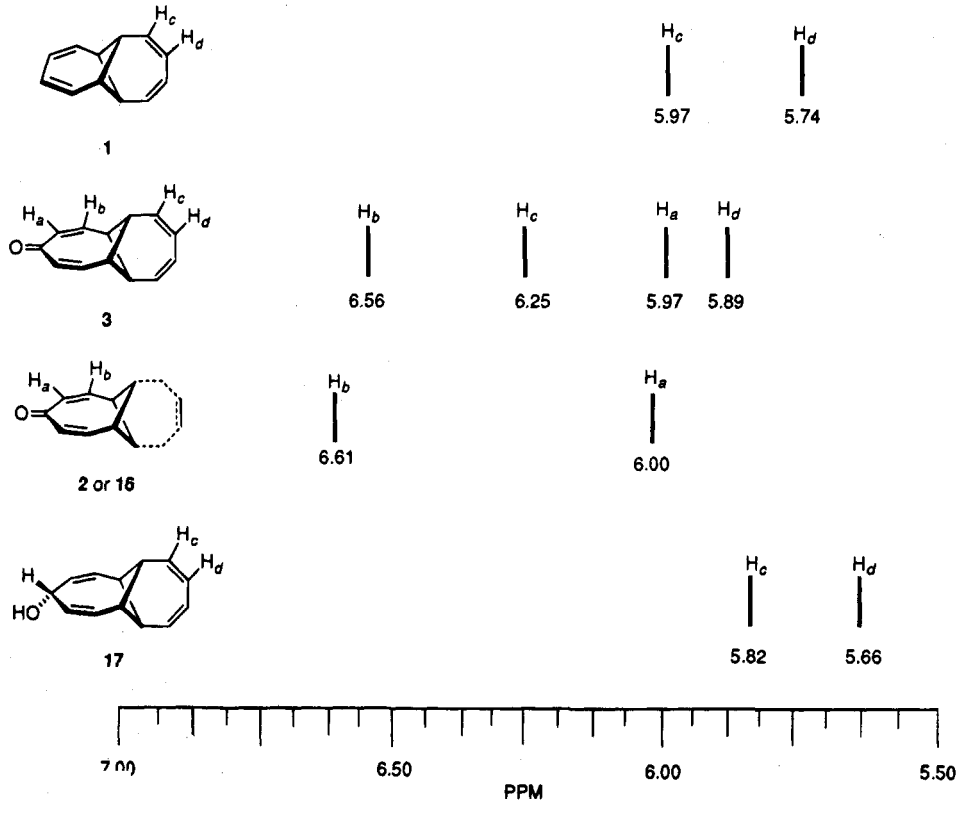


Figure 4. *Comparison of the ^1H chemical shifts of the olefinic protons in* **1**–**3**, **16**, *and* **17**.

of the ketone carbonyl. Similar effects are evident upon inspection of the data for **2** and **3**. Thus, the more distal carbon from the bridge labeled as *a* appears at essentially the same locale in both spectra. There is greater variance in the shifts arising from C_b because of bridge proximity and difference in local anisotropy caused by the presence or absence of a 1,3-diene bridge. To a first approximation, therefore, ^{13}C NMR spectroscopy indicates that **3** enjoys no special electronic character.

The same conclusion is arrived at by ^1H NMR (Figure 4). The upfield shifts for H_c in **1** and **17** can be viewed as normal in the context of additional olefinic centers on the second bridge. In **3**, both of these signals experience a modest downfield displacement, the more so for H_c, because of the electron-withdrawing contribution of the carbonyl group and the relative distances involved. For this reason, it is perhaps more significant to focus on the relative positions held by H_a and H_b in **3**. These are so very closely mirrored by the corresponding resonances in **2** and **16**, with the minor exception of the diene field effect on H_b in **3** as to be considered reflective of the absence of detectable polarization.

Conclusions

The major thrust of this study has been an attempt to prepare the first belted [4,5]dihomotropones and to define the importance of through-bond electronic interaction to

their ground-state character. The larger of these systems, *viz.* **3**, predicted by molecular mechanics methods to be conformationally planar in both of its unsaturated rings, proved nevertheless to be kinetically unstable. Although not exceptionally strained, this tetraenone was seen to decompose over a short time upon storage at 0 °C. We conclude from its infrared and NMR characteristics that **3** does not profit from potential polarization through its cyclobutane σ bonds.[2] A clearcut feature of the experimental evidence is the virtually complete absence of recognition on the part of the dienone subunit that a 1,3-butadiene belt is positioned orthogonally in close proximity to its β carbons. This conclusion is, of course, only as good as the model systems selected for comparison. In our view, however, ketone **16** and alcohol **17** are well designed and suitably functionalized to probe the issues involved.

We presume that our inability to obtain **4** rests on the unsuitability of the Ramberg–Bäcklund rearrangement in this particular context. One might therefore inquire how stable **4** might be if produced by some alternative method. Its intrinisic strain, which induces the cyclooctadienone ring to be substantially puckered, should be adequate to preclude its prolonged survival under ordinary laboratory conditions. If this proves indeed to be the case, as is expected, the criteria for through-bond dihomoaromaticity would be present in very few select molecules and hardly widespread. We had hoped that the actual scenario would be otherwise.

Experimental Section

Melting points are uncorrected. IR spectra were recorded on Perkin-Elmer 1300 or 1600 series FTIR spectrometers. ^{1}H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra at 75 MHz unless otherwise noted. High resolution and fast atom bombardment mass spectra were obtained at The Ohio State University Campus Chemical Instrumentation Center. Elemental analyses were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark. The column chromatographic separations were carried out on silica gel (40 μm, 230–400 mesh) obtained from Scientific Absorbents Incorporated. Solvents were reagent grade and in most cases dried prior to use.

5-Hydroxytricyclo[5.5.0.0^{2,8}]dodec-10-en-4-one (11). Sodium–potassium alloy was prepared by refluxing a mixture of sodium (0.60 g) and potassium (0.60 g) in anhydrous benzene (50 mL) until silver droplets had formed. After being cooled, the mixture was treated during 1 h with a solution of **10**[3a] (750 mg, 2.9 mmol) and chlorotrimethylsilane (2.3 mL) in dry C_6H_6 (10 mL). Upon completion of the addition, the reaction mixture was refluxed for 24 h during which time a purple color developed, cooled, and filtered through glass wool (subsequently flushed with 50 mL of ether). The combined organic solutions were evaporated and the residue was taken up in THF (10 mL), treated with 5% HCl (4 mL), and refluxed for 1 h. After being cooled, this solution was neutralized with calcium carbonate (1 g) and the THF was evaporated. The residue was triturated with ether (3 × 10 mL) and these extracts were dried and concentrated to give **11** as a colorless oil (342 mg, 60% over two steps): IR (CCl_4, cm^{-1}) 3490, 2660, 1446; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.51 (s, 2 H), 4.73–4.64 (m, 1 H), 3.61 (d, J = 4.4 Hz, 1 H), 2.79 (dd, J = 15, 6 Hz, 1 H), 2.69–2.51 (m, 3 H), 2.27 (m, 2 H), 2.22 (m, 2 H), 2.07 (m, 2 H), 1.63 (d, J = 4 Hz, 1 H), 1.48 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 213.3, 125.3, 125.0, 75.3, 45.5, 42.3, 39.1, 38.0, 37.5, 35.0, 33.4, 32.8; MS m/z (M$^+$) calcd 192.1150, obsd 192.1146.

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.51; H, 8.46.

5-Bromotricyclo[5.5.0.0^{2,8}]dodec-10-en-4-one (12). A cold (0 °C), nitrogen-blanketed solution of methanesulfonyl chloride (0.15 mL, 2.10 mmol) in anhydrous CH_2Cl_2 (2 mL) was treated sequentially with anhydrous pyridine (0.38 mL, 4.40 mmol) and a solution of **11** (203 mg, 1.05 mmol) in dry CH_2Cl_2 (1 mL). The reaction mixture was stirred at 0 °C for 3 days, quenched with water (3 mL), and neutralized with 10% HCl. The product was extracted into CH_2Cl_2 (3 × 5 mL), washed with saturated $NaHCO_3$ solution (2 mL), dried, and evaporated.

A mixture of the residual oil from above, anhydrous LiBr (1.0 g), and acetone (5 mL) was refluxed under N_2 for 4 h, cooled to rt, stirred for 24 h, evaporated, and diluted with water (2 mL). The product was extracted into CH_2Cl_2 (3 × 2 mL) and the combined organic phases were dried and concentrated. The residue was subjected to chromatography on silica gel (elution with 8% ethyl acetate in hexanes) to furnish 112 mg (42% overall) of **12** as a colorless oil: IR (CCl_4, cm^{-1}) 1716, 1422; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.56 (s, 2 H), 5.03 (dd, J = 11, 7 Hz, 1 H), 2.91 (dd, J = 14, 5 Hz, 1 H), 2.68–2.57 (m, 2 H), 2.46–2.08 (series of m, 8 H), 1.96–1.94 (m, 1 H); ^{13}C NMR (75 MHz, cm^{-1}) ppm 203.8, 125.3, 125.0, 55.0, 45.9, 40.7, 40.4, 40.1, 38.1, 34.9, 33.0, 32.7; MS m/z (M$^+$) calcd 254.0306, obsd 254.0300.

Ethyl 6-Bromo-5-oxotricyclo[6.5.0.0^{2,9}]tridec-11-ene-4-carboxylate (13). A solution of **12** (81 mg, 0.318 mmol) in CH_2Cl_2 (1.6 mL, 1.59 mmol) was cooled to 0 °C under N_2, mixed with freshly distilled boron trifluoride etherate (0.20 mL), and treated dropwise during 1 h with a solution of ethyl diazoacetate (0.17 mL, 1.59 mmol) in CH_2Cl_2 (1 mL). The reaction mixture was stirred at 0 °C for 30 min and at rt overnight, quenched with water (2 mL), and stirred overnight. After dilution with more CH_2Cl_2, the organic phase was separated, dried, and evaporated. The residue was purified by silica gel chromatography (elution with 10% ethyl acetate in petroleum ether) to give 87 mg (80%) of **13** as a white solid, mp 130–131 °C: IR (CCl_4, cm^{-1}) 1732, 1709, 1258; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.49 (s, 2 H), 4.54 (dd, J = 12, 6 Hz, 1 H), 4.20–4.06 (m, 3 H), 2.73–2.63 (m, 1 H), 2.44–2.39 (m, 1 H), 2.35–2.03 (series of m, 10 H), 1.21 (t, J = 7 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 205.8, 169.1, 125.2 (2 C), 61.6, 50.5, 49.8, 41.7, 39.9, 38.4, 37.5, 35.8, 34.4, 33.9, 33.8, 13.9; MS m/z (M$^+$) calcd 340.0674, obsd 340.0642.

Anal. Calcd for $C_{16}H_{21}BrO_3$: C, 56.32; H, 6.20. Found: C, 56.24; H, 6.33.

Tricyclo[6.5.0.0^{2,9}]tridec-11-en-5-one (14). A mixture of **13** (80 mg, 0.234 mmol), ether (13 mL), acetic acid (1.34 mL), and zinc dust (0.67 g) was stirred rapidly at rt for 1 h under N_2. The solid was separated by filtration, and the filtrate was washed with water (3 × 3 mL), dried, concentrated, and used directly.

The above β-keto ester in acetone (5 mL) was treated with 5 M HCl (5 mL), refluxed for 4 h, cooled , and evaporated. The remaining aqueous solution was extracted with CH_2Cl_2 (3 × 5 mL), and the combined organic layers were dried and evaporated to afford 36 mg (80% over two steps) of **14**. An analytical sample was obtained by silica gel chromatography (elution with 10% ethyl acetate in petroleum ether): colorless oil; IR (CCl_4, cm^{-1}) 1698, 1421, 1350; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.52 (s, 2 H), 2.58 (t, J = 6 Hz, 4 H), 2.33–2.04 (series of m, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 219.7, 125.6, 39.7, 38.6, 38.5, 34.2, 29.8; MS m/z (M$^+$) calcd 190.1358, obsd 190.1364.

4′,6′,11′,12′-Tetrabromospiro[1,3-dioxolane-2,5′-tricyclo-[6.5.0.0^{2,9}]tridecane] (15). A solution of **14** (36 mg, 0.19 mmol), ethylene glycol (0.5 mL), and *p*-toluenesulfonic acid (1 mg) in benzene (10 mL) was refluxed under a Dean–Stark trap for 24 h. After cooling, solid Na_2CO_3 was added to achieve neutralization and the benzene was evaporated. The residue was triturated with pentane (3 × 10 mL) and ether (10 mL). The combined organic solutions were dried and evaporated to leave 36 mg (80%) of the dioxolane.

A cooled (0 °C) solution of the dioxolane (277 mg, 1.2 mmol) in diethyl ether (3 mL) containing ethylene glycol (0.10 mL) was treated with 9 equiv (0.54 mL) of bromine via syringe. The reaction mixture was maintained at rt for 24 h, poured into pentane (30 mL) containing Na_2CO_3 (1.0 g), stirred until the orange color no longer persisted, and diluted with water

(50 mL). The product was extracted into ether (3 × 20 mL), dried, and concentrated. The residue was chromatographed on silica gel to give **15** (300 mg, 46%) as a white solid, mp 170–210 °C with slow decomposition: IR (CCl_4, cm^{-1}) 2959, 2928, 2872; ^1H NMR (300 MHz, $CDCl_3$) δ 4.85–4.78 (m, 2 H), 4.58–4.47 (m, 2 H), 4.37–4.25 (m, 4 H), 2.85–2.55 (series of m, 4 H), 2.30 (m, 6 6 H), 2.19–2.10 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 110.6, 110.5, 68.4, 68.3, 57.1, 56.8, 56.1, 55.9, 42.5, 42.1, 39.5, 39.3, 38.7, 37.0, 36.9; FAB MS *m/z* (M^+ + 1) calcd 548.82, obsd 548.85.

Anal. Calcd for $C_{15}H_{20}Br_4O_2$: C, 32.64; H, 3.65. Found: C, 32.90; H, 3.75.

Tricyclo[6.5.0.0^{2,9}]trideca-3,6,10,12-tetraen-5-one (3). To a cooled (0 °C), nitrogen-blanketed solution of **15** (51 mg, 0.091 mmol) in THF (2 mL) was added 1.0 M potassium *tert*-butoxide in THF (0.73 mL, 8 equiv). The reaction mixture was stirred at rt for 3 h, quenched with water (3 mL), and extracted with pentane (3 × 5 mL). The combined organic layers were shaken with cold 8% H_2SO_4 for 30 min and neutralized with saturated $NaHCO_3$ solution (2 × 10 mL) prior to drying and concentration in vacuo. Flash chromatography of the residue (silica gel, elution with 5% ethyl acetate in hexanes) gave rise to 5 mg (30%) of **3** as a colorless crystalline solid, mp 92–93 °C: IR (CCl_4, cm^{-1}) 1654; UV $\lambda 2^{EtO}_{max}$ 240 (log ε 3.70) and 2.90 (log ε 3.35); ^1H NMR (300 MHz, $CDCl_3$) δ 6.56 (dd, *J* = 13, 8.5 Hz, 2 H), 6.25 (m, 2 H), 5.97 (d, *J* = 13 Hz, 2 H), 5.89 (m, 2 H), 2.81 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 195.3, 143.4, 136.7, 130.4, 123.8, 39.4, 36.3; MS *m/z* (M^+) calcd 184.0887, obsd 184.0882.

Tricyclo[6.5.0.0^{2,9}]trideca-3,6,11-trien-5-one (16). Tetrabromo ketal **15** (10 mg) was added to a mixture of predried LiBr (10 mg, 0.018 mmol) and lithium carbonate (10 mg) in dimethylacetamide (1 mL), and the solution was heated at 120 °C for 10 min. The cooled reaction mixture was diluted with water (3 mL) and extracted with ether (1 mL). The ethereal phase was shaken with cold 7% H_2SO_4 (10 mL) for 10 min, dried, filtered, and concentrated to give **16**, whose spectra were immediately recorded: ^1H NMR (300 MHz, $CDCl_3$) δ 6.59 (dd, *J* = 13, 8 Hz, 2 H), 5.99 (d, *J* = 13 Hz, 2 H), 5.58 (s, 2 H), 2.55 (dd, *J* = 11, 2Hz, 2 H), 2.46 (s, 2 H), 2.35 (d, *J* = 2 Hz, 4 H); GC/MS *m/z* (M^+) calcd 186.25, obsd 186.15.

Tricyclo[6.5.0.0^{2,9}]trideca-3,6,10,12-tetraen-5-ol (17). A solution of **3** (10 mg, 0.018 mmol) in cold (0 °C) 0.4 M $CeCl_3$ in methanol (1 mL) was treated with sodium borohydride (5 mg), stirred for 5 min, and diluted with chloroform. After the solution was washed with ice water (2 × 5 mL), the $CHCl_3$ was immediately dried and concentrated, and the resulting alcohol was examined spectroscopically at 0 °C without delay: ^1H NMR (300 MHz, $CDCl_3$) δ 6.33–6.19 (m, 2 H), 5.96 (br s, 1 H), 5.86–5.64 (m, 6 H), 3.62–3.57 (m, 1 H), 2.62 (d, *J* = 6 Hz, 2 H), 2.48–2.44 (m, 1 H); GC/MS *m/z* (M^+) calcd 186.25, obsd 186.18.

***endo,endo*-4-Bromo-7,8-bis(bromomethyl)bicyclo[4.1.1]octan-3-one (19).** A cold (0 °C), nitrogen-blanketed solution of **18** (2.0 g, 5.4 mmol), triethylamine (7.5 mL, 9 equiv), and 4-(dimethylamino)pyridine (20 mg) in dry CH_2Cl_2 (30 mL) was treated dropwise with methanesulfonyl chloride (2.11 mL, 27 mmol) during 1 h. The reaction mixture was washed with water (3 × 50 mL) and saturated $NaHCO_3$ solution (50 mL), dried, and evaporated.

A mixture of the above mesylate, tetrabutylammonium bromide (3.48 g, 10.8 mmol), and benzene (50 mL) was refluxed under N_2 for 6 h and evaporated. Following the addition of water (30 mL), the product was extracted into ethyl acetate (3 × 20 mL), the combined organic layers were dried and concentrated, and the residue was carried on.

Triphenylphosphine (3.4 g, 12.9 mmol) was placed in CH_2Cl_2 and cooled to 0 °C. Bromine (0.65 mL, 2.3 equiv) was added until a pale yellow color persisted. A solution of the α-bromo ketone in CH_2Cl_2 (10 mL) was introduced was allowed to warm to rt, stirred for 3 h, absorbed directly onto silica gel, and directly chromatographed (elution with 20% ethyl acetate in hexanes). There was obtained 1.51 g (71% overall) of **19** as a white solid, mp 130–131 °C (from ethyl acetate): IR (film, cm^{-1}) 1717, 1320; ^1H NMR (300 MHz, $CDCl_3$) δ 4.84 (dd, *J* = 10, 7 Hz, 1 H), 3.51 (d, *J* = 9 Hz, 2 H), 3.39 (d, *J* = 9 Hz, 2 H), 2.90 (dd, *J* = 13, 5 Hz, 1 H), 2.64–2.60 (m, 2 H), 2.57–2.54 (m, 1 H), 2.21–2.07 (series of m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 202.0, 54.1, 45.9, 45.0, 42.9, 40.54, 40.52, 36.1, 35.7, 35.6; FAB MS *m/z* (M^+ − Br) calcd 322.93, obsd 322.85.

Anal. Calcd for $C_{10}H_{13}Br_3O$: C, 30.88; H, 3.37. Found: C, 31.09; H, 3.42.

***endo,endo*-8,9-Bis(bromomethyl)bicyclo[5.1.1]nonan-4-one (20).** A solution of **19** (1.42 g, 3.7 mmol) in CH_2Cl_2 (30 mL) was cooled to 0 °C under N_2, mixed with freshly distilled boron trifluoride etherate (2.26 mL, 18.5 mmol), and treated dropwise during 1 h with a solution of ethyl diazoacetate (2.26 mL, 18.5 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred at 0 °C for 30 min longer and at rt overnight, quenched with water (20 mL), and stirred for 1 h. After dilution with more CH_2Cl_2, the organic layer was separated, dried, and evaporated.

The residue was taken up in ether (180 mL), treated with acetic acid (18 mL) and zinc dust (8.92 g), stirred under N_2 at rt for 1 h, and filtered. The filtrate was washed with water (3 × 30 mL), dried, and concentrated to leave an oil that was carried on.

A solution of the β-keto ester in benzene (50 mL) was treated with 48% HBr (50 mL), heated to reflux for 3 h, cooled, and freed of benzene under reduced pressure. The resulting aqueous solution was extracted with ethyl acetate (3 × 30 mL), and the combined organic layers were dried and concentrated. Purification of the residue by silica gel chromatography (elution with 20% ethyl acetate in hexanes) afforded **20** (765 mg, 66% overall) as a yellowish oil: IR (neat, cm^{-1}) 1698, 1246; ^1H NMR (300 MHz, $CDCl_3$) δ 3.45 (d, *J* = 8 Hz, 4 H), 2.69 (t, *J* = 6 Hz, 4 H), 2.46–2.41 (m, 2 H), 2.16–2.11 (m, 4 H), 1.94–1.90 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 218.9, 41.4, 41.0, 40.1, 38.2, 32.7; MS *m/z* (M^+) calcd 325.9527, obsd 325.9529.

Anal. Calcd for $C_{11}H_{16}Br_2O$: C, 40.77; H, 4.98. Found: C, 41.11; H, 5.08.

Spiro[1,3-dioxolane-2,5′-[11]thiatricyclo[6.4.0.0^{2,9}]dodecane] (21). A solution of **20** (500 mg, 1.54 mmol), ethylene glycol (2 mL), and *p*-toluenesulfonic acid (1 mg) in benzene (50 mL) was refluxed for 24 h under a Dean–Stark trap. The cooled reaction mixture was neutralized with solid Na_2CO_3, and the benzene was evaporated. The residue was placed in water (50 mL) and extracted with pentane (3 × 150 mL) and ether (30 mL). The combined organic phases were dried and evaporated to leave a residue that was carried on.

Sodium sulfide (1.1 g, 4.62 mmol) was heated to 120 °C under vacuum (20 Torr) in HMPA (30 mL) with exclusion of moisture until a deep blue color persisted. The mixture was cooled, the unpurified ketal dissolved in HMPA (10 mL) was introduced, and heating to 110 °C was resumed for 3 h. After return to rt, water (60 mL) was introduced and the product was extracted with petroleum ether (3 × 40 mL). The organic solutions were dried and concentrated, and the residue was purified by chromatography on silica gel (elution with 20% ethyl acetate in hexanes) to give 277 mg (75% overall) of **21** as a colorless crystalline solid, mp 78–79 °C: ^1H NMR (300 MHz, $CDCl_3$) δ 3.88 (s, 4 H), 3.28 (narrow m, 4 H), 2.32 (narrow m, 4 H), 1.86–1.80 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 111.6, 64.1, 401, 38.7, 38.1, 33.1, 24.0; MS *m/z* (M^+) calcd 240.1184, obsd 240.1195.

Anal. Calcd for $C_{13}H_{20}O_2S$: C, 64.96; H, 8.39. Found: C, 65.19; H, 8.50.

4′,6′-Dibromo-10′-chlorospiro[1,3-dioxolane-2,5′-[11]thiatricyclo[6.4.0.0^{2,9}]dodecane] 11,11-Dioxide (22). Sulfide **21** (53 mg, 0.221 mmol) was added to a magnetically stirred solution of *N*-chlorosuccinimide (29 mg, 0.221 mmol) in CCl_4 (10 mL) under N_2 and lowered into an oil bath preheated to 90 °C for 15 min. The reaction mixture was cooled, filtered, added directly to a solution of *m*-chloroperbenzoic acid (114 mg, 0.663 mmol) in CH_2Cl_2 (30 mL) containing $NaHCO_3$ (111 mg, 1.32 mmol), and stirred at rt for 2 h. Water (40 mL) was added, and the organic phase was washed with saturated $NaHCO_3$ solution (40 mL) and brine (40 mL), dried, and concentrated to leave a tacky white solid.

This solid was taken up in ether (20 mL), treated with ethylene glycol (2 drops) and bromine (0.045 mL, 0.884 mmol), stirred for 12 h, poured into ethyl acetate (30 mL) containing

Na_2CO_3 (5 g), and stirred for an additional 5 h. The reaction mixture was washed with water (3 × 70 mL), dried, and concentrated to afford 74 mg (72%) of **22** as a colorless solid that melts with decomposition at 195 °C: IR (film, cm^{-1}) 1319, 1063; ^1H NMR (300 MHz, $CDCl_3$) δ 5.25 (d, J = 4 Hz, 1 H), 4.71–4.63 (m, 2 H), 4.35–4.30 (m, 4 H), 3.75 (t, J = 3 Hz, 2 H), 2.89–2.45 (series of m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 110.2, 110.1, 109.8, 82.1, 81.9, 68.55, 68.51, 68.4, 68.3, 65.6, 65.40, 65.37, 65.33, 56.0, 55.2, 55.0, 54.9, 54.7, 45.1, 44.6, 44.5, 40.1, 39.4, 39.1, 38.8, 38.0, 37.3, 35.6, 35.5, 35.21, 35.17, 35.09, 35.02, 34.94, 34.91, 34.88, 34.78; MS m/z (M^+) calcd 465.8766, obsd 465.8806.

Anal. Calcd for $C_{13}H_{17}Br_2ClO_4S$: C, 33.61; H, 3.69. Found: c, 33.59; H, 3.82.

***trans*-4′,6′-Dibromospiro[1,3-dioxolane-2,5′-tricyclo-[6.3.0.0^{2,9}]undec[10]ene] (23) and *trans*-4′,6′-Dibromospiro[1,3-dioxolane-2,5′-tricyclo[6.3.0.0^{2,11}]undec[9]ene] (24).** A cold (−78 °C), nitrogen-blanketed solution of **22** (30 mg, 0.646 mmol) in THF (1 mL) was treated with potassium *tert*-butoxide dissolved in THF (1 mL of 1.0 M, 1.0 mmol). After 10 min, the reaction mixture was quenched with water (10 mL) and warmed to 0 °C, at which point cold (0 °C) ether (5 mL) was introduced prior to washing with ice water (5 mL). The organic phase was concentrated in the absence of light. The residue was immediately dissolved in cold $CDCl_3$ and examined by NMR spectroscopy at 0 °C, thereby confirming that **23** had been produced: ^1H NMR (300 MHz, $CDCl_3$) δ 7.05 (m, 2 H), 4.73 (m, 2 H), 4.31 (m, 4 H), 2.97 (m, 2 H), 2.66 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 146.7, 110.4, 68.0, 56.3, 47.7, 35.7, 29.7.

After 3 h, the spectra were rerecorded; complete isomerization to **24** was noted: ^1H NMR (300 MHz, $CDCl_3$) δ 5.88 (d, J = 5 Hz, 1 H), 5.31 (d, J = 5 Hz, 1 H), 5.15 (dd, J = 10, 3 Hz, 1 H), 4.33 (d, J = 7 Hz, 1 H), 4.26 (m, 2 H), 4.03 (m, 2 H), 3.11 (m, 1 H), 2.54 (m, 1 H), 2.16 (m, 1 H), 2.03 (m, 1 H), 1.94 (m, 1 H), 1.68 (m, 2 H), 0.66 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 135.3, 133.6, 110.7, 67.5, 65.6, 59.0, 56.0, 42.9, 37.1, 35.1, 32.6, 27.0, 24.4; MS m/z (M^+) calcd 363.9497, obsd 363.9489.

10′-Chlorospiro[1,3-dioxolane-2,5′-[11]thiatricyclo-[6.4.0.0^{2,9}]dodeca[3,6]diene] 11′,11′-Dioxide (25). Lithium bromide (87 mg, 0.72 mmol) was dried at 140 °C under high vacuum for 4 h, cooled to rt, and added to lithium carbonate (51 mg, 0.72 mmol), sulfone **22** (30 mg, 0.065 mmol), and dimethylacetamide (10 mL). The mixture was heated at 120 °C under N_2 for 6 h, cooled, and freed of solvent in vacuo. The residue was taken up in ethyl acetate (20 mL), washed with water (3 × 20 mL), dried, and concentrated to leave an oil that was purified chromatographically on silica gel (elution with 20% ethyl acetate in petroleum ether). There was isolated 18 mg (94%) of **25** as a white solid that slowly yellows upon standing at rt: IR (film, cm^{-1}) 1318, 1116; ^1H NMR (300 MHz, $CDCl_3$) δ 6.02–5.92 (m, 4 H), 5.30 (d, J = 5 Hz, 1 H), 4.07–3.96 (m, 4 H), 3.81 (d, J = 3 Hz, 2 H), 3.49–3.45 (m, 1 H), 3.24–3.16 (m, 2 H), 3.01–2.97 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) pm 136.1, 135.7, 132.3, 131.5, 104.6, 82.7, 66.2, 64.5, 64.3, 43.4, 41.0, 39.3, 34.5; MS m/z (M^+) calcd 304.0320, obsd 304.0335.

10-Chloro-11-thiatricyclo[6.4.0.0^{2,9}]dodeca-3,6-dien-5-one 11,11-Dioxide (26). Ketal **25** (18 mg, 0.053 mmol) was dissolved in THF, treated with 8% H_2SO_4 (0.4 mL), stirred for 2 min, and neutralized with saturated $NaHCO_3$ solution. The product was extracted into ethyl acetate (2 × 5 mL), dried, and concentrated to furnish 8 mg (60%) of **26** as a light- and heat-sensitive solid: IR (film, cm^{-1}) 1662, 1626; ^1H NMR (300 MHz, THF-d_8) δ 6.52–6.44 (m, 2 H), 6.04 (d, J = 13 Hz, 2 H), 5.54–5.51 (m, 1 H), 3.84 (d, J = 4 Hz, 2 H), 3.36–3.32 (m, 1 H), 3.10–3.05 (m, 1 H), 2.74–2.65 (m, 2H); ^{13}C NMR (75 MHz, THF-d_8) ppm 195.0, 138.6, 137.9, 133.3 (2 C), 83.9, 67.6, 43.0, 42.0, 40.1, 36.2; MS m/z (M^+) calcd 260.0088, obsd 260.0082.

Attempts to implement Ramberg–Bäcklund rearrangement of **24** were undertaken immediately following isolation of the compound.

***trans*-4′,6′-Dibromospiro[1,3-dioxolane-2,5′-[11]thiatricyclo[6.4.0.0^{2,9}]dodecane] 11′,11′-Dioxide (27).** To a stirred mixture of *m*-chloroperbenzoic acid (114 mg, 0.663 mmol) and $NaHCO_3$ (111 mg, 1.32 mmol) in CH_2Cl_2 (30 mL) was added **21** (53 mg, 0.221 mmol). After 2 h of stirring, water (40 mL) was introduced and the organic phase was washed with saturated $NaHCO_3$ solution (40 mL) and brine (40 mL), dried, and concentrated. There was obtained 60 mg (99%) of the sulfone ketal as a colorless solid, mp 195 °C dec: IR (film, cm^{-1}) 1297; ^1H NMR (300 MHz, $CDCl_3$) δ 3.90 (s, 4 H), 3.69 (narrow m, 4 H), 2.62 (narrow m, 2 H), 2.45 (narrow m, 2 H), 1.91–1.83 (m, 8 H)′ ^{13}C NMR (75 MHz, $CDCl_3$) ppm 110.8, 67.1, 64.2, 39.2, 35.6, 32.7, 23.2; MS m/z (M^+) calcd 272.1082, obsd 272.1063.

Anal. Calcd for $C_{13}H_{20}O_4S$: C, 57.33; H, 7.40. Found: C, 57.12; H, 7.39.

To a solution of the sulfone ketal (58 mg, 0.21 mmol) in ether (20 mL) were added ethylene glycol (2 drops) and bromine (0.045 mL, 0.84 mmol). The reaction mixture was stirred for 12 h, poured into ethyl acetate (30 mL) containing Na_2CO_3 (5 g), and agitated for 5 h more prior to being washed with water (3 × 70 mL), dried, and concentrated to give 90 mg (99%) of **27** as a colorless solid, mp 230 °C dec: IR (neat, cm^{-1}) 1306, 1118; ^1H NMR (300 MHz, $CDCl_3$) δ 4.65 (d, J = 10 Hz, 2 H), 4.38–4.29 (m, 4 H), 3.70 (s, 4 H), 2.74–2.71 (m, 4 H), 2.58–2.46 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 110.5, 68.6, 65.3, 55.3, 40.0, 35.5, 34.8; MS m/z (M^+) calcd 431.9256, obsd 431.9209.

Anal. Calcd for $C_{13}H_{18}Br_2O_4S$: C, 36.30; H, 4.22. Found: C, 36.33; H, 4.40.

Spiro[1,3-dioxolane-2,5′-[11]thiatricyclo[6.4.0.0^{2,9}dodeca-[3,6]diene] 11′,11′-Dioxide (28). Lithium bromide (114 mg, 0.928 mmol) was dried in vacuo at 140 °C for 4 h, cooled to rt, and added to a mixture of Li_2CO_3 (110 mg, 1.48 mmol), **25** (30 mg, 0.069 mmol), and dimethylacetamide (10 mL). This mixture was heated under N_2 at 120 °C for 6 h, cooled, and freed of solvent in vacuo. The residue was partitioned between ethyl acetate (20 mL) and water (20 mL), and the organic layer was washed with water (2 × 20 mL), dried, and concentrated. The residue was chromatographed on silica gel (elution with 20% ethyl acetate in petroleum ether) to give 15 mg (83%) of **28**: ^1H NMR (300 MHz, $CDCl_3$) δ 5.93 (narrow m, 4 H), 3.97 (s, 4 H), 3.75 (narrow m, 4 H), 3.21 (narrow m, 2 H), 3.07 (narrow m, 2 H); ^{13}C NMR ($CDCl_3$) ppm 135.4, 132.8, 104.8, 66.3, 64.3, 42.1, 34.0; MS m/z (M^+) calcd 268.0738, obsd 268.0753.

11-Thiatricyclo[6.4.0.0^{2,9}]dodeca-3,6-dien-5-one 11,11-Dioxide (29). To a solution of **28** (18 mg, 0.067 mmol) in THF (1 mL) was added 8% H_2SO_4 (0.4 mL), and the mixture was stirred for 2 min before being neutralized with saturated $NaHCO_3$ solution. The product was extracted into ethyl acetate (2 × 5 mL), dried, and concentrated to leave 9 mg (60%) of **29** as a light- and heat-sensitive compound: IR (film, cm^{-1}) 1662, 1627; ^1H NMR (300 MHz, $CDCl_3$) δ 6.52–6.45 (m, 2 H), 6.00 (d, J = 13 Hz, 2 H), 3.57 (s, 4 H), 3.22–3.17 (m, 2 H), 2.57–2.54 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 195.6, 137.9, 132.6, 67.0, 41.9, 33.8; MS m/z (M^+) calcd 224.0504, obsd 224.0508.

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Supplementary Material Available: Copies of ^1H and ^{13}C NMR spectra of those compounds lacking combustion data (16 pages). This material is contained in libraries on microfich, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.