tempted via encounter with the triplet excited state of chloranil (CHL), an approach used successfully in previous picosecond spectroscopic investigations to generate cation radicals of organic molecules.[53] When an acetonitrile solution containing 20 mM CHL and 70 mM DMEU was excited at 355 nm, the initial generation of ^{1}CHL* followed by its rapid conversion to ^{3}CHL* was observed in the expected manner.[53] The triplet-triplet absorption band of ^{3}CHL* at 510 nm decayed with concomitant appearance of the 450-nm band of CHL$^{\bullet+}$ and a new, weak absorption band in the 600–760-nm region, which increased from shorter to longer wavelengths. On the basis of previous behavior of electron donors in the presence of ^{3}CHL*, it appears likely that this weak 600–760-nm absorption band is a doublet doublet transition of DMEU$^{\bullet+}$.

With the detection of an absorption band attributable to DMEU$^{\bullet+}$, the prompt increase of the absorption in the 650–750-nm region resulting after 355-nm excitation of **1**–DMEU (Figure 6) could be due to the generation of DMEU$^{\bullet+}$ and α-$PW_{12}O_{40}^{4-}$. The decrease in the absorbance change occurring within 75 ps of excitation and remains constant for times longer than 1 ns after excitation may be the result of further reaction of DMEU$^{\bullet+}$ while α-$PW_{12}O_{40}^{4-}$ persists on this time scale. In the case of **1**–DMEU, it appears that both the oxidized donor and the reduced acceptor are detected within the excitation laser pulse, a behavior expected for an EDA complex.[47,51] The picosecond spectroscopic experiments reveal that photoredox chemistry of **1**–NMP and **1**–DMEU occurs on a subnanosecond time scale. Specific experiments to address other photophysical and photochemical features of these catalytic and radiant energy conversion systems are in progress.

Acknowledgment. C.L.H. thanks the National Science Foundation (Grant CHE-8715322) for support. E.F.H. and J.A.S. thank the National Science Foundation (Grant CHE-8605560) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support. Grants from the National Science Foundation were used in part to purchase the 200- and 360-MHz spectrometers.

Registry No. **1**·6NMP, 110401-80-4; **1**·6TMU, 115140-67-5; **1**·6DMeU, 115140-68-6; α-$H_3PW_{12}O_{40}$, 1343-93-7.

Supplementary Material Available: Tables of anisotropic thermal parameters, calculated hydrogen positions, torsion angles, nonbonded distances, atomic coordinates, and bond lengths and angles, crystal data collection parameters, and a packing diagram of unit cell for $[(TMU)_2H]_3[\alpha$-$PW_{12}O_{40}]$ (**1**–TMU) (16 pages); listings of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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Through-Bond Interaction via Cyclobutane Relay Orbitals as a Means of Extending Conjugation. Synthesis of Tricyclo[5.5.0.0^{2,8}]dodecatetraene, Tricyclo[5.3.0.0^{2,8}]deca-3,5,9-triene, and 9,10-Dimethylenetricyclo[5.3.0.0^{2,8}]deca-3,5-diene

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Abstract: The title hydrocarbons have been prepared from dimethyl ϵ-truxillate. Stepwise belting of a preformed all-trans 1,2,3,4-tetrasubstituted cyclobutane with proper differentiation of the 1,3- and 2,4-positions permits the necessary twofold annulation to be accomplished with relative ease. The efficiency of the syntheses has made available quantities of **8–10** sufficiently large for physicochemical study.

As a consequence of pioneering work carried out during the last 20 years by Hoffmann,[2] Simmons,[3] Semmelhack,[4] Heilbronner,[5] Nakajima,[6] and Gleiter,[7] we have come to recognize that two π systems linked perpendicularly by a common tetrahedral carbon atom[8] can exhibit through-space interaction. The magnitude of this phenomenon, termed spiroconjugation, is controlled by the interaction matrix term itself ($\beta_{spiro}^{\mu\nu} = \langle \pi_A^{\mu} | H | \pi_A^{\nu} \rangle$) and the dependence upon degenerate or at least nearly degenerate basis orbital energies. The manifestations of spiroconjugation are therefore at a maximum when $\beta_{spiro}^{\mu\nu}$ is large and the π fragments within the system are identical.[7a]

Indeed, spiro[4.4]nonatetraene (**1**) exhibits a splitting of its highest filled (and highest unfilled) diene π (π^*) orbitals amounting to 1.23 eV, as revealed by its UV[4d] and PE spectra.[5c]

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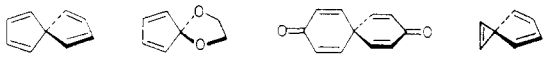
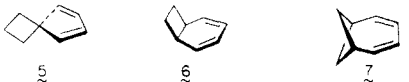
The ethylene ketals of cyclopentadienone, e.g., **2**, also exhibit spiroconjugation, as seen by a red shift of 30 nm in the lowest energy electronic transition.[3a] In these molecules, the lone-pair oxygen orbitals interact with the 1,3-diene orbitals so as to provide a bonding orbital of higher energy without significantly perturbing the LUMO.[3a,10] In agreement with the qualitative orbital description for **1**, Gerson et al. did not observe delocalization of negative charge over both rings in the ESR spectrum of radical anions of **3**.[11] Additionally, examination of lower homologous systems related to **4** has shown spiroconjugation to be too weak a stabilizing factor to override the destabilization brought on by charge transfer.[4c,12-15] Thus, convincing evidence for spiroconjugation has only been found for **1** and **2**.



1 **2** **3** **4**

In spiroconjugation, the spiro carbon spacer places a stringent limitation on the proximity of the termini of the mutually perpendicular π-ribbons and consequently on the extent of their overlap. Replacement of this insulating structural element by a suitable orbital relay network through which the π-ribbons could communicate more efficiently has been proposed more recently by Gleiter et al.[16] Intriguingly, the cyclobutane ring was noted by them to fulfill all the criteria necessary for efficient through-bond orbital interaction:[17] (i) the Walsh orbitals of four-membered carbocycles[18] lie relatively close in energy to the molecular orbitals of cyclic alkenes and 1,3-alkadienes;[7b] (ii) the puckered cyclobutane ring has the same D_{2d} symmetry as the two mutually perpendicular π-ribbons; and (iii) the cyclobutane relay orbitals are only one C–C single bond removed from the π-ribbon termini, thereby allowing for more pronounced overlap.

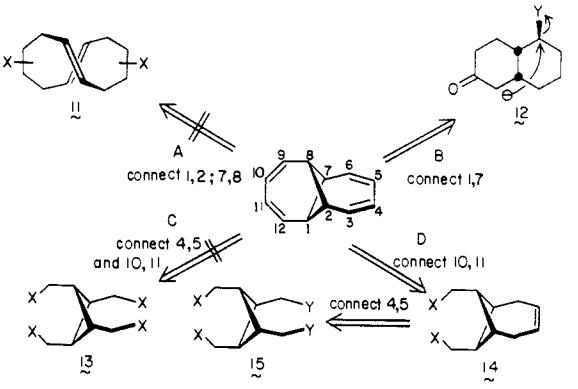
That π-bonds can indeed interact with a cyclobutane ring as suggested had been aptly demonstrated by photoelectron spectroscopic (PE) analysis of numerous vinylcyclobutanes.[19,20] Of the three ways in which a π-ribbon can be linked to a four-membered ring, as represented by **5**,[19a] **6**,[20,21] and **7**, the latter



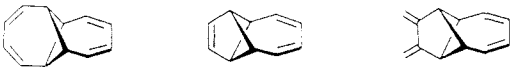
5 **6** **7**

system deserved special consideration and was, in fact, synthesized by Volz in 1977.[22,23] The 7,7-dimethyl analogue of **7**, prepared a year earlier by Young and Borden,[24] has been subjected to thermal and photochemical scrutiny.[25] The *endo,endo*-7,8-diphenyl derivative prepared by Chasey,[26] for which an X-ray crystal structure analysis is available, has been subjected to similar study. Of particular relevance, the level of interaction between the Walsh orbitals of the cyclobutane ring and diene moiety in **7** is best described by a resonance integral (β) of −1.9 eV.[22] The substantial magnitude of this interaction is in agreement with expectation[19a,b] and compares very closely to that found between a cyclopropane ring and double bond.[27]

Scheme I



As in spiroconjugated systems, the level and consequences of through-bond interaction between two π-ribbons linked orthogonally across a cyclobutane ring is intimately related to the total number of electrons involved. Whereas the basis orbital energies calculated for tetraene **8** predict that the system should be destabilized, those present in **9** were anticipated to be marginally stabilizing.[16] Not only the termini of a π-ribbon, but also its



8 **9** **10**

central carbons, can be connected to the cyclobutane ring. Tetraene **10** is isomeric with **8**. Its two-carbon bridge can be approximated to be 1.53 Å in length, somewhat longer than the ethylene bridge in **9** (ca. 1.36 Å).[2b,6] The ring strain in **10** should, therefore, be intermediate between that residing in **8** and **9**. On the other hand, the energy levels of the MO's in **10** resemble more closely those of **8** and the symmetries of the FMO's in both **8** and **10** are opposite to those present in **9**. Consequently, **10** offers a unique opportunity to gain information on the relative importance of ring strain and electronic character in these systems.

Tricyclo[5.5.0.0^{2,8}]dodecatetraene (8).[28] This hydrocarbon has been predicted to be a benzene dimer of reasonable stability.[16] However, its attempted acquisition by several research groups[29] has consistently been thwarted by serious synthetic complication. Any route must ultimately deal with the timing of cyclobutane ring installation. Those disconnections that we and others have considered are shown in Scheme I. Intramolecular photocyclization of a suitably functionalized cyclododeca-1,6-diene (**11**) was fully expected to lead to the linear 6-4-6 tricyclic system[30]

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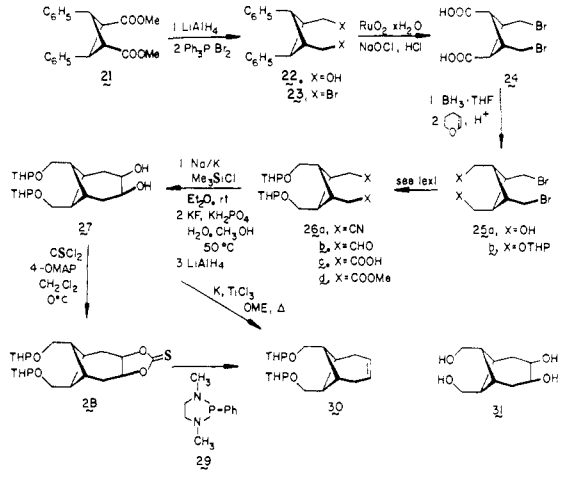
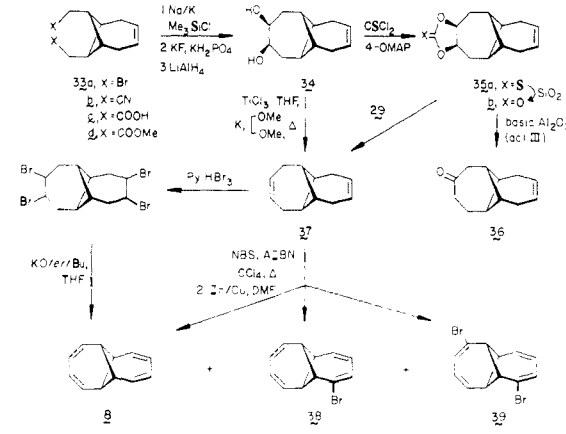
Scheme II

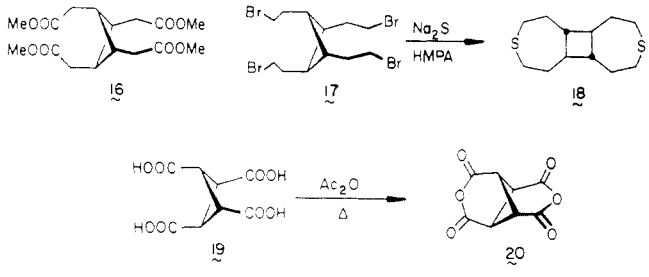


Scheme III



rather than the desired cross-cyclized product and was not given serious consideration. The particular pathway followed is known to depend heavily on ring size.[31-34] The intramolecular S_N2 displacement exemplified by **12** (path B) yields tricyclo-[4.4.0.0^{2,7}]decanes with reasonable efficiency and served as the conceptual basis for Heathcock's synthesis of copaene and ylangene.[35] The conversion of benzsuberone to the tricyclo-[5.4.0.0^{2,8}]undecane framework has more recently been achieved in comparable fashion.[36] Although enlargement of both bridges would become necessary in the present context, this protocol could, in principle, prove serviceable. However, the process lacks the flexibility we desired and was also not pursued.

In their plan to synthesize truncated tetrahedrane, Woodward, Scott,[29g] and Brousseau[29f] made recourse to a stratagem dependent on proper cyclization of an all-trans 1,2,3,4-tetrasubstituted cyclobutane such as **13**. However, no tricyclic product was isolated from attempted Dieckmann or acryloin cyclization of tetraester **17**, while exposure of tetrabromide **17** to sodium sulfide in HMPA afforded only **18**. These findings illustrate an important feature



of cyclobutane chemistry. The unsubstituted four-membered ring is not flat (D_{4h}) but puckered (D_{2d}) by 35°,[37-39] with a barrier to planarization of about 1.5 kcal/mol as determined by IR[40] and Raman spectroscopy.[41] This puckering destroys the equivalency of geminal substituents and differentiates axial and equatorial positions. An all-trans 1,2,3,4-tetrasubstituted cyclobutane is therefore strongly expected to prefer the all-equatorial conformation in order to avoid the intense repulsive 1,3-transannular interactions experienced in the all-axial conformation.[42] Thus, whenever 1,2-bridging is geometrically feasible, it is virtually certain to dominate kinetically over 1,3-bridging, and by a substantial margin. Only when the bridge size becomes too short for 1,2-closure will 1,3-annulation perhaps operate. The conversion of tetraacid **19** to dianhydride **20**[43] nicely illustrates the last point.

In our view, *stepwise* belting of two chains to alternate carbon atoms of the four-membered ring (path D, Scheme I) offered the greatest promise for leading to **8–10**. To achieve double cyclization in that manner appropriate for all-axial annulation, the substituents must necessarily be divided into two discrete sets (see **15**). By differentiating the 1,3- and 2,4-positions in this way, the system can initially bridge only in the desired fashion. Competing 1,2-cyclization is conveniently skirted, and the subsequent second-stage belting of **14** was expected to be geometrically feasible.

A cyclobutane precursor that aptly fulfills the conditions demanded by path D is dimethyl ϵ-truxillate (**21**).[26,44] Its transformation to monocyclized intermediate **31** is outlined in Scheme II. Notable points include the unreactivity of the bromine atoms in **23** while both phenyl groups are oxidatively degraded by ruthenium tetraoxide,[45] the nonnecessity of high dilution conditions during acyloin cyclization of **26d**, and the preferability of the McMurry conditions[46] relative to those developed by Corey and Hopkins[47] for the olefination of diol **27**. The cis arrangement of the hydroxyls in **27**, the assignment to which is complicated somewhat by the asymmetry introduced by the 2-tetrahydropyranyloxy groups, was achieved by hydrolysis[48] to **31**. This tetrol displayed seven lines in its broad-band-decoupled ^{13}C NMR spectrum, as expected uniquely for a C_s symmetric molecule.

The bicyclo[4.1.1]octene part structure of **30** was left at the monounsaturated stage during the second chain homologation sequence to obtain **33d** (Scheme III) in order to avoid labilizing the cyclobutane bonds. Again as in the olefination of the first bridge, direct deoxygenation of diol **34** with the titanium trichloride–tris(tetrahydrofuran) complex[49] and potassium in re-

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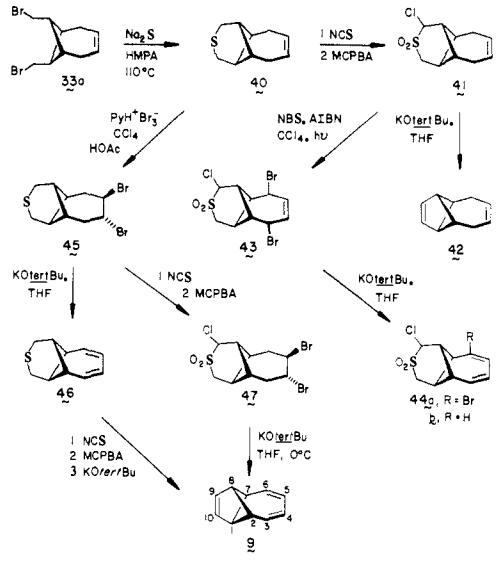
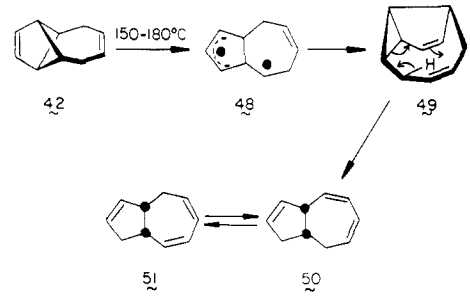
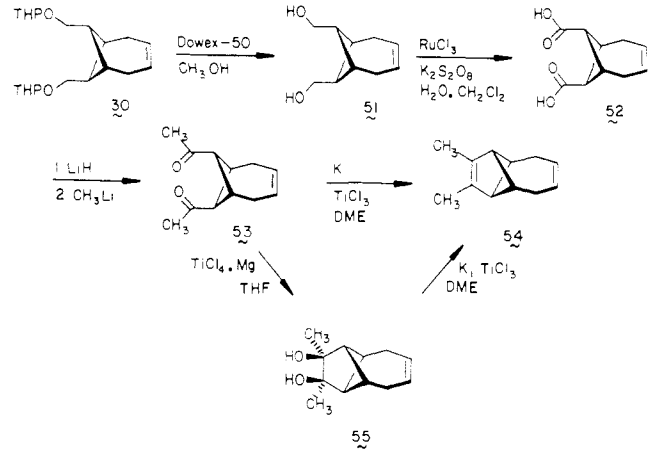
Scheme IV



Scheme V



Scheme VI



fluxing deimethoxyethane avoided the complications associated with thiocarbonate formation. In a very clean reaction, diene **37** can be obtained directly from **34** in 77% yield.

Diene **37** proved to be a colorless crystalline solid. For the first time, the high D_{2d} symmetry of the target tetraene was made evident from the simplified ^1H and ^{13}C NMR spectra of **37**.

Allylic bromination of **37** with 4.0–4.7 equiv of *N*-bromosuccinimide and a catalytic quantity of azobisisobutyronitrile under sunlamp irradiation and heat afforded an extensive mixture of bromides. Direct treatment of this mixture with freshly prepared zinc–copper couple in anhydrous dimethylformamide at room temperature[50a] for 12 h delivered tetraene **8** (12%), monobromide **38** (34%), and the dibromo derivative **39** (4%). Coaddition of potassium iodide and iodine[50b] had no major effect on the outcome of this reaction. However, when the reduction was allowed to proceed for almost 4 days, only tetraene **8** could be isolated in 57% yield. It was of crucial importance to exclude oxygen at all times. Also, all manipulations at elevated temperatures (50 °C and above) and exposure to laboratory light had to be avoided.

Tricyclo[5.5.0.0^{2,8}]dodecatetraene (**8**), a soft white solid with an intense musty odor, was easily identified by the simplificity of its ^{13}C NMR spectrum (three lines) and by the strong resemblance of the olefinic portion of its ^1H NMR spectrum to that of bicyclo[4.1.1]octa-2,4-diene (**7**).[22,23b] The locus of the bromine atom in **38** was determined from the coupling pattern of its olefinic protons and by comparison with data reported for 3-bromobicyclo[4.1.1]octadiene.[23b] The identity of dibromide **39**, which was not obtained completely pure, was again inferred from its ^1H NMR spectrum.

Attention is called to the fact that **11** has the same D_{2d} symmetry as allene. The C_2-symmetric dibromide **39** is therefore chiral and in principle resolvable. As expected, **38** and **39** were most efficiently metalated and protonated under Seebach's conditions (2 equiv of *tert*-butyllithium, THF, −78 °C; CH_3OH).[51] Direct treatment of the allylic bromide mixture with *tert*-butyllithium afforded **8** in 53% yield. The least problematic route to **8** proved to be bromination with pyridinium perbromide followed by dehydrobromination with potassium *tert*-butoxide.[26]

Tricyclo[5.3.0.0^{2,8}]deca-3,5,9-triene (9).[52] It was envisioned that Ramberg–Bäcklund rearrangement of a derived α-chloro sulfone might be performed under conditions sufficiently mild[53] to preserve the structural integrity of the product. Accordingly, **33a** was heated with a solution of anhydrous sodium sulfide in HMPA,[54] and **40** was obtained quantitatively (Scheme IV). Following the acquisition of **41**, exposure to potassium *tert*-butoxide in tetrahydrofuran resulted in very rapid conversion to **42**.[50] This diene proved to be thermally labile. Complete rearrangement occurred during attempted GC purification at 150 °C. The ^1H NMR spectrum of the resulting nonsymmetric isomer indicated the product to be 3,6-dihydroisobullvalene (**49**; Scheme V), the product of a formal [1,3] migration presumably mediated by biradical **13**. When **49** was heated to somewhat higher temperatures (≥170 °C), two additional hydrocarbons identified spectroscopically as **50** and **51**[56] began to make their appearance.

When attempts to achieve allylic bromination in **42** failed,[57] the pair of bromine atoms were introduced instead at the α-chloro sulfone stage.[58] However, exposure of **43** to potassium *tert*-butoxide in tetrahydrofuran resulted in unexpectedly rapid monodehydrobromination, thereby demonstrating that desulfonylative ring contraction was, in fact, the slower of the two processes.

These complications were bypassed entirely by initial electrophilic bromination of the double bond in **40**. Preliminary studies on **45** made clear the fact that base-promoted twofold dehydrobromination could be performed satisfactorily. Because the conversion of diene sulfide **46** into α-chloro sulfone **44b** could be effected only inefficiently (45%), it proved more expedient first to prepare **47** and *to accomplish the three chemical steps necessary to arrive at* **9** *in a single maneuver*. When **47** was treated with potassium *tert*-butoxide in THF-d_8 at −78 to −30 °C in an NMR tube, desulfonylative ring contraction was seen to occur to the virtual exclusion of dehydrobromination. At the preparative level, **9** was obtained efficiently at 0 °C, although admixed with ap-

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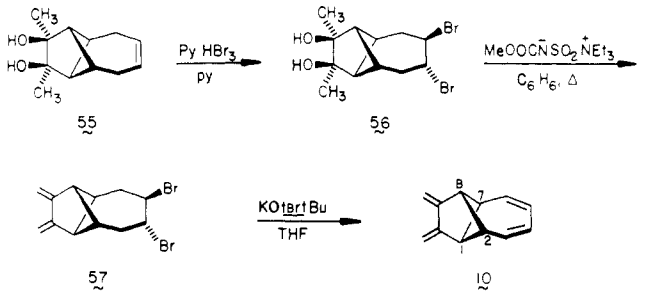
Scheme VII



proximately 10% of **42**. Pure **9** that was not contaminated with **42** could be obtained by installing the diene bridge first and then forming the monoene bridge, i.e., by Ramberg–Bäcklund ring contraction of **44b**.

9,10-Dimethylenetricyclo[5.3.0.0^{2,8}]deca-3,5-diene (10).[59] From among the several methodologies available for introducing vicinal *exo*-dimethylene double bonds, that due to Capozzi and Hogeveen[60] appeared most compatible with our general strategy of belting an all-trans tetrasubstitued cyclobutane in stepwise fashion. Adaptation of this procedure required the availability of dimethyl diene **54**, and Scheme VI outlines the crafting of this tricyclic molecule from **30**.

Although the tetrahydropyranyl groups in **30** could be removed by heating with *p*-toluenesulfonic acid in ethanol for 26 h,[61] Beier and Mundy's method[48] involving stirring with acid-washed Dowex-50 resin in methanol proved milder, faster (1 h), and more efficient. Although the diol was only marginally soluble in methylene chloride, the conversion to diacid **52** by oxidation with potassium ruthenate[62] proceeded smoothly. Following preparation of the dilithium salt of **52** by reaction with excess lithium hydride, addition of methyllithium[63] gave **53**.

The first method selected for effecting the critical ring closure involved heating **53** with potassium metal and the $TiCl_3$·3THF complex in dimethoxyethane[64] with vigorous exclusion of oxygen and moisture. However, only 13% of impure **54** could be isolated. Since neither the yield nor the purity of this diene could be improved, recourse was made instead to pinacolic coupling as promoted by titanium tetrachloride and magnesium in tetrahydrofuran.[65] These conditions led cleanly to diol **55** whose cis stereochemistry and resultant C_s symmetry are transparently obvious on the basis of its nine-line ^{13}C NMR spectrum. Submission of **55** to the McMurry deoxygenation conditions provided **54** in high purity, although again in undistinguished yield (18% based on recovered **55**). Although application of the Capozzi–Hogeveen bromination/dehydrobromination protocol to **54** did lead to **57**, no further use was made of **54** as a precursor to **10**.

Instead, dibromide **57** was prepared much more efficiently by reaction of **55** with pyridinium perbromide and heating of the resulting polyfunctional compound **56** in benzene with the Burgess reagent[66] (Scheme VII). Ultimate dehydrobromination of **57** with potassium *tert*-butoxide in tetrahydrofuran was also achieved without complication. Tetraene **10**, which has proven to be a fairly stable substance, was easily identified on the basis of its ^1H NMR spectrum.

The photoelectron spectroscopy of **8–10** is discussed in detail in the ensuing paper.[66]

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Experimental Section

1-*r*,3-*c*-Bis(bromomethyl)-2-*t*,4-*t*-diphenylcyclobutane (23). A solution containing diester **21** (2.57 g, 7.92 mmol) in 10 mL of anhydrous tetrahydrofuran was added dropwise to a refluxing slurry of lithium aluminum hydride (650 mg, 17.12 mmol) in 50 mL of tetrahydrofuran, and the mixture was kept under nitrogen and at the reflux temperature for 30 h. Excess hydride reagent was destroyed with ethyl acetate, the reaction mixture was cooled to room temperature, and crystals of hydrated sodium sulfate were added as stirring was maintained. After the salts had turned white, the mixture was filtered, and the tetrahydrofuran was evaporated to leave crystalline diol **22** in quantitative yield: mp 93.5–94.5 °C (from hexane–dichloromethane); IR (CH_2Cl_2, cm^{-1}) 3350, 3020, 2920, 1600, 1490, 1440, 1050, 1000; ^1H NMR (300 MHz, $CDCl_3$) δ 7.30 (s, 10 H), 3.75 (d, J = 5 Hz, 4 H), 3.40–2.40 (m, 4 H), 1.93–1.66 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 143.2, 128.6, 127.2, 126.4, 64.0, 49.2, 41.0; MS, m/z (M^+) calcd 268.1463, obsd 268.1470.

Comparable reaction of 221 g of **21** in one lot gave **22** in 96% yield.

Under a blanket of nitrogen, bromine (120 mL, 2.34 mol) was added dropwise to a cold (0 °C) solution of triphenylphosphine (600 g, 2.27 mol) in 3 L of methylene chloride until a drop was not longer discolored (some triphenylphosphine dibromide precipitated as a white solid). Diol **23** (214 g, 0.800 mol) was dissolved in 0.9 L of methylene chloride and added within 30 min. After another 30 min at 0 °C, the clear yellow solution was stirred at room temperature for 20 h, and the solvent was evaporated. The remaining solids were triturated with a total volume of 4 L of petroleum ether. Evaporation of the organic extracts and recrystallization from petroleum ether–chloroform yielded 254 g (81%) of **23** as colorless crystals: mp 62.5–63.5 °C; IR (CH_2Cl_2, cm^{-1}) 3035, 2960, 1600, 1490, 1455, 1430, 745, 695; ^1H NMR (300 MHz, $CDCl_3$) δ 7.32 (s, 10 H), 3.58 (d, J = 5 Hz, 4 H), 3.40–2.55 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 141.3, 128.7, 127.4, 127.0, 48.2, 47.2, 35.7; MS, m/z (M^+) calcd 391.9776, obsd 391.9783. Anal. Calcd for $C_{18}H_{18}Br_2$: C, 54.89; H, 4.60. Found: C, 54.86; H, 4.63.

2-*t*,4-*t*-Bis(bromomethyl)-1-*r*,3-*c*-cyclobutanedimethanol (25a). A 5-L three-necked, round-bottomed flask equipped with an overhead stirrer, a reflux condenser, and a 500-mL addition funnel was charged with dibromide **23** (40 g, 0.10 mol), ruthenium dioxide hydrate (1.5 g, ca 8.2 mmol), and 300 mL of methylene chloride. With vigorous stirring, ca. 4 L of Chlorox solution (0.76 M aqueous sodium hypochlorite, 3.0 mol) was added at such a rate that the methylene chloride was maintained at reflux (the oxidation is initially very exothermic and usually takes 7–8 h). The end-point was reached when the solution no longer changed color from golden-orange to black within a 5-min period. The ruthenium tetraoxide was extracted with methylene chloride (5 × 200 mL) and quenched with ether. The volume of the aqueous phase was reduced to ca. 1 L on a rotary evaporator. Then 100 mL of concentrated hydrochloric acid was added to precipitate the diacid (CAUTION: chlorine gas evolution), and the remainder was removed by suction filtration. After the air-dried solid had been taken up in 800 mL of ether, the organic phase was dried over magnesium sulfate, decolorized with charcoal, and filtered through a Celite pad. Evaporation of the ether yielded dicarboxylic acid **24** as a white paste that was directly utilized in the ensuing reduction.

Under a nitrogen atmosphere and with vigorous agitation from a Hershberg stirrer, borane–THF complex (1.3 L of 1 M, 1.3 mol) was added within 1.5 h to a cold (0 °C) solution of **24** (the material as obtained from four oxidation runs) in anhydrous tetrahydrofuran (200 mL). Stirring was continued for 1 h at 0 °C and for 4 h at room temperature. When polymeric intermediates were formed, stirring was continued until these dissolved. The pale yellow reaction mixture was poured onto crushed ice (500 g) and stirred overnight. The solution was neutralized with sodium carbonate. The solvent was evaporated, and the still hot two-phase system was extracted with 1.8 L of boiling chloroform. Drying of the solution over magnesium sulfate, filtration, and evaporation yielded a yellow, tacky solid. For recrystallization purposes, this solid was suspended in 400 mL of methylene chloride and completely dissolved in chloroform at the boiling point. Petroleum ether was added until the solution turned cloudy. There was isolated 85 g (70%) of **25a** as small, pale yellow, hard crystals: mp 93.5–94 °C (from hexane–dichloromethane); IR (KBr, cm^{-1}) 3300, 2900, 1430, 1360, 1220, 1055, 990, 610; ^1H NMR (300 MHz, C_5D_5N) δ 5.89 (s, 2 H), 2.98 (d, J = 5 Hz, 4 H), 3.72 (d, J = 6 Hz, 4 H), 3.00–1.80 (m, 4 H); ^{13}C NMR (75 MHz, C_5D_5N, ppm) 62.7, 47.0, 38.9, 38.7; MS, m/z (M^+ + H) calcd 300.9438, obsd 300.9433. Anal. Calcd for $C_8H_{14}Br_2O_2$: C, 31.81; H, 4.67. Found: C, 31.87; H, 4.68.

Dimethyl 2-*t*,4-*t*-Bis[[(tetrahydro-2*H*-pyran-2-yl)oxy]methyl]-1-*r*,3-*c*-cyclobutanediacetate (26d). Diol **25a** (50 g, 0.17 mol), pyridinium tosylate (6.15 g, 24.5 mmol), and dihydropyran (83 g, 1.0 mol) were dissolved in 1 L of methylene chloride and stirred at room temperature for 20 h. The yellow, cloudy reaction mixture was washed with water

(3 × 200 mL) and brine (200 mL). Drying over magnesium sulfate and evaporation of the solvent yielded 81.9 g of an orange oil. This material can be purified by chromatography on silica gel (elution with dichloromethane–ethyl acetate, 20:1) and obtained as a colorless oil: IR (neat, cm^{-1}) 2920, 2860, 1460, 1450, 1440, 1380, 1350, 1220, 1190, 1120, 1060, 1020, 890, 860, 800; ^1H NMR (300 MHz, $CDCl_3$) δ 4.65–4.50 (m, 2 H), 4.05–3.22 (series of m, 12 H), 2.50–1.30 (series of m, 16 H).

The unpurified dibromide **25b** from above was dissolved in 200 mL of anhydrous dimethyl sulfoxide under argon. When 66.6 g (1.36 mol) of freshly ground sodium cyanide was added, the solution turned orange and heated up. After 6.5 h of heating at 90–100 °C in an oil bath, the dark brown solution (solidification occurred on cooling) was partitioned between 500 mL of water and 200 mL of ether. The aqueous phase was extracted with a total volume of 1.3 L of ether, and the combined ethereal phases were washed with water (100 mL) and brine (2 × 150 mL) prior to drying. Evaporation of the solvent yielded 62.7 g of **26a** as a brown oil. Although not routinely done, this material can be purified by chromatography on silica gel (elution with dichloromethane–ethyl acetate, 4:1) and obtained as a colorless oil: IR (neat, cm^{-1}) 2920, 2850, 2230, 1460, 1450, 1435, 1350, 1250, 1190, 1130, 1070, 1020, 890, 860, 800, 730; ^1H NMR (300 MHz, $CDCl_3$) δ 4.65–4.40 (m, 2 H), 4.00–3.25 (m, 8 H), 2.70–1.25 (series of m, 20 H).

Aqueous potassium hydroxide solution (372 g of potassium hydroxide in 450 mL of water) was slowly added to a solution of the crude dinitrile **26a** obtained above dissolved in 450 mL of methanol. A highly exothermic reaction was noted, and ammonia was evolved. The orange emulsion was heated to reflux for 15 h in a sand bath. After evaporation of the methanol, the water-insoluble material was extracted with 200 mL of ether. The aqueous phase was cooled to 0 °C, diluted with 200 mL of water, and acidified to pH 4–5 with concentrated hydrochloric acid. The voluminous precipitate was extracted with a total of 1.5 L of ether. Washing with brine, drying over magnesium sulfate, and evaporation of the solvent left 54.4 g (80% yield from **25a**) of **26c** as a pale yellow solid, mp 120–121 °C.

A 2-L Erlenmeyer flask containing a suspension of **26c** (43.8 g, 0.10 mol) in 100 mL of ether was treated with ethereal diazomethane until nitrogen evolution ceased. The excess diazomethane was destroyed with acetic acid. Following drying and evaporation of the reaction mixture, silica gel chromatography (elution with 50% ether in petroleum ether) afforded **26d** as a colorless oil: IR (neat, cm^{-1}) 2940, 2860, 1735, 1430, 1350, 1250, 1190, 1120, 1070, 1020, 890, 860, 800; ^1H NMR (300 MHz, $CDCl_3$) δ 4.65–4.50 (m, 2 h), 4.00–3.25 (m, with s at 3.67, 14 H), 2.70–1.30 (series of m, 20 H). Anal. Calcd for $C_{22}H_{36}O_8$: C, 61.66; H, 8.47. Found: C, 61.42; H, 8.61.

(1*R*,4*S*,7s_n,8s_n)-7,8-Bis[[(tetrahydro-2*H*-pyran-2-yl)oxy]methyl]bicyclo[4.1.1]octane-3,4-diol (27). Under an atmosphere of argon, anhydrous ether (250 mL) was placed into a 1-L three-necked Morton flask equipped with an Allen condenser and a Hershberg stirrer. With rapid stirring, 60 mL of a sodium–potassium (1:1) alloy was injected. The apparatus was equipped with a 250-mL pressure equalizing addition funnel filled with trimethylsilyl chloride (freshly distilled from calcium hydride, 135 mL, 1.05 mol) and a 250-mL Hershberg addition funnel filled with diester **26d** (86 g, 0.20 mol) in anhydrous ether (75 mL). At the maximum speed of the compressed air stirrer, both solutions were added within 4 h (exothermic reaction). Stirring was continued for 12 h before the purple solids were allowed to settle for 4 h. A 1-L three-necked round-bottomed flask was equipped with a 500-mL pressure equalizing funnel topped by an Allen condenser, charged with potassium dihydrogen phosphate (5.4 g), potassium fluoride dihydrate (7.5 g), water (200 mL), and methanol (150 mL), and flushed with argon. The supernatant acyloin condensation solution was transferred by cannula (15 gauge) into the vigorously stirred hydrolysis vessel by applying a weak vacuum (the hydrogen evolved by the hydrolysis of unreacted sodium potassium alloy regulated the rate of transfer automatically). The acyloin condensation residue was triturated with anhydrous ether (3 × 50 mL) and finally decomposed by sequential injection of 2-propanol (100 mL), methanol (100 mL), and water (100 mL) while the hydrogen was vented into a brisk flow of argon. With vigorous magnetic stirring of both phases, the hydrolysis mixture was heated at 70 °C for 10 h. During that time most of the ether collected in the addition funnel. The residual ether and methanol were removed on a rotary evaporator, 300 mL of ether was added, and the aqueous phase was saturated with sodium chloride. Extraction with more (2 × 100 mL) ether, drying of the combined ether phases, and evaporation yielded 105 g of a pale yellow paste. Reduction with lithium aluminum hydride (5.7 g, 0.15 mol) in anhydrous tetrahydrofuran (150 mL) at 0 °C for 30 min, hydrolysis with saturated aqueous ammonium chloride solution, and Soxhlet extraction of the insolubles with tetrahydrofuran for 12 h yielded 80 g of a yellow viscous oil. Flash chromatography of 0.26 g of this crude oil on silica gel (elution with 80% ethyl acetate in petroleum ether) afforded 0.1m g of **27** as a pale yellow oil that spontaneously solidified. Accordingly, the total yield was 52.3 g (71%). Colorless crystals, mp 105–107 °C, were obtained following recrystallization from hexane–dichloromethane; IR (CH_2Cl_2, cm^{-1}) 3400, 2880, 1620, 1110, 1010; ^1H NMR (300 MHz, $CDCl_3$) δ 4.60–4.40 (m, 2 H), 4.35–4.05 (m, 2 H), 4.00–3.25 (m, 8 H), 2.95–2.20 (m, 2 H), 2.15–1.25 (m, 20 H); MS, m/z (M^+ + H) calcd 371.2433, obsd 371.2433. Anal. Calcd for $C_{20}H_{34}O_6$: C, 64.83; H, 9.25. Found: C, 64.56; H, 9.24.

(3*R*,4*S*,7s_n,8s_n)-3,4-Dihydroxybicyclo[4.1.1]octane-7,8-dimethanol (31). A solution of **27** (91.6 mg, 0.248 mmol) and pyridinium tosylate (13 mg, 0.05 mmol) in 2 mL of absolute ethanol was stirred at 55 °C for 26 h, and the solvent was evaporated. The residue was dissolved in ethyl acetate, filtered through a short plug of silica gel to remove the catalyst, evaporated again, and purified by MPLC (25% methanol–ethyl acetate, silica gel). A glassy solid (42.8 mg, 86%) was isolated and recrystallized from acetone to give colorless plates: mp 126.5–127.5 °C; IR (KBr, cm^{-1}) 3640–3060, 3030, 2920, 1380, 1035, 1020; ^1H NMR (300 MHz, CD_3OD) δ 4.11 (t, J = 5.1 Hz, 2 H), 3.55 (dd, J = 8.3, 5.9 Hz, 4 H), 2.74–2.62 (m, 1 H), 1.90–1.70 (m, 7 H); ^{13}C NMR (75 MHz, CD_3OD, ppm) 74.63, 66.88, 66.82, 44.74, 44.49, 36.71, 36.21; MS, m/z ($M^+ - 3H_2O$) calcd 148.0888, obsd 148.0915. Anal. Calcd for $C_{10}H_{18}O_4$: C, 59.39; H, 8.97. Found: C, 59.57; H, 8.96.

Cyclic *O*,*O*-[(3*R*,4*S*,7s_n,8s_n)-7,8-Bis[[(tetrahydro-2*H*-pyran-2-yl)oxy]methyl]bicyclo[4.1.1]oct-3,4-ylene] Thiocarbonate (28). Freshly sublimed 4-(dimethylamino)pyridine (7.90 g, 64.8 mmol) and diol **27** (10.0 g, 27.0 mmol) were dissolved in 100 mL of anhydrous methylene chloride under nitrogen and cooled to 0 °C. An 85% thiophosgene solution in carbon tetrachloride (2.5 mL, 32.4 mmol) was slowly injected with vigorous stirring. The intensively orange-red emulsion quickly faded and a solid precipitated. After one night at 0 °C, 100 mL of ether was added dropwise at 0 °C to precipitate as much 4-(dimethylamino)-pyridine hydrochloride as possible. The suspension was filtered through a sintered-glass funnel, and the solids were washed with ether (3 × 50 mL). The combined filtrates were evaporated and chromatographed on silica gel (ether solution) to give 13.0 g of a pale yellow, viscous oil (theoretical yield, 11.1 g). No further purification was necessary for the olefination. A purified sample displayed the following spectrum: ^1H NMR (300 MHz, $CDCl_3$) δ 5.28–5.21 (m, 2 H), 4.54–4.50 (m, 2 H), 3.91–3.75 (m, 4 H), 3.57–3.43 (m, 4 H), 2.44–2.35 (m, 2 H), 2.19–2.10 (m, 5 H), 1.84–1.49 (m, 13 H); MS, m/z (M^+) calcd 412.1919, obsd 412.1926.

2,2′-[(7s_n,8s_n)-Bicyclo[4.1.1]oct-3-en-7,8-ylenebis(methyleneoxy)]bis[tetrahydro-2*H*-pyran] (30). A. Application of Corey–Hopkins Methodology. 2,5-Dimethyl-1-phenyl-2,5-diazaphospholidine (29, 9.8 mL, 54 mmol) was added to crude thiocarbonate **28** (13 g, max of 27 mmol) under an atmosphere of nitrogen. After a short induction period, the initially pale yellow solution turned orange-yellow, a highly exothermic reaction started, and gas was evolved. After overnight stirring at room temperature, another 3 mL of **29** was added, and the mixture was heated to 40 °C for 1 h. The reaction mixture was dissolved in 150 mL of methylene chloride, adsorbed on 30 g of silica gel, and poured onto a column packed with 100 g of silica gel. At first, the thiophospholidine eluted with methylene chloride to be followed by the reaction product with ether–petroleum ether (1:1). Rotary evaporation yielded **30** as a colorless oil that solidified in a freezer (7.85 g, 86.5% from diol **27**): mp 35.5–38.5 °C; IR (neat, cm^{-1}) 3035–2800, 1135, 1115, 1075, 1050, 1025; ^1H NMR (300 MHz, $CDCl_3$) δ 5.56 (br s, 2 H), 4.65–4.54 (m, 2 H), 4.00–3.80 (series of m, 4 H), 3.66–3.56 (m, 2 H), 3.56–3.42 (m, 2 H), 2.27 (s, 4 H), 2.13 (br t, J = 10 Hz, 2 H), 2.01 (td, J = 6.0, 2.0 Hz, 2 H), 1.88–1.42 (series of m, 20 H); MS, m/z (M^+ – dihydropyran) calcd 252.1725, obsd 252.1710.

B. Application of McMurry Methodology. A mechanically stirred solution of titanium trichloride (50 g, 0.32 mol) in anhydrous dimethoxyethane (430 mL) was blanketed with argon and treated portionwise with potassium metal (51 g, 1.30 mol). The dark black mixture that resulted after heating at the reflux temperature for 2 h was treated with a solution of **27** (10.0 g, 27 mmol) in 70 mL of dimethoxyethane and reheated to reflux for 36 h. The black insoluble byproducts were removed by filtration through Celite (CAUTION: flammable solid) and triturated with tetrahydrofuran (4 × 100 mL) and finally dichloromethane (100 mL). Evaporation of the combined organic solutions left 8.45 g of a yellow oil, chromatography of which on silica gel (elution with 25–50% ethyl acetate in petroleum ether) afforded 6.36 g (70%) of **30**, whose spectral properties were identical with those described above.

(7s_n,8s_n)-7,8-Bis(bromomethyl)bicyclo[4.1.1]oct-3-ene (33a).[67] Triphenylphosphine (12.3 g, 46.9 mmol) was dissolved in 100 mL of methylene chloride under nitrogen and cooled to 0 °C. Bromine (2.4 mL,

(67) Sonnet, P. E. *Synth. Commun.* **1976**, *6*, 21.

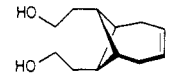
46.9 mmol) was added with a pipette until a drop was no longer discolored. The excess bromine was reacted by adding a few crystals of triphenylphosphine. Bis(tetrahydropyranyl ether) **30** (7.15 g, 21.3 mmol) was dissolved in 20 mL of methylene chloride and added dropwise at 0 °C. After 5 min, the mixture was allowed to warm to room temperature and stirred for 2.5 h. The intensively yellow, clear reaction mixture was adsorbed onto 50 mL of silica gel and packed on top of 800 mL of silica gel. Flash chromatography (petroleum ether elution) yielded 5.1 g (82%) of **33a** as colorless crystals, mp 63.5–66 °C (from hexane–dichloromethane); IR (CCl_4, cm^{-1}) 2950, 2860, 1440, 1420, 650, 610; ^1H NMR (300 MHz, $CDCl_3$) δ 5.57 (s, 2 H), 3.61 (d, J = 8.6 Hz, 4 H), 2.32 (d, J = 0.9 Hz, 4 H), 2.25–2.10 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 125.3, 42.9, 39.4, 37.8, 34.0; MS, m/z (M^+) calcd 291.9463, obsd 291.9467. Anal. Calcd for $C_{10}H_{14}Br_2$: C, 40.84; H, 4.80. Found: C, 41.18; H, 4.93.

($7s_n$,$8s_n$)-Bicyclo[4.1.1]Oct-3-ene-7,8-diacetonitrile (33b). A reaction mixture consisting of dry dimethyl sulfoxide (100 mL), unpurified dibromide **33a** (5.10 g, 17.5 mmol), and finely ground sodium cyanide (3.42 g, 69.9 mmol) was heated to 70–100 °C for 2 h with the exclusion of moisture. After being cooled to room temperature, the mixture was partitioned between water (200 mL) and ether (100 mL). The aqueous phase was extracted with ether (3 × 100 mL). The combined organic phases were washed with water (50 mL) and brine (50 mL), filtered through a magnesium sulfate cone, and evaporated to leave 3.85 g of a yellow, partially crystalline material (theoretical yield 3.25 g) that could be used without further purification. An analytically pure sample was obtained by MPLC on silica gel (30% ethyl acetate in petroleum ether) and subsequent recrystallization from methanol: mp 71.5 °C; IR (CH_2Cl_2, cm^{-1}) 2990, 2900, 2810, 2230, 1420; ^1H NMR (300 MHz, $CDCl_3$) δ 5.62 (s, 2 H), 2.66 (d, J = 8.7 Hz, 4 H), 2.36 (s, 4 H), 2.25 (br s, 2 H), 2.15 (td, J = 8.6, 1.3 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 125.1, 118.4, 39.2, 36.7, 33.6, 23.1; MS, m/z (M^+) calcd 186.1156, obsd 186.1163. Anal. Calcd for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58. Found: C, 77.13; H, 7.56.

Dimethyl ($7s_n$,$8s_n$)-Bicyclo[4.1.1]oct-3-ene-7,8-diacetate (33d). A heterogeneous mixture of unpurified dinitrile **33b** (3.85 g, max 17.5 mol), methanol (40 mL), and aqueous potassium hydroxide solution (50 mL, from 37 g of potassium hydroxide and 45 mL of water) was refluxed vigorously in a sand bath (140–150 °C). After 10 h, the methanol was evaporated, and the aqueous phase was extracted with ether (discarded), cooled to 0 °C, acidified with concentrated hydrochloric acid (42 mL), and extracted again with ether (5 × 100 mL). Evaporation of the dried ether phases yielded a green-brown solid. A suspension of the solid in 100 mL of ether was esterified with diazomethane. The diester was purified by flash chromatography (silica gel, 15% ethyl acetate in petroleum ether) to give 3.58 g of a mobile colorless oil (81% from **33a**): IR (neat, cm^{-1}) 2990, 2900, 2810, 1735, 1430, 1100; ^1H NMR (300 MHz, $CDCl_3$) δ 5.57 (br s, 2 H), 3.64 (s, 6 H), 2.66 (d, J = 8.3 Hz, 4 H), 2.32–2.23 (m, 4 H), 2.15–2.06 (m, 2 H), 2.04 (br s, 2 H); MS, m/z (M^+) calcd 252.1361, obsd 252.1367.

***cis*-Tricyclo[5.5.0.$0^{2,8}$]dodec-10-ene-4,5-diol (34).** A dry, 1-L three-necked Morton flask equipped with an Allen condenser, a Hershberg stirrer, and a 15-cm glass extension was charged with 350 mL of ether (freshly distilled from sodium benzophenone). Under a dynamic nitrogen atmosphere and with rapid stirring by a compressed-air high-speed motor, 3 mL of sodium–potassium (1:4) alloy was injected. After 30 min, the alloy had become very fine, gray-white dispersion. Two dry, nitrogen-flushed 30-mL syringes were filled respectively with an ethereal solution of dry trimethylsilyl chloride (5 mL, 40 mmol, freshly distilled from calcium hydride, diluted to 30 mL with anhydrous ether) and an ethereal solution of diester **33d** (0.50 g, 0.20 mmol, total volume 30 mL). These syringes were mounted on a dual syringe pump, and the tips of their 30-cm needles were placed directly above the dispersion. Both solutions were added simultaneously within 3 h. The dark gray suspension was stirred for another 3 h. Hydrolysis was performed as for diester **26d** with potassium dihydrogen phosphate (5.4 g), potassium fluoride dihydrate (7.5 g), water (200 mL), and methanol (200 mL) at 70 °C for 24 h. The workup with ether (100 + 2 × 70 mL) and brine (50 mL) was followed by drying. Reduction with lithium aluminum hydride (0.25 g, 6.6 mmol) in anhydrous tetrahydrofuran (10 min at 0 °C), quenching with saturated aqueous ammonium chloride solution, and Soxhlet extraction with tetrahydrofuran left a pasty solid after rotary evaporation. This material was triturated with ether (4 × 3 mL) and filtered through a sintered-glass funnel. The amorphous residue amounted to 0.16 g of **34**. The combined ether phases were concentrated, and that residue was subjected to MPLC (ethyl acetate, silica gel) to give an additional 0.09 g (total yield (81%) of **34** and 0.05 g of open chain diol **58**.

For **34**: colorless crystals; mp 152–156 °C (from ethyl acetate); ^1H NMR (300 MHz, $CDCl_3$) δ 5.53 (s, 2 H), 4.38–4.20 (m, 2 H), 3.70–3.60 (m, 2 H), 2.24–1.68 (series of m, 12 H); MS, m/z (M^+) calcd 194.1306, obsd 194.1313. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.01; H, 9.21.



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For **58**: IR ($CDCl_3$, cm^{-1}) 3620, 3700–3200, 3000, 2930, 2890, 2820, 1420, 1050, 1030; ^1H NMR (300 MHz, $CDCl_3$) δ 5.55 (br s, 2 H), 3.61 (t, J = 6.8 Hz, 4 H), 2.23 (br d, J = 1.9 Hz, 4 H), 2.04–1.88 (m, 6 H), 1.80–1.68 (m, 2 H), 1.32 (s, 2 H); MS, m/z (M^+) calcd 196.1463, obsd 196.1509.

($7s_n$,$8s_n$)-Bicyclo[4.1.1]oct-3-ene-7,8-diacetaldehyde (26b). A. Oxidation of Diol 47. A solution of diol **47** (55 mg, 0.28 mmol) in hot chloroform (2 mL) was added while under argon to a stirred suspension of ground, activated 3-Å molecular sieves (0.28 g) and pyridinium chlorochromate (0.36 g, 1.7 mmol) in dry methylene chloride (2 mL). After 30 min, the supernatant solution was decanted from the dark red-black gum, and the latter was triturated with ether (3 × 2 mL). The combined organic phases were filtered through Florisil and eluted with 20 mL of ether to yield 11 mg (20%) of **26b** as a colorless oil: IR ($CDCl_3$, cm^{-1}) 3000, 2900, 2880, 2820, 2720, 1720, 1420; ^1H NMR (300 MHz, $CDCl_3$) δ 9.68 (t, J = 1.6 Hz, 2 H), 5.65–5.50 (m, 2 H), 2.80 (dd, J = 8.1, 1.5 Hz, 4 H), 2.31 (br s, 4 H), 2.21 (br t, J = 6.9 Hz, 2 H), 2.02 (br s, 2 H); MS, m/z (M^+) calcd 192.1146, obsd 192.1130.

B. Reduction of Dinitrile 26a. Under argon, dinitrile **26a** (100 mg, 0.537 mmol) was dissolved in 4 mL of anhydrous benzene and cooled to 10 °C in an ice bath. Diisobutylaluminum hydride (1 M in hexanes, 1.2 mL, 1.2 mol) was injected dropwise. The intensively yellow, clear solution was stirred at room temperature for 6 h. The mixture was cannulated into vigorously stirred 5% aqueous sulfuric acid (rinsed with 2 × 5 mL of anhydrous ether), stirred until all solids had dissolved (ca 10 min), and extracted with ether (3 × 3 mL). The combined organic phases were washed with brine (3 mL), dried, filtered, and evaporated to leave 75 mg (73%) of a pale, yellow oil that was pure by ^1H NMR analysis.

Cyclic *O,O-cis*-Tricyclo[5.5.0.$0^{2,8}$]dodec-10-en-4,5-ylene Thiocarbonate (35a). Under argon, **34** (100 mg, 0.515 mmol) and 4-(dimethylamino)pyridine (151 mg, 1.24 mmol) were dissolved in 3 mL of anhydrous methylene chloride and cooled to 0 °C. Thiophosgene–carbon tetrachloride (85%, 0.06 mL, 0.62 mmol) was injected dropwise. The orange-red suspension that formed was stirred for 3 h at 0 °C and then warmed up to room temperature and chromatographed on Florisil with ether elution to afford 84 mg (72%) of **35a** as pale yellow crystals: mp 155–156 °C; IR ($CDCl_3$, cm^{-1}) 3010, 2920, 2805, 1295, 1280; ^1H NMR (300 MHz, $CDCl_3$) δ 5.63–5.48 (m, 2 H), 5.28–5.18 (m, 2 H), 2.47–2.14 (series of m, 9 H), 2.07 (br s, 2 H), 1.85–1.77 (m, 1 H); MS, m/z (M^+) calcd 236.0871, obsd 236.0877.

When chromatographed on silica gel, **35a** underwent partial hydrolysis to **35b**, a white solid: mp 122–125 °C; IR ($CDCl_3$, cm^{-1}) 2920, 1800, 1025; ^1H NMR (300 MHz, $CDCl_3$) δ 5.61–5.54 (m, 2 H), 5.11–5.04 (m, 2 H), 2.40–2.06 (series of m, 11 H), 1.81–1.80 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 154.6, 125.50, 124.93, 80.85, 41.05, 39.12, 37.71, 33.38, 33.63, 32.91; MS, m/z (M^+) calcd 220.1100, obsd 220.1111.

Tricyclo[5.5.0.$0^{2,8}$]dodec-10-en-4-one (36). Exposure of **35a** to basic alumina (activity III) overnight and purification by MPLC (silica gel, 16% ethyl acetate–petroleum ether) yielded **36** as a volatile, colorless oil: IR ($CDCl_3$, cm^{-1}) 3010, 2990, 2830, 1690; ^1H NMR (300 MHz, $CDCl_3$) δ 5.58 (br s, 2 H), 2.71 (t, J = 6.9 Hz, 2 H), 2.58 (d, J = 4.0 Hz, 2 H), 2.39–2.23 (m, 4 H), 2.19–2.12 (m, 3 H), 2.09–2.03 (m, 1 H), 1.89 (5 d, J = 6.9, 3.5 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 213.87, 125.54, 47.82, 40.97, 39.65, 35.34, 33.38, 28.96; MS, m/z (M^+) calcd 176.1201, obsd 176.1205.

Tricyclo[5.5.0.$0^{2,8}$]dodeca-4,10-diene (37). A. From Thiocarbonate 35a. Under argon, a suspension of **35a** (87 mg, 0.37 mmol) in 0.5 mL of 1,3-dimethyl-2-phenyldiazaphospholidine was stirred at 48 °C for 3.5 h and left to stand at room temperature overnight. The homogeneous reaction mixture was diluted with pentane (3 mL), adsorbed on silica gel, and flash chromatographed (silica gel, pentane) to leave 42 mg (71%) of **37** as a white solid, mp 41.5–43.5 °C, after rotary evaporation (room temperature, 100 mmHg): ^1H NMR (200 MHz, $CDCl_3$) δ 5.55 (s, 4 H), 2.26 (s, 8 H), 2.05 (s, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$, ppm) 26.1, 39.2, 33.8; MS, m/z (M^+) calcd 160.1251, obsd 160.1256. Anal. Calcd for $C_{12}H_{16}$: C, 92.26; H, 7.74. Found: C, 91.99; H, 7.65.

B. Deoxygenation of Diol 34. Under argon, a 500-mL Schlenk flask equipped with a reflux condenser and stir bar was charged with titanium trichloride–tetrahydrofuran complex (23 g, 62 mmol) and potassium (9.6 g, 0.25 mol). After the addition of anhydrous dimethoxyethane (200 mL, freshly distilled from sodium–potassium–benzophenone under argon), the

stirred mixture was heated to reflux for 1 h. Diol **34** (1.00 g, 5.15 mmol) was dissolved in hot, anhydrous dimethoxyethane (total 30 mL) and added by cannula to the reduction mixture that had been removed from the oil bath. After 18 h of reflux, the black suspension was cooled to room temperature, diluted with 200 mL of distilled pentane, and decanted onto a glass frit covered with Celite under a brisk flow of argon. Suction was applied at such a rate that the filter residue was always covered with solvent in order to avoid contact of the unreacted potassium with the humid air and ignition of the solvent vapors. The filter residues were rinsed with distilled pentane (200 mL), and the combined clear colorless filtrates were washed with water (250 mL). The aqueous phase was extracted with pentane (100 mL), and the combined organic phases were washed with water (2 × 100 mL) and brine (100 mL). The bulk of the solvent was evaporated at 150 mmHg and room temperature, the remainder at 60 mmHg. After evacuation at 20 mmHg for 10 min, the material was twice distilled bulb-to-bulb (0.05 mmHg, 50 °C, receiver cooled to −78 °C) to yield 0.64 g (77%) of **37**, a white, soft solid, homogeneous by GC and ^{1}H NMR analyses.

Tricyclo[5.5.0.0^{2,8}]dodeca-3,5,9,11-tetraene (8). A. Reductive Debromination with Zinc–Copper Couple. Under argon, a stirred slurry of **37** (105 mg, 0.655 mmol), *N*-bromosuccinimide (516 mg, 2.9 mmol), and azobisisobutyronitrile (17 mg, 0.10 mmol) in 12 mL of dry carbon tetrachloride was irradiated with a sun lamp for 1.5 h. During that time, the inner temperature of the reaction mixture rose to 56 °C. Filtration of the suspension through silica gel (elution with carbon tetrachloride) and evaporation of the solvent at 50 °C yielded 304 mg of a bromide mixture as a white paste. No attempt was made to separate the multitude of possible isomers, but instead the mixture was used as such.

For the subsequent manipulations, exposure to UV light had to be avoided. Therefore, ceiling lights were shut off, and the reaction apparatus was wrapped in aluminum foil.

In a glovebox (argon), 83% zinc–copper couple (0.50 g) was added to the bromide mixture (145 mg, max 0.305 mmol) under argon, dimethylformamide (5 mL, freshly distilled from calcium hydride under argon) was injected, and the suspension was stirred at room temperature. After 1 h, no starting material remained according to TLC, and after 3.9 days no tetraene bromide remained according to GC (1.7 m × 1.5 mm 3% OV-101 on 100-120 Gaschrom Q, 120 °C). The reaction mixture was distributed between water (3 mL) and redistilled pentane (4 mL), and the combined pentane phases were washed with water (3 × 3 mL). Drying, removal of solvent in a lyophylizer (760–20 mmHg, receiver cooled to −78 °C), and sublimation of the residue (room temperature, 0.03–0.01 mmHg, trapped in V-tube cooled to −78 °C) yielded 27 mg (57% from **37**) of **8** as colorless, musty smelling plates: mp 33.5–35.5 °C; IR (neat, cm^{-1}) 3020, 2940, 1580, 1370, 1280, 1050, 825, 780, 665; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.03–5.92 (m, 4 $H_{3,6,9,12}$), 5.80–5.70 (m, 4 $H_{4,5,10,11}$), 2.60–2.50 (m, 4 $H_{1,2,7,9}$) (assigned by homodecoupling); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 134.39, 123.11, 32.93; UV [cyclohexane; λ_{max}, nm (ϵ)] 228 (8900), 318 (3000); MS, *m/z* (M^+) calcd 156.0939, obsd 156.0926.

B. Reductive Debromination with *tert*-Butyllithium. Under argon, the bromide mixture (165 mg, 0.328 mmol) was dissolved in anhydrous tetrahydrofuran (5 mL) and cooled to −78 °C. *tert*-Butyllithium (1.6 M in pentane, 0.87 mL, 1.4 mmol) was injected dropwise. After 10 min, the dark-red reaction mixture was quenched with 0.1 mL of methanol at −78 °C, warmed to room temperature, and washed with brine (2 × 3 mL). The solution was diluted with redistilled pentane (5 mL) and dried over magnesium sulfate. After evaporation of the solvent (bulk at 160 mmHg, rest at 30 mmHg), sublimation (45 °C, 0.03 mmHg) afforded 28.5 mg (53% from **37**) of tetraene **8**.

C. Bromination–Dehydrobromination of 37. Diene **37** (20 mg, 0.13 mmol) was dissolved in 4 mL of carbon tetrachloride and 4 mL of glacial acetic acid. After the addition of pyridinium bromide perbromide (88 mg, 0.29 mmol), the suspension was stirred at room temperature for 1.5 h and partitioned between 10 mL of carbon tetrachloride and 10 mL of water. The organic phase was washed with 10 mL of saturated aqueous sodium bicarbonate solution, dried, and evaporated to leave 54% mg (90%) of tetrabromide as a white solid, mp 236–238 °C dec, that was poorly soluble in carbon tetrachloride, cold chloroform, or ether and very soluble in benzene or tetrahydrofuran. According to ^{13}C NMR spectral data, the ratio of the two possible diastereomers was 54:46: IR (KBr, cm^{-1}) 2910, 2840, 1430, 1110, 750, 635; ^{1}H NMR (300 MHz, benzene-d_6) δ 3.96–3.85 (m, 4 H), 2.12–2.00 (m, 4 H), 1.65–1.52 (m, 3 H), 0.94–0.90 (m, 4 H); ^{13}C NMR (75 MHz, benzene-d_6) major (54%) 56.08, 41.66, 39.24; minor (46%) 56.17, 41.48, 39.42 ppm; MS, *m/z* (M^+ − HBr_2) calcd 318.9520, obsd 318.9501.

Under argon, potassium *tert*-butoxide (1.6 M in tetrahydrofuran, 0.60 mL, 0.96 mmol) was injected into a cold (0 °C) solution of the above tetrabromide (56 mg, 0.12 mmol) in anhydrous tetrahydrofuran (5 mL). The orange-brown suspension was warmed to room temperature, stirred for 30 min, and partitioned between 10 mL of water and 10 mL of redistilled pentane. The organic phase was washed with water (5 mL) and half-saturated aqueous ammonium chloride solution (2 × 5 mL), dried, and filtered through 20 × 10 mm of Florisil. Solvent evaporation was carried out at 0 °C and 120 Torr until only about 1–2 mL of liquid was left. The residue was evacuated briefly in a Kugelrohr distillation apparatus at room temperature (30 Torr) for 2 min to remove most of the tetrahydrofuran and then distilled into a bulb cooled to −20 to −35 °C. Resublimation at room temperature and 0.02 Torr yielded 13 mg (68%) of **8** as a white semisolid containing only minimal impurities, especially no solvent or diene by 300-MHz ^{1}H NMR spectroscopy.

3-Bromotricyclo[5.5.0.0^{2,8}]dodeca-3,5,9,11-tetraene (38). Again all manipulations were done with exclusion of lighting. From an incomplete reductive debromination with zinc–copper couple, tetraene bromide could be isolated by reversed-phase HPLC (250 × 4.6 mm C_{18} 5 μm Zorbax 008, 1.5 mL/min, 90% methanol–water; retention time 8.23 min, compare for **8**, 7.62 min). The combined fractions were extracted with distilled pentane (3 × 10 mL), and pentane phases were washed with water (3 × 10 mL) and brine (5 mL) prior to drying. After evaporation of the solvent, the residue was distilled at 0.01 mmHg and 60 °C. The ^{1}H NMR signals were assigned by homodecoupling techniques: IR ($CDCl_3$, cm^{-1}) 3040, 2960, 2850, 1595, 1580, 1275, 1065, 825, 680; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.21 (dd, $J_{4,5}$ = 7.6 Hz, $J_{4,2}$ = 2.0 Hz, $J_{4,6}$ = 0.7 Hz, 1 H_4), 6.04 (br dd, $J_{6,5}$ = 11.1 Hz, $J_{6,7}$ = 8.2 Hz, 1 H_6), 6.00–5.90 (m, 2 $H_{9,12}$), 5.82–5.73 (m, 2 $H_{10,11}$), 5.55 (ddd, $J_{5,6}$ = 11.1 Hz, $J_{5,4}$ = 7.6 Hz, $J_{5,7}$ = 0.7 Hz, 1 H_5), 2.92 (br dd, $J_{2,7}$ = 4.8 Hz, $J_{2,4}$ = 2.0 Hz, 1 H_2), 2.76–2.67 (m, 2 $H_{1,8}$), 2.56 (ddd, $J_{7,6}$ = 8.2 Hz, $J_{7,2}$ = 4.8 Hz, $J_{7,5}$ = 0.7 Hz, 1 H_7); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 135.06, 132.94, 127.61, 125.15, 123.53, 122.07, 44.57, 33.75, 32.86; UV [cyclohexane; λ_{max}, nm (ϵ)] 234 (6850), 244 (sh, 4780), 324 (2210); MS, *m/z* (M^+) calcd 236.0024, obsd 236.0023.

3,9-Dibromotricyclo[5.5.0.0^{2,8}]dodeca-3,5,9,11-tetraene (39). All manipulations were performed with protection from light. Under argon, the unpurified allylic tetrabromide (0.12 g, max 0.25 mmol), prepared from diene **37** (40 mg, 0.25 mmol) in the predescribed manner, was dissolved in anhydrous tetrahydrofuran (3 mL), cooled to 0 °C, and treated with potassium *tert*-butoxide in the same solvent (1.6 M, 0.6 mL, 4 mmol). After 15 min at 0 °C, the dark brown mixture was partitioned between pentane (10 mL) and water (10 mL). The aqueous phase was extracted with pentane (5 mL), and the combined organic phases were washed with water (2 × 5 mL) and brine (5 mL). After evaporation, pentane (3 mL) was added, and the material seemed to polymerize. The suspension was dried, filtered, and evaporated to leave 71 mg of a dark brown oil. Flash chromatography (silica gel, pentane elution) yielded 30 mg (38%) of a pale yellow oil that still exhibited a strong tendency to polymerize (this dimerization/polymerization tendency seemed to increase in going from **8** to **38** to **39**) and contained impurities according to ^{1}H NMR analysis: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.23 (dd, $J_{4,5}$ = 7.6 Hz, $J_{4,2}$ = 1.7 Hz, 2 H_4), 6.03 (dd, $J_{6,5}$ = 11.3 Hz, $J_{6,1}$ = 8.5 Hz, 2 H_6), 5.58 (dd, $J_{5,6}$ = 11.1 Hz, $J_{5,4}$ = 7.6 Hz, 2 H_5), 3.05 (dd, $J_{2,1}$ = 5.8 Hz, $J_{2,4}$ = 1.4 Hz, 2 H_2), 2.70 (dd, $J_{1,6}$ = 8.4 Hz, $J_{1,2}$ = 5.6 Hz, 2 H_1); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 135.88, 126.04, 125.57, 122.51, 45.14, 33.58.

10-Thiatricyclo[5.4.0.0^{2,8}]undec-4-ene (40). A 100-mL three-necked round-bottomed flask equipped with a distillation apparatus was charged with finely ground sodium sulfide monohydrate (4.04 g, 16.8 mmol) and HMPA (50 mL). Under a vacuum of 30 mmHg, the stirred suspension was slowly heated to 140 °C until all the water had distilled over. After cooling to room temperature, the vacuum was released to argon, and the distillation apparatus was replaced by a rubber septum. A solution of **33a** (1.65 g, 5.61 mmol) in anhydrous HMPA (10 mL) was cannulated into the reaction flask. After 2.75 h at 110 °C, the mixture was cooled to room temperature and partitioned between water (70 mL) and petroleum ether (50 mL). The aqueous phase was extracted with 50 mL of petroleum ether, and the combined organic phases were washed twice with 50 mL of water, dried, and evaporated. The residue was distilled in a Kugelrohr apparatus at 60 °C (0.02 mmHg) to afford 908 mg (99%) of **40** as a colorless liquid that crystallized in the freezer. Bulb-to-bulb resublimation yielded a foul-smelling, analytically pure, white solid, mp 28 °C; IR (neat, cm^{-1}) 3000, 2960–2840, 2820, 1440, 1420, 1255, 1155, 1075, 925, 855, 655; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.56–5.52 (br s, 2 H), 3.30 (d, J = 3.0 Hz, 4 H), 2.39–2.35 (br s, 2 H), 2.34–2.29 (m, 4 H), 2.23–2.17 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 126.11, 40.46, 38.53, 37.44, 23.47; MS, *m/z* (M^+) calcd 166.0817, obsd 166.0845. Anal. Calcd for $C_{19}H_{14}S$: C, 72.23; H, 8.49. Found: C, 72.16; H, 8.45.

9-Chloro-10-thiatricyclo[5.4.0.0^{2,8}]undec-4-ene 10,10-Dioxide (41). Sulfide **40** (503 mg, 3.03 mmol) was α-chlorinated with *N*-chlorosuccinimide (406 mg, 3.03 mmol) in 10 mL of anhydrous carbon tetrachloride and heated to 90 °C under argon for 10 min. After being cooled to room temperature, the mixture was filtered with exclusion of moisture

and cooled to 0 °C. The clear, colorless solution warmed significantly when treated with 99% *m*-chloroperbenzoic acid (0.84 g, 5.76 mmol). After 18.5 h of being stirred at room temperature under argon, the thick slurry was partitioned between 20 mL of dichloromethane and 30 mL of saturated aqueous potassium carbonate solution–saturated aqueous sodium sulfite solution–water (6:6:18). The aqueous phase was extracted with dichloromethane (2 × 10 mL), and the combined organic phases were dried and evaporated. The residue was subjected to flash chromatography (20% ethyl acetate in petroleum ether), and 443 mg (63%) of **41** was isolated as a white solid: mp 117–121 °C; IR ($CDCl_3$, cm^{-1}) 3010, 2880, 2820, 1350, 1140; ^1H NMR (300 MHz, $CDCl_3$) δ 5.59 (m, 2 H), 5.29 (d, J = 4.3 Hz, 1 H), 3.79 (d, J = 3.4 Hz, 2 H), 2.94–2.84 (m, 1 H), 2.72–2.65 (m, 1 H), 2.57–2.42 (series of m, 5 H), 2.42–2.34 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 125.13, 124.69, 83.39, 66.57, 45.68, 39.19, 36.98, 36.91, 31.86, 31.68; MS, m/z (M^+) calcd 232.0324, obsd 232.0340.

Tricyclo[5.3.0.0^{2,8}]deca-4,9-diene (42). A solution of **41** (434 mg, 1.86 mmol) in anhydrous tetrahydrofuran (5 mL) was cooled to 0 °C under argon, treated with potassium *tert*-butoxide (1.6 M in THF, 1.7 mL, 2.8 mmol), and warmed to room temperature. After 1.8 h, another 4 mL of potassium *tert*-butoxide solution (6.4 mmol) was added. Partitioning of the thick, orange-brown slurry between 20 mL of water and 20 mL of distilled pentane, extraction of the aqueous phase with distilled pentane (2 × 10 mL), and washing of the combined organic phases with water (2 × 20 mL) and brine (10 mL) was followed by filtration through neutral alumina (activity I). The eluate was concentrated to ca. 5 mL at 0 °C (150 mmHg); most of the solvent was removed by brief (5 min) evaporation in a Kulgerohr distillation apparatus at 0 °C (40 mmHg), and diene **42** was subjected to bulb-to-bulb distillation at room temperature and 0.1–0.2 mmHg into a receiver cooled to −45 to −50 °C. Redistillation at room temperature and 0.1–0.05 mmHg yielded 201 mg (82%) of **42** as a solvent-free mobile liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 7.13 (t, J = 2.2 Hz, 2 H), 5.58 (br s, 2 H), 2.91 (br s, 2 H), 2.58 (t, J = 2.2 Hz, 2 H), 2.45 ('d', J = 1.8 Hz, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 147.65, 126.87, 78.49, 50.43, 32.10; MS, m/z (M^+) calcd 132.0939, observed 132.0946. Anal. Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.64; H, 9.37.

Thermal Isomerization of 42. During an attempt to purify **42** by preparative GC (5 m × 4 mm 10% SE-30 on Chromosorb P), rearrangement occurred to give the isomeric hydrocarbons **49–51** in ratios depending on the column temperature: at 170 °C, 20.8:1:2.5; at 230 °C, 1:2.4:3.6.

For 2a,2b,3,6,6a,6b-Hexahydrocycloprop[*cd*]azulene (**49**): ^1H NMR (300 MHz, CD_2Cl_2) δ 6.77–5.66 (m, 2 H), 5.66–5.54 (m, 1 H), 5.47–5.36 (m, 1 H), 3.28–3.18 (br s, 1 H), 2.78–2.65 (m, 1 H), 2.47–2.33 (m, 1 H), 2.29–2.14 (m, 1 H), 2.14–2.00 (m, 1 H), 2.00–1.92 (m, 1 H), 1.62–1.52 (m, 1 H), 1.47–1.34 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 138.33, 130.39, 129.34, 128.72, 44.99, 31.11, 28.96, 23.69, 22.45.

For *cis*-1,3a,8,8a-tetrahydroazulene (**50**) and *cis*-1,3a,4,8a-tetrahydroazulene (**51**): ^1H NMR (300 MHz, $CDCl_3$ on the mixture) δ 6.15–5.62 (series of m, 6 H, **50** and **51**), 3.50–3.43 (m, 1 H, **50**), 3.11–2.99 (m, 1 H, **51**), 2.92–2.78 (m, 1 H, **50** and **51**), 2.68–2.55 (m, 1 H, **50** and **51**), 2.36–1.90 (series of m, 3 H, **50** and **51**); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) (**50**) 136.01, 134.52, 132.86, 128.75, 127.67, 125.25, 50.64, 50.25, 41.22, 33.42; (**51**) 136.87, 135.33, 133.73, 128.60, 127.38, 123.72, 52.06, 44.11, 40.69, 30.80.

9-Chloro-3,6-dibromo-10-thiatricyclo[5.4.0.0^{2,8}]undec-4-ene 10,10-Dioxide (43). A mixture of chloro sulfone **41** (25.5 mg, 0.109 mmol), *N*-bromosuccinimide (41 mg, 0.23 mmol), and azobisisobutyronitrile (3.6 mg, 0.022 mmol) in anhydrous carbon tetrachloride (4 mL) was irradiated under argon with a sun lamp for 2.3 h. After being cooled to room temperature, the colorless suspension was filtered through a short Florisil column (30% ethyl acetate in petroleum ether as eluant) to leave 46.3 mg of a colorless oil. Usually this mixture was used directly for further reaction. For characterization, the material was purified by preparative TLC (silica gel, 30% ethyl acetate in petroleum ether) to give two UV active components:

A (R_f 0.65–0.53, 15.8 mg (37.1%) of a white solid, a mixture of at least two isomers): ^1H NMR (300 MHz, $CDCl_3$) δ 5.80 (br s, 4 H), 5.33 (d, J = 3.6 Hz, 1 H), 5.31 (d, J = 3.9 Hz, 1 H), 5.14–5.04 (m, 4 H), 3.90–3.84 (m, 4 H), 3.32–3.29 (m, 2 H), 3.10–3.05 (m, 2 H), 2.88–2.83 (m, 2 H), 2.78–2.70 (m, 1 H).

B (R_f 0.47–0.41, 10.2 mg (23.9%) of colorless oil, probably one diastereomer only): ^1H NMR (300 MHz, $CDCl_3$) δ 5.81 (d, J = 1.9 Hz, 2 H), 5.26 (d, J = 3.9 Hz, 1 H), 5.04–4.96 (m, 2 H), 3.91 (d, J = 3.3 Hz, 2 H), 3.32 (t, J = 4.7 Hz, 1 H), 3.06 (t, J = 4.7 Hz, 1 H), 3.05–3.00 (m, 1 H), 2.52 (dd, J = 6.0, 4.0 Hz, 1 H).

3-Bromo-9-chloro-10-thiatricyclo[5.4.0.0^{2,8}]undeca-3,5-diene 10,10-Dioxide (44a). Dibromide **43** (4.5 mg, 12 mmol) in 1.5 mL of anhydrous tetrahydrofuran was cooled to 0 °C under argon, treated with potassium *tert*-butoxide (1.6 M in tetrahydrofuran, 7 μL, 12 mmol), and warmed to room temperature. After 12 h, more potassium *tert*-butoxide solution (4 μL, 6 mmol) was injected, until no starting material was left according to analytical TLC. The solvent was evaporated, and the residue was taken up in 20% ethyl acetate in petroleum ether and filtered through a pipet filled with Florisil (20% ethyl acetate in petroleum ether). The eluate was further purified by MPLC (silica gel, 20% ethyl acetate in petroleum ether), resulting in separation of the two epimers.

A (R_f 0.42, 1.0 mg (28%) of a yellow oil): ^1H NMR (300 MHz, $CDCl_3$) δ 6.48 (dd, J = 6, 1 Hz, 1 H), 6.27 (dd, J = 10, 9 Hz, 1 H), 5.83 (dd, J = 10, 6 Hz, 1 H), 5.40 (d, J = 5.1 Hz, 1 H), 3.85–3.79 (m, 2 H), 3.66 (dd, J = 5, 1 Hz, 1 H), 3.07 (dd, J = 9, 6 Hz, 1 H), 2.50 (dd, J = 6, 4 Hz, 1 H), 2.40–2.35 (m, 1 H); MS, m/z (M^+) calcd 309.9253, obsd 309.9256.

B (R_f 0.24, 0.6 mg (17%) of a white solid): ^1H NMR (300 MHz, $CDCl_3$) δ 6.45 (dd, J = 7, 2 Hz, 1 H), 6.22 (ddd, J = 11.5, 6.5, 2 Hz, 1 H), 5.83 (dd, J = 11, 7 Hz, 1 H), 5.31 (d, J = 4.5 Hz, 1 H), 3.83–3.79 (m, 2 H), 3.41–3.34 (m, 2 H), 2.51 (dd, J = 6, 4.5 Hz, 1 H), 2.38 (dd, J = 6.5, 3.5 Hz, 1 H); MS, m/z (M^+) calcd 309.9253, obsd 309.9279.

***trans*-4,5-Dibromo-10-thiatricyclo[5.4.0.0^{2,8}]undecane (45).** A suspension of sulfide **40** (396 mg, 2.39 mmol) and pyridinium bromide perbromide (804 mg, 2.63 mmol) in carbon tetrachloride (6 mL) and glacial acetic acid (6 mL) was stirred at room temperature for 1 h and then partitioned between 20 mL of water and 20 mL of carbon tetrachloride. The organic phase was washed with 10 mL of saturated aqueous sodium bicarbonate solution, dried, and evaporated. Ultimate evacuation to 0.01 mmHg (50 °C, 3 h) left 722 mg (93%) of **45** as an off-white solid. This material could be used as such. Flash chromatography on silica gel (10% ethyl acetate in petroleum ether) afforded pure **45** as a white solid: mp 116.5–117.5 °C; IR ($CDCl_3$, cm^{-1}) 2920, 2850, 1435, 1245; ^1H NMR (300 MHz, $CDCl_3$) δ 4.58–4.46 (m, 2 H), 3.28–3.16 (m, 4 H), 2.84 (dt, J = 15, 4.5 Hz, 2 H), 2.39 (br s, 4 H), 2.33 (br dd, J = 15, 8.5 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 56.15, 41.83, 40.04, 37.79, 35.63; MS, m/z (M^+) calcd 325.9162, obsd 325.9137. Anal. Calcd for $C_{10}H_{14}Br_2S$: C, 36.82; H, 4.33. Found: C, 36.43; H, 4.19.

10-Thiatricyclo[5.4.0.0^{2,8}]undeca-3,5-diene (46). Under argon, a solution of dibromide **45** (179 mg, 0.550 mmol) in anhydrous tetrahydrofuran (7 mL) was cooled to 0 °C and treated with potassium *tert*-butoxide (1.6 M in tetrahydrofuran, 1.0 mL, 1.60 mmol). After being stirred for 35 min at room temperature, the solution was partitioned between 20 mL of water and 20 mL of pentane. The organic phase was washed with water (2 × 10 mL) and saturated aqueous ammonium chloride solution (10 mL), dried, and evaporated. Bulb-to-bulb distillation (0.01 mmHg, 50 °C) of the residue left 85 mg (94%) of **46** as a white, smelly solid that melted at 33.0–35.5 °C after two additional sublimations: IR ($CDCl_3$, cm^{-1}) 3020, 2920, 2840, 1360, 1235, 1005, 860, 670; ^1H NMR (300 MHz, $CDCl_3$) δ 6.22–6.11 (m, 2 H), 5.91–5.83 (m, 2 H), 3.33–3.22 (m, 4 H), 2.75–2.68 (m, 2 H), 2.05–1.99 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 135.88, 124.44, 42.03, 34.29, 29.36; MS, m/z (M^+) calcd 164.0660, obsd 164.0667.

9-Chloro-10-thiatricyclo[5.4.0.0^{2,8}]undeca-3,5-diene 10,10-Dioxide (44b). Sulfide **46** (23.4 mg, 0.143 mmol) dissolved in anhydrous carbon tetrachloride [4 mL, filtered through basic alumina (activity I) together with sulfide] was heated to 85 °C under argon for 1.3 h with *N*-chlorosuccinimide (19.1 mg, 0.143 mmol). After the mixture was cooled to room temperature, 99% *m*-chloroperbenzoic acid (50 mg, 0.25 mmol) was added in three portions, and stirring at room temperature was continued overnight. The mixture was diluted with 10 mL of carbon tetrachloride and washed with 10 mL of saturated aqueous potassium carbonate solution–saturated aqueous sodium sulfite solution–water (2:1:7). The aqueous phase was extracted with 2 mL of carbon tetrachloride, and the combined organic phases were dried. Solvent evaporation yielded 28.2 mg of a solid, MPLC of which on silica gel (30% ethyl acetate in petroleum ether) afforded 14.9 mg (45%) of **44b** as a white sticky solid: mp 160–165 °C; IR ($CDCl_3$, cm^{-1}) 3030, 2940, 1330, 1320, 1120; ^1H NMR (300 MHz, $CDCl_3$) δ 6.27–6.11 (m, 2 H), 6.05–5.95 (m, 2 H), 5.32 (d, J = 4.0 Hz, 1 H), 3.83–3.72 (m, 2 H), 3.33 (dd, J = 8.3, 5.8 Hz, 1 H), 3.05 (dd, J = 8.4, 5.8 Hz, 1 H), 2.32 (dd, J = 6.1, 4.1 Hz, H), 2.23–2.15 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 132.92, 132.01, 125.95, 125.35, 80.90, 62.55, 40.37, 38.57, 35.98, 27.76; MS, m/z (M^+) calcd 232.0139, obsd 232.0139.

(2*R,4*R**,*R**,7*S**)-4,5-Dibromo-9-chloro-10-thiatricyclo[5.4.0.0^{2,8}]-undecane 10,10-Dioxide (47). A. Bromination of 41.** A solution of chloro sulfone **41** (15.6 mg, 66.9 mmol) and pyridinium bromide perbromide (22 mg, 70 mmol) in carbon tetrachloride (0.5 mL) and glacial acetic acid (0.5 mL) was stirred at room temperature for 30 min and then partitioned between carbon tetrachloride (1.5 mL) and water (1 mL). The organic phase was washed with half-saturated aqueous potassium carbonate solution (2 × 1 mL) and brine (1 mL), dried, and evaporated

to leave 23.5 mg of a colorless oil that still contained about 14% of starting material according to ^{1}H NMR data. The mixture was therefore resubmitted to the bromination conditions [0.3 mL of carbon tetrachloride, 0.3 mL of glacial acetic acid, 3.1 mg (10.1 mmol) of pyridinium bromide perbromide (10.1 mmol); 4 h and 40 min] to yield after workup and MPLC (silica gel, 30% ethyl acetate in petroleum ether) 23.2 mg (88%) of **47** as a colorless foam: IR ($CDCl_3$, cm^{-1}) 2920, 1325, 1125; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.23 (d, J = 4.0 Hz, 1 H), 4.75–4.65 (m, 2 H), 3.73 (d, J = 4.2 Hz, 2 H), 3.20–3.14 (m, 1 H), 3.05–2.84 (series of m, 4 H), 2.75–2.71 (m, 1 H), 2.62–2.45 (series of m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 80.99, 80.89, 64.02, 63.95, 53.49, 53.38, 44.14, 44.10, 40.27, 40.14, 38.79, 38.68, 36.23, 36.11, 35.98, 35.53; MS (CI), m/z (M^+) calcd 391.87, obsd 392.66.

B. Chlorination–Oxidation of 45. Sulfide **45** (722 mg, 2.1 mmol) and *N*-chlorosuccinimide (297 mg, 2.21 mmol) in anhydrous carbon tetrachloride (10 mL) were heated to 90 °C under argon for 10 min. After being cooled to room temperature, the reaction suspension was filtered through a dry, cotton-plugged Pasteur pipet with exclusion of moisture and cooled to 0 °C. *m*-Chloroperbenzoic acid (99%, 950 mg, 5.52 mmol) was added at 0 °C, and the mixture was stirred for 2 h at room temperature. The reaction mixture was partitioned between saturated aqueous potassium carbonate solution–aqueous sodium sulfite solution–water (1:1:3) and chloroform to yield after drying and careful rotary evaporation 730 mg (84%) of **47** as a white frothy foam that was pure by TLC and spectroscopically identical with the material prepared in part A.

Tricyclo[5.3.0.0^{2,8}]deca-3,5,9-triene (9). A. Directly from 47. While at 0 °C under argon and protected from direct light, 1.5 mL of 1.6 M potassium *tert*-butoxide in tetrahydrofuran (2.4 mmol) was injected dropwise into a solution of **12** (100 mg, 0.25 mmol) in the same solvent (3 mL). After 1 h of stirring, the black reaction mixture was partitioned between cold, distilled pentane (10 mL) and cold water (10 mL) with chilled glassware in a cold room (2–4 °C). The orange organic phase was washed with water (2 × 5 mL) and filtered through a pipet filled with 2 cm of Florisil that had been equilibrated with cold pentane. The solvent was rotary evaporated (0 °C, 70 mmHg), and the brown residue was distilled in a Kulgerohr apparatus (distillation flask cooled to 0 °C, receiver flask cooled to −40 °C, 0.05 mmHg) after brief evacuation (20 mmHg, 0 °C, 2 min). Redistillation (distillation flask cooled to 0 °C, receiver tube cooled to −40 °C) afforded in high yield a colorless oil with a strong musty odor that consisted of a mixture of triene **9**, diene **42**, and isobullvalene in a ratio of 10:2:1 (^{1}H NMR): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (t, J = 2.3 Hz, 2 H), 6.34–6.24 (m, 2 H), 6.24–6.15 (m, 2 H), 3.56–3.49 (m, 2 H), 1.17 (t, J = 2.3 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.36, 136.26, 126.29, 78.37, 29.61.

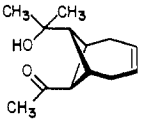
B. Ramberg–Bäcklund Rearrangement of 44b. A solution of **44b** (16 mg, 69 mmol) in anhydrous tetrahydrofuran (1 mL) was cooled to −10 °C and treated with 1.6 M potassium *tert*-butoxide in tetrahydrofuran (88 μL, 0.14 mmol). After 10 min, the solution was quenched at −10 °C with cold saturated brine/water (1:1, 2 mL) and stirred vigorously with cold distilled pentane (2 + 2 × 1 mL). The lower aqueous phase was withdrawn by pipet and transferred into another cold flask. In the same manner, the combined organic phases were washed with cold saturated brine–water (1:1, 2 × 1 mL) and brine (1 mL) and rotary evaporated (−10 °C, 60 mmHg) to a volume of ca. 0.3 mL. After the addition of ca. 50 mg of magnesium sulfate and subsequent filtration, the remaining solvent was rotary evaporated (0 °C, 30 mmHg). Distillation by the Kugelrohr technique as before furnished an 11:1 mixture of triene **9** and isobullvalene in good yield.

(7*s*$_n$,8*s*$_n$)-Bicyclo[4.1.1]oct-3-ene-7,8-dimethanol (51). Bis(tetrahydropyranyl) ether **30** (2.98 g, 8.84 mmol) was stirred with acid-washed Dowex 50 × 4-400 resin (0.5 g) in 13 mL of methanol at room temperature. After 1 h, the mixture was filtered through Celite. The filtrate was rotary evaporated and evacuated (room temperature, 0.03 mmHg) to leave 1.82 g of a clear, pale yellow oil. Purification by MPLC (silica gel, ethyl acetate) afforded 1.36 g (91%) of **51** as a white solid: mp 98.5–100.0 °C (from chloroform); IR ($CDCl_3$, cm^{-1}) 3605, 3600–3100, 3000, 2880, 2815, 1420, 1070, 1020; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.59 (br s, 2 H), 3.81 (d, J = 7.0 Hz, 4 H), 2.29 (s, 4 H), 2.14 (br s, 2 H), 2.05–1.87 (m, 4 H); MS, m/z (M^+) calcd 168.1146, obsd 168.1147. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.52; H, 9.40.

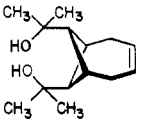
(7*s*$_n$,8*s*$_n$)-Bicyclo[4.1.1]oct-3-ene-7,8-dicarboxylic Acid (52). A solution of **51** (400 mg, 2.38 mmol) in dichloromethane was added to the golden orange solution of ruthenium trichloride hydrate (27 mg, 0.10 mmol), potassium persulfate (3.4 g, 14 mmol), and potassium hydroxide (5.2 g, 93 mmol) in water (140 mL). After 5 h of vigorous stirring, the dark-brown reaction mixture had turned orange again. The excess oxidant was quenched with sodium thiosulfate (1.89 g, 15 mmol). The aqueous phase was saturated with sodium chloride. Residual organic impurities were extracted with ether (2 × 50 mL), and the aqueous phase was acidified at 0 °C with concentrated hydrochloric acid (20 mL, 0.24 mol). Extraction with ether (3 × 50 mL), drying of the combined extracts, and solvent evaporation afforded 411 mg (87%) of **52** as a white solid, dec >250 °C: IR (KBr, cm^{-1}) 3800–2300, 1695, 1425, 1325, 1290, 1220; ^{1}H NMR (300 MHz, acetone-d_6) δ 5.65 (br s, 2 H), 3.13 (br s, 2 H), 2.51 ('t', J = 2.1 Hz, 2 H), 2.38 ('d', J = 1.7 Hz, 4 H); ^{13}C NMR (75 MHz, acetone-d_6, ppm) 175.63, 126.23, 45.49, 38.22, 33.92; MS, m/z (M^+) calcd 196.0735, obsd 196.0755.

(7*s*$_n$,8*s*$_n$)-7,8-Diacetylbicyclo[4.1.1]oct-3-ene (53). Diacid **52** (411 mg, 2.10 mmol) was added to a suspension of lithium hydride (53 mg, 7.6 mmol) in anhydrous tetrahydrofuran (10 mL) and stirred at room temperature for 30 min. After cooling to 0 °C, 1.5 M of methyllithium in ether (7.8 mL, 11.8 mmol) was injected dropwise over 5 min. The yellow suspension was stirred at room temperature for 10 h, diluted with more anhydrous tetrahydrofuran (10 mL), and stirred for another 10 h. For hydrolysis, the reaction mixture was added by cannula to a vigorously stirred solution of water (40 mL), 10% aqueous hydrochloric acid (20 mL), and saturated aqueous ammonium chloride solution (10 mL). After neutralization with sodium carbonate, the tetrahydrofuran was removed by rotary evaporation. The aqueous phase was extracted with ether (3 × 50 mL). Drying of the combined organic phases and solvent evaporation afforded 404 mg of a yellow oil that spontaneously crystallized. Purification by MPLC (silica gel, 50% ethyl acetate in petroleum ether) yielded 210 mg (53%) of **53** that crystallized as white, colorless needles, mp 102–104 °C. A sample of analytical purity was obtained by preparative GC (1.1 m × 4 mm 5% SE-30 on 60–80-mesh Chromosorb W, 120 °C); IR ($CDCl_3$, cm^{-1}) 3000, 2940, 2880, 2820, 1700, 1420, 1355, 1275, 1215, 1180; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.66 (br s, 2 H), 3.16 (br s, 2 H), 2.56 (t, J = 2.1 Hz, 2 H), 2.41 (br d, J = 1.7 Hz, 4 H), 2.13 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 208.15, 125.57, 53.15, 35.65, 33.30, 27.11; MS, m/z (M^+) calcd 192.1150, obsd 192.1165. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.39; H, 8.27.

In addition to **53**, varying amounts of the over-addition products **59** and **60** were isolated as more polar components.



59



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For **59**: white solid; mp 94.0–95.5 °C; IR ($CDCl_3$, cm^{-1}) 2970, 2930, 2875, 2820, 1690, 1190; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.66 (br s, 2 H), 2.87 (br s, 2 H), 2.53–2.49 (m, 1 H), 2.38 (br AB, J_{AB} = 18.4 Hz, 2 H), 2.27 (br AB, J_{AB} = 18.3 Hz, 2 H), 2.13 (s, 3 H), 1.66–1.62 (m, 1 H), 1.12 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 211.70, 125.77, 69.75, 52.69, 51.58, 34.28, 33.75, 27.11, 26.90; MS, m/z ($M^+ - CH_3$) calcd 193.1229, obsd 193.1247; MS (CI), m/z ($M + H^+$) calcd 209.15, obsd 209.08.

For **60**: soft, white needles; IR ($CDCl_3$, cm^{-1}) 3360, 2970, 2930, 2870, 2810, 1700, 1420, 1365, 1150; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.61 (br s, 2 H), 4.13 (br s, 2 H), 2.77–2.68 (m, 2 H), 2.21 (br 'd', J = 1.6 Hz, 4 H), 1.62 (t, J = 2.9 Hz, 2 H), 1.17 (s, 12 H); MS, m/z ($M^+ - CH_3$) calcd 209.1542, obsd 209.1537.

9,10-Dimethyltricyclo[5.3.0.0^{2,8}]deca-4,9-diene (54). A. From Diol 55. Titanium trichloride–tris(tetrahydrofuran) complex (0.19 g, 0.51 mmol) and potassium (86 mg, 2.2 mmol) were weighed into an oven-dried 25-mL Schlenk flask under argon by the Schlenk technique. The flask was equipped with a reflux condenser and stir bar, and all joints were secured by springs or wire. After the addition of dimethoxyethane [7 mL, freshly distilled from Na–K (1:1) benzophenone under argon], the blue suspension was refluxed for 1.5 h. A solution of **55** (10 mg, 0.052 mmol) in anhydrous dimethoxyethane (1 mL) was added by cannula, and the black suspension was refluxed for another 18 h. After cooling to room temperature, the titanium residues were precipitated with pentane (15 mL). The supernatant solution was siphoned off by cannula and filtered through a cotton plug. The residue was triturated with more pentane (2 × 25 mL). The combined organic phases were washed with water (3 × 10 mL), dried, evaporated (0 °C, 100–60 mmHg), and purified by preparative GC (1.1 m × 4 mm 5% SE-30 on 60–80-mesh Chromosorb W, 80 °C) to give 1 mg (12%) of **54** as a colorless oil: IR ($CDCl_3$, cm^{-1}) 3020, 2920, 2880, 2820, 1455, 1420; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.55 (br s, 2 H), 2.85–2.82 (br s, 2 H), 2.45–2.33 (m, 4 H), 2.31 (s, 2 H), 1.84 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 147.48, 126.99, 74.41, 54.33, 32.18, 12.97; MS, m/z (M^+) calcd 160.1252, obsd 160.1240.

The combined aqueous phases and trituration residue were extracted with ether (40 mL total). The organic phase was washed with water (20 mL) and brine (10 mL), dried, and evaporated. The resulting brown oil afforded 3.3 mg (33%) of unreacted **55** after flash chromatography

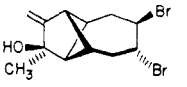
(grade silica gel, 40% ethyl acetate in petroleum ether).

B. From Diketone 53. In the same apparatus, titanium trichloride–tris(tetrahydrofuran) complex (0.41 g, 1.1 mmol) and potassium (0.17 g, 4.4 mmol) were refluxed in anhydrous dimethoxyethane (7 mL) for 1 h. At room temperature, diketone **53** (24 mg, 0.13 mmol) dissolved in anhydrous dimethoxyethane (3 mL) was added by cannula. The reaction mixture was refluxed for 15 h and worked up in analogous fashion to give 2.3 mg (13%) of diene **54** (less pure) and 1.5 mg (7%) of diol **55**.

***cis*-9,10-Dimethyltricyclo[5.3.0.0^{2,8}]dec-4-ene-9,10-diol (55).** A suspension of magnesium powder (70-80 mesh, 50 mg, 2.1 g-atom) and mercuric chloride (16 mg, 0.057 mmol) was stirred under argon in anhydrous tetrahydrofuran (2 mL) at room temperature for 15 min. The cloudy supernatant solution was siphoned off by syringe, and the dark amalgam was washed with anhydrous tetrahydrofuran (3 × 3 mL) and finally suspended in more of the same solvent (3 mL). After cooling to −15 to −10 °C, freshly distilled titanium tetrachloride was injected dropwise in a very exothermic reaction. Diketone **53** (50 mg, 0.26 mmol) in anhydrous tetrahydrofuran (3 mL) was added rapidly by cannula at −10 °C. After 7 h of stirring at 0 °C, no starting material was left by TLC analysis. The pitch-black mixture was stirred with saturated aqueous potassium carbonate solution (0.5 mL) for 15 min at 0 °C. A blue-black, granular precipitate settled. After the addition of ether (total 20 mL), the supernatant solution was suction filtered through Celite. The clear, colorless filtrate was washed with brine (7 mL), dried, filtered, evaporated, redissolved in ether, and again dried. MPLC purification (silica gel, 50% ethyl acetate in petroleum ether) afforded 38 mg (76%) of **55** as a white crystalline solid: mp 119–121 °C; IR ($CDCl_3$, cm^{-1}) 3600, 3600–3160, 3000, 2940, 2860, 1380, 1130, 1065; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.64–5.50 (m, 2 H), 3.01 (br s, 2 H), 2.74–2.66 (m, 1 H), 2.60–2.53 (m, 2 H), 2.53–2.45 (m, 2 h), 2.13 (s, 2 H), 2.04–1.94 (m, 1 H), 1.41 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 127.01, 125.99, 78.77, 56.54, 44.58, 42.21, 30.72, 30.58, 21.90; MS (CI), *m/z* (M^+) calcd 194.14, obsd 194.06. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.02; H, 9.43.

(4*R,5*R**,9*R**,10*S**)-4,5-Dibromo-9,10-dimethyltricyclo[5.3.0.0^{2,8}]-decane-9,10-diol (56).** A solution of **55** (28 mg, 0.14 mmol) in pyridine (1 mL) was cooled to 0 °C and treated with portions of pyridinium bromide perbromide (48 mg, 0.15 mmol). After 1 h at room temperature, the pale yellow suspension was partitioned between water (10 mL) and ether (10 mL). The organic phase was washed with water (2 × 5 mL) and brine (5 mL), dried, filtered, and evaporated. The remaining solids were purified by MPLC (silica gel, 50% ethyl acetate in petroleum ether) to yield 33 mg (66%) of **56** as a white, hard crystalline solid: mp 159–162 °C dec; IR ($CDCl_3$, cm^{-1}) 3600, 3600–3160, 2940, 1420, 1375, 1160, 1135; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.73–4.63 (m, 2 H), 3.04 (dt, *J* = 16.0, 3.4 Hz, 1 H), 2.97 (dt, *J* = 16.1, 3.5 H, 1 H), 3.13–2.90 (br s, 2 H), 2.72–2.66 (m, 1 H), 2.59 (s, 2 H), 2.59–2.39 (series of m, 2 H), 2.00–1.92 (m, 1 H), 1.39 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 77.88, 77.80, 55.62, 55.34, 54.81, 54.76, 44.86, 42.90, 34.65, 34.60, 22.0 (not all the peaks for the two possible diastereomers were resolved); MS, the molecular ion was too fleeting for accurate mass measurement.

***trans*-4,5-Dibromo-9,10-dimethylenetricyclo[5.3.0.0^{2,8}]decane (57).** In an oven-dried 25-mL flask was placed 101 mg (0.286 mmol) of **25**, 13 mL of dry benzene, and 277 mg (1.162 mol) of Burgess reagent. The flask was fitted with an oven-dried condenser and heated to reflux under nitrogen for 1 h. When cool, the mixture was poured into water (60 mL) and extracted with methylene chloride (2 × 60 mL). The combined organic layers were dried, filtered, and concentrated to leave a yellow oil. Flash chromatography (silica gel, elution with petroleum ether followed by 30% ethyl acetate in petroleum ether) provided **57** (60 mg, 66%) and allylic alcohol **61** (22 mg, 23%). The allylic alcohol could be treated with 2 equiv of the Burgess reagent to provide additional **57** in 50% yield.



61

For **57**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.13 (s, 2 H), 4.91 (s, 2 H), 4.77–4.72 (m, 2 H), 3.32 (s, 2 H), 2.11–3.02 (m, 2 H), 2.57–2.45 (m, 2 H), 2.21–2.15 (m, 2 H); MS, *m/z* ($M + H^+$) calcd 318.9519, obsd 318.9528.

For **61**: Anal. Calcd for $C_{12}H_{16}Br_2O$: C, 42.88; H, 4.80. Found: C, 42.75; H, 4.61.

9,10-Dimethylenetricyclo[5.3.0.0^{2,8}]deca-3,5-diene (10). In an oven-dried 25-mL flask was placed a solution of **57** (60 mg, 0.189 mmol) in anhydrous tetrahydrofuran (6.5 mL). In a separate flask was prepared a solution of freshly sublimed potassium *tert*-butoxide (1.131 g, 10.09 mmol) in 10 mL of the same solvent. The flask containing **26** was cooled to 0 °C, and 1.5 mL of base solution was slowly introduced via syringe. The mixture was stirred for 10 min at 0 °C, poured into water (30 mL), and extracted with methylene chloride (2 × 30 mL). The combined organic layers were dried, filtered, and carefully concentrated to leave a yellow oil, flash chromatography of which on silica gel (pentane elution) gave 26 mg (86%) of **10** after brief evacuation to 0.20 mmHg at −10 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 5.96–5.81 (m, 4 H), 5.27 (s, 2 H), 4.90 (s, 2 H), 2.76 (d, *J* = 6.1 Hz, 2 H), 1.68 (s, 2 H); ^{13}C NMR (75 MHz, C_6D_6, ppm) 152.76, 132.79, 126.26, 99.03, 55.72, 34.65; MS, *m/z* (M^+) calcd 156.0939, obsd 156.0909.

Acknowledgment. We acknowledge with thanks the financial support of the National Science Foundation that made this research possible.