In Quest of Tricyclo[4.4.1.0^{4,11}]undeca-1,3,5,7,9-pentaene, a Highly Strained, Cyclic 10π-Electron, Polyunsaturated Hydrocarbon. Synthesis of a Methoxyl-Substituted Dihydro Derivative

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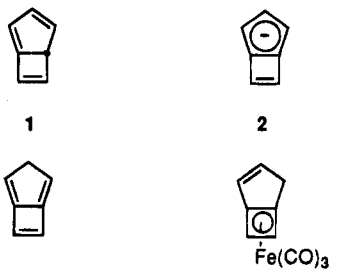
Received August 5, 1994[⊗]

Ketone **9**, which can be rapidly prepared from 2-cyclohexenone in three steps, has been examined for its suitability as a template for the generation of the title hydrocarbon **5**. The stepwise regiocontrolled introduction of two bromine atoms has resulted in the acquisition of **17**, **22**, or **23** depending upon conditions. The tribromo enone **18** has also been generated, although the more pivotal intermediate **24** has not been seen. Dehydrobromination experiments performed on these halogenated products have given rise to dienone **15** and trienone **19**, both of which have proven to be rather sensitive compounds. The O-methylation of **19** could be accomplished to give **26**, the maximally unsaturated member of this series generated to date. This tetraene polymerizes rapidly in its pure oily state or in solution when exposed to air.

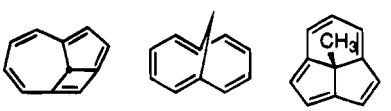
Bicyclo[3.2.0]hepta-1,3,6-triene (**1**) is known to be an unstable compound that dimerizes rapidly upon its formation.[2] Deuteration of its anion **2** returns **1**-d_1.[3] The quenching of **2** with acids of various strength enabled a pK_a of 29 to be approximated for **1**. This value is 11 units higher than that exhibited by cyclopentadiene. The dramatically decreased acidity of **1** has been appropriately attributed to the antiaromatic character of cyclobutadiene which destabilizes several of the resonance forms available to **2**.



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

The isomeric bicyclo[3.2.0]hepta-1,4,6-triene (**3**) was subsequently shown to be less labile. Synthesized by pyrolysis of 1,2-diethynylcyclopropane, **3** has been isolated as an oil which, although stable in solution for days at 0 °C, is reactive toward oxygen and polymerizes in neat form.[4] The deprotonation of **3** leads via **2** to **1**.[5] Heating **3** with $Fe_3(CO)_{12}$ in hexane affords the cyclobutadiene complex **4** with rearrangement of the double bonds.[6] Notwithstanding, **4** exhibits a significantly decreased tendency to polymerize.

A possible alternative means for exploring these reactive building blocks would be to incorporate them into a larger carbon framework. An interesting prospect is tricyclo[4.4.1.0^{4,11}]undeca-1,3,5,7,9-pentaene (**5**), an example of a [10]annulene in which **1** is conjoined at its 4- and 6-positions with a 1,3-butadiene tether. The deviation from planarity and ring strain in **5** are considerably more elevated than the levels present in 1,6-methano-[10]annulene (**6**)[7] or 7b-methyl-7b*H*-cyclopent[*cd*]indene (**7**).[8]



5 **6** **7**

The ^{1}H NMR spectra of **6** and **7** reflect the presence of a diamagnetic ring current, viz. downfield shifting of the peripheral protons (δ 8.2–7.4) and a marked upfield displacement of the methylene and methyl protons above the ring at δ −0.5 and −1.67, respectively. Although complete planarization is not possible in either **6** or **7**, the bond lengths between the constituent conjugated carbon atoms reflect the existence of π-electron delocalization. In this context, the physical and chemical properties of **5** command interest. Further, since a single sp^3-hybridized carbon atom is positioned roughly at the midpoint of its π-perimeter, the opportunity exists in principle for examining as well its anion, cation, and radical should stability consideration be favorable.

Ketone **9**, which is available in only three steps from 2-cyclohexenone,[9] appeared suitably functionalized to constitute a reasonable starting material for the potential preparation of **5**. As before, submission of alcohols **8** (endo/exo = 2:1) to anionic oxy-Cope conditions proceeded with loss of methanol to give **9** as the only characterizable product (65%, Scheme 1). The kinetic enolate formed in the course of this transformation could be captured as the silyl enol ether **10**. Although attempts to transform this derivative into the α,β-unsaturated ketone with Pd(OAc)$_2$[10] or DDQ[11] resulted in decomposition, **12** and **13** could be arrived at instead by debromination[12] of α-bromo

⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1994.

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(10) (a) Ito, Y.; Hirao, T.; Saegusa, T. *J. Org. Chem.* **1978**, *43*, 1011. (b) Sugimura, T.; Paquette, L. A. *J. Am. Chem. Soc.* **1987**, *109*, 3017.

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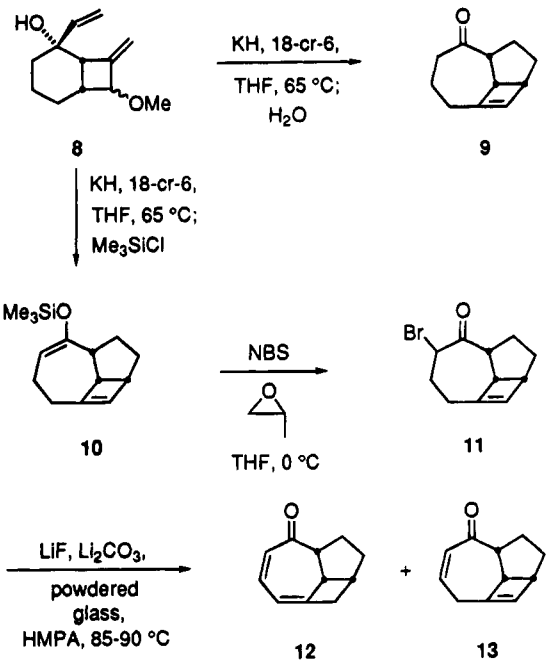
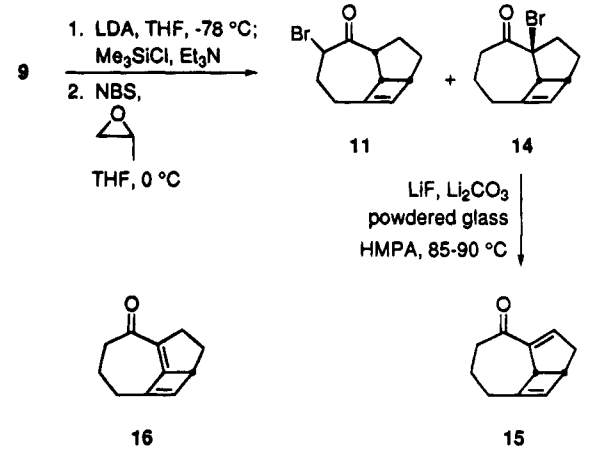
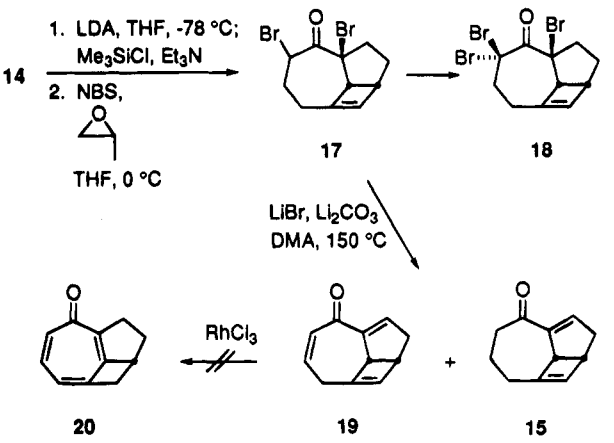
Scheme 1



Scheme 2



Scheme 3



ketone **11** produced by the action of N-bromosuccinimide.[13] Key features of the spectral properties of **11** are the appearance of the proton geminal to the halogen as a doublet of doublets at δ 4.59 and the downfield position of its associated carbon atom (57.4 ppm) in $CDCl_3$ solution.

Although the R_f's of **12** and **13** are quite similar, these dienones can be separated by careful chromatography on silica gel. The ^1H NMR spectrum of **12** showed the three olefinic protons to be mutually coupled, indicating that the cyclobutene double bond had migrated into conjugation. This conclusion was reinforced by the increased deshielding (now 152.4 ppm) of the quaternary olefinic carbon, a consequence of its terminal position in the dienone chromophore. In contrast, the ^1H NMR spectrum of **13** displayed typical enone coupling, as well as a singlet absorption for the cyclobutene proton at δ 5.81. It appears that **12** is the more thermodynamically stable of the two isomers, since extension of the heating time for dehydrobromination from 3 to 5 h increased its proportion in the mixture from 66% to > 97%.

Synthesis of the regioisomeric α-bromo ketone **14** was realized by bromination of the TMS enol ethers generated by the direct deprotonation of **9**. Interestingly, this route produced **11** and **14** in equal amounts, indicating that no preference exists for one α-position over the other (Scheme 2). In fact, the same end result materialized regardless of whether thermodynamic (Et_3N, TMSCl, DMF, or *i*-Pr_2NMgBr/Et_2O)[14,15] or kinetic conditions were utilized.[16] Spectral support for the fact that the bromine atom in **14** resides at the fully substituted α position was derived from the appearance of the quaternary carbon signal at 69.7 ppm.

Dehydrobromination of **14** gave rise in 32% yield to dienone **15** in which the new double bond resides exocyclic to the seven-membered ring. Its two fully substituted olefinic carbons were evident in the ^{13}C NMR spectrum. The significantly more strained isomer **16** was not seen. However, the low yield realized does allow for its competitive production with subsequent rapid polymerization.

In order to arrive at **5** in reasonably expedient fashion, increased levels of unsaturation had to be introduced rapidly. To this end, **14** was transformed into dibromide **17** (β/α = 3:1) since twofold elimination of this intermediate would incorporate three of the requisite double bonds (Scheme 3). Furthermore, all resources could be directed toward **17**, since it proved possible to transform the unneeded **11** formed concurrently back into **9** simply by stirring the bromo ketone with NaI and TMSCl in acetonitrile.[17]

In early experiments, the unwanted formation of tribromide **18** complicated matters. On several occasions, it proved to be the sole product, even when only 1 equiv

(11) Fleming, I.; Paterson, I. *Synthesis* **1979**, 736.
(12) King, P. F.; Paquette, L. A. *Synthesis* **1977**, 279.
(13) Reuss, R. H.; Hassner, A. *J. Org. Chem.* **1974**, *39*, 1785.
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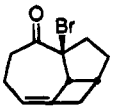
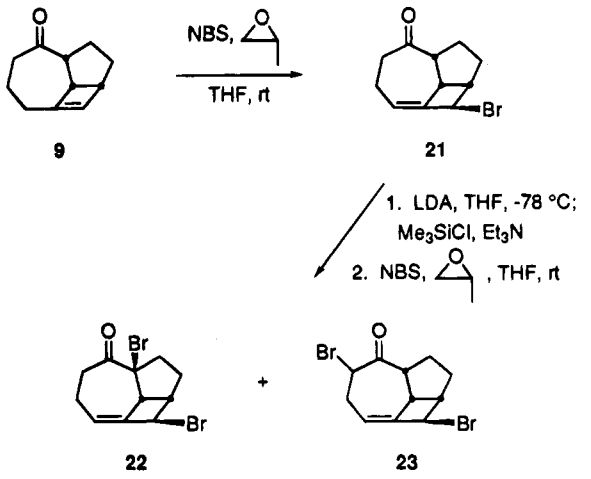
(16) When the product mixtures were purified by chromatography on alumina instead of silica gel, bromo enone **i** made an appearance (10% maximum) at the expense of **14**. It is possible that double bond isomerization materialized on the column, although this possibility was not established by proper experiment.



i

(17) Olah, G. A.; Arvanaghi, M.; Vankar, Y. D. *J. Org. Chem.* **1980**, *45*, 3531.

Scheme 4



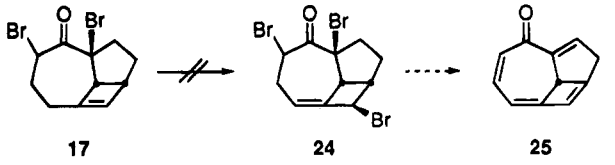
of NBS was used. It was subsequently determined that the conditions employed for isolation of the TMS enol ether were critically relevant to product formation. When the THF solvent was evaporated and the enol ether was extracted into pentane from the precipitated lithium chloride, subsequent concentration and bromination gave almost exclusively **18** (44%). If the THF solution was poured instead into saturated $NaHCO_3$ solution and extracted into ether, then identical processing afforded the desired **17** free of **18**. The structural features of **18** were secured by X-ray crystallographic analysis.[25]

Dehydrohalogenation of **17** with LiBr and Li_2CO_3 in hot dimethylacetamide[18] afforded **19** in low yield (17%) accompanied by a lesser amount of **15** (10%), the result of reductive loss of one bromine atom. Although the spectral features of **19** convincingly showed that the cyclobutene double bond had not migrated into conjugation, this trienone proved to be very unstable, decomposing within days at 0 °C. In an attempt to induce isomerization within **19** to the tropone **20**, the former was stirred with $RhCl_3$ in ethanol.[19] Unfortunately, decomposition ensued instead.

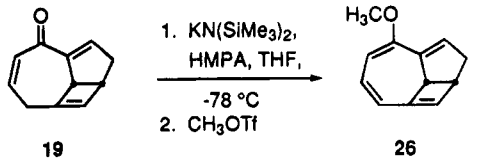
In order to heighten the level of brominative substitution at sites more distal to the carbonyl, **9** was treated with NBS in THF containing propylene oxide at rt for 20 h. Smooth conversion to **21** occurred in 62% yield (Scheme 4). COSY, CH-correlation, and selective DEPT 45 experiments confirmed that the entry of bromine was accompanied by double bond isomerization. The attraction offered by **21** was the availability of two α positions for the introduction of a second and third bromine substituent. Quite unexpectedly, however, the O-silylating **21** could be accomplished only with great difficulty and in low yield. Subsequent treatment with NBS produced a co-eluting 5:1 mixture of **22** and **23** in 10% combined yield. This route was therefore clearly not acceptable.

A still more advanced ploy would be to engage **17** in allylic bromination. Should **24** become available in this very direct way (Scheme 5), its exhaustive dehydrobromination was to be explored as a means of obtaining **25** or an isomer thereof. The mere stirring of **17** with NBS in THF, the conditions previously successful in providing

Scheme 5



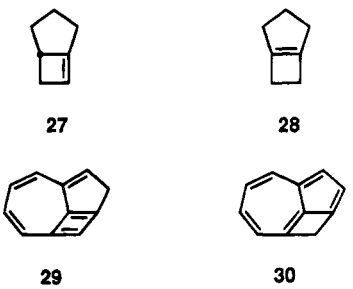
Scheme 6



21, failed completely. More aggressive procedures including irradiation with and without AIBN in CCl_4 furnished only succinimide and uncharacterized materials lacking olefinic absorptions.

For the above reasons, we turned our investigation to an examination of the capability of **19** for enolate anion formation and O-methylation. This trienone was found to undergo ready deprotonation in cold (−78 °C) THF solution containing potassium hexamethyldisilazide. The subsequent introduction of methyl triflate[20] afforded methoxytetraene **26** in 40% yield following chromatography on Florisil (Scheme 6). This polyolefin exhibits five well-separated olefinic proton absorptions. Its cyclobutene methylene protons are notable in that they appear at δ 3.25 (in $CDCl_3$), further downfield than usual due perhaps to a combination of ring strain and their allylic nature. As expected, **26** proved to be a highly sensitive substance, polymerizing rapidly in neat condition or when its solutions are exposed to air.

The proclivity for decomposition exhibited by many of the compounds generated during the course of this research is construed to be an indicator of the extensive bond angle strain inherent in this tricyclic hydrocarbon framework. Since the incremental introduction of unsaturation exacerbates the problem, the generation of **26** can be regarded as an achievement of some significance.



Although pentaene **5** has eluded us presently, its acquisition in the future does not appear to be entirely ruled out. Calculations on the bicyclic olefins **27**[21] and **28** suggest that the double bond prefers to be positioned centrally as in **28** by 3.8 kcal/mol.[22] Such a disposition for the fifth π linkage in tricyclo[4.4.1.0^{4,11}]undecapentaenes (as in **29**) is not at all likely since cyclobutadiene character is present, 10π peripheral electronic character is lost, and the entire framework must experience

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considerable planarization. Finally, once target compound **5** is attained, the possible migration of the central hydrogen atom to give azulene **30** would warrant evaluation. Should this shift occur rapidly, it would be necessary to introduce a methyl group at that site[23] in order to preserve structural integrity.

Experimental Section[24]

(1a*R*,3a*R*,7b*S*)-1a,2,3,3a,5,6,7,7b-Octahydro-4*H*-cyclobut[*cd*]azulen-4-one (9). A solution of alcohols **8** (2.14 g, 11 mmol) in THF (50 mL) was added via cannula to a mixture of potassium hydride (1.10 g, 27.5 mmol) and 18-crown-6 (7.26 g, 27.5 mmol) in dry THF (100 mL). The mixture was heated to reflux for 6 h, cooled, and quenched by careful addition of saturated NH_4Cl solution, and extracted with ether. The combined organic phases were dried and concentrated, then chromatographed on silica gel (elution with 20% ethyl acetate in hexanes) to afford 1.17 g (65%) of **9**; IR (neat, cm^{-1}) 1694, 1610; ^1H NMR (300 MHz, $CDCl_3$) δ 5.68 (d, J = 2.0 Hz, 1 H), 3.18–3.12 (m, 2 H), 2.52–2.42 (m, 3 H), 2.40–2.31 (m, 1 H), 2.22–2.15 (m, 1 H), 2.00–1.89 (m, 2 H), 1.79–1.65 (m, 2 H), 1.60–1.53 (m, 1 H), 1.40–1.30 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 215.5, 148.0, 129.8, 52.2, 47.3, 44.9, 42.7, 30.0, 28.4, 26.1, 23.5; MS m/z (M^+) calcd 162.1045, obsd 162.1049.

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.17; H, 8.82.

(1a*R*,3a*R*,5*R*,7b*S*)-5-Bromo-1a,2,3,3a,5,6,7,7b-octahydro-4*H*-cyclobut[*cd*]azulen-4-one (11). To a mixture of potassium hydride (0.532 g, 13.7 mmol) and 18-crown-6 (3.70 g, 14.0 mmol) in dry THF (30 mL) was added the alcohols **8** (0.533 g, 2.75 mmol) dissolved in THF (20 mL). The stirred reaction mixture was refluxed for 4 h, cooled to −78 °C, and quenched by the addtion via cannula of premixed trimethylsilyl chloride (1.75 mL, 13.7 mmol) and triethylamine (0.48 mL, 3.5 mmol). After being warmed to rt, the mixture was poured into saturated $NaHCO_3$ solution and extracted with ether. The organic layers were dried and evaporated to yield an oil that was immediately dissolved in dry THF (10 mL) and propylene oxide (0.20 mL, 2.9 mmol) at 0 °C. N-Bromosuccinimide (511 mg, 2.89 mmol) was added to the solution, the cooling bath was removed, and the mixture was stirred at rt for 5 h. The reaction mixture was poured into saturated $NaHCO_3$ solution and extracted with CH_2Cl_2 (3 × 5 mL), and the extracts were dried and concentrated to leave an oil that was chromatographed on silica gel (elution with 10% ethyl acetate in hexanes) to afford 351 mg (53%) of **11**; IR (neat, cm^{-1}) 1690, 1400, 1425, 1250, 830, 790; ^1H NMR (300 MHz, $CDCl_3$) δ 5.71 (t J = 1 Hz, 1 H), 4.59 (dd, J = 7.4 Hz, 1.6 Hz, 1 H), 3.50 (dd, J = 7.3 Hz, 3.1 Hz, 1 H), 3.17–3.13 (m, 1 H), 2.81–2.72 (m, 1 H), 2.57–2.45 (m, 1 H), 2.40–2.31 (m, 1 H), 2.20–1.87 (m, 4 H), 1.60–1.53 (m, 1 H), 1.45–1.32 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 206.6, 147.6, 130.2, 57.4, 49.1, 46.6, 45.1, 31.7, 29.5, 27.1, 26.1; MS m/z (M^+) calcd 242.0130, obsd 242.0134.

(1a*R*,3a*R*,7b*S*)-1,1a,2,3,3a,7b-Hexahydro-4*H*-cyclobut[*cd*]azulen-4-one (12) and (1a*R*,3a*R*,7b*S*)-1a,2,3,3a,7,7b-Hexahydro-4*H*-cyclobut[*cd*]azulen-4-one (13). A stirred mixture of **11** (122 mg, 0.506 mmol), lithium fluoride (138 mg, 5.31 mmol), lithium carbonate (393 mg, 5.31 mmol), powdered glass (200 mg), and HMPA (5 mL) was heated to 90 °C for 3 h. The cooled reaction mixture was poured into brine (15 mL) and extracted with ether (3 × 10 mL). The organic phases were washed with saturated $CuSO_4$ solution, dried, concentrated, and chromatographed on silica gel (elution with 10% ethyl acetate in hexanes). Dienone **13** (10 mg, 12%) was the first compound to elute; ^1H NMR (300 MHz, $CDCl_3$) δ 6.05 (dd, J = 10.1 Hz, 3.3 Hz, 1 H), 5.81 (s, 1 H), 5.70 (td, J = 9.8 Hz, 3.3 Hz, 1 H), 3.87–3.80 (m, 1 H), 3.63 (dd, J = 7.6 Hz, 3.5 Hz, 1 H), 3.27–3.24 (m, 1 H), 2.89–2.82 (m, 1 H), 2.78–2.69 (m, 1 H), 2.10–2.01 (m, 1 H), 1.98–1.88 (m, 1 H), 1.72–1.66 (m, 1 H), 1.63–1.50 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 209.9, 145.0, 131.3, 125.1, 124.9, 51.2, 46.8, 45.5, 44.4, 28.4, 25.6; MS m/z (M^+) calcd 160.0888, obsd 160.0852.

The second compound to elute was the conjugated dienone **12**; IR ($CDCl_3$, cm^{-1}) 1725, 1660, 1635, 1465, 1450, 1310, 920; ^1H NMR (300 MHz, $CDCl_3$) δ 6.42 (ddd, J = 12.4 Hz, 6.5 Hz, 0.6 Hz, 1 H), 5.93 (d, J = 12.4 Hz, 1 H), 5.77–5.72 (m, 1 H), 3.55–3.53 (br m, 1 H), 3.15–3.06 (m, 1 H), 2.87–2.77 (m, 1 H), 2.71–2.62 (m, 1 H), 2.33–2.17 (m, 2 H), 2.00–1.92 (m, 1 H), 1.84–1.70 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 203.4, 152.4, 137.3, 129.4, 118.4, 57.2, 46.4, 36.7, 33.2, 30.4, 27.8; MS m/z (M^+) calcd 160.0888, obsd 160.0935.

(1a*R*,3a*S*,7b*R*)-3a-Bromo-1a,2,3,3a,5,6,7,7b-octahydro-4*H*-cyclobut[*cd*]azulen-4-one (14). A. Purification on Silica Gel. A solution of n-butyllithium in hexanes (1.0 mL, 1.3 mmol) was added via syringe to a solution of dry diisopropylamine (0.2 mL, 1.4 mmol) in dry THF (3 mL) at −78 °C and stirred for 10 min. Ketone **9** (196 mg, 1.21 mmol) in anhydrous THF (1 mL) was added via cannula, and stirring was maintained for 20 min prior to treatment with premixed trimethylsilyl chloride (0.35 mL, 2.7 mmol) and triethylamine (0.55 mL, 4.0 mmol). After 30 min at rt, the solvent was evaporated. The residual lithium chloride slurry was repeatedly triturated with aliquots of pentane that were subsequently combined and concentrated. The resultant oil was dissolved immediately in dry THF (5 mL) containing propylene oxide (0.09 mL, 1.3 mmol) at 0 °C. After the addition of N-bromosuccinimide (225 mg, 1.27 mmol), the mixture was stirred for 15 min, poured into saturated $NaHCO_3$ solution, and extracted with CH_2Cl_2. The combined extracts were dried and concentrated, and the residual oil was chromatographed on silica gel (elution with 10% ethyl acetate in hexanes) to afford 93 mg (32%) of **11** followed closely by 102 mg (35%) of **14**; IR (neat, cm^{-1}) 1715, 1435, 1255, 845; ^1H NMR (300 MHz, $CDCl_3$) δ 5.73 (d, J = 1.2 Hz, 1 H), 3.51 (d, J = 2.3 Hz, 1 H), 3.38–3.31 (m, 1 H), 2.85 (br t, J = 12.0 Hz, 1 H), 2.62–2.56 (m, 1 H), 2.48–2.28 (m, 3 H), 2.18–2.00 (m, 2 H), 1.99–1.84 (m, 1 H), 1.68–1.52 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 206.8, 149.7, 131.2, 69.7, 57.9, 45.2, 40.6, 36.5, 29.3, 25.4, 24.6; MS m/z (M^+) calcd 240.0150, obsd 240.0123.

Anal. Calcd for $C_{11}H_{13}BrO$: C, 54.79; H, 5.43. Found: C, 54.36; H, 5.41.

B. Workup on Neutral Alumina. A solution of n-butyllithium in hexanes (5.8 mL, 1.6 M, 9.3 mmol) was added via syringe to a solution of dry diisopropylamine (1.4 mL, 9.7 mmol) in dry THF (15 mL) at −78 °C and stirred for 15 min. Ketone **9** (1.37 g, 8.42 mmol) in anhydrous THF (5 mL) was added via cannula and stirring was maintained for 15 min prior to treatment with premixed trimethylsilyl chloride (1.3 mL, 0.010 mmol) and triethylamine (0.50 mL, 3.4 mmol). After being warmed to rt, the reaction mixture was evaporated and the residual lithium chloride slurry was repeatedly triturated with aliquots of pentane that were subsequenly combined and concentrated. The resultant oil was dissolved immediately into dry THF (20 mL) and propylene oxide (1.65 g, 9.3 mmol) at 0 °C. After the addition of N-bromosuccinimide (1.65 g, 9.26 mmol), the mixture was stirred for 15 min, kept in the freezer overnight, and evaporated. The residue was filtered through neutral alumina and subjected to MPLC separation (elution with 5% ethyl acetate in hexanes). The first compound to elute was **11** (470 mg, 23%), followed closely by **i**[16] (161 mg, 8%), and finally **14** (561 mg, 28%).

For **i**: ^1H NMR (300 MHz, $CDCl_3$) δ 5.24–5.23 (m, 1 H) 3.91–3.88 (m, 1 H), 3.35–3.25 (m, 1 H), 2.96–2.88 (m, 2 H), 2.51–2.10 (m, 7 H), 1.78–1.71 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 205.3, 139.2, 121.0, 72.5, 56.4, 36.7, 35.8, 34.5, 34.2, 30.8, 27.9.

(1a*R*,7b*R*)-1a,2,5,6,7,7b-Hexahydro-4*H*-cyclobut[*cd*]-azulen-4-one (15). A mixture of bromo ketone **14** (65.6 mg, 0.274 mmol), lithium fluoride (74 mg, 2.9 mmol), lithium carbonate (211 mg, 2.86 mmol), and powdered glass (100 mg) in HMPA (4 mL) was stirred and heated to 90 °C for 5 h. The cooled reaction mixture was poured into brine (15 mL) and water (10 mL to transfer) and extracted with ether. The

(23) This suggestion was offered by a reviewer of this paper.

(24) For general information, see: Paquette, L. A.; Thompson, R. C. *J. Org. Chem.* **1993**, *58*, 4952.

(25) The author has deposited atomic coordinates for **18** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

extracts were washed with saturated $CuSO_4$ solution, dried, and concentrated. The resulting oil was chromatographed on silica gel (elution with 10% ethyl acetate in hexanes) to afford 14 mg (32%) of **15**; IR (neat, cm^{-1}) 1685, 1610; ^1H NMR (300 MHz, $CDCl_3$) δ 6.22–6.21 (m, 1 H), 5.64 (s, 1 H), 3.70 (d, J = 2.7 Hz, 1 H), 3.37–3.32 (m, 1 H), 2.68–2.54 (m, 3 H), 2.49–2.34 (m, 2 H), 2.26–2.15 (m, 1 H), 2.06–1.96 (m, 1 H), 1.67–1.52 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 201.5, 159.9, 147.3, 136.2, 128.0, 54.9, 43.9, 42.2, 34.4, 31.2, 25.6; MS m/z (M^+) calcd 160.0933, obsd 160.0916.

(1a*R*,3a*S*,5*R*,7b*R*)-3a,5-Dibromo-1a,2,3,3a,5,6,7,7b-octahydro-4*H*-cyclobut[*cd*]azulen-4-one (17). A solution of **14** (608 mg, 2.52 mmol) in anhydrous THF (3 mL) was added to a solution of lithium diisopropylamide (2.65 mmol) [prepared by the addition of a solution of *n*-butyllithium in hexanes (1.89 mL, 2.65 mmol) to a solution of dry diisopropylamine (0.37 mL, 2.65 mmol)] in dry THF (12 mL) at −78 °C. After being stirred for 30 min, the reaction mixture was quenched by the addition of premixed trimethylsilyl chloride (0.34 mL, 2.7 mmol) and triethylamine (0.095 mL, 0.68 mmol). The mixture was warmed to rt over 2 h, poured into saturated $NaHCO_3$ solution, and extracted with ether. Drying and evaporation of the solvent afforded an oil that was dissolved immediately in anhydrous THF (15 mL) and propylene oxide (0.2 mL, 3 mmol) at −78 °C. N-Bromosuccinimide (470 mg, 2.65 mmol) was added and stirring was maintained for 2 h. The solvent was evaporated and the residue was chromatographed on silica gel (elution with 10% ethyl acetate in hexanes) to yield 54 mg (67%) of **17**; IR (neat, cm^{-1}) 1700, 1430, 1245, 1155, 1100, 1030, 905, 840; ^1H NMR (300 MHz, $CDCl_3$) δ 5.77 (d, J = 2.1 Hz, 1 H), 4.72 (dd, J = 7.1, 1.2 Hz, 1 H), 3.96 (d, J = 2.5 Hz, 1 H), 3.37–3.32 (m, 1 H), 2.67–2.55 (m, 1 H), 2.41–2.28 (m, 3 H), 2.27–2.16 (m, 1 H), 1.99–1.85 (m, 2 H), 1.60 (dd, J = 5.3, 3.3 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 201.2, 131.4, 66.3, 56.6, 54.3, 45.0, 38.3, 31.2, 26.3, 24.0; MS m/z (M^+) calcd 317.9255, obsd 317.9278.

(1a*R*,3a*S*,7b*R*)-3a,5,5′-Tribromo-1a,2,3,3a,5,6,7,7b-octahydro-4*H*-cyclobut[*cd*]azulen-4-one (18). A solution of *n*-butyllithium in hexanes (4.7 mL, 6.1 mmol) was added via syringe to a solution of dry diisopropylamine (0.90 mL, 6.4 mmol) in anhydrous THF (35 mL) at −78 °C and stirred for 15 min. Bromo ketone **14** (1.40 g, 5.82 mmol) in dry THF (5 mL) was added via cannula, and stirring was maintained for 30 min before the addition via cannula of premixed trimethylsilyl chloride (0.83 mL, 6.5 mmol) and triethylamine (0.22 mL, 1.6 mmol). After 30 min of stirring at rt, the solvent was evaporated and the residual lithium chloride slurry was repeatedly triturated with pentane. The combined pentane extracts were concentrated and the resulting oil was dissolved immediately in dry THF (30 mL) containing propylene oxide (0.45 mL, 6.5 mmol) at 0 °C. N-Bromosuccinimide (1.16 g, 6.5 mmol) was added and the mixture was stirred for 30 min. Solvent evaporation followed by chromatography of the residue on silica gel (elution with 5% ethyl acetate in hexanes) funished 1.02 g (44%) of **18**; ^1H NMR (300 MHz, $CDCl_3$) δ 5.78 (d, J = 2.1 Hz, 1 H), 3.86 (s, 1 H), 3.38–3.34 (m, 1 H), 3.05–2.96 (m, 1 H), 2.72–2.52 (m, 1 H), 2.50–2.26 (m, 4 H), 1.98–1.88 (m, 1 H), 1.60 (dd, J = 13.2 Hz, 6.3 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 193.2, 147.2, 131.8, 71.3, 64.1, 56.5, 46.1, 45.4, 39.6, 29.4, 23.4; MS m/z (M^+ − Br) calcd 316.9177, obsd 316.9183.

Reductive Debromination of 11. A mixture of **11** (1.031 g, 4.28 mmol), sodium iodide (1.923 g, 12.8 mmol), and trimethylsilyl chloride (1.61 mL, 8.6 mmol) in acetonitrile (30 mL) was stirred at rt for 2 h, poured into 10% $Na_2S_2O_3$ solution, and extracted with ether (3 × 20 mL). The extracts were washed consecutively with water and brine, then dried. Rotary evaporation yielded an oil that was chromatographed on silica gel (elution with 20% ethyl acetate in hexanes) to afford 0.54 g (77%) of **9**.

(1a*R*,7b*R*)-1a,2,7,7b-Tetrahydro-4*H*-cyclobut[*cd*]azulen-4-one (19). A stirred mixture of **17** (232 mg, 0.723 mmol), lithium bromide (157 mg, 1.81 mmol) [dried at 140 °C and 1 Torr overnight prior to use], and lithium carbonate (161 mg, 2.17 mmol) in N,N-dimethylacetamide (10 mL) was heated to 150 °C until the bromo ketone was no longer detectable by t.l.c. analysis. The cooled mixture was poured into water (100 mL) and extracted with ether. The combined extracts were washed consecutively with water and brine, dried, and concentrated. Chromatography of the residual oil on silica gel (elution with 10% ethyl acetate in hexanes) afforded 12 mg (10%) of **15** followed by 20 mg (17%) of **19**; IR (CH_2Cl_2, cm^{-1}) 1635, 1610, 1565, 1435, 1325, 1265, 895, 830; ^1H NMR (300 MHz, C_6D_6) δ 6.19–6.08 (m, 2 H), 5.97–5.95 (m, 1 H), 5.20–5.16 (m, 1 H), 3.56–3.51 (m, 1 H), 2.87–2.77 (m, 1 H), 2.39–2.25 (m, 2 H), 2.02–1.94 (m, 1 H), 1.90–1.79 (m, 1 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 189.3, 152.4, 145.7, 137.7, 134.2, 130.6, 115.8, 52.2, 39.2, 38.0, 30.5; MS m/z (M^+) calcd 158.0732, obsd 158.0734.

(1*R*,1a*S*,3a*R*,7b*R*)-1-Bromo-1,1a,2,3,3a,5,6,7b-octahydro-4*H*-cyclobut[*cd*]azulen-4-one (21). Ketone **9** (200 mg, 1.23 mmol) was stirred under N_2 with N-bromosuccinimide (230 mg, 1.29 mmol) and propylene oxide (0.1 mL, 1.4 mmol) in THF (5 mL) for 20 h. The solvent was evaporated and the residue was chromatographed on silica gel (elution with 10% ethyl acetate in hexanes) to furnish 185 mg (62%) of **21**; IR (neat, cm^{-1}) 1700, 1440, 1340, 1305, 1190, 1160, 1120; ^1H NMR (300 MHz, C_6D_6) δ 5.18 (d, J = 2.8 Hz, 1 H), 4.11 (d, J = 1.3 Hz, 1 H), 3.56–3.50 (m, 1 H), 2.75–2.68 (m, 1 H), 2.56–2.45 (m, 1 H), 2.36–2.28 (m, 1 H), 1.94–1.81 (m, 3 H), 1.79–1.65 (m, 2 H), 1.30–1.14 (m, 2 H); ^{13}C NMR (C_6D_6) ppm 209.9, 142.1, 126.4, 57.9, 50.4, 49.1, 45.5, 39.8, 31.1, 28.1, 27.8; MS m/z (M^+) calcd 340.0150, obsd 240.0145.

Anal. Calcd for $C_{11}H_{13}BrO$: C, 54.79; H, 5.43. Found: C, 54.64; H, 5.55.

(1a*R*,7b*R*)-1a,7b-Dihydro-4-methoxy-2*H*-cyclobut[*cd*]azulene (26). To a solution of trienone **19** (17.8 mg, 0.113 mmol) and dry HMPA (0.04 mL, 0.23 mmol) in THF (1 mL) at −78 °C was added dropwise a solution of potassium hexamethyldisilazide in toluene (0.3 mL, 0.15 mmol). The reaction mixture was stirred for 15 min, treated with methyl triflate (0.04 mL, 0.28 mmol), and stirred for an additional 15 min before being warmed to rt. Evaporation of the solvent afforded an oily residue that was chromatographed on Florisil (elution with 5% ether and 2% triethylamine in hexanes) to afford 8 mg (40%) of **26** as a yellowish oil; ^1H NMR (300 MHz, C_6D_6) δ 6.19 (d, J = 11.4 Hz, 1 H), 5.87 (dd, J = 11.2 Hz, 9.0 Hz, 1 H), 5.58 (s, 1 H), 5.38 (t, J = 2.6 Hz, 1 H), 4.98 (d, J = 8.8 Hz, 1 H), 3.31–3.22 (m, 2 H), 3.20 (s, 3 H), 2.40 (ddm, J = 11.3 Hz, 1 H), 1.76 (ddm, J = 18.9 Hz, 3.5 Hz, 1 H); ^{13}C NMR (125 MHz, C_6D_6) ppm 153.6, 140.7, 126.5, 125.8, 123.0, 119.7, 96.9, 54.6, 50.9, 41.7; MS m/z (M^+) calcd 172.0888, obsd 172.0885.

Acknowledgment. We acknowledge with gratitude the support of this investigation by the National Science Foundation. In addition, we thank Professor Robin Rogers (Northern Illinois University) for the X-ray crystallographic analysis and Dr. Kurt Loening for nomenclature expertise.

Supplementary Material Available: ORTEP drawing of **18** and copies of ^1H and ^{13}C NMR spectra of **11**–**13**, **15**, **17**–**19**, and **26** (17 pages). This material is contained in libraries on microfiche, 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.