Is Through-Bond Dihydroaromaticity Attainable? Preparation of [4,5]Dihomotropone, Investigation of Its Ground-State Properties, and an Attempt To Generate the Dihomotropylium Cation

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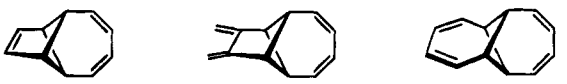
Construction of the first dihomotropone (**6**) has been accomplished. The key elements of the synthesis were a regiocontrolled expansion of a [4.1.1] bicyclic α-bromo ketone and introduction of the dienone double bonds by means of the Garbisch method. The spectral properties of **6** under neutral and strongly acidic conditions are described and interpreted in terms of a lack of dihomoaromatic character. The parent bicyclo[5.1.1]nonadienyl cation is unstable and experiences ready Wagner–Meerwein rearrangement to the bicyclo[4.2.1]nonadien-7-yl cation. These features appear well suited to the ultimate evaluation of through-bond interaction in tricyclic homologues of **6** that carry perpendicular π arrays in the third ring.

Exploration of the myriad of options available for fostering interaction between nonconjugated π networks has preoccupied the attention of leading research groups for three decades. The search for homoconjugation, the result of through-space interaction across proximal, disjointed π systems was spearheaded by Winstein in the 1960s.[2] Somewhat later, pioneering work by several other investigators called attention to the remarkable fact that perpendicularly oriented π fragments linked together by a common tetrahedral carbon atom could also exhibit through-space interaction (spiroconjugation) under the proper circumstances.[3]

In a seminal paper published in 1968, Hoffmann recognized that π units also have the capacity for communicating electronically through σ frameworks (through-bond interaction).[4] Gleiter in the late 1970s presented theoretical arguments showing that orthogonally oriented π networks should also find it possible to interact through the bonds of a cyclobutane ring, the consequences being opposite to those witnessed in spiroconjugated ensembles.[5] The existence of a relay orbital effect has since been substantiated in these laboratories[6] and those of Gleiter.[7] Thus, 2-fold annulation of a cyclobutane core across its 1,3- and 2,4-positions as in **1–3** serves to lock the individual π ribbons into a perpendicular relationship. Stabilization is intrinsically linked to the number of π electrons involved and materializes when the total count is $4n$, but not $(4n + 2)$.



1 **2** **3**

Since the method of choice for assessing the level of interaction present in neutral hydrocarbons such as **1–3** is photoelectron spectroscopy (PE),[8] one is necessarily dealing with the respective radical cations. Consequently, charge dispersal must be factored into the already complicated interplay of bonding and antibonding electronic levels. For this reason, we have been attracted to seeking out ground-state effects that could rival those at play within the confines of a PE spectrometer. Much in the way that tropone is generally regarded to be a representative nonbenzenoid aromatic system,[9] ketone **4** or **5** (but unlikely both) could exhibit enhanced polarization because the prevailing orbital exchange contributions are well suited to long-range interaction through the Walsh orbitals of the four-membered ring.

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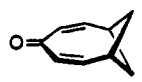
4

5

As a prelude to this effort, we describe herein the preparation of **6**, the key structural component of **4** and **5**.[10] The spectral properties of this cross-conjugated ketone reveal that interruption of the tropone π network with a pair of methano bridges does not give rise to a dihomoaromatic entity.[11] Consequently, the absence of measurable ground-state perturbations in **6** qualify it as an entirely suitable constituent for our eventual examination of **4** and **5**.

The availability of **6** has also provided us with an opportunity to examine whether the related cations **7a** and **7b** are entirely classical or gain stability on the basis of charge delocalization into the cyclobutane Walsh orbitals as implied by the dashed lines in **8**.[12] Unfortunately, the rapidity with which **7a** and **7b** experience structural isomerization has precluded experimental evaluation of their electronic character.



6

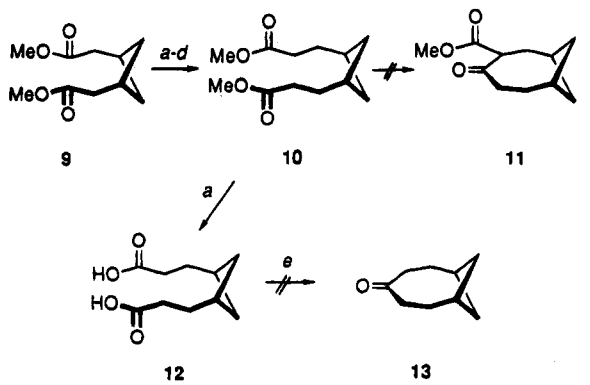
7a, R = OH
b, R = H

8a, R = OH
b, R = H

Results

Synthetic Considerations. Widely different pathways are potentially available for conversion of the known cyclobutane diester **9**[13] into dienone **6**, and several of these were investigated. One option considered to be quite direct involves homologation of both functionalized chains in **9** so as to produce symmetrical diester **10**, followed by Dieckmann cyclization as a means of generating keto ester **11** (Scheme 1). While application of the Arndt–Eistert sequence to **9** proved entirely workable, various attempts to achieve ring closure even under high dilution conditions[14] were to no avail. Unreacted **10** was returned in every instance, presumably because the preferred diequatorial status of both propionate residues serves as a powerful deterrent to ring closure. A similar fate accompanied the heating of diacid **12** with barium hydroxide up to 260 °C at atmospheric pressure and under reduced pressure.[15] These conditions led to tarry polymer formation.

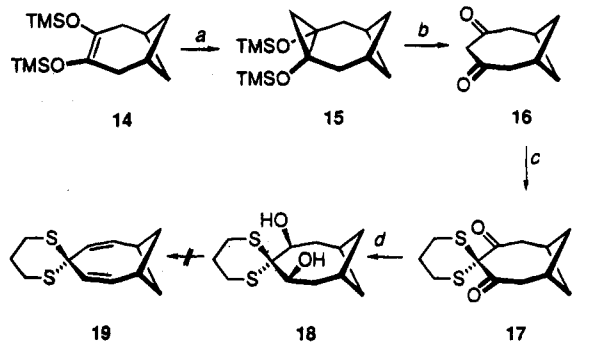
Scheme 1



9 10 11 12 13

[a] KOH, H_2O; H_2SO_4. [b] $SOCl_2$, C_6H_6. [c] CH_2N_2. [d] AgOAc, Et_3N, CH_3OH. [e] $Ba(OH)_2$, Δ.

Scheme 2



14 15 16 19 18 17

[a] CH_2I_2 (5 eq), $(C_2H_5)_2Zn$, Et_2O, 35 °C. [b] $FeCl_3$, DMF, rt. [c] KOAc, $TsS(CH_2)_3STs$, EtOH, reflux. [d] $LiAlH_4$, THF.

In light of these developments, the decision was made to capitalize on the efficiency with which **9** undergoes the acyloin reaction to give **14**.[13] Simmons–Smith cyclopropanation[16] of this intermediate and direct Saegusa oxidation[17] of **15** successfully gave rise to **16** in an optimized overall yield of 55% (Scheme 2). At this juncture, the β-diketone underwent smooth condensation with trimethylene dithiotosylate[18] as long as the usual strongly basic promoters[19] were replaced with potassium acetate in refluxing ethanol.[20] Since **17** proved unreactive to diisobutylaluminum hydride, reduction to diol **18** was effected with $LiAlH_4$. In addition to **18**, two other products were formed, neither of which was the trans diol. These byproducts were identified as **20** and **21**. The overreduction likely arises via retroaldol cleavage of the monoreduced intermediate **22** and further hydride attack at the aldehyde carbonyl unmasked in this manner. The α-keto dithiane part structure presumably exists as an enolate while the reduction proceeds and is therefore

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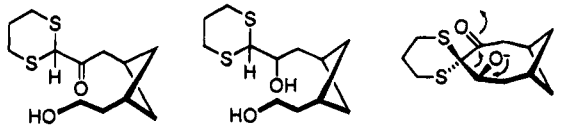
insulated from more advanced reduction. For this reason, the conversion of **20** to **21** is considered to take place during the hydrolytic workup. Unexpectedly, all attempts to effect the dehydration of **18** did not lead to **19**.[21] Nor were experiments aimed at unmasking the latent carbonyl in **18** successful.



20 **21** **22**

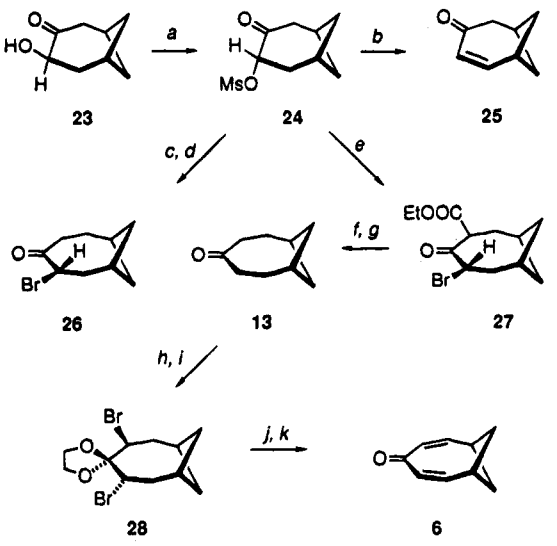
The route that ultimately proved workable began by hydrolysis of **14** to α-hydroxy ketone **23** as previously described.[13] The conversion of this readily available intermediate into the bromide via mesylate **24** proved uneventful (Scheme 3). Although enone **25** could be produced from the mesylate, this attractive compound could not be enticed into further useful chemistry.[21] Similarly, the direct ring expansion of the α-bromo ketone to **26** with diazomethane[22] was not adequately regioselective for our purposes. In contrast, recourse instead to the lesser reactive ethyl diazoacetate in the presence of boron trifluoride etherate[22] induced smooth ring expansion to give only **27** (88% isolated yield). As anticipated, the latter was obtained as a keto–enol mixture of both possible diastereomers.

Reductive debromination of **27** with zinc dust in acetic acid and subsequent heating of the resultant β-keto ester in 5 M HCl proved highly suited to acquisition of the tetrahydro precursor **13**. The C_{2v} symmetry of this ketone was evident from its simplified ^{1}H NMR and five-line ^{13}C NMR spectra. In order to apply the Garbisch protocol,[23] **13** was converted to its ethylene ketal and reacted in turn with 2 equiv of bromine in ethylene glycol as solvent. The trans disposition of the two bromines in the exclusive product of this very clean halogenation was likewise immediately recognized on the basis of its ^{13}C NMR spectrum. The observed six lines require that a C_2 axis be present. The C_s-symmetric cis isomer would be represented instead by eight carbon signals.

The 2-fold dehydrobromination of **28** with potassium *tert*-butoxide in warm DMSO was also achieved without complication. Hydrolytic removal of the ethylenedioxy group had necessarily to be accomplished rapidly under conditions as mildly acidic as possible because of the acid sensitivity of **6** (see below). Brief shaking (5 min) with 3% aqueous sulfuric acid emerged as a reasonable compromise.

Spectral Characteristics of 6. The infrared carbonyl stretching frequency of **6** in CCl_4 solution is located at 1653 cm^{-1}, a somewhat higher wavenumber relative to the values reported for 2,6-cycloheptadienone (1647 cm^{-1}) and 2,7-cyclooctadienone (1640 cm^{-1}).[23] By comparison, the carbonyl absorption of tropone makes its appearance at 1597 cm^{-1}; this lowering has been construed as indicative of contributions from the polarized form. The modest gravitation of **6** in the opposite direction quite probably arises from the greater conformational strain present in the bicyclo[5.1.1]nonadienone framework.[24] The same trend is evident in the stretching

Scheme 3

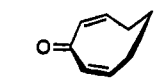


23 **24** **25** **26** **13** **27** **28** **6**

[a] CH_3SO_2Cl, py, CH_2Cl_2, 0 °C. [b] LiBr, Li_2CO_3, DMSO, 70-100 °C. [c] LiBr, acetone, reflux. [d] CH_2N_2, CH_3OH. [e] $N_2CHCOOEt$, BF_3•OEt_2, CH_2Cl_2. [f] Zn, HOAc, Et_2O. [g] 5M HCl, acetone, reflux. [h] $HOCH_2CH_2OH$, (TsOH), C_6H_6, reflux. [i] Br_2 (2 equiv), $HOCH_2CH_2OH$. [j] KO*t*-Bu, DMSO, 50 °C. [k] 3% H_2SO_4, shaking 5 min.

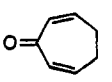
frequencies of the double bonds in these conjugated dienones. This absorption, which appears at 1623 cm^{-1} in **6**, is displaced by 10 wavenumbers relative to that at 1613 cm^{-1} seen in both simpler structural analogues.

The dihomotropone is characterized by a single ultraviolet absorption maximum in ethanol at 245 nm (log ε 3.71). This electronic behavior mirrors that exhibited by **29** and is bracketed by the two bands reported for **30**.[25] A comparison of these data with the electronic spectrum of 4,5-homotropone (**31**)[26] is informative. We conclude that these experimental determinations provide no hint of charge separation in the ground state of **6**.



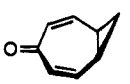
29

λ_{max}^{EtOH} 243.5 (log ε 4.03)



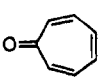
30

λ_{max}^{EtOH} 266 (log ε 3.40)
235 (log ε 4.03)



31

λ_{max}^{EtOH} 290 sh (log ε 3.66)
264 (log ε 3.88)



32

The NMR spectral parameters for **29** and **30** should model well the olefinic proton chemical shifts of **6** should it lack dipolar character. As seen in Table 1, the similarities between **6** and **30** in $CDCl_3$ solution are striking. The overlapping of the α and β protons observed for **29** can be attributed to those conformational readjustments required to bring this dienone to its global energy minimum geometry. Notwithstanding, none of the above

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(24) For comparison, see: Chasey, K. L.; Paquette, L. A.; Blount, J. F. *J. Org. Chem.* **1982**, *47*, 5262.
(25) Krabbenhoft, H. O. *J. Org. Chem.* **1979**, *44*, 4285.
(26) Chapman, O. L.; Fugiel, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 215.

Table 1. High Field ^1H and ^{13}C NMR Data for Selected Unsaturated Medium-Ring Ketones ($CDCl_3$ Solutions; Values in ppm)

	6	29	30	32
^1H NMR	6.61 (dd, 2 H)	6.10 (m, 4 H)[a]	6.60 (m, 2 H)[a]	6.82 (m, 2 H)
(300 MHz)	6.00 (d, 2 H)		6.08 (d, 2 H)	6.67 (m, 4 H)
	3.01 (m, 2 H)	2.25 (m, 4 H)	2.45 (m, 4 H)	
	2.88 (m, 2 H) exo	1.70 (m, 2 H)		
	1.82 (m, 2 H) endo			
^{13}C NMR	194.98	193.23[a]	192.50[a]	187.35
(75 MHz)	146.78	141.59	144.33	141.28
	130.70	135.93	133.50	135.60
	31.68 (d)	27.14	27.30	134.15
	30.09 (t)	25.04		

[a] Reference 25.

Table 2. Compilation of Chemical Shift Data for 6, 29, 30, and 32 in Acidic Media (300 and 75 MHz; Values in ppm)

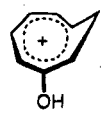
	6	29	30	32
^1H NMR	8.39 (m, 2 H)[a]	7.98 (dt, 2 H)[b]	8.17 (br d, 2 H)[c]	
FSO_3H	6.75 (m, 2 H)	6.95 (d, 2 H)	7.05 (d, 2 H)	
ppm	3.65 (m, 2 H)	2.46 (m, 6 H)	3.17 (br s, 4 H)	
	3.38 (m, 2 H) exo			
	1.59 (m, 2 H) endo			
^1H NMR	7.13 (dd, 2 H)[d]	6.88 (dt, 2 H)[d]		8.64 (m, 2 H)[d]
CF_3CO_2D	6.28 (d, 2 H)	6.57 (d, 2 H)		8.48 (dd, 2 H)
ppm	3.26 (m, 2 H)	2.47 (m, 4 H)		8.39 (d, 2 H)
	3.09 (m, 2 H) exo	2.00 (m, 2 H)		
	1.90 (m, 2 H) endo			
^{13}C NMR	e	199.46[d]		184.70[d]
CF_3CO_2D	158.23[d]	150.41		152.49
ppm	130.22	135.75		148.06
	34.12 (d)	30.30		141.30
	30.28 (t)	27.15		

[a] Measurement made at −78 °C. [b] Measurement made at 0 °C. [c] Reference 27. [d] Measurement made at 25 °C. [e] Signal too weak to be observed because of ongoing decomposition.

dienones feature an induced ring current suggested by the rather dramatic deshielding exhibited by tropone (**32**).

The protonation studies carried out on **6** were more limited than usual because of the inherent sensitivity of this dienone to acid. In FSO_3H at −78 °C, however, it was possible to observe the formation of **7a** and to record the ^1H NMR (but not ^{13}C NMR) spectrum of this cation prior to the onset of decomposition. As seen in Table 2, the protonation of **6** is accompanied by downfield shifting of the α-vinylic ($\Delta\delta$ −1.78 ppm), β-vinylic ($\Delta\delta$ −0.75 ppm), bridgehead ($\Delta\delta$ −0.64 ppm), and exo-methylene protons ($\Delta\delta$ −0.50 ppm) but not the endo-methylene protons which in contrast experience modest shielding ($\Delta\delta$ +0.23 ppm). The chemical shift displacements observed for the lateral protons find close analogy in the effects encountered following comparable protonation of **29** and **30**.[27] As a consequence of the close structural similarities of these reference cations, e.g. **33**, the comparison is considered to be direct and not beset with gross assumptions.

33



34

The usual diagnostic of homoaromatic character is the chemical shift difference observed for those protons positioned on the bridging carbon.[2,28] Notwithstanding the lack of detailed knowledge of the origin of ring current effects[29] and possible contributions from local anisotropic influences, large $\Delta\delta$ values for exo/endo proton pairs have rather indiscriminately been interpreted in terms of induced diamagnetic ring current effects.[30] X-ray crystallographic studies of monosubstituted homotropylium ions by Childs and co-workers[31] have confirmed that cyclic charge delocalization[32] does indeed operate in these systems. Consequently, the very large $\Delta\delta$ for the C-8 protons in the parent homotropylium cation (5.86)[33] can unquestionably be attributed in part to homoconjugation. *However, local anisotropic contributions are now recog-*

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Table 3. ^{1}H NMR Analysis of the Cyclopentene and 1,3-Cycloheptadiene Effects in Bisannulated Cyclobutanes

X				
	1.69	3.53	1.27	1.23
	Δδ -1.84		Δδ +0.04	
	1.85	3.76	1.17	2.48
	Δδ -1.91		Δδ -1.31	
	1.85	3.45	1.27	2.23
	Δδ -1.60		Δδ -0.96	
	----	2.48	2.11	2.01
			Δδ +0.10	
H—	----	----	1.24	1.44
H—			Δδ -0.20	
	2.42	3.54	2.55	2.48
	Δδ -1.12		Δδ +0.07	

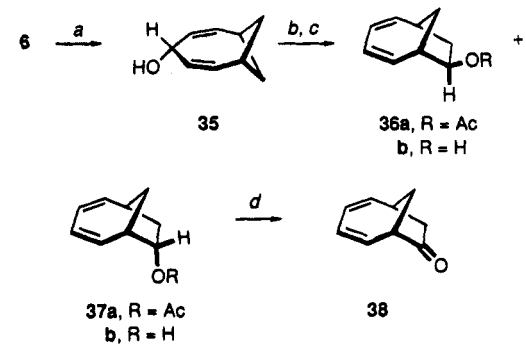
nized to account for more than 40% of the total chemical shift difference.[34]

In the present context, the need exists to call attention to the striking interplay of local magnetic anisotropy effects and chemical shift that operates in 1,3:2,4-bisannulated cyclobutanes (Table 3).[6g,35] Several interpretations have been accorded to the considerable deshielding that can accompany the placement of a methine proton above a region of unsaturation. Anisotropic field effects, differing degrees of steric compression, varying strain contributions, and orbital interactions through the filled cyclobutane orbitals have all been implicated. While these interpretations must currently be regarded as speculative, it is clear that wide variations in chemical shift often accompany structural modifications within molecules of this general type.

The magnitude of the shift differences between the exo and endo protons in **6** (Δδ 1.06) and **7a** in FSO_3H solution (Δδ 1.79) are considered to be a reflection of the greater delocalization that accompanies conversion to a pentadienyl cation subunit. The greater spread in Δδ for **7a** does not appear to be indicative of dihomoaromatic status for this species. This is tantamount to saying that charge density is not being propagated into the four-membered ring in the manner implicated in structure **8a**. This conclusion is supported by the virtually identical chemical shift of the methylene carbons in **6** (30.09 ppm) and its protonated ion (30.28 ppm). The various pieces of evidence, when taken together, indicate that the cation in question is classical, although no good model system against which to compare **8a** exists at present.

In CF_3CO_2D solution at 25 °C, it was possible to observe **7a** for a more prolonged period of time. The ^{1}H NMR spectrum recorded under these conditions (see Table 2) differs from that recorded in superacidic FSO_3H medium in that the chemical shift changes are considerably less pronounced. Most notably, the Δδ for the exo/endo methylene protons is reduced to 1.19 ppm. This is as expected if these shift parameters are directly related to the extent to which the carbonyl group is protonated. Childs et al. have generated complexes involving 2,3-homotropone and Lewis acids having different charge-stabilizing abilities and shown the chemical shifts of the methylene protons to be directly linked to the donor properties of the O–LA$^-$ substituent.[34] The greater acid strength of FSO_3H relative to CF_3COOH would shift the equilibrium more extensively in the direction of **7a**.

Scheme 4



[a] $NaBH_4$, $CeCl_3 \cdot 7H_2O$, CH_3OH. [b] Ac_2O, HOAc, (TsOH). [c] NaOH, CH_3OH, H_2O. [d] MnO_2, $CDCl_3$.

Studies Aimed at Generation of the Parent Dihomotropylium Cation. Hydroxyl-substituted cations such as **33** and **34** are not the most ideal models for the assessment of delocalization because a substantial component of the positive charge resides on their oxygenated carbon atoms. For this reason, independent evaluation of the parent cations is often sought in order to gain a more rigorous appreciation of the electronic state of affairs unperturbed by substitution.

In an effort to investigate the relative merits of **7b** and **8b**, **6** was reduced with sodium borohydride in the presence of cerium trichloride to give **35** (Scheme 4). This sensitive dienol was immediately dissolved in acetic anhydride containing 25% of glacial acetic acid and treated with a catalytic quantity of *p*-toluenesulfonic acid.[36] The ensuing reaction did not give the acetate of **35** but resulted instead in the formation of a 30:70 mixture of the *exo*- and *endo*-bicyclo[4.2.1]nona-2,4-dien-7-yl acetates **36a** and **37a**. Major component **37a** was easily identified by means of its 300 MHz ^{1}H NMR spectrum. The signals from the admixed **36a** were too weak and overlapping to be definitive. However, once saponification to generate the respective alcohols had been accomplished, the identity of **36b** was clearly revealed.[37] Additional confirmation of these structural assignments was realized by manganese dioxide oxidation of the combined **36b/37b** sample *exclusively* to **38**. This ketone had earlier been prepared in several laboratories.[37–39]

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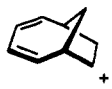
The driving force that underlies the bicyclo[5.1.1]-nonadienyl to bicyclo[4.2.1]nonadien-7-yl rearrangement is necessarily thermodynamic in origin. Although this may appear unusual at first glance since **7b** presumably enjoys pentadienylic delocalization and **39** can only profit from homoconjugation, the 1,2-alkyl shift that leads to **39** is accompanied by considerable strain release.



39

Summary. The first dihomotropone has been synthesized. The preparative aspects of this study reflect the workability of a regioselective ring expansion involving a functionalized acyloin. The two key elements of the successful scheme were the use of ethyl diazoacetate as a reagent of choice for arrival at a suitably functionalized bicyclo[5.1.1]nonan-4-one and the serviceability of the Garbisch procedure for introduction of the double bonds. With arrival at **6**, it proved possible to demonstrate by UV and NMR spectroscopy that this dienone is not measurably polarized in its ground state. Nor does its relatively unstable protonated form give evidence of dihomoaromatic character. The parent cation is particularly sensitive to Wagner–Meerwein rearrangement. Thus, by all indications, **6** can be looked upon as a dienone that is not electronically different from simpler monocyclic analogues. The structural building block represented by **6** is consequently suitable for the assessment of possible electronic perturbations brought on by relay orbital interactions of the type anticipated for **4** or **5**. These issues are considered in the ensuing paper.[40]

Experimental Section

Melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 1320 spectrometer. ^{1}H NMR spectra were recorded at 300 MHz and ^{13}C spectra at 75 MHz on a Bruker AC-300 instrument. Mass spectra were recorded on a Kratos MS-30 spectrometer at The Ohio State University Chemical Instrument Center. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark. All separations were carried out under flash chromatography conditions on Fluka silica gel H. The organic extracts were dried over anhydrous magnesium sulfate. Solvents were reagent grade and in many cases dried prior to use.

***cis*-1,3-Cyclobutanediacetic Acid.** High quality diacid could be routinely prepared by the saponification of highly purified **9**[13] as follows. To a warm (60 °C) solution of KOH (680 mg) in water (1.2 mL) was added dropwise during 5 min 600 mg (3.0 mmol) of neat diester. The reaction mixture was refluxed for 20 h and concentrated to dryness. The residual solid was taken up in water (4 mL), acidified with concentrated sulfuric acid (850 mg) in water (2 mL), refluxed for 1 h, cooled, and filtered to separate a white solid. This material and the concentrated filtrate were stirred in ether (100 mL), filtered, evaporated, and dried to give 516 mg (100%) of the diacid as white plates, mp 154.5–155.5 °C (from water): IR (KBr, cm^{-1}) 3300, 2850, 1680; ^{1}H NMR (300 MHz, CD_3COCD_3) δ 2.60–2.40 (m, 2 H), 2.40-2.25 (m, 6 H), 1.5–1.4 (m, 2 H); ^{13}C NMR (75 MHz, CD_3COCD_3) ppm 173.5, 41.2, 35.0, 29.1; MS m/z ($M^+ - H_2O$) calcd 154.0630, obsd 154.0640.

Anal. Calcd for $C_8H_{12}O_4$: C, 55.81; H, 7.02. Found: C, 56.11; H, 7.05.

Dimethyl *cis*-1,3-Cyclobutanedipropionate (10). The preceding diacid (357 mg, 2.07 mmol) was suspended in dry benzene (15 mL), treated with thionyl chloride (1.5 mL) and pyridine (2 drops) via cannula, stirred at rt for 12 h, and refluxed for 90 min. The homogeneous orange solution was concentrated on a rotary evaporator, evacuated at 0.3 Torr for several hours, dissolved in dry benzene (15 mL), and transferred during 30 min into a cold (−10 °C) dry reaction flask containing diazomethane (>25 mmol in 80 mL of ether) by filtration through a cotton plug under nitrogen. After the cessation of gas evolution, the reaction mixture was stirred at 0 °C for 2 h and at 10 °C overnight prior to concentration to a volume of approximately 25 mL. The insolubles were separated by filtration and the filtrate was concentrated, dissolved in absolute ethanol (20 mL), and treated portionwise with batches of silver acetate (0.1 g) and anhydrous triethylamine (2 mL). At this point, the mixture was refluxed for 45 min, cooled, filtered through a Celite plug, concentrated, and directly chromatographed on silica gel (elution with 4% ethyl acetate in petroleum ether). There was obtained 300 mg (63%) of **10** as a colorless oil: IR (neat, cm^{-1}) 1740, 1440; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.63 (s, 6 H), 2.18 (t, J = 7.6 Hz, 4 H), 2.20–1.95 (m, 4 H), 1.64 (q, J = 7.5 Hz, 4 H), 1.16 (qd, J = 8.8, 1.9 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 174.0, 51.3, 34.1, 32.4, 31.9, 31.3; MS m/z (M^+) calcd 228.1361, obsd 228.1347.

Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83. Found: C, 62.90; H, 8.84.

***cis*-1,3-Cyclobutanedipropionic Acid (12).** A magnetically stirred solution of **10** (220 mg, 0.96 mmol) in absolute methanol (0.4 mL) was treated at rt with KOH (0.4 g) dissolved in water (1 mL), stirred for 20 h, concentrated to dryness, and processed in the manner described above. The resultant white solid was dried overnight in vacuo at 80 °C over P_2O_5 to give 192 mg (99%) of **12** as colorless flakes, mp 112.0–112.5 °C (from water): IR (KBr, cm^{-1}) 3300, 2860, 1695, 1430, 1415, 1305, 1240, 1205; ^{1}H NMR (300 MHz, CD_3COCD_3) δ 2.40–2.05 (m, 4 H), 2.17 (t, J = 7.6 Hz, 4 H), 1.62 (q, J = 7.4 Hz, 4 H), 1.28–1.12 (m, 2 H); ^{13}C NMR (75 MHz, CD_3COCD_3) ppm 174.8, 34.7, 33.2, 32.1, 32.0; MS m/z ($M^+ - H_2O$) calcd 182.0943, obsd 182.0943.

Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 59.77; H, 7.99.

Bicyclo[5.1.1]nonane-3,5-dione (16). Into a dry three-necked flask was placed 36.4 mL of diethylzinc (1.1 M in toluene, 40 mmol) followed by unpurified **14**[13] (8 mmol at a maximum) dissolved in dry ether (15 mL). This solution was stirred in a water bath as a solution of diiodomethane (12.34 g, 46 mmol) in dry ether (5 mL) was introduced dropwise during 15 min under N_2. The reaction mixture was stored at 35 °C for 3 h, cooled to 0 °C, and quenched with cold saturated NH_4Cl solution (3 mL). The insoluble white solid was separated by filtration and washed thoroughly with ether (3 × 30 mL). The combined filtrates were washed with cold saturated NH_4Cl solution (20 mL) and brine (20 mL) prior to drying and filtration. There remained 2.46 g of **15** as a thick yellow oil.

Ferric chloride was dried by overnight reflux in thionyl chloride and evacuation to 1 mm at 100 °C for 24 h. A 2.88 g sample of this material was slurried under N_2 with anhydrous DMF (12 mL, freshly distilled from CaH_2) at 20 °C for 15 min before being treated with the **15** prepared above dissolved in anhydrous THF (8 mL). After 3 h of stirring at rt, the dark orange solution was treated with 10% HCl (30 mL) and extracted with $CHCl_3$ (5 × 25 mL). The combined organic extracts were washed with 10% HCl (20 mL), a saturated $NaHCO_3$ solution (20 mL), and brine (20 mL) prior to drying and concentration. The residual DMF was distilled under reduced pressure and the residue was purified by silica gel chromatography (elution with 30% ethyl acetate in petroleum ether) to give 670 mg (55%) of **16** as a colorless crystalline solid, mp 98–99 °C (from ether): IR (KBr, cm^{-1}) 1710, 1650, 1345, 1280, 1240, 1090; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.85 (s, 2 H), 2.85–2.60 (m, 6 H), 1.85–1.70 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 202.2, 59.3, 49.6, 29.4, 27.5; MS m/z (M^+) calcd 152.0837, obsd 152.0819.

Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.68; H, 7.95.

(40) Paquette, L. A.; Watson, T. J. *J. Org. Chem.*, following paper in this issue.

Bicyclo[5.1.1]nonane-3,4,5-trione 4-(Propylene dithioketal) (17). A mixture of **16** (152.2 mg, 1.0 mmol), trimethylene dithiotosylate (477 mg, 1.145 mmol),[18] potassium acetate (723 mg), and absolute ethanol (8 mL) was refluxed for 24 h, concentrated to dryness, and partitioned between water (10 mL) and CH_2Cl_2 (15 mL). The water layer was further extracted with CH_2Cl_2 (4 × 15 mL), and the combined organic phases were dried and concentrated. Chromatography of the residue on silica gel (elution with 10% ethyl acetate in petroleum ether) afforded **17** (231 mg, 90%) as a colorless crystalline solid, mp 151–151.5 °C (from ether–petroleum ether): IR (KBr, cm^{-1}) 1680, 1440, 1425, 1410, 1265, 1165, 1125, 1085; ^1H NMR (300 MHz, $CDCl_3$) δ 2.92 (t, J = 5.2 Hz, 4 H), 2.74 (br s, 4 H), 2.56 (br s, 4 H), 1.95–1.85 (m, 2 H), 1.48 (br d, J = 8.5 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 199.0, 69.4, 43.3, 30.3, 28.8, 27.2, 24.2; MS m/z (M^+) calcd 256.0592, obsd 256.0572.

Anal. Calcd for $C_{12}H_{16}O_2S_2$: C, 56.22; H, 6.29. Found: C, 56.06; H, 6.34.

Hydride Reduction of 17. To a cold (−15 °C), stirred suspension of $LiAlH_4$ (68 mg) in dry THF (3 mL) was added dropwise under N_2 a solution of **17** (150 mg, 0.585 mmol) in the same solvent (5 mL). After 4 h at this temperature, saturated Na_2SO_4 solution (1.5 mL) was introduced and the suspension was allowed to warm to rt. The insoluble white solid was separated by filtration and washed extensively with THF (6 × 10 mL). The combined filtrates were concentrated and the residue was chromatographed on silica gel (elution with 40% ethyl acetate in petroleum ether) to give 117 mg of a 2:1 mixture of **18** and **20** and 21 mg (14%) of **21**. Recrystallization of the mixture from ether–petroleum ether afforded 76 mg (50%) of pure **18**. In a similar reaction carried out at −78 °C, it proved possible to isolate **20** in pure condition from the mother liquors of the first crystallization.

For 18: colorless crystals, mp 147.5–148.5 °C; IR (KBr, cm^{-1}) 3200, 1470, 1440, 1410, 1300, 1290, 1085, 1075, 890; ^1H NMR (300 MHz, $CDCl_3$) δ 4.43 (t, J = 4.8 Hz, 2 H), 3.74 (br s, 2 H), 2.93–2.88 (m, 4 H), 2.55–2.48 (m, 4 H), 2.46–2.32 (m, 3 H), 2.30–2.26 (m, 2 H), 2.03–1.95 (m, 2 H), 1.87–1.80 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 77.6, 64.1, 36.4, 30.3, 29.1, 29.0, 26.8, 25.5, 23.9; MS m/z (M^+) calcd 260.0905, obsd 260.0933.

Anal. Calcd for $C_{12}H_{20}O_2S_2$: C, 55.35; H, 7.74. Found: C, 55.16; H, 7.74.

For 20: colorless crystals, mp 68.5–69.5 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 4.17 (s, 1 H), 3.55 (t, J = 6.7 Hz, 2 H), 3.25–3.16 (m, 2 H), 2.72 (d, J = 7.3 Hz, 2 H), 2.62–2.54 (m, 3 H), 2.35–2.19 (m, 3 H), 2.14–1.94 (m, 2 H), 1.67–1.57 (m, 2 H), 1.46 (s, 1 H), 1.38–1.30 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 201.8, 61.1, 47.4, 46.9, 40.2, 35.0 (2 C), 29.4, 28.3, 26.2 (2 C), 25.2; MS m/z (M^+) calcd 260.0905, obsd 260.0918.

For 21: colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 3.86 (d, J = 6.2 Hz, 1 H), 3.80–3.74 (m, 1 H), 3.54 (t, J = 6.7 Hz, 2 H), 2.95–2.85 (m, 2 H), 2.80–2.68 (m, 2 H), 2.40–2.15 (m, 4 H), 2.10–1.75 (series of m, 4 H), 1.68–1.58 (m, 4 H), 1.37–1.25 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 71.1, 61.2, 52.7, 41.5, 40.3, 35.4, 34.9, 29.4, 29.2, 28.6, 28.1, 25.7; MS m/z (M^+) calcd 262.1061, obsd 262.1058.

4-Bromobicyclo[4.1.1]octan-3-one. A cold (0 °C), nitrogen-blanketed solution of methanesulfonyl chloride (7.0 mL) in anhydrous CH_2Cl_2 (10 mL) was treated sequentially with anhydrous pyridine (9.7 mL) and **23**[13] (3.0 g, 21.4 mmol) in dry CH_2Cl_2 (10 mL). The reaction mixture was stirred at 0 °C for 3 days, quenched with water (100 mL), and neutralized with 10% HCl. The product was extracted into CH_2Cl_2 (3 × 100 mL), washed with saturated $NaHCO_3$ solution (100 mL), dried, and evaporated. There was obtained 3.0 g (64%) of **24** as a colorless crystalline solid, mp 112–113 °C (from CH_2Cl_2–petroleum ether): IR (KBr, cm^{-1}) 1720, 1360, 1175, 995, 985, 970, 855; ^1H NMR (300 MHz, $CDCl_3$) δ 5.61 (dd, J = 7.4, 10.6 Hz, 1 H), 3.22 (s, 3 H), 2.76–2.47 (m, 6 H), 2.50–2.35 (m, 1 H), 1.90–1.72 (m, 2 H), 1.23–1.18 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 205.7, 82.7, 46.3, 39.4, 35.0, 31.5, 30.3, 29.1, 28.3; MS m/z (M^+) calcd 218.0613, obsd 218.0668.

Anal. Calcd for $C_9H_{14}O_4S$: C, 49.52; H, 6.46. Found: C, 49.64; H, 6.58.

A mixture of **24** (1.0 g, 4.6 mmol), anhydrous LiBr (2.3 g), and acetone (25 mL) was refluxed under N_2 for 4 h, cooled to rt with stirring during 24 h, evaporated, and diluted with water (20 mL). The product was extracted with CH_2Cl_2 (3 × 20 mL), the combined organic layers were dried and concentrated, and the residue was subjected to column chromatography on silica gel (elution with 25% ethyl acetate in petroleum ether) to furnish 0.50 g (61%) of the α-bromo ketone as a colorless oil: IR (neat, cm^{-1}) 1720; ^1H NMR (300 MHz, $CDCl_3$) δ 4.96 (dd, J = 6.8, 10.9 Hz, 1 H), 2.85–2.75 (m, 1 H), 2.70–2.39 (m, 6 H), 1.99 (td, J = 1.5, 7.5 Hz, 1 H), 1.80–1.69 (m, 1 H), 1.30–1.20 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 203.8, 54.6, 46.4, 39.9, 33.4, 31.2, 28.8, 28.5; MS m/z (M^+) calcd 201.9993, obsd 202.0028.

Bicyclo[4.1.1]oct-3-en-4-one (25). A slurry of **24** (322 mg, 1.52 mmol), anhydrous LiBr (1.32 g, 15.2 mmol), lithium carbonate (1.19 g, 15.65 mmol), and dry DMSO (5 mL) was stirred for 3 h at 70 °C and subsequently for 2.5 h at 100 °C under N_2. After cooling, the mixture was partitioned between water (10 mL) and ether (20 mL). Insoluble material was removed by filtration and washed thoroughly with ether. The aqueous phase was extracted with ether (3 × 20 mL), and the combined organic solutions were washed with water (3 × 10 mL), dried, and concentrated. Bulb-to-bulb distillation of the residue gave 84 mg (43%) of **25**, bp 35–40 °C (1.5 Torr), as a colorless solid, mp 38.5–39.5 °C: ^1H NMR (300 MHz, $CDCl_3$) δ 7.18 (dd, J = 8.7, 11.5 Hz, 1 H), 6.00 (d, J = 11.5 Hz, 1 H), 3.05–2.85 (m, 1 H), 2.85–2.65 (m, 5 H), 1.75–1.55 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 156.1, 131.1, 46.6, 35.6, 34.4, 30.3 (carbonyl peak not seen); MS m/z (M^+) calcd 122.0732, obsd 122.0761.

Ethyl 3-Bromo-4-oxobicyclo[5.1.1]nonane-5-carboxylate (27). Bromo ketone **24** (2.48 g, 12.3 mmol) dissolved in CH_2Cl_2 (50 mL) was cooled to 0 °C under N_2, mixed with freshly distilled boron trifluoride etherate (7.5 mL), and treated dropwise during 1 h with a solution of ethyl diazoacetate (6.4 mL) in CH_2Cl_2 (10 mL). The mixture was stirred at 0 °C for 30 min and at rt overnight, quenched with water (25 mL), and stirred for 1 h. After dilution with more CH_2Cl_2, the organic layer was separated, dried, and evaporated. The residue was purified by silica gel chromatography (elution with 10% ethyl acetate in petroleum ether) to give 3.01 g (88%) of **27** as a colorless oil: IR (neat, cm^{-1}) 1745, 1715, 1650; MS m/z (M^+) calcd 288.0361, obsd 288.0373.

Bicyclo[5.1.1]nonan-4-one (13). A dry 1 L flask equipped with a magnetic stirring bar was charged with **27** (4.29 g, 14.8 mmol), ether (720 mL), acetic acid (72.1 mL), and zinc dust (35.7 g). This mixture was stirred under N_2 at rt for 4 h and filtered. The solid was washed with water (8 × 200 mL), dried, and concentrated to give 2.69 g (87%) of the β-keto ester, which can be directly utilized. Purification for analysis was achieved by flash column chromatography on silica gel (elution with 5% ethyl acetate in petroleum ether) to give the product as a colorless oil: IR (neat, cm^{-1}) 3360, 1745, 1705, 1640; ^1H NMR (300 MHz, $CDCl_3$) δ 4.12 (q, J = 7.1 Hz), 3.97 (dd, J = 6.8, 10.3 Hz), 2.85–2.65 (m), 2.65–2.30 (m), 2.30–2.15 (m), 2.15–1.90 (m), 1.80–1.65 (m), 1.55–1.40 (m), 1.21 (t, J = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 214.2, 170.2, 61.0, 55.4, 40.0, 35.6, 32.3, 30.3, 30.2, 28.8, 27.7, 14.0; MS m/z (M^+) calcd 210.1256, obsd 210.1237.

Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.29; H, 8.80.

A solution of the β-keto ester (2.69 g, 12.8 mmol) in acetone (25 mL) was added to 5 M HCl (25 mL), and the resulting soltuion was heated to reflux for 4 h, cooled, and evaporated. The resulting aqueous solution was extracted with CH_2Cl_2 (3 × 25 mL), and the combined organic layers were dried and evaporated to give 1.65 g (82%) of **13**. An analytically pure sample of the colorless solid, mp 89–91 °C, was obtained by bulb-to-bulb distillation and preparative GC: IR (KBr, cm^{-1}) 1700; ^1H NMR (300 MHz, $CDCl_3$) δ 2.63 (t, J = 6.1 Hz, 4 H), 2.59–2.37 (m, 4 H), 2.10–1.90 (m, 4 H), 1.70–1.55 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 220.3, 40.1, 32.4, 30.1, 28.8.

Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 59.71; H, 7.99.

Dibromo Ketal 28. A solution of **13** (500 mg, 3.6 mmol), ethylene glycol (4 mL), and *p*-toluenesulfonic acid (1 crystal) in benzene (10 mL) was refluxed under a Dean–Stark trap for 24 h. After cooling, solid Na_2CO_3 was added to achieve neutralization, and the benzene was evaporated. The residue was extracted with pentane (3 × 50 mL) and then with ether (50 mL). The combined organic layers were dried and evaporated to leave 520 mg (80%) of the ethylene ketal. Purification for analysis was achieved by preparative GC leading to a colorless oil: IR (neat, cm^{-1}) 1448, 1380, 1290, 1220; ^1H NMR (300 MHz, $CDCl_3$) δ 3.94 (s, 4 H), 2.44 (m, 2 H), 2.32 (m, 2 H), 1.98 (m, 4 H), 1.70 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 64.0, 34.5, 30.9, 30.3, 28.5, 27.6; MS *m/z* (M^+) calcd 182.1307, obsd 182.1315.

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.09; H, 9.90.

A solution of the above ketal (124.6 mg, 0.68 mmol) in ethylene glycol (1.5 mL) was cooled to 0 °C under N_2, treated dropwise with bromine (1 mL) during 15 min, and warmed to rt. After 20 min, the mixture was poured into a stirred slurry of Na_2CO_3 (450 mg) in pentane (10 mL). After the orange color had faded, the mixture was washed with water (2 × 10 mL), dried, and evaporated. Purification by silica gel chromatography (elution with 10% ethyl acetate in petroleum ether) afforded 190 mg (82%) of **28** as colorless crystals, mp 107–108 °C (from ethyl acetate–petroleum ether): ^1H NMR (300 MHz, $CDCl_3$) δ 4.98 (dd, J = 10.0, 1.7 Hz, 2 H), 4.40–4.25 (m, 4 H), 2.65–2.30 (m, 8 H), 1.80 (br d, J = 12 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 110.9, 68.2, 58.1, 38.2, 32.6, 28.8; MS *m/z* (M^+) calcd 339.9496, obsd 339.9542.

Anal. Calcd for $C_{11}H_{16}Br_2O_2$: C, 38.85; H, 4.74. Found: C, 39.17; H, 4.87.

Bicyclo[5.1.1]nona-2,5-dien-4-one (6). A solution of **28** (146 mg, 0.63 mmol) and potassium *tert*-butoxide (300 mg) in dry DMSO (5 mL) was stirred at 50 °C for 15 h, cooled, poured into brine (10 mL), and extracted with pentane (2 × 20 mL). The combined organic extracts were dried and concentrated to give 50 mg (65%) of the diene ketal, which was directly shaken with 3% sulfuric acid (2 mL) for 5 min, immediately extracted with ether (2 × 10 mL), dried, and concentrated. Silica gel chromatography (elution with 10% ethyl acetate in petroleum ether) gave 18 mg (47%) of **6**, a colorless oil that was further purified by preparative GC: IR (neat, cm^{-1}) 1653, 1623; ^1H NMR (300 MHz, $CDCl_3$) δ 6.61 (dd, J = 12.8, 8.6 Hz, 2 H), 6.00 (dd, J = 13.1, 0.8 Hz, 2 H), 3.05–2.75 (m, 4 H), 1.83 (dm, J = 12.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 195.0, 146.8, 130.8, 31.7, 30.1; MS *m/z* (M^+) calcd 134.0731, obsd 134.0769.

Bicyclo[5.1.1]nona-2,5-dien-4-ol (35). To 1 mL of a 0.4 M solution of $CeCl_3 \cdot 7H_2O$ in methanol were added sequentially 10 mg of **6** and 5 mg of sodium borohydride. After 5 min, water (1 mL) was added, the product was extracted into ether (3 × 2 mL), and the combined organic phases were dried and evaporated to produce **35** as a white solid that yellowed quickly at rt. This material was therefore directly acetylated.

Acetylative Rearrangement of 35. The alcohol sample from above was dissolved in 1 mL of a 4:1 acetic anhydride–glacial acetic acid mixture. *p*-Toluenesulfonic acid (1 mg) was introduced, and the mixture was stirred at rt for 24 h, evaporated in vacuo, and diluted with ether (3 mL). The ethereal solution was washed with water (3 × 3 mL) and 5% Na_2CO_3 solution prior to drying and solvent evaporation. There was isolated 10 mg of a 30:70 mixture of **36a** and **37a** as a colorless mobile oil. **For 37a**: ^1H NMR (300 MHz, $CDCl_3$) δ 6.08 (br dd, J = 11, 8 Hz, 1 H), 5.88 (dd, J = 12, 7 Hz, 1 H), 5.72–5.62 (m, 2 H), 5.06 (ddd, J = 9, 7, 7 Hz, 1 H), 3.02 (br ddd, J = 7, 7, 6 Hz, 1 H), 2.61 (br dddd, J = 9, 8, 7, 3 Hz, 1 H), 2.28 (ddd, J = 14, 9, 9 Hz, 1 H), 2.12 (br ddd, J = 13, 7, 6 Hz, 1 H), 2.03 (s, 3 H), 1.92 (br d, J = 13 Hz, 1 H), 1.85 (dddd, J = 14, 7, 3, 2 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 171.2, 139.8, 132.7, 127.0, 123.7 86.4, 42.5, 40.2, 35.0, 29.7, 21.0; GC-MS *m/z* (M^+) calcd 178.10, obsd 178.20.

The acetate mixture (10 mg) was dissolved in 50% aqueous methanol (1 mL) to which KOH (50 mg) was added. The mixture was stirred at rt for 1 h, concentrated in vacuo, and triturated with ether (3 × 3 mL). The combined organic layers were dried and evaporated to leave 6 mg of a 30:70 mixture of **36b** and **37b** as a colorless mobile oil.

For 36b: ^1H NMR (300 MHz, $CDCl_3$) δ 6.11 (br dd, J = 11, 8.5 Hz, 1 H), 5.92 (br dd, J = 12, 7.5 Hz, 1 H), 5.75 (ddd, J = 12, 7, 1 Hz, 1 H), 5.64 (dd, J = 11, 7 Hz, 1 H), 4.34 (br d, J = 6 Hz, 1 H), 2.84 (br ddd, J = 8.5, 8.5, 7 Hz, 1 H), 2.59 (br dd, J = 7.5, 6 Hz, 1 H), 2.39 (br ddd, J = 12, 7, 6 Hz, 1 H), 2.23 (br dd, J = 14.5, 6 Hz, 1 H), 1.88 (br dd, J = 14.5, 8.5 Hz, 1 H), 1.67 (br d, J = 12 Hz, 1 H).

For 37b: ^1H NMR (300 MHz, $CDCl_3$) δ 6.12 (br dd, J = 11, 8 Hz, 1 H), 6.03 (dd, J = 12, 7 Hz, 1 H), 5.79 (br dd, J = 12, 7 Hz, 1 H), 5.66 (dd, J = 11, 7 Hz, 1 H), 4.40 (ddd, J = 9, 7, 7 Hz, 1 H), 2.92 (br ddd, J = 7, 7, 6 Hz, 1 H), 2.58 (br dddd, J = 9, 8, 7, 3 Hz, 1 H), 2.26 (ddd, J = 14, 9, 9 Hz, 1 H), 2.10 (br ddd, J = 13, 7, 6 Hz, 1 H), 1.89 (br d, J = 13 Hz, 1 H), 1.68 (dddd, J = 14, 7, 3, 2 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 140.9, 132.6, 128.6, 123.1, 85.1, 44.8, 44.7, 35.8, 29.7; MS *m/z* (M^+) calcd 136.0888, obsd 136.0889.

Bicyclo[4.2.1]nona-2,5-dien-7-one (38). The above alcohol mixture (6 mg) was placed in $CDCl_3$ (0.5 mL) and treated with activated manganese dioxide (10 mg). The mixture was stirred at rt for 24 h and filtered through a small Celite pad into an NMR tube. **38**: ^1H NMR (300 MHz, $CDCl_3$) δ 6.20 (br dd, J = 11, 8 Hz, 1 H), 5.96 (dd, J = 11, 7 Hz, 1 H), 5.88 (br dd, J = 11, 8 Hz, 1 H), 5.82 (ddd, J = 11, 7, 1 Hz, 1 H), 3.38 (br dd, J = 8, 8 Hz, 1 H), 2.96 (ddddd, J = 8.5, 8, 6, 2.5, 1 Hz, 1 H), 2.55 (ddd, J = 18.5, 8.5, 1 Hz, 1 H), 2.42 (br d, J = 18.5 Hz, 1 H), 2.37 (br ddd, J = 12.5, 8, 6 Hz, 1 H), 1.83 (dd, J = 12.5, 2.5 Hz, 1 H); MS *m/z* (M^+) calcd 134.0732, obsd 134.0735.

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Supplementary Material Available: 300-MHz ^1H and 75-MHz ^{13}C NMR spectra of those compounds lacking combustion data (8 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.