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Photochemical and Thermal Rearrangements of Protonated 2,3-Homotropones

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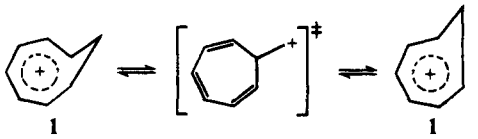
Abstract: The 2-hydroxyhomotropylium cation **10** and 8-*endo*-methyl-, 8-*exo*-methyl-, 8,8-dimethyl-, 1,8,8-trimethyl-, and 3,8,8-trimethyl-2-hydroxyhomotropylium cations, **12, 11, 13, 14,** and **15,** respectively, were prepared by protonation of the corresponding 2,3-homotropones in FSO_3H. On the basis of a comparison of the ^1H NMR spectra of the 2-hydroxyhomotropylium ions with nonaromatic systems it is concluded that they can properly be regarded as homoaromatic cations. Ions **10, 11, 12,** and **13** isomerized when irradiated in FSO_3H to give the corresponding 1-hydroxyhomotropylium cations **19, 21, 22,** and **23,** respectively. The thermal isomerization of these ions has been investigated. Cation **22** was shown to isomerize to **21** at -39.5 °C ($k = 4.3 \times 10^{-4}$ s^{-1}). An equilibrium was set up between these two ions consisting of 6% **22** and 94% **21** at 0 °C. At higher temperatures **21** rearranged to protonated 1-phenylpropanal ($k = 2.5 \times 10^{-4}$ s^{-1} at 37 °C). The 8,8-dimethyl cation **23** isomerized back to **13** ($k = 3.1 \times 10^{-4}$ s^{-1} at -23 °C), which underwent a further series of rearrangements to give eventually protonated 8,8-dimethylbicyclo[3.1.0]octa-3,6-dien-2-one (**29**). The symmetrical 8,8-dimethyl-4-hydroxyhomotropylium cation **32** was observed as an intermediate in the isomerization of **13** to **29.** On the basis of the thermal isomerizations of **14** and **15** it was concluded that the 8,8-dimethyl-3-hydroxyhomotropylium cation must also be an intermediate in the conversions of **13** to **29** and **13** to **32.**

The purpose of this study was to see whether circumambulatory rearrangements could be detected with homotropylium cations,[1] eq 1. Interest in these potential migrations stems from



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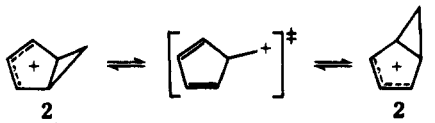

(2)

the observation of facile, highly stereoselective, cyclopropyl merrry-go-round reactions of the bicyclo[3.1.0]hexenyl cations, eq 2.[2] The characterization of such rearrangements with **1** would be of value in assessing the importance of homoaromaticity and orbital symmetry in the two systems.

Circumambulatory isomerizations of the bicyclo[3.1.0]-hexenyl cations readily occur. The measured barrier to isomerization of **2** is only 15 kcal/mol[2b] and substituted derivatives of **2** exhibit activation energies which can range down to values which are formally below zero.[2,3]

At the outset of this work, no circumambulatory rearrangements of **1** or its derivatives had been detected. Berson and co-workers[4] had examined deuterated derivatives of the parent cation and concluded that the barrier to such a migration must be greater than 26–27 kcal/mol, a limit set by the onset of rapid decomposition of **1.** Calculations performed by Hehre[5] suggested that the barrier to migration would be of the order of 40 kcal/mol. Since our preliminary communication of these results[6] Scott and Brunsvold[7] have observed a circumambulatory rearrangement with a ring-fused homotropylium cation.

Why should the degenerate rearrangements of **1** have such a larger activation energy than those of **2**? Two primary reasons can be suggested: the constraints put on the system by the dictates of orbital symmetry[8] and the greater homoaromatic stabilization of the ground state of **1** as compared to **2.**

The importance of both factors can readily be seen by comparing the relative stabilities of the ground and formal transition states shown for the migrations in eq 1 and 2. For a concerted migration there are two possible geometries of the transition state and these are not equally attractive. The *bisected* structure which involves inversion at the migrating carbon can be readily attained from either **1** or **2.** The formation of the alternative *eclipsed* structure involves a more difficult non-least-motion movement of the migrating carbon.[9] For orbital symmetry to be conserved in thermally induced migrations, **1** is required to rearrange by the higher energy *eclipsed* transition state, whereas **2** can isomerize by the least motion allowed *bisected* pathway. On the other hand, homoaromatic stabilization of **1** will have the effect of increasing the energy gap between the ground state of **1** and the transition state for migration as compared to the comparable ground and transition states of the nonaromatic **2.**[1,10]

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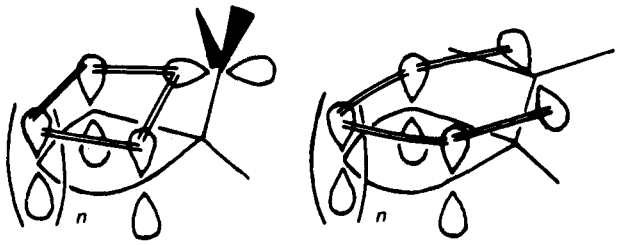


eclipsed transition state
non-least motion

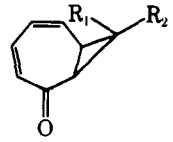
bisected transition state
least motion

In this paper we explore two ways of minimizing these adverse factors to the circumambulatory rearrangements of **1**. The orbital symmetry imposed constraint can in principle be removed in the first excited state and we indeed show this to be the case. Secondly, by placing electron-donating substituents at C_8 of **1** the activation energy for the migration can be reduced, allowing thermally induced migrations to occur.[5]

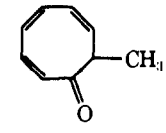
Results and Discussion

The parent homotropylium cation **1** has been shown to rearrange on irradiation to give a bicyclo[3.3.0]octadienyl cation.[11] If any degenerate isomerizations of **1** had occurred under these conditions, they would not have been detected. In order to provide a ring marker we chose to work with the 2-hydroxyhomotropylium cations which can be obtained on protonation of 2,3-homotropones.[12]

Preparation of Homotropones. Ketones **3–5** were prepared by the procedure of Franck-Neumann.[13] The *exo*-methyl compound **4** as prepared by this method contained some of the corresponding *endo*-methyl isomer **6** (10–20%). The addition of diazoethane to tropone itself gave in our hands a mixture of 8-methylcyclooctatrienone (**7**, ~60%), **6**, and **4**,[14] which



3, $R_1 = R_2 = H$
4, $R_1 = H$; $R_2 = CH_3$
5, $R_1 = R_2 = CH_3$
6, $R_1 = CH_3$; $R_2 = H$



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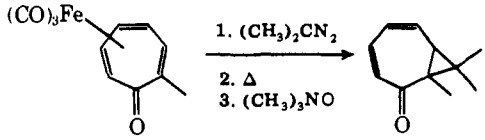
eventually yielded a mixture containing **6** (80–90%) and **4** (10–20%).

The two homotropones **8** and **9** were prepated from 2-methyltroponeiron tricarbonyl[15] as indicated in eq 3.



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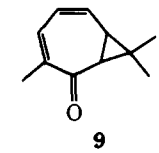

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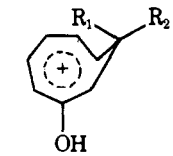
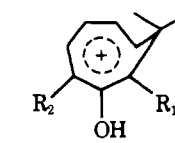
(3)

Protonation of Homotropones. Dissolution of the homotropones **3–6**, **8**, and **9** at low temperature in FSO_3H gave the corresponding 2-hydroxyhomotropylium cations **10–15**. The ^1H NMR spectra of all the cations were in agreement with the assigned structures (Table I) or in the case of **10** with that previously reported.[12]

Cations **10–12** were all found to be thermally stable at room temperature. No evidence for the interconversion of the *exo*- and *endo*-methyl isomers **11** and **12** could be detected up to 80 °C, at which temperature both cations underwent general decomposition. Knowing the rate of decomposition it was possible to put an upper limit on the rate of conversion of **12** → **11**, $k < 2 \times 10^{-4}$ s^{-1} at 83 °C ($\Delta G^{\ddagger} > 27$ kcal/mol).



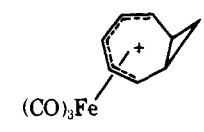
10, $R_1 = R_2 = H$
11, $R_1 = H$; $R_2 = CH_3$
12, $R_1 = CH_3$; $R_2 = H$
13, $R_1 = R_2 = CH_3$



14, $R_1 = CH_3$; $R_2 = H$
15, $R_1 = H$; $R_2 = CH_3$

Before proceeding further it is necessary to address the question of the degree of homoaromaticity in these protonated homotropones. Although in the past they have been regarded as homoaromatic systems,[1,14] it could be argued that most of the positive charge is localized on the oxygen atom and cyclic delocalization is unimportant. The usual test of cyclic delocalization in homoaromatic systems has been the magnitude of the chemical-shift difference of resonances of the exo and endo substituents on the bridging carbon in the NMR spectrum of a system. The recent paper of Haddon[16] which links the ring current to the resonance energy of an aromatic system has strengthened the use of this criterion. The chemical-shift difference of the C_8 substituent resonances of a range of homotropylium species are presented in Table II. As can be seen, this chemical-shift difference is attenuated by about a factor of 2 on introduction of the hydroxy group onto C_2 of the homotropylium cation ($\Delta\delta = 5.86$ for **1** compared to 3.1 for **10**). Nevertheless, a chemical-shift difference between the exo and endo protons of **10** of 3.1 ppm is still appreciable.

Some idea of the difference to be expected in these systems in the absence of cyclic delocalization can be gained from a consideration of the corresponding iron tricarbonyl complexes. Cyclic delocalization in **16** is prevented by the iron tricarbonyl



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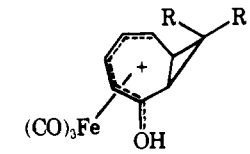


17, R = H
18, R = CH_3

function and the chemical-shift difference has been shown to be very small.[1,17] Similarly, we find that there is no difference in the chemical shifts of the C_8 methylene proton resonances of the O-protonated iron tricarbonyl complex of 2,3-homotropone **17**. A comparable pattern of shifts exists for the C_8 substituted systems, e.g., **13** and **18**.[18]

Overall it would appear that the hydroxy group on C_2 of a homotropylium cation reduces but by no means eliminates cyclic delocalization. Protonated 2,3-homotropones may be classified as homoaromatic cations.

Photoisomerizations. Protonated 2,3-homotropones exhibit intense long-wavelength absorptions at ca. 360 nm (Table III). Irradiation of FSO_3H solutions of these cations at low temperature with broad-spectrum light led to the formation of complex mixtures of products. However, much cleaner photoreactions were observed when longer wavelength light was used ($\lambda > 360$ nm).

In the case of **10** the photoproduct was identified as **19** by the similarity of its ^1H NMR spectrum to that previously reported.[20] Cyclooctatrienone was recovered when the irradiated solutions were quenched with aqueous base.

Table I. ^{1}H NMR Spectral Data

		chemical shifts, ppm								
compd	solvent	H_1	H_2	H_3	H_4	H_5	H_6	H_7	$H_{8\text{-exo}}$	$H_{8\text{-endo}}$
6	CS_2	2.30 m		5.91 d	6.30 m	6.00 t	6.3 m	1.96 m	1.96 m	(1.02 d)
12	FSO_3H	3.55 m		7.03 m	7.78 dd	7.03 m	7.50 dd	3.55 m	4.12 m	(0.52 d)
11	FSO_3H	3.40 m		7.00 m	7.68 dd	7.00 m	7.65 dd	3.65 m	(1.69 d)	0.99 m
21	FSO_3H		7.44 m	8.02 m	7.44 m	8.02 m	7.44 m	5.60	(1.78 d)	1.29 dq
22	FSO_3H				7.2–8.4 m			6.08 t	5.15 m	(0.22 d)
5	CS_2	2.06 d		5.90 d	6.22 q	5.78 t	6.40 q	1.60 t	(1.03 s)[a]	(1.36 s)[a]
13	FSO_3H	3.23 d		7.10 d	7.67 q	6.99 t	7.52 q	3.42 t	(1.92 s)	(0.68 s)
23	FSO_3H				7.25–8.35 m			5.53 d	(2.10 s)	(0.15 s)
30	CS_2	2.66 m		5.30 ddd	6.94 dd	2.66 m	6.50 dd	5.83 dd	(1.20 s)	(1.20 s)
29	FSO_3H	3.63 m		6.57 dd	8.78 dd	3.63 m	7.22 t	6.48 dd	(1.42 s)	(1.54 s)
33	CS_2	1.63 dd	6.30 m	5.85 d		5.85 d	6.30 m	1.63 dd	(1.32 s)[a]	(0.83 s)[a]
32	FSO_3H	3.33 d	8.00 bt	7.11 d		7.11 d	8.00 bt	3.33 d	(2.03 s)	(0.41 s)
8	CS_2	(1.13 s)[a]			5.6–6.45 m			1.24 d	(0.91 s)[a]	(1.24 s)[a]
9	CS_2	2.25 d		(1.28 s)[a]		5.6–6.4		1.62 t	(1.03 s)[a]	(1.38 s)[a]
14	FSO_3H	(1.71 s)			7.00–7.60 m			3.35 d	(1.98 s)	(0.35 s)
15	FSO_3H	(3.10 d)		(1.82 s)	7.72 d	6.80 t	7.20 t	3.45 t	(2.27 s)	(0.53 s)
34	FSO_3H	3.39 m	7.92 d	(1.95 s)		7.04 d	7.92 m	3.39 m	(2.36 s)	(0.23 s)
37	CS_2	2.73 dd		(1.56 d)	6.66 dq	2.60 dd	6.55 dd	5.90 dd	(1.16 s)	(1.20 s)
38	CS_2	(1.13 s)[a]		5.40 d	6.97 dd	2.67 dd	5.60 dd	5.50 dd	(1.04 s)[a]	(0.97 s)[a]
35	FSO_3H	3.63 d		(2.00 s)	8.50 dd	3.50 m	7.23 t	6.50 t	(1.35 s)[a]	(1.48 s)[a]
36	FSO_3H	(1.27 s)[a]		6.50 d	8.78 dd	3.55 m	7.23 m	6.11 d	(1.40 s)[a]	(1.43)[a]

	coupling constants, Hz									
compd	$J_{1,2}$	J_{17}	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6,7}$	J_{18}	J_{CH_3H}	other
6				12	8				5	
12				12	8	11	6		6	
11				12	8	11	6		6	
21							9	9	7	
22							9	9	7	
5		9				11	7			
13		8		11	10	10	7			
23							10			
30		3.3		9.6	6.5	3.2	5.9			0.8, 1.0[b]
29		2		10	6.5	2	4			
33	5		12							3[c]
32	8		11							
8							7			
9		8					8			
14							7.5			
15		7			9	7	7			
34						10				
37		3			7	4	6		2	
38				9	6	3	5			
35		3.5			6.5	4	4			
36				10	7	4	5			

All chemical shifts referred to tetramethylsilane (CS_2 solvent) or internal CH_2Cl_2 taken as δ 5.3 (FSO_3H solvent). Chemical shifts of methyl resonances in parentheses. s, singlet; d, doublet; t, triplet; m, multiplet. [a] Assignment may be reversed. [b] $J_{3,5}$ and $J_{1,3}$. [c] $J_{2,7} = J_{1,7}$.

Table II. Differences in ^{1}H Chemical Shifts of the Exo and Endo Substituent Resonances

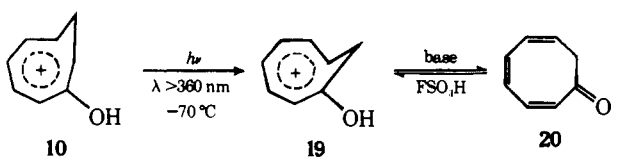
cation	$\Delta\delta$, ppm[a]	cation	$\Delta\delta$, ppm[a]
10	3.10	**16**	0.18
17	0.00	**13**	1.24
1	5.86	**18**	0.16

[a] $\Delta\delta = \delta_{exo} - \delta_{endo}$ for C_8 methylene proton resonances or, in the cases of **13** and **18**, methyl resonances.

Table III. UV Spectra of Cations[a]

cation	λ_{max}, nm	log ϵ
10	362	3.34
11	355	3.56
19	350	3.74
21	345	3.48

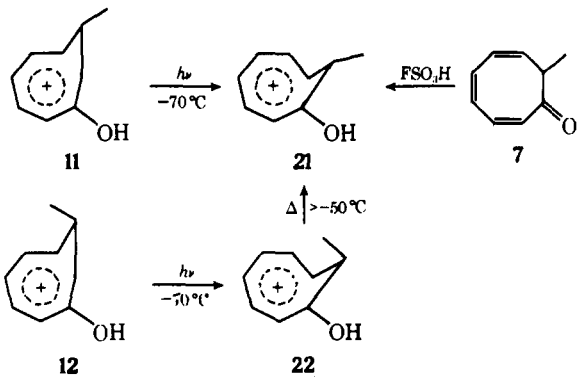
[a] All spectra obtained in H_2SO_4 at room temperature.



10 **19** **20**

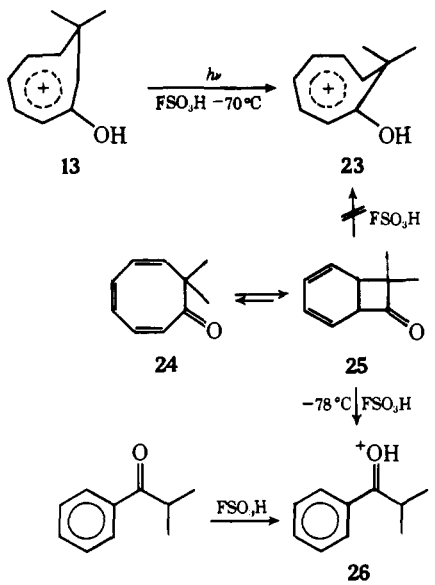
Irradiation of **11** led to a similar photoreaction to that found for **10.** The product was identified as **21** on the basis of its similarity to **19** and by its independent generation on protonation of **7.** The assignment of the C_8-methyl group to the exo position was made on the basis of the C_8 methine and methyl proton resonances, particularly when compared to those of the corresponding *endo*-methyl cation.

Similar irradiations of FSO_3H solutions of **12** (containing some **11**) at −70 °C led to the formation of **21** and a new cation. This new cation had a ^{1}H NMR spectrum which was comparable to that of **21,** except for the positions of the C_8 methyl and methine proton resonances (Table I). The high-field position of the methyl group resonance and low-field position of the C_8 methine proton strongly suggest that this

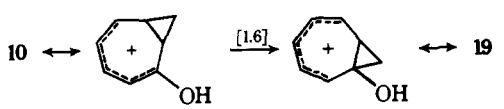


cation has the structure indicated by **22.** At temperatures above −50 °C **22** isomerizes rapidly to **21.** Endo-C_8-substituted homotropylium cations are known to be thermodynamically less stable than the corresponding exo isomers and the occurrence of such an endo → exo isomerization is well precedented.[1,21,22]

A single product was obtained on irradiation of **13** which was identified as **23** on the basis of its ^{1}H NMR spectrum. In this case it was not possible to generate **23** independently by protonation of the corresponding cyclooctatrienone **24.** This ketone exists very largely as its bicyclic valence tautomer **25,**[17] and **26** was produced on protonation of **25** in FSO_3H at very low temperatures.



Stereoselectivity of Photoisomerization. The photochemical isomerization of 2-hydroxyhomotropylium to 1-hydroxyhomotropylium cations described above can best be understood in terms of a circumambulatory rearrangement of the bridging C_8 carbon around the "seven-membered" ring. Alternative possibilities involving photoinduced hydride or methyl shifts cannot readily account for these isomerizations. Formally this circumambulation can be considered to involve a [1.6]-sigmatropic shift of a hydroxybicyclo[5.1.0]octadienyl cation and



in this regard it was of interest to determine the stereoselectivities of these photodriven circumambulations.

With the monomethyl substituted systems, the conversion of **11** to **21** is not particularly informative about the stereoselectivity of this type of conversion as both cations are the thermodynamically preferred isomers.[22] The same is not true of the photoisomerization of **12** to **22.** Analysis of the stereoselectivity of this rearrangement was complicated by the thermal instability of the product **22,** even at −70 °C, the limiting temperature of our photochemical equipment, and by the presence of **11** as an impurity which underwent photoisomerization to give **21** during the course of the experiment. To correct for the first factor, the rate of isomerization of **22** to **21** was measured at −70 °C ($k \approx 2 \times 10^{-5}$ s^{-1} at −70 °C). The photoisomerization of **12** was repeated at −70 °C and the composition of the solutions carefully determined by NMR spectroscopy (Table IV). After allowing for the thermal isomerization of **22** to **21,** the corrected composition of the final solution is shown in line 3 of Table IV. If the isomerization of **12** to **22** occurred with no loss of steric integrity at C_8, then the amount of **22** present after irradiation should correspond to the drop in concentration of **12** (Table IV, line 4). Thus the final solution should contain 31% of **22** but as is shown only 29% of **22** was produced, indicating that the photoisomerization of **12** to **22** occurred with a 94% stereoselectivity.

Table IV. Irradiation of **12** at −70 °C

	composition, %[a]			
	12	**22**	**11**	**21**
initial	79	0	21	0
after 4.5 h *hν*	48	26	12	14
corrected for thermal reaction	48	29	12	11
expected for completely stereoselective reaction	48	31	12	9

[a] Error ±1%.

It is thus clear that this circumambulatory rearrangement of hydroxyhomotropylium cations occurs with inversion of configuration at C_8, the migrating center, which gives an overall retention of stereochemistry at C_8. In other words, this photoinduced rearrangement proceeds very largely by the "bisected" transition state just as is preferred by orbital symmetry and least motion considerations.

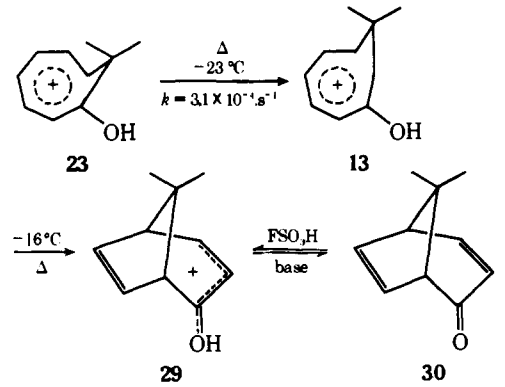
In passing it is of interest that Paquette and Cox[23] have reported that the parent homotropone **3** undergoes photoisomerization to give cyclooctatrienone among other products.

Thermal Isomerizations. During the course of this work a variety of thermal isomerizations of these hydroxyhomotropylium cations were encountered. One which has been referred to already is the isomerization of the *endo*-methyl-1-hydroxy cation **22** to the corresponding exo isomer. The rate constant for this reaction was measured at −39.5 °C and found to be 4.3×10^{-4} s^{-1} ($\Delta G^{\ddagger}$ = 17.1 kcal/mol). The much lower barrier to inversion of **22** as compared to that of the parent homotropylium cation **1** ($\Delta G^{\ddagger}$ = 22.3 kcal/mol)[24] or the corresponding conversion of **12** → **11** ($\Delta G^{\ddagger} > 27$ kcal/mol) can most reasonably be attributed to the stabilization of the planar cyclooctatrienyl cation transition state for the ring inversion process. The barrier to inversion of **22** to **21** is similar to that reported by Brookhart and Atwater for the 1-methoxyhomotropylium cation.[21]

The conversion of **22** to **21** did not proceed to completion but an equilibrium was set up between the two cations consisting of 6% **22** and 94% **21** at 0 °C. At 0 °C, the difference in energy between **22** and **21** is only 1.48 kcal/mol, which represents a much smaller energy difference than has been reported for other C_8 monosubstituted homotropylium cations.[22] Careful examination of the solution obtained on protonation of **7** in FSO_3H showed that a mixture of the same composition was formed.

At room temperature and above, **21** rearranged to give protonated propiophenone (**27**) ($k = 2.5 \times 10^{-4}$ s^{-1}, $\Delta G^{\ddagger}$ = 23.2 kcal/mol at 37 °C). The product **27** was identified by its ^{1}H NMR spectrum and its independent generation by protonation of propiophenone (**28**).

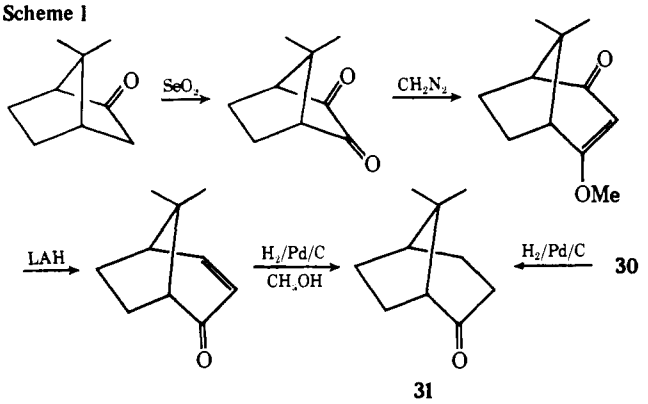
A much more complicated series of isomerizations took



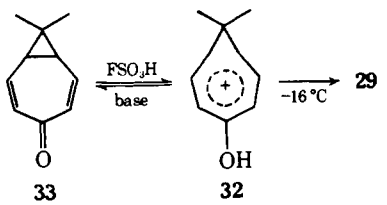
place with the C_8-dimethyl substituted systems. In the first place, cation **23** was found to isomerize back to **13** when heated to temperatures exceeding −30 °C ($k = 3.1 \times 10^{-4}\,s^{-1}$ at −23 °C). At somewhat higher temperatures **13** underwent a further series of reactions to give eventually a new cation **29.** Neutralization of the FSO_3H after this rearrangement had occurred led to the recovery of **30** in high yield.

The structure of **30** was suggested by its spectroscopic properties.[30] Confirmation of this structure was made by catalytic reduction of **30** to the known ketone **31.**[25] An authentic sample of **31** was prepared from fenchocamphorone by the route shown in Scheme I and found to be identical with that obtained by reduction of **30.**

Scheme I



Examination of the ^1H NMR spectra obtained during the course of the rearrangement of **13** to **29** showed that another species was present. This cation grew to a maximum concentration of 16% and subsequently decayed to **29** (Figure 1). Using spectral subtraction techniques it proved possible to obtain the ^1H NMR spectrum of this intermediate. The isomerization of **13** was stopped after about 1 half-life and on neutralization of the acid solution three ketones were obtained which were identified as **5, 30,** and **33.** The properties of **33** were entirely consistent with the symmetrical homotropone and **32** was regenerated on its protonation in FSO_3H. This cation had an identical spectrum with that obtained by the subtraction techniques. The cation **32** isomerized to **29** on warming to −16 °C. No **13** was detected during this isomerization.[19]



To gain further insight into the mechanism of these isomerizations, the rearrangements of the methyl-substituted cations **14** and **15** were examined. Cation **14** was prepared in an

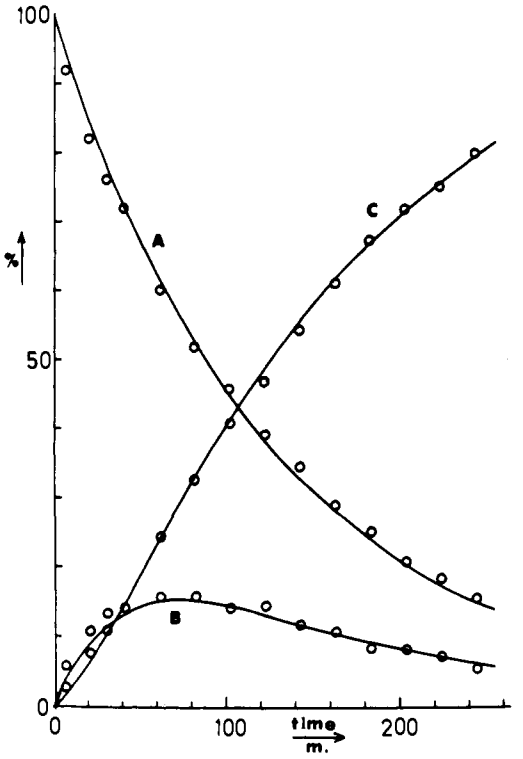
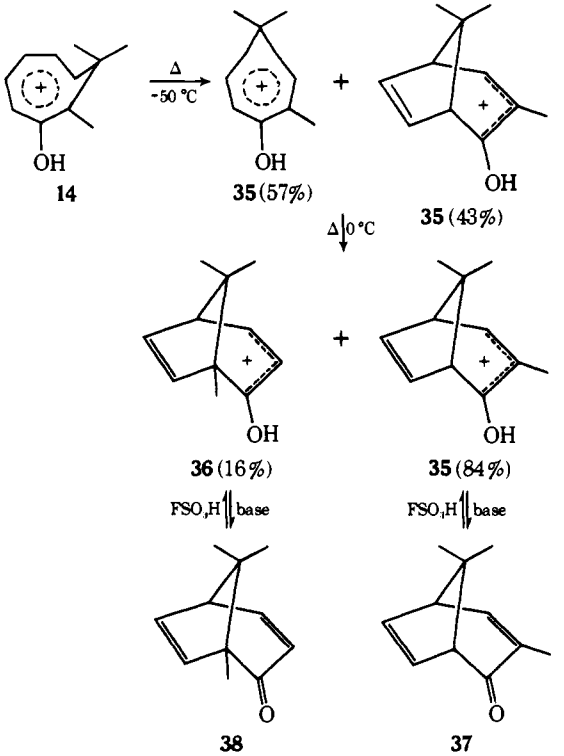


Figure 1. Rate of isomerization of **13.** Open circles (O), experimental data; solid lines, calculated concentrations. Curve A, decay of **13;** curve B, intermediate cation 32; curve C, final product **29.**

FSO_3H/SO_2 mixture and found to be stable at temperatures below −70 °C. On warming the solution to −50 °C for 1.5 h, **14** completely rearranged to a mixture of two ions which were identified as **34** (57%) and **35** (43%). Both **34** and **35** were stable at −50 °C; however, at higher temperatures **34** rearranged to give **35** and a small amount of an additional cation, **36.** The final composition of the solution obtained after 12 min at 0 °C was **35** (84%) and **36** (16%).

Neutralization of the acid solution of **35** and **36** gave the two ketones **37** and **38,** which were separated and characterized.

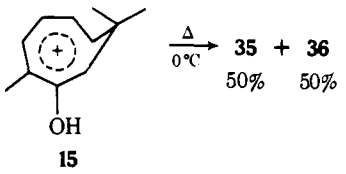


The properties of these ketones were very similar to that of **30**. The positions of the additional methyl groups were readily assigned on the basis of their ^{1}H NMR spectra (Table I). Protonation of **37** and **38** in FSO_3H gave **35** and **36**, respectively, the NMR spectra of which confirmed the structural assignments.

The structure of **34** is based upon its ^{1}H NMR spectrum (Table I), which was obtained by a series of spectral subtractions. The ^{1}H NMR spectra of **34** is very similar to that of **32**, differing in the replacement of a vinyl-proton resonance by a methyl-group signal.

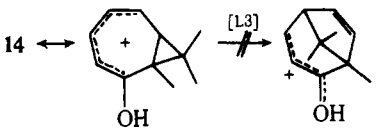
FSO_3H solutions of **35** and **36** were stable at 0 °C for the time periods involved in the isomerization of **14**. When left for longer times, further isomerizations of these cations were observed in their ^{1}H NMR spectra. However, there was no detectable interconversion of the two ions. As a result, it must be concluded that **36** comes from rearrangement of **34** and not directly from **14**. Examination of the composition of the solutions at the two stages of the rearrangement indicates that **34** rearranges to give **35** (72%) and **36** (28%).

The isomerization of **15** proceeded more slowly than that of **14**. After 30 min at −20 °C, only some 30% of **15** had rearranged. The same products were observed as were obtained from **14** but in different proportions. The higher temperatures required for the rearrangement of **15** meant that **34** was thermally labile and this product only built up to a 10% level during the reaction. On keeping the FSO_3H solution of **15** at 0 °C for 45 min, a 1:1 mixture of **35** and **36** was obtained.



15

These isomerizations of **14** and **15** provided information about the mechanism of the rearrangements of 8,8-dimethyl substituted homotropones. The thermal stability of **34** at −50 °C, at which temperature **35** is produced from **14**, rules out the possibility that **34** is an intermediate in the conversion of **14** to **35**. That is, the protonated 4,5-homotropones observed in the rearrangments of the protonated 2,3-homotropones do not lie on the direct pathway between the latter cations and the protonated bicyclo[3.2.1]octadienones. The results obtained with **14** and **15** also rule out the possibility that the protonated bicyclo[3.2.1]octadienones are produced directly from the protonated 2,3-homotropones by what could be regarded as a [1.3]-sigmatropic shift process. Such a pathway would require that **14** isomerize to give **36** at −50 °C and not **35** as has been observed.

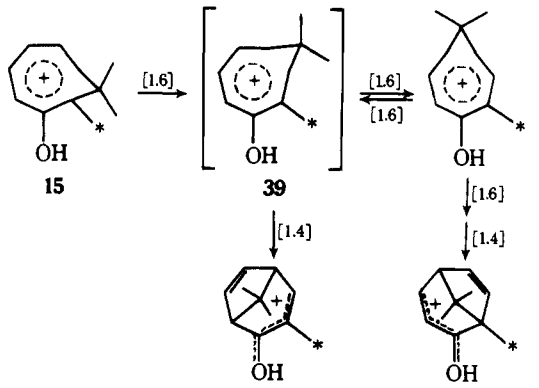


36

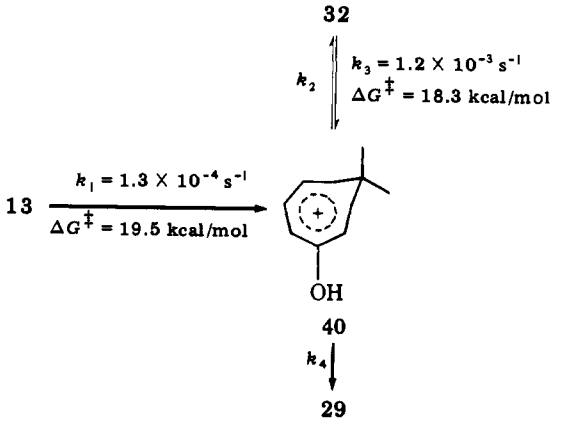
The simplest scheme which can account for the observed transformations is shown in Scheme II. (For brevity in this scheme the various resonance forms of the protonated homotropones have not been shown; however, the rearrangements can be thought of as proceeding via the bicyclo[5.1.0]octadienyl-type structures.) A 3-hydroxyhomotropylium cation is suggested as a key intermediate. This cation could either rearrange to give the protonated 4,5-homotropone or undergo a [1.4]-sigmatropic shift to give the bicyclooctadienones. Such a scheme fully accounts for the observations made with the methyl-labeled ions **14** and **15**.

The rate constants of the isomerizations of **13** were evaluated

Scheme II



Scheme III



all reactions at −16 °C

$k_2/k_4 = 2.5$

$k_2/k_3 > 100$

using a kinetics simulation program[26] and matching the observed and calculated time/concentration plots (Figure 1). For this approach it was necessary to assume a mechanistic scheme and one directly comparable to that shown in Scheme II was used. As a result, the rate constants presented here differ from those given in our preliminary publication where the straightforward isomerization path of **13** → **32** → **29** was used as a basis for the simulation. It was not possible to evaluate the exact magnitude of the two fast rate constants (k_2 and k_4) but only their relative magnitudes. The results obtained by this approach are shown in Scheme III.

The reactions described above of the 8,8-dimethyl substituted homotropylium cations provide several examples of thermally initiated circumambulatory rearrangements (e.g., **23** → **13** → **40** → **32**). It has been tacitly assumed in the previous discussion that these arrangements involve a single-step [1.6]-sigmatropic shift of C_8 around the periphery of the cycloheptadienyl resonance form of the homotropylium species. There are alternative multistep pathways possible which involve the stepwise movement of the cyclopropane; however, many of these are ruled out by the observed stability of the bicyclo[3.2.1]octadienyl systems. For example, the conversion of **13** to **32**, which could formally proceed by successive [1.3] shifts, is ruled out by the stability of **29**. Rather it would appear that these circumambulatory rearrangements proceed via the single-step migration of C_8 around the "seven-membered ring" in a [1.6]-sigmatropic shift. Just as the calculation of Hehre indicated, these circumambulatory shifts in homotropylium cations become energetically possible when C_8 bears charge-stabilizing groups.[5] Indeed the activation energies associated with these shifts are not far removed from the 13 kcal/mol figure estimated by Hehre.

The importance of substitution at C_8 for these circumam-

bulatory rearrangements can be seen by comparing the barrier to circumambulation of **23** → **13** with that of **21** → **11.** Cation **21** was observed to isomerize to **27** with a rate constant of 2.5×10^{-4} s^{-} at 37 °C. No **11** was detected during the course of this reaction even though **11** is known to be stable under these conditions. As the formation of 5% of **11** could be detected the rate of isomerization of **21** → **11** must be less than 1.25×10^{-5} s^{-1} at 37 °C, $\Delta G^{\ddagger} > 25.0$ kcal/mol. This $\Delta G^{\ddagger}$ should be compared to the comparable isomerization of **23** to **13** ($\Delta G^{\ddagger} = 18.5$ kcal/mol). The difference in free energy of 6.5 kcal/mol represents the minimum energy difference for the circumambulatory migration of C_8 with one and two methyl groups. The magnitude of this energy difference indicates that the localization of positive charge on C_8 is very substantial in the transition state for these migrations.[7] A similar charge localization has been found for the circumambulatory rearrangements of the bicyclo[3.1.0]hexenyl cations.[2,3]

In conclusion it is worth pointing out that the overall rearrangement of the hydroxyhomotropylium cations to protonated bicyclo[3.2.1]octadienones observed in this work has implications in terms of the energetic importance of homoaromaticity. The bicyclo[3.2.1]octadienyl cations have been considered to be "antibishomoaromatic" or at best nonaromatic cations[27] and yet in this work they are thermodynamically more stable than the hydroxyhomotropylium ions. We are currently examining the thermochemistry of these systems and will report on the results in a forthcoming paper.

Experimental Section

General. ^{1}H NMR spectra were obtained on Varian HA-100 and EM-390 instruments and both ^{1}H and ^{13}C NMR spectra with a Bruker WH90 instrument. Probe temperature was measured with a copper/constantan thermocouple or in the case of the EM-390 with a methanol sample. Spectral subtractions were carried out using the dual display overlay part of the Bruker FT NMR program. Proton chemical shifts in the acid solutions are referred to internal tetramethylammonium tetrafluoroborate taken as δ 3.10. UV and IR spectra were obtained using Cary 14 and Perkin-Elmer 283 instruments, respectively. Preparative GLC was performed on a Varian Aerograph A-90-P3 instrument fitted with either column A, 15% SE-30 on Chromosorb W, or column B, 15% Carbowax 20M on Chromosorb W. Protonation of the ketones in FSO_3H was achieved by adding cooled FSO_3H (~0.7 mL) to the ketone (10–20 mg) in an NMR tube kept at −78 °C. Solution of the ketone was achieved by stirring the acid with a thin glass rod.

Rate Measurements. These were carried out by following the isomerizations by ^{1}H NMR spectroscopy. The temperature of the probe was measured before and after the kinetic run. In all cases except the isomerization of **13 to 29,** the data were treated by a first-order kinetic treatment. For the **13** → **29** reaction, the time-concentration plots were matched using the kinetics program ZAUBER written by D. P. Santry.[26] A good estimate of the first-order decay of **13** was made on the basis of the available data and values of the other rate constants were varied until the calculated rate/concentration plot matched the experimental data.

Photoisomerizations were carried out using a Phillips SP 500-W superpressure mercury lamp using the apparatus previously described.[28] A Corning glass filter CS 0-51 (4 mm) was used for all the photoreactions. The samples were contained in 5-mm NMR tubes and the course of the reactions was followed by ^{1}H NMR spectroscopy directly on the irradiated samples. The solutions were not degassed.

Photoisomerization of 10. 2,3-Homotropone (**3,** 15 mg), in FSO_3H (0.75 mL) was irradiated for 6 h at −70 °C. The ^{1}H NMR spectrum of the solution after the irradiation showed **10** (75%) and **19** (25%) to be present. The FSO_3H solution was added to a stirred slurry of methanol (15 mL) and $NaHCO_3$ (2 g) at −78 °C; the temperature of solution was allowed to rise to 0 °C when water (20 mL) was added. The solution was extracted with ether (3 × 15 mL), the extracts were washed with water (10 mL) and dried (K_2CO_3), and the ether was evaporated through a short column. The ^{1}H NMR spectrum of the resulting oil showed **3** (80%) and **20** (20%) to be present.

Addition of Diazoethane to Tropone. A dried solution of diazoethane in ether (30 mL) (prepared by reaction of *N*-ethyl-*N*-nitrosourea (3.1 g) with aqueous NaOH)[29] was added to tropone[30] (2.0 g) and kept at −10 °C for 3 days. The ether was removed to give an oil (2 g). ^{1}H NMR analysis of the oil showed that it contained **7** (60%) and 8-methyl-2,3-homotropones **6** and **4.** The oil was chromatographed on neutral alumina, activity 2, using petroleum ether (30–60 °C)/ether mixtures. Elution of the column with 1% ether/petroleum ether gave a yellow fraction which on evaporation of the solvent gave **7** (^{1}H NMR, Table I).[14] Elution of the column with 5% ether/petroleum ether gave a second yellow fraction which yielded an oil on evaporation. Further purification of this second fraction was carried out using thick layer chromatography plates coated with silica gel (80–200 mesh). The plates were eluted with 5% ether/petroleum ether, the major yellow band was scraped off the plate, and the silica gel was extracted with ether. Evaporation of the ether and bulb-to-bulb distillation of the residue (100–120 °C, 8 mm) gave a yellow oil (150 mg) consisting of **6** (80–90%) and **4** (10–20%).

1,8,8- and 3,8,8-Trimethylbicyclo[5.1.0]octa-3,5-dien-2-ones (8 and 9). 2-Methylcycloheptatrienoneiron tricarbonyl (2.5 g), prepared by the reaction of 2-methylcycloheptatrienone[31] with iron enacarbonyl,[15] in ether (50 mL) was treated with an ether solution of diazopropane prepared from acetone hydrazone (15 g).[32] The reaction mixture was kept at 0 °C for 24 h. The ether was removed in vacuo to give a dark brown residue which was dissolved in toluene (50 mL) and refluxed for 20 min. The toluene was removed in vacuo and the residue chromatographed on neutral alumina (activity 2) eluting with a mixture of benzene (25%) in hexane (75%). The major orange band eluted was collected, and the solvent was evaporated in vacuo to give a thick oil (1 g) which was dissolved in anhydrous benzene (60 mL) and stirred for 18 h with anhydrous triethylamine *N*-oxide (2.5 g).[33] The mixture was filtered through Celite, the filtrate washed with water (3 × 25 mL) and dried over $MgSO_4$, and the solvent evaporated. The residue was chromatographed on neutral alumina (activity 2) eluting with 2% ether in petroleum ether. The first fraction gave on evaporation an oil which was distilled, bulb to bulb, 110–130 °C (10 mm), to give **8** as a yellow liquid (100 mg): IR (CS_2) 1642, 1615, 1394, 1378, 1336, 1199, 1078, 959, 873, 847, 793, 698 cm^{-1}; mass spectrum M^+ 162.1029 (calcd M^+ 162.1045).

The second fraction eluted from the column was **8** (~70%) plus **9** (~30%). This was purified by preparative GLC at 130 °C using column A to give **9** (retention time 20 min) as a yellow liquid, mass spectrum M^+ 162.1034 (calcd M^+ 162.1045).

8,8-Dimethylbicyclo[3.2.1]octa-3,6-dien-2-one (30). 8,8-Dimethylbicyclo[5.1.0]octa-3,5-dien-2-one (**5,** 0.5 g) dissolved in CH_2Cl_2 (3 mL) was added dropwise to FSO_3H (5 mL) which was stirred at −78 °C. The two-phase system was heated to 0 °C for 1.5 h, cooled to −78 °C, and added dropwise to rapidly stirred ice/water (100 mL) containing $NaHCO_3$ (15 g) kept at 0 °C. The resulting mixture was extracted with ether (3 × 20 mL), the ether extracts were combined and dried ($MgSO_4$), and the ether was removed by distillation to give an oily solid. Sublimation at 50 °C (10 mm) gave **30** as a pale yellow solid: mp 30–34 °C; 0.4 g; IR (film) 1680, 1370, 1303, 1260, 1234, 1160, 1113, 855 cm^{-1}. ^{13}C NMR (ppm from Me_4Si): 21.4, 26.6 (CH_3); 52.6, 67.8 (bridgehead); 125.3, 132.0, 145.4, 156.7 (vinyl); 216.9 (carbonyl).

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found, C, 81.23; H, 8.11.

8,8-Dimethylbicyclo[5.1.0]octa-2,5-dien-4-one (33). 8,8-Dimethylbicyclo[5.1.0]octa-3,5-dien-2-one (**5,** 0.1 g) dissolved in CH_2Cl_2 (1 mL) was added to rapidly stirred FSO_3H (2 mL) at −78 °C. The two-phase system was warmed to −16 °C for 1 h, cooled to −78 °C, and added dropwise to a stirred slurry of sodium bicarbonate (6 g) in methanol (20 mL) at −78 °C. The methanol slurry was allowed to warm to 0 °C and water (35 mL) added. The ketones present were extracted with ether (3 × 20 mL), the ether solution was dried ($MgSO_4$), and solvent was evaporated to give a yellow oil (70 mg). Preparative GLC (column A) at 130 °C gave **30** (retention time 4.2 min), **5** (retention time 8.7 min), and **33** (retention time 9.8 min) in a ratio 12:72:16. **33** was a pale yellow oil, mass spectrum M^+ 148.089 36 (calcd for $C_{10}H_{12}O$, 148.088 09).

8,8-Dimethylbicyclo[3.2.1]octan-2-one (31). 8,8-Dimethylbicyclo[3.2.0]octa-3,6-dien-2-one (**30,** 40 mg) in methanol (10 mL) was hydrogenated at room temperature and atomospheric pressure using 5% Pd/C catalyst (5 mg). The catalyst was removed by filtration through Celite and the methanol evaporated to give a pasty solid. Preparative GLC (column B) at 155 °C gave **31** (retention time 18

min), which was finally purified by sublimation at 100 °C (8 mm): yield of **31** 25 mg; mp 133.5–134.5 °C[25] (no depression on admixture with authentic material prepared below); IR (KBr) 1710, 1457, 1392, 1327, 1175 cm^{-1}, superimposable on IR spectrum of authentic sample; ^1H NMR (CS_2) δ 0.91, 0.97 (each 3 H, s, CH_3) 1.5–2.3 (10 H, m).

7,7-Dimethylbicyclo[2.2.1]heptane-2,3-dione.[34] α-Fenchocamphorone[35] (4 g) in acetic anhydride (10 mL) was refluxed for 8 h with SeO_2 (4 g). Additional SeO_2 (2 × 1 g) was added after 3- and 6-h reflux. The reaction mixture was cooled and filtered and the filtrate neutralized with aqueous Na_2CO_3. Extraction of the resulting solution with CH_2Cl_2 (3 × 15 mL) gave a yellow solution which was washed with water (2 × 10 mL) and dried ($MgSO_4$). Removal of the solvent gave a yellow solid which was purified by sublimation (100 °C, 10 mm) to give the title compound (1.2 g): mp 133–134.5 °C; IR (KBr) 1775, 1745, 1453, 1300, 1209, 1070, 980, 911, 782 cm^{-1}; ^1H NMR (CS_2) 1.14, 1.07 (each 3 H, s, CH_3), 1.63, 2.12, 2.43 (each 2 H, m, CH_2).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found, C, 70.77; H, 7.77.

4-Methoxy-8,8-dimethylbicyclo[3.2.1]oct-3-en-2-one.[36] The above compound (0.4 g) in benzene (2 mL) and methanol (1 mL) was treated with diazomethane in benzene (prepared by treatment of *N*-methyl-*N*-nitrosourea (1 g)). The solution was kept at 0 °C for 3 h and allowed to warm up to room temperature overnight. The solvent was evaporated and the residue chromatographed on alumina (activity 11) eluting with 25% ether in petroleum ether to give an oil. This was distilled (bulb to bulb 125 °C, 10 mm) to give the title compound (0.32 g): IR (film) 1665, 1607, 1378, 1226, 1209, 990, 828 cm^{-1}; ^1H NMR (CS_2) δ 0.97, 1.06 (each 3 H, s, CH_3), 1.35–2.25 (6 H, m, ring H), 3.63 (3 H, s, OCH_3), 4.90 (1 H, s, vinyl H).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.03; H, 9.01.

8,8-Dimethylbicyclo[3.2.1]oct-3-en-2-one. The previous compound (0.2 g) in anhydrous ether (4 mL) was added to $LiAlH_4$ (0.1 g) in ether (2 mL). The reaction mixture was stirred for 2.5 h at 25 °C and cooled to −10 °C and water (1.8 mL) and concentrated H_2SO_4 (1.8 mL) were added. The resulting mixture was stirred at −10 °C for 0.5 h, excess water was added (15 mL), and the organic materials were extracted into ether (2 × 10 mL). After the extract was dried (K_2CO_3), the ether was removed to give an oily solid. This was shown by GLC to consist of two compounds, the desired enone being the major 85% component. Purification by preparative GLC (column B) at 155 °C gave the title compound (retention time 18 min): 120 mg; mp 107–108 °C; IR (KBr) 1675, 1375, 1298, 1248, 1119, 840 cm^{-1}; ^1H NMR δ 0.94, 0.98 (each 3 H, s, CH_3), 1.47 (2 H, m), 2.18 (4 H, m), 5.72 (1 H, d, J = 10 Hz, C_3 H), 6.91 (1 H, dd, J = 10 and 7 Hz, C_4 H).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found, C, 79.58; H, 9.40.

8,8-Dimethylbicyclo[3.2.1]octan-2-one (Homoapocamphor, 31). The above enone (50 mg) in methanol (10 mL) was hydrogenated at room temperature and pressure using a 5% Pd/C catalyst. The solvent was evaporated after the catalyst had been removed by filtration through Celite. Purification was accomplished by preparative GLC (column B) at 155 °C to give **31** (25 mg), mp 133.5–134.5 °C, identical in all respects with the same material described above.

Rearrangement of 1,8,8-Trimethylbicyclo[5.1.0]octa-3,5-dien-2-one (14). Ketone **14** (100 mg) was dissolved in pentane (concentrated H_2SO_4 washed) (1 mL) and extracted in FSO_3H (1.5 mL) at −78 °C. The solution was warmed to 0 °C for 0.5 h, cooled to −78 °C, and poured into a rapidly stirred mixture of water (10 mL)/$NaHCO_3$ (3 g) at 0 °C. The product ketones were extracted into ether (3 × 7.5 mL), the extracts were dried (K_2CO_3), and the ether was evaporated to give an oily solid (75 mg). Preparative GLC (column A) at 115 °C showed two compounds to be present in a ratio of 85:15 and these were collected and shown to be **37** and **38**, respectively. **37**: IR (CS_2) 3028, 3022, 1680, 1369, 1347, 1308, 1262, 1217, 1163, 1072, 863, 799, 672, and 651 cm^{-1}; mass spectrum M^+ 162.1035 (calcd for $C_{11}H_{14}O$, 162.1045). **38**: IR (CS_2) 3065, 3038, 1681, 1369, 1364, 1094, 1060, 846, 801, 728, 670, cm^{-1}; mass spectrum M^+ 162.1036 (calcd for $C_{11}H_{14}O$, 162.1045).

Acknowledgment. We would like to thank Professor D. P. Santry for provision of the kinetic program ZAUBER prior to its publication, Mr. B. Sayer for the spectral subtraction work, and the National Science and Engineering Research Council of Canada for financial assistance.

Supplementary Material Available: Copies of spectra illustrating the photo- and thermal isomerization of **13** (2 pages). Ordering information is given on any current masthead page.

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