

polarization should be decreased since the polarization of the ketyl radicals can decay before it is transferred to K. These considerations are borne out by strong, unbroadened emission signals observed during irradiation of K in acidic solutions containing Q. This signal direction is compatible with the radical pair theory ($\mu, \epsilon, a_{CF_3} > 0; g_K > g_Q$), while the signal intensity follows the relative yield of triplet quenching (Figure 1) at quencher concentrations where no CIDNP effects are observed in the absence of acid.

We close with a comment on a recent report by Closs and Czeropski^{3f} who eliminated the interference of line broadening by accumulating the NMR data while interrupting the UV irradiation. This technique promises to be exceedingly useful. However, in the unique system K-Q the two effects carry different information: the line broadening reflects the yield of triplet quenching; the spin polarization is evidence for an unusual polarization mechanism. In this special case, elimination of the broadening would destroy essential information.

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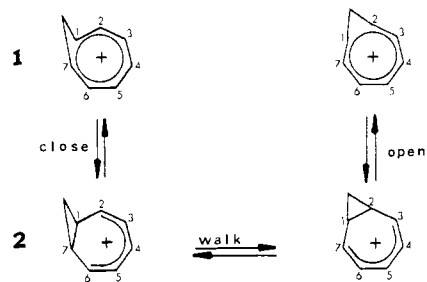
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Circumambulatory Rearrangements of 1,7-Bridged Homotropylium Cations

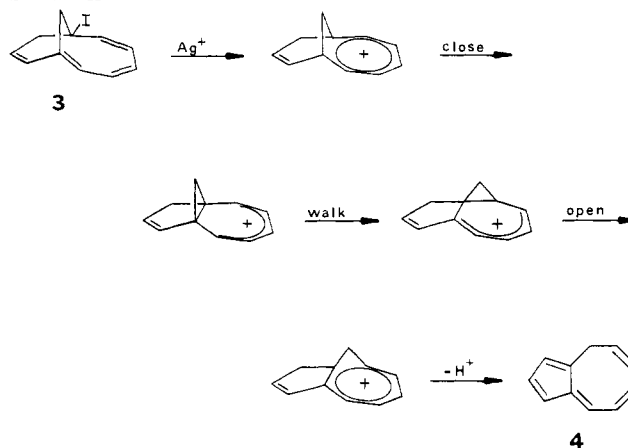
Sir:

Experimental studies by Berson and Jenkins¹ have established that thermal circumambulatory rearrangement of homotropylium cation (Scheme I) must be impeded by an energy barrier (ΔF^\ddagger) of at least 27 kcal/mol. On the basis of ab initio molecular orbital calculations, Hehre² estimates a value of fully 43 kcal/mol for this symmetry allowed process³ in the parent ion. Temporary disruption of aromaticity has been cited as a possible explanation for this high barrier;^{1,2} however, there still remains some disagreement⁴ as to whether the "open" structure **1** or the "closed" structure **2** better represents the preferred geometry for homotropylium cation.

Scheme I



Scheme II

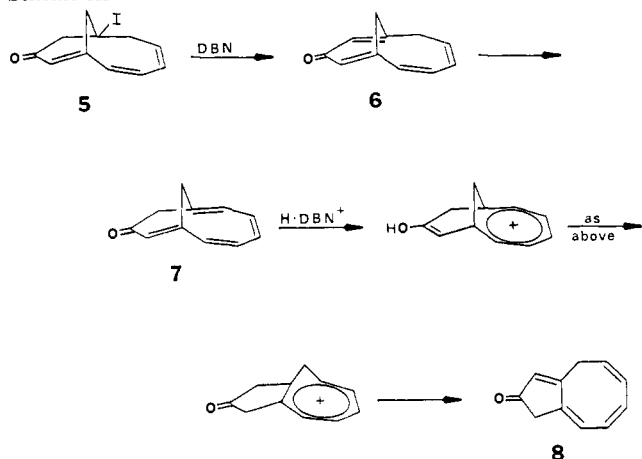


Until this year, the search for ground-state circumambulatory rearrangements in homotropylium cations has gone unrewarded.^{1,5} Success was finally achieved by Childs and Rogerson⁶ who prepared a homotropylium cation bearing substituents specifically designed to favor circumambulatory rearrangement by *electronic* effects. We have found that *steric* effects can also favor circumambulatory rearrangements in homotropylium cations and herein present evidence to support the following conclusions; (1) Homotropylium cations can be constrained in the closed form **2** by incorporation of an additional three-atom bridge across the homoconjugation gap, i.e., between positions 1 and 7 in **2** (cf. analogously constrained norcaradienes).⁷ (2) Circumambulatory rearrangement or "cyclopropane walk" in such closed homotropylium cations is an inherently facile process. (3) The large energy barrier to thermal circumambulatory rearrangement in unconstrained homotropylium cations, therefore, must be associated with the ring-closure step (**1** \rightarrow **2**, $\Delta F^\ddagger > 27$ kcal/mol). (4) It follows, then, that the open structure **1**, rather than the closed structure **2**, better represents the preferred ground-state geometry of unconstrained homotropylium cations.

Our concern with this problem arose inadvertently while exploring synthetic approaches to 1,5-methano[10]annulene.⁸ Thus, iodotetraene **3** was prepared⁹ and treated with various reagents in an effort to remove the elements of HI. With silver ion (AgOAc, acetone, 25 °C, 15 min) we found that iodide **3** gives pentaene **4**¹⁰ (39% yield), the formation of which might best be explained by the mechanism depicted in Scheme II. Ionization and ring closure may occur either sequentially, as illustrated, or concertedly;¹¹ however, the subsequent cyclopropane walk¹² must proceed with little difficulty for neither lower temperature (0 °C) nor added base (*i*-Pr₂NEt) suppresses this unwelcomed rearrangement.

An analogous rearrangement was observed on treatment of iodotrienone **5**¹³ with mild base (DBN, CHCl₃, 25 °C, 5 min). Scheme III outlines a mechanism which could account for the formation of tetraenone **8**¹⁴ in this reaction (85% yield). Presumably, elimination of HI from **5** produces the desired tetraenone **7**, either directly or via **6**, but subsequent proton

Scheme III



transfer from the conjugate acid of DBN generates a bridged homotropylum cation capable of circumambulatory rearrangement as in Schemes I and II. In agreement with this mechanism, it was found that rearrangement to **8** can be completely avoided by use of the stronger base (weaker conjugate acid) *i*-Pr₂NLi in THF. Under these conditions, however, only dimeric products could be isolated.

In sum, we have discovered two unexpected skeletal reorganizations which can reasonably be explained by circumambulatory rearrangements of homotropylum cations. Although lacking *direct* experimental evidence for the intermediates postulated in Schemes II and III, we believe our results strongly support the conclusions enumerated above.

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Supplementary Material Available: A more thorough discussion of the structural assignments for compounds **4** and **8**, including hydrogenation of **4** and Eu-shift studies on **8** (5 pages). Ordering information is given on any current masthead page.

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- 7-Iodobicyclo[5.3.1]undeca-1,3,5,9-tetraene (**3**) was prepared from tricyclo[5.3.1.0^{1,7}]undeca-2,4,9-triene⁸ (I₂, Cu(OAc)₂, HOAc; then CF₃COOH, CHCl₃; 53% yield); ¹H NMR (CCl₄ (Δ 2/5)) [br d, J = 18 Hz, 1 H of CH₂C=C, 2.65 (d, J = 9 Hz, 1 bridging H), 2.92 (d, J = 9 Hz, 1 bridging H), 3.08 (d of t, J = 2, 18 Hz, 1 H of CH₂C=C), 5.3–5.6 (m, 1 vinyl H), 5.8–6.3 (m, 6 vinyl H's); IR (neat) 3070 (m), 2960 (m), 1625 (w), 1615 (w), 1405 (m), 1295 (m), 1129 (s), 962 (m), 906 (m), 868 (m), 786 (m), 740 (s), 722 (s), 696 (s, br) cm⁻¹; UV (hexane) λ_{max} 223 nm (ε 18 000), 319 (4600); mass spectrum parent peak, *m/e* 270.
- Bicyclo[6.3.0]undeca-1,3,5,8,10-pentaene (**4**): ¹⁵NMR (CCl₄) δ 2.90 (d, J = 7 Hz, 2 H), 5.4–6.8 (m, 8 H); IR (neat) 3080 (m), 3000 (m), 1630 (m), 1495 (s), 1435 (m), 1340 (s), 1200 (s), 1110 (m), 782 (s), 765 (vs), 734 (s), and 694 cm⁻¹ (m); UV (ethanol) λ_{max} 232 nm (ε 12 700), 255 (sh, 7200), 323 (6500), 420 (br sh, 270); mass spectrum parent peak, *m/e* 142. Of the seven possible double-bond isomers of this ring system, five have previously been reported: D. Schönleber, *Chem. Ber.*, **102**, 1789 (1969); H. Dürr and G. Scheppers, *ibid.*, **103**, 380 (1970).
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- Cyclopropane walk in the opposite direction would lead to the same product via a less fully conjugated tricyclic cation.
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- Bicyclo[6.3.0]undeca-1,3,5,8-tetraen-10-one (**8**): ¹⁵NMR (CCl₄) δ 2.92 (s, 2 H, CH₂C=O), 3.25 (d, J = 7 Hz, 2 H, CH₂CH=C), 5.5–6.25 (m, 6 vinyl H); IR (neat) 3040 (m), 2990 (w), 1670 (vs), 1560 (vs), 1425 (m), 1378 (m), 1220 (s), 1200 (s), 933 (m), 855 (m), 836 (m), 792 (m), 755 (vs), 719 (m) cm⁻¹; UV (hexane) λ_{max} 246, 303 nm; mass spectrum *m/e* (rel intensity) 158 (38), 157 (32), 131 (20), 130 (74), 129 (100), 128 (62), 127 (26), 117 (16), 116 (54), 115 (100), 103 (18), 91 (25), 77 (33).
- See paragraph at end of this paper regarding supplementary material.

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Stereospecific Total Synthesis of *dl*-Pentalenolactone

Sir:

The sesquiterpene antibiotic, tumor inhibitory agent, pentalenolactone (**1**) is a member of a growing class of pentalenopyranones which includes pentalenolactone G^{1a} and quadron.^{1b} It may also be perceived as bearing a structural similarity to the hirsutanes^{1c} and to coriolin.^{1d} The structure of pentalenolactone was deduced, by an Upjohn group^{2a} by crystallographic analysis of its tetrahydrobromohydrin derivative, whose relationship to the natural product was ascertained by spectroscopic methods.^{2b}

The challenges inherent in an enterprise of total synthesis directed at pentalenolactone are apparent on inspection of its compactly housed functionality, and recognition of its five centers of chirality. A stereospecific total synthesis of *dl*-pentalenolactone (**1**) is described herein.

Our operating strategy, rested on the assumption that prototropically dependent transformations of an intermediate such as **19** might be differentiable, so as to allow for its conversion to **24**, and that, in some way, the properly configured epoxy-methylene group could be obtained from **24** (Scheme I). We thus sought an intermediate bearing, implicitly, the essential stereochemical information for reaching **19** through a variety of possibilities. We envisioned that compound **6** would fulfill these criteria and it was with the synthesis of this substance that we were first concerned.

Compound **2**,³ itself readily available through the Diels-Alder reaction of dimethyl acetylenedicarboxylate with cyclopentadiene, was transformed into **3**^{4,5} by the indicated steps^{6–8} in 46% overall yield. Compound **3** now served as a dienophile toward the diene, **4**, in whose development our

Scheme I

