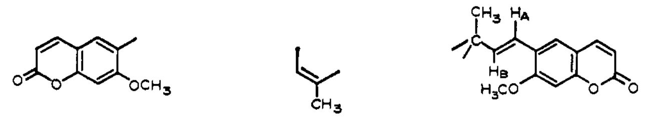
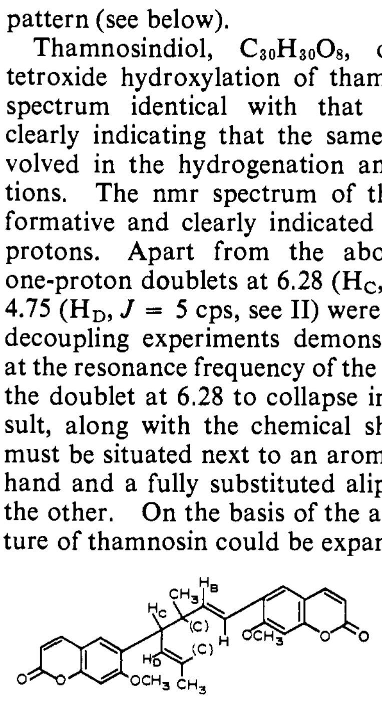


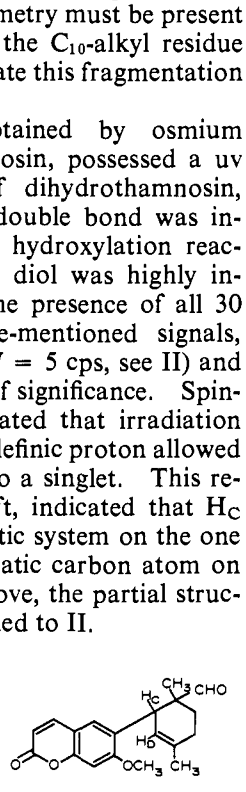
I

It is appropriate to note at this time that the mass spectrum of thamnosin was very striking, since there were virtually no peaks between the molecular ion (*m/e* 484, 8% abundance) and the base peak (*m/e* 242). This important result suggested that thamnosin was cleaved, under electron impact, into two equal halves, and therefore some structural symmetry must be present in this molecule. The nature of the C_{10}-alkyl residue mentioned above must accommodate this fragmentation pattern (see below).

Thamnosindiol, $C_{30}H_{30}O_8$, obtained by osmium tetroxide hydroxylation of thamnosin, possessed a uv spectrum identical with that of dihydrothamnosin, clearly indicating that the same double bond was involved in the hydrogenation and hydroxylation reactions. The nmr spectrum of the diol was highly informative and clearly indicated the presence of all 30 protons. Apart from the above-mentioned signals, one-proton doublets at 6.28 (H_C, J = 5 cps, see II) and 4.75 (H_D, J = 5 cps, see II) were of significance. Spin-decoupling experiments demonstrated that irradiation at the resonance frequency of the olefinic proton allowed the doublet at 6.28 to collapse into a singlet. This result, along with the chemical shift, indicated that H_C must be situated next to an aromatic system on the one hand and a fully substituted aliphatic carbon atom on the other. On the basis of the above, the partial structure of thamnosin could be expanded to II.



II

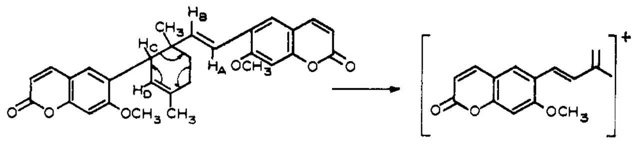


III

Periodic acid oxidation of thamnosindiol provided two aldehydic compounds designated as aldehyde I and aldehyde II. High-resolution mass spectra of these compounds established their molecular formulas as $C_{11}H_8O_4$ and $C_{19}H_{20}O_4$, respectively, and provided conclusive evidence that this reaction cleaves the diol into two compounds *without* any loss of carbon.

Aldehyde I, λ_{max}^{MeOH} 255, 308, and 329 mμ, nmr [$(CF_2Cl)_2C(OD)_2$] −0.23 (Ar-*CHO*), 6.01 (CH_3O), was tentatively assigned the structure 7-methoxycoumarin-6-carboxaldehyde and this was established by comparison (mixture melting point, tlc, superimposable uv and ir spectra) with an authentic sample.[5]

Aldehyde II resisted crystallization, but data were obtained on tlc-pure material: ir 1720 and 1615 cm^{-1} (coumarin, saturated aldehyde); uv λ_{max}^{MeOH} 229, 254 (sh), 296 (sh), and 328 mμ; nmr signals: 0.73 (1 H, singlet, CHO), 2.45 (1 H, doublet, J = 9.5 cps, H–C_4 of coumarin), 2.85 (1 H, singlet, H–C_5 of coumarin), 3.31 (1 H, singlet, H–C_8 of coumarin), 3.84 (1 H, doublet, J = 9.5 cps, H–C_3 of coumarin), 4.76 (1 H, multiplet, $H_DC{=}C{-}$), 5.84 (1 H, doublet, $H_CC<$), 6.2 (3 H, singlet, CH_3O–C_7 of coumarin), 8.21 (3 H, singlet, $CH_3C{=}C{-}$), 8.82 (3 H, singlet, $CH_3C<$). These data, when taken in conjunction with the above results (only C_2H_4 and one degree of unsaturation still remain unaccounted in thamnosin), establish structure III for aldehyde II and, in turn, IV for thamnosin.



IV V

The mass spectrum of thamnosin is now readily explained by the well-known retro-Diels–Alder fragmentation process as indicated in IV → V (*m/e* 242). It is to be noted that such a fragmentation would be expected to be extremely facile in this instance, since benzylic and allylic bonds are involved and a highly stabilized ion (V) results. In fact, on the basis of the mass spectrum, structure IV was strongly favored even before much of the above data had been accumulated.

Numerous confirmatory experiments (epoxidation, further reduction, ozonization, etc.) were conducted to support the above proposals, but these will be presented in our detailed paper. In brief, the most important experiment in this regard involved controlled ozonolysis of dihydrothamnosin followed by catalytic reduction of the ozonide to yield a *single* compound which from spectral data was shown to be a keto aldehyde. In particular, nmr signals for the aldehydic proton (0.02, 1 H, doublet, J = 2 cps), a methyl ketone (7.87, 3 H, singlet), and the proton H_C (see IV) which appeared as a doublet (5.76, J = 2 cps, $>CH_CCHO$) should be noted. Decoupling experiments established that the carbon atom bearing H_C in thamnosin could only be connected to an aromatic system, a tetrasubstituted carbon atom, and a trisubstituted double bond whose olefinic proton was in turn coupled with H_C. The formation of the keto aldehyde, therefore, conclusively established the presence of the trisubstituted double bond in a cyclohexene system as postulated in IV.

Thamnosin represents a novel system which to the best of our knowledge has not been previously encountered in any natural source. A biosynthetic study on this molecule could be very interesting and is anticipated.

Acknowledgment. Financial aid from the National Research Council of Canada is gratefully acknowledged.

---

(5) We are very grateful to Dr. F. E. King, Forest Products Research Laboratory, Aylesbury, Bucks, England, for supplying us with an authentic sample.

(6) Enquiries about this work should be directed to this author.

James P. Kutney,[6] Tadanobu Inaba
Chemistry Department, University of British Columbia
Vancouver 8, Canada

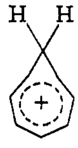
David L. Dreyer
Fruit and Vegetable Chemistry Laboratory
U. S. Department of Agriculture
Pasadena, California

Received November 27, 1967

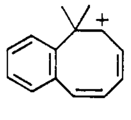
A Benzohomotropylium Cation

Sir:

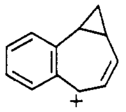
The inclusion of the homoallylic interaction in the homotropylium cation I allows for the explanation of two unusual and significant features displayed by this system.[1] It allows for the formation of an aromatic π-electron system which is now stable enough so that salts of the cation can be isolated; in common with a very select few other such carbonium ions the species can coexist with an anion without the benefit of solvation forces. Secondly, the extraordinarily large difference in chemical shift (5.8 ppm) displayed by the two methylene protons can be readily interpreted as being due to the system possessing an aromatic ring current associated with the homoallylic bond. It was earlier shown that cation I is readily formed following addition of a proton to cyclooctatetraene;[1] we wish to report now the extension of those studies to the protonation of benzocyclooctatetraene.



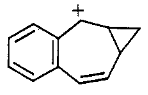
I



II



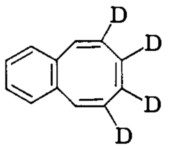
III



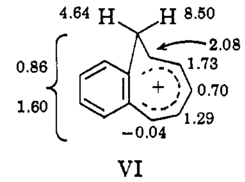
IV

Both simple perturbation MO theory[2] and SCF MO theory[3] predict that protonation of benzocyclooctatetraene should occur at C_8 to yield the cation II. If, however, homoallylic interactions were to be significant, then structures III and IV would have to be considered as possible products of protonation. Stabilization of cationic centers by cyclopropyl groups is well known, and III and IV are homoaromatic systems in which the contribution by the σ-bonded canonical form is represented.

Benzocyclooctatetraene was prepared as described earlier[4] by addition of cyclobutadiene to benzocyclobutadiene followed by isomerization of the resulting benzotricyclooctadiene. The nmr spectrum of benzocyclooctatetraene in H_2SO_4 consisted of a doublet at τ -0.04 (area 1), a complex set of bands in the range 0.7–2.1 (area 8), a quartet at 4.64 (area 1), and a triplet at 8.50 (area 1). In order to better understand the spectrum, 4,5,6,7-tetradeuteriobenzocyclooctatetraene (V) was prepared using the synthesis previously mentioned but employing tetradeuteriocyclobutadieneiron tricarbonyl in place of cyclobutadieneiron tricarbonyl.[5]



V

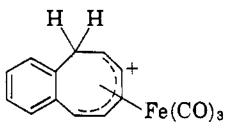


VI

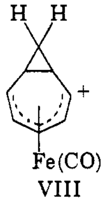
The simplified spectrum of compound V in H_2SO_4 and D_2SO_4, together with decoupling experiments, allows an assignment to be made of the chemical shifts to the protons of interest.[6] In particular compound V in H_2SO_4 displays absorption at τ 4.6 and 8.5, both absorptions being doublets (J = 10.4 cps for each) and each having an area equivalent to one proton. The absorption at τ -0.04 is also present and is now a singlet, whereas in the parent system this appeared as a doublet. In D_2SO_4 (98%) it is readily seen that deprotonation of the cation did not occur.

The data are consistent with a nonplanar formulation VI for the cation with the assignments as indicated. When compound V is dissolved in D_2SO_4 at ~0° and the spectrum obtained rapidly, the absorption at τ 8.5 is almost zero in area, but at room temperature this rapidly increases in intensity to a value of 0.5 with a corresponding decrease in intensity of absorption at τ 4.6 from 1 to 0.5. Protonation therefore takes place such that the added proton initially becomes the inside proton (H_a), but ring inversion occurs and protons H_a and H_b become exchanged *via* this intramolecular process. Similar effects have been previously observed for the parent system I.[7]

Protonation of benzocyclooctatetraene therefore adds in the manner expected based on the classical system; however, three independent features point to a homoallylic bond existing between carbons 1 and 7 in the cation. First, the large difference in chemical shift between protons H_a and H_b (3.9 ppm) suggests the presence of a ring current. Part of this difference could result from the nonsymmetrical disposition of H_a and H_b with respect to the benzene nucleus. However, it might be noted that in the iron carbonyl complex of the cation VII[8] the difference in chemical shift between H_a and H_b is only 1.6 ppm and in the complex VIII[9] the difference between H_a and H_b is small (0.18 ppm), indicating a very small anisotropic effect of the pentadienyliron tricarbonyl unit in the region of interest. Assuming similar geometries for the cations VI and VII the effect of the benzene ring alone would not then account for the difference of 3.9 ppm for the methylene protons in VI.



VII



VIII

A second feature is associated with the coupling constants of H_a and H_b in VI. In the metal carbonyl complex VIII[9] there appears to be no ring current present and J_{ab} = 4.86 cps, which is in the normal range of such cyclopropane protons. In the complex VII J_{ab} = 14.0 cps, which is again normal for nonstrained methylene protons.[10] In the cation I and VI the J_{ab} coupling constants are in intermediate ranges between fully formed cyclopropyl systems and acyclic methylenes, *viz.*, 6.7 and 10.4 cps, respectively. Finally the uv spectrum of the cation VI bears a very strong similarity to that of the benzotropylium cation: the absorption

---

[1] J. L. von Rosenberg, Jr., J. E. Mahler, and R. Pettit, *J. Am. Chem. Soc.*, **84**, 2842 (1962).

[2] M. J. S. Dewar, *ibid.*, **74**, 3357 (1952).

[3] M. J. S. Dewar and J. A. Hashmall, private communication.

[4] W. Merk and R. Pettit, *J. Am. Chem. Soc.*, **89**, 4787 (1967).

[5] J. C. Barborak and R. Pettit, *ibid.*, **89**, 3080 (1967).

[6] The full details of V in acid are (a) in D_2SO_4 τ -0.04 (s) (1 H), 0.86–1.60 (m) (4 H), 4.64 (s) (0.5 H), 8.50 (s) (0.5 H); (b) in H_2SO_4 -0.04 (s) (1 H), 0.86–1.60 (m) (4 H), 4.64 (d) (1 H), and 8.50 (d) (1 H).

[7] S. Winstein, C. G. Kreiter, and J. I. Brauman, *J. Am. Chem. Soc.*, **88**, 3047 (1966).

[8] Prepared by protonation of benzocyclooctatetraeneiron tricarbonyl which in turn was prepared from the reaction of benzocyclooctatetraene with $Fe(CO)_5$: W. Merk and R. Pettit, unpublished.

[9] A. Davison, W. McFarland, L. Pratt, and J. Wilkinson, *J. Chem. Soc.*, 4821 (1962).

[10] The coupling constants of *gem*-cyclopropyl protons typically range between 3.1 and 6.0 cps [D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3218 (1963)], while nonstrained methylene protons are between 12 and 15 cps [J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965].

maxima (and log ε values) of the former occur at 233 (4.25), 280 (3.91), 315 (3.38), and 400 mμ (3.43), while for the latter cation they appear at 234 (4.30), 282 (4.74), 338 (3.54), and 426 mμ (3.25).[11,12]

Evidence therefore suggests that cation VI does possess a homoaromatic structure; however, as might be expected, the presence of the benzene ring strongly dampens the extent of the homoallylic interaction.

(11) H. H. Rennhard, E. Heilbronner, and A. Eschenmoser, *Chem. Ind.* (London), 415 (1955).

(12) The resemblance to the uv spectrum of the benzotropylium cation is closer than that which is shown by the bicyclo[5.4.1]dodecapentaenylium cation: W. Grimme, H. Hoffmann, and E. Vogel, *Angew. Chem.*, 77, 348 (1965).

(13) We thank the National Science Foundation, the U. S. Army Research Office (Durham), and the Robert A. Welch Foundation for financial support. We also thank Badische Anilin und Soda Fabrik and General Aniline and Film Corporation for generous gifts of cyclooctatetraene and iron carbonyl, respectively.

W. Merk, R. Pettit[13]
Department of Chemistry, The University of Texas
Austin, Texas 78712

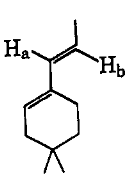
Received December 13, 1967

Concerning the Structure of "Isomeric" Molecular Ions of Unsaturated Hydrocarbons

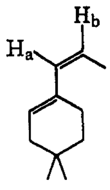
Sir:

One of the more intriguing problems connected with electron-impact fragmentation mechanisms is concerned with the nature of "isomeric" molecular ions. *cis–trans* isomeric olefins often give essentially identical mass spectra, and the view has been expressed that the isomerism is eliminated in the ionized molecules due to rotation about the electron-deficient π bond.[1] In addition it has been observed that the relative abundances of the molecular ions of *cis* olefins are smaller than those of the corresponding *trans* isomers when the latter are more stable by at least 2–3 kcal/mole.[1c] This was explained on the basis of the disappearance of the isomerism in the molecular ion; the energy resulting from steric hindrance in the *cis* isomer would thereby be released and used in the decomposition processes.[1c] However, these data are not incompatible with the decomposition of molecular ions which maintain the geometric integrity of the un-ionized molecules. More recently Smith and Thornton have studied the retro-Diels–Alder (RDA) reaction of 4-vinylcyclohexene; the possibility of isomeric activated complexes (*e.g.*, *s-cis* and *s-trans*) was considered.[2] We wish to present evidence that the conformation of an olefinic side chain can markedly influence the course of the RDA fragmentation of cyclohexene derivatives.

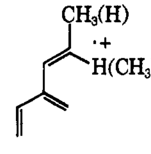
The compounds chosen for study were *trans*- and *cis*-1-propenylcyclohexenes (**1** and **2**, respectively).[3] Dreiding models clearly indicate that large nonbonded repulsions exist in conformations of **2** in which the double bonds are coplanar. Strong evidence for a more twisted *s-trans* conformation in the *cis* isomer than in the *trans* isomer is provided by the ultraviolet spectra; **1** has λ_{max} 232.5 mμ (ε 19,200), whereas **2** has λ_{max} 224.5 mμ (ε 13,700) (both in hexane).[4] In addition, the nmr doublet for H_a, located at τ 3.88 and 4.15 for **1** (J_{ab} = 16.0 Hz), is shifted upfield to τ 4.21 and 4.40 for **2** (J_{ab} = 11.5 Hz); the two nmr spectra are virtually identical in all other respects. This shift is interpreted as resulting from H_a in the *cis* isomer being affected less by the anisotropy of the endocyclic π bond due to the fact that it is twisted farther out of the nodal plane of the bond.[5] The infrared spectra provide further evidence for these relative conformations; the *trans* isomer shows a sharp unsymmetrical doublet at 1650 and 1625 cm^{-1} due to vibrational coupling of the double bonds[6] while the *cis* isomer shows only a single broadened peak at 1638 cm^{-1}, the coupling having been largely eliminated by the twisting.



1



2



m/e 94

3

m/e 56

4

Another manifestation of the twisted equilibrium conformation of **2** is the free energy of isomerization of 3.0 ± 0.25 kcal/mole at 25.0° for the conversion **1** → **2**. This was determined by equilibrium studies (starting from each side of the equilibrium mixture) in solutions of 0.5 *N* potassium *t*-butoxide in hexamethylphosphoramide.[7] This result constitutes further evidence for a significant π delocalization energy in dienes[8] since the nonbonded repulsions can be greatly reduced by twisting the propenyl group, but only at the expense of decreased π overlap.

The greater stability of the *trans* isomer is, as expected, reflected in the greater relative abundance (% Σ_{27}) of its molecular ion (8.20) relative to that of the *cis* isomer (6.72).[9] In addition, these dienes display the expected odd-electron fragments at *m/e* 94 (the base peak) and 56 which result from the RDA reaction.[10]

Since Hückel molecular orbital calculations indicate that the π-electron energy of ion **3** decreases to a greater extent with twisting of the propenyl group than does that of the corresponding neutral fragment,[11] the degree of departure from coplanarity of the propenyl group in the activated complexes for the respective RDA reac-

---

(1) (a) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 151; (b) J. Momigny, *Nature*, **191**, 1089 (1961); (c) P. Natalis in "Mass Spectrometry," R. I. Reed, Ed., Academic Press Inc., New York, N. Y., 1965, p 379, and references cited therein.

(2) E. P. Smith and E. R. Thornton, *J. Am. Chem. Soc.*, **89**, 5079 (1967).

(3) All new compounds have been fully characterized; syntheses will be published at a later time.

(4) A λ_{max} of 232 mμ is predicted for these dienes using empirical rules: R. B. Woodward, *J. Am. Chem. Soc.*, **64**, 72 (1942). For a closely related pair of isomers see E. N. Marvell and J. Tashiro, *J. Org. Chem.*, 30, 3991 (1965).

(5) J. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, p 129.

(6) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1964, p 40.

(7) S. Bank, A. Schriesheim, and C. A. Rowe, Jr., *J. Am. Chem. Soc.*, **87**, 3244 (1965).

(8) (a) S. W. Staley, *ibid.*, **89**, 1532 (1967); (b) P. S. Carleton, Ph.D. Thesis, Yale University, 1966. The study by Carleton (and W. von E. Doering) involved sterically hindered styryl derivatives.

(9) These values (corrected for isotopes) were obtained at 70 eV using an LKB 9000 mass spectrometer. A Varian M-66 instrument (utilizing a different geometry) gave very similar results.

(10) (a) H. Budzikiewicz, J. I. Brauman, and C. Djerassi, *Tetrahedron*, **21**, 1855 (1959); (b) T. J. Kinstle and R. E. Stark, *J. Org. Chem.*, **32**, 1318 (1967).

(11) The π-electron energies of the ions were calculated using the ω technique (A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 115) and utilizing a computer program written by J. P. Erdman of this laboratory.