posed β-elimination mechanism.

(8) S. B. Horwitz and P. B. Schiff, Albert Einstein College of Medicine, personal communication.

(9) Note Added in Proof. A recent total synthesis of racemic steganone via isosteganone has been achieved by L. R. Hughes and R. A. Raphael, *Tetrahedron Lett.*, 1543 (1976). Professor Raphael has kindly informed us that the spectroscopic and chemical properties of their isosteganone, as well as their independent x-ray structure determination of isosteganol, are in full accord with our results.

Andrew S. Kende,* Lanny S. Liebeskind
Clifford Kubiak, Richard Eisenberg
Department of Chemistry, University of Rochester
Rochester, New York 14627

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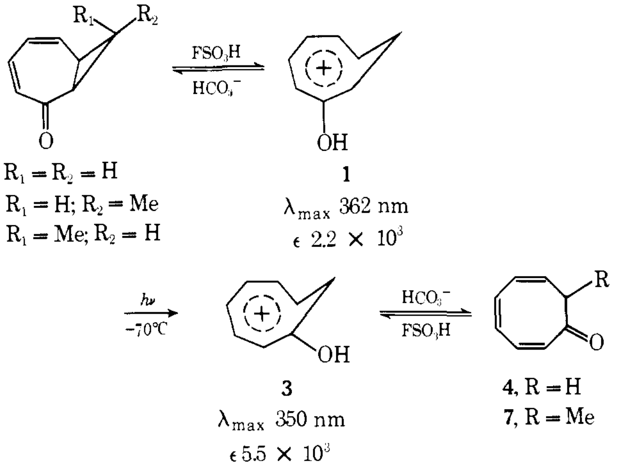
Circumambulatory Rearrangements of Homotropylium Cations: Photoisomerization of 2-Hydroxyhomotropylium Cations[1]

Sir:

While the thermally induced circumambulations of a cyclopropyl around the periphery of the five-membered ring of a bicyclo[3.1.0]hexenyl cation are well known,[2] comparable peregrinations have not been detected with homotropylium cations.[3] Previous attempts to detect such a degenerate rearrangement of homotropylium cations have been restricted to the ground-state manifold;[3] however, there is good reason to expect on the basis of a consideration of least motion[4] and orbital symmetry[5] that such a reaction would be more likely to occur in the first excited state. To this end we have examined the photochemistry of some labeled homotropylium cations and report here our results with the 2-hydroxy systems.[6]

The 2-hydroxyhomotropylium cation (**1**), generated by the protonation of **2** in FSO_3H,[7] was irradiated at −70 °C with light of wavelength greater than 360 nm.[8] Only one product could be detected by ^1H NMR and this was shown to be **3** on the basis of its spectrum.[9] Cyclooctatrienone (**4**) was recovered on neutralization of the acid solution of the photoproduct. Under the conditions of the photoisomerization, **3** was both thermally and photochemically stable.



2, $R_1 = R_2 = H$
5, $R_1 = H$; $R_2 = Me$
6, $R_1 = Me$; $R_2 = H$

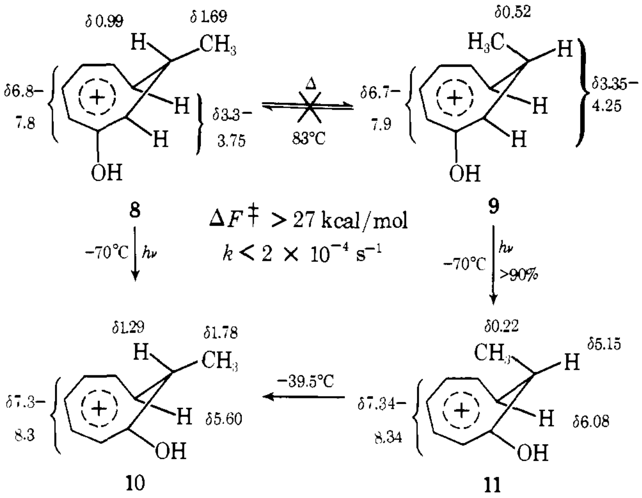
1
λ_{max} 362 nm
ϵ 2.2 × 10^3

3
λ_{max} 350 nm
ϵ 5.5 × 10^3

4, R = H
7, R = Me

In order to label the methylene carbon of **1**, the methyl-substituted cations were prepared by the protonation of the corresponding homotropones **5** and **6**. Contrary to a previous report,[10] the addition of diazoethane to tropone gives not only **7** but also substantial amounts of **6** and a smaller proportion of **5**. Separation of these isomers was difficult, but by a combination of column and thick-layer chromatography, samples of **6** containing some 10–20% of **5** were obtained. The exo isomer **5** was prepared using a comparable procedure to thay recently described.[11]

Dissolution of **5** and **6** in FSO_3H gave cations **8** and **9**, respectively, each of which exhibited a ^1H NMR spectrum completely consistent with the assigned structures. The acid solutions of **8** and **9** were stable up to 80 °C. At this temperature each underwent a general decomposition without there being any evidence for the interconversion of **8** and **9**.



$\Delta F^{\ddagger} > 27$ kcal/mol
$k < 2 \times 10^{-4}\ s^{-1}$

$k = (4.3 \pm 0.3) \times 10^{-4}\ s^{-1}$
$\Delta F^{\ddagger} = 17.1$ kcal/mol

Irradiation of a FSO_3H solution of **8** (−70 °C, $\lambda > 360$ nm) caused it to isomerize to give **10**. The product was identified as **10** on the basis of the similarity of its ^1H NMR spectrum to that of **3** and by the independent production of this cation by the protonation of **7** in FSO_3H. The stereochemistry at C(8) was evidenced by the chemical shifts of the C(8) proton and methyl resonances.

A mixture of **8** and **9** in FSO_3H at −70 °C was photochemically converted to **10** and a further cation. This new cation, which exhibited a ^1H NMR spectrum completely consistent with that expected for **11**, was thermally unstable and rearranged quantitatively to give **10** in a first-order process (at −39.5 °C, $k = 4.3 \times 10^{-4}\ s^{-1}$, $\Delta F^{\ddagger} = 17.1$ kcal/mol). Such a rearrangement is not unexpected in view of the low barrier reported for the interconversion of the 8-*exo*- and 8-*endo*-deuterio-1-methoxyhomotropylium cations[12] and the known preference for C(8) substituents to adopt the exo position in homotropylium cations.[13] The thermal conversion of **11** to **10** also occurred under the irradiation conditions ($t_{1/2} \simeq 10$ h at −70 °C); however, correcting for this thermal rearrangement, the photoisomerization of **9** to **11** was found to proceed with greater than 90% stereoselectivity.

The conversions of **8** and **9** to **10** and **11**, respectively, show that these photoisomerizations involve a basic skeletal rearrangement in which C(8) and its attendant substituents migrate around the "seven-membered" ring.[14] Formally such a rearrangement can be thought of as involving a photoinduced [1,6]-sigmatropic shift of a bicyclo[5.1.0]octadienyl resonance form of **8** and **9**. If orbital symmetry were to be obeyed, such a reaction should proceed with inversion of configuration at C(8), leading to an overall retention of stereochemistry at the migrating center. This is indeed the steric result observed; however, it should be pointed out that this is also the stereochemistry expected for the least motion pathway. While it is difficult to gauge the relative importance of least motion and orbital symmetry in this type of cyclopropyl circumambulation, it would seem that the former factor is important and should be taken into account in these reactions.[15]

As can be seen from a comparison of the barriers to ring inversion of **9** ($\Delta F^{\ddagger} > 27$ kcal/mol) and **11** ($\Delta F^{\ddagger} = 17.1$ kcal/mol), the ground-state properties of the 1- and 2-hydroxyhomotropylium cations are quite different. Such differences in behavior can most reasonably be attributed to the effect the hydroxy group has on the "degree of openness" of the internal "cyclopropane" bond of these systems.[16]

References and Notes

(1) Research supported by a grant from the National Research Council of Canada.

(2) D. W. Swatton and H. Hart, *J. Am. Chem. Soc.*, **89**, 5075 (1967); R. F. Childs and S. Winstein, *ibid.*, **90**, 7146 (1968); **96**, 6409 (1974); P. Vogel, M. Saunders, N. M. Hasty, Jr., and J. A. Berson, *ibid.*, **93**, 1551 (1971), and cited references.

(3) J. A. Berson and J. A. Jenkins, *J. Am. Chem. Soc.*, **94**, 8907 (1972); W. J. Hehre, *ibid.*, **96**, 5207 (1974).

(4) F. O. Rice and E. Teller, *J. Chem. Phys.* **6**, 489 (1938); **7**, 199 (1939). For reviews of later work, S. I. Miller, *Adv. Phys. Org. Chem.*, **6**, 185 (1968); O. S. Tee, *J. Am. Chem. Soc.*, **91**, 7144 (1969).

(5) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1969.

(6) The photoisomerization of the homotropylium cation has been previously reported (H. Hogeveen and C. J. Gaasbeek, *Recl. Trav. Chim. Pays-Bas*, **89**, 1079 (1970); P. A. Christensen, Y. Y. Huang, A. Meesters, and T. S. Sorensen, *Can. J. Chem.*, **52**, 3424 (1974)); however, in the absence of any ring labels, no "cyclopropyl walk" was detected.

(7) J. D. Holmes and R. Pettit, *J. Am. Chem. Soc.*, **85**, 2531 (1963).

(8) A Phillips S.P. 500-W super pressure mercury lamp in conjunction with a Corning Glass Filter, CS 0-51 (4 mm), was used for the irradiations.

(9) M. Brookhart, M. Ogliaruso, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 1965 (1967).

(10) M. Franck-Neumann, *Tetrahedron Lett.*, 2143 (1970); cf. L. J. Luskus and K. N. Houk, *ibid.*, 1925 (1972).

(11) M. Franck-Neumann and D. Martina, *Tetrahedron Lett.*, 1759 (1975).

(12) M. S. Brookhart and M. A. M. Atwater, *Tetrahedron Lett.*, 4399 (1972).

(13) R. Huisgen and J. Gasteiger, *Tetrahedron Lett.*, 3661 (1972).

(14) A comparable cyclopropyl migration could also be involved in the photoisomerization of 2,3-homotropone to cyclooctatrienone in aprotic solvents: L. A. Paquette and O. Cox, *J. Am. Chem. Soc.*, **89**, 5633 (1967).

(15) M. Kato, M. Funakura, M. Tsuji, and T. Miwa, *J. Chem. Soc., Chem. Commun.*, 63 (1976); F. Klärner, *Angew. Chem., Int. Ed. Engl.*, **13**, 268 (1974).

(16) The 1-hydroxyhomotropylium cations do not isomerize back to the 2-hydroxy isomers on irradiation ($\lambda > 330$ nm), but undergo an as yet incompletely defined ring contraction reaction.

Ronald F. Childs,* Carol V. Rogerson

Department of Chemistry, McMaster University
Hamilton L8S 4M1, Ontario, Canada

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Experimental Study of the Negative Ion States of Styrene. A Test of the Pairing Theorem

Sir:

Low energy electron scattering methods provide a means to determine the energies of the temporary negative ion states associated with the low-lying, normally unfilled π^* orbitals of unsaturated hydrocarbons. In this communication we report values for the four lowest electron affinities (EA's) of styrene as determined by electron transmission spectroscopy (ETS) in the format devised by Sanche and Schulz.[1] This technique has been employed in recent measurements of the EA's of benzene[2,3] and its azine analogues,[3] substituted benzenes,[4] ethylene,[5] butadiene,[5] formaldehyde,[6] and selected cyclic dienes.[7]

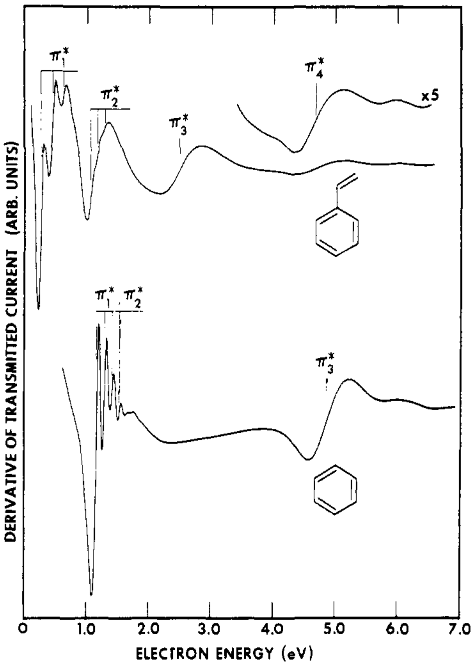

Figure 1. The derivative with respect to energy of the electron current transmitted through styrene (upper curve) and benzene (lower curve) as a function of electron impact energy.

In applying this technique to more complicated molecules, styrene is of interest since it may be viewed as two interacting functional groups, namely, the ethylenic and phenyl moieties. Each of the "constituent" molecules, ethylene and benzene, has already been well characterized in the gas phase by ETS. Furthermore, because styrene is an alternant hydrocarbon, its π and π^* orbitals, as described by PPP theory, obey the pairing theorem.[8] Our determination of the anion energies, together with the known ionization potentials (IP's), allows a direct experimental test of this relationship.

In Figure 1, we present the electron transmission spectra of styrene and, for comparison, benzene. The ethylene spectrum has been published elsewhere.[5] The temporary occupation of one of the unfilled π^* orbitals in these molecules is manifested by a rapid, "resonant", variation in the total scattering cross section. The visibility of such variations is enhanced by measuring the derivative with respect to energy of the electron current transmitted through a cell containing the appropriate gas.[1]

The structure near 1 eV in the benzene spectrum corresponds to the capture of an incident electron into the doubly

Table I. Vertical Electron Affinities and Ionization Potentials of Ethylene, Benzene and Styrene

Compound	Electron affinity (eV) Exptl	Electron affinity (eV) Theory[a]	Ionization potential (eV) Exptl[b]	Ionization potential (eV) Theory[a]	EA + IP Exptl	EA + IP Theory[a]
Ethylene	−1.78 ± 0.1[c]	−1.60	10.52	9.73	8.74	8.13
Benzene	−1.15 ± 0.05	−1.07	9.24	9.19	8.09	8.12
	−4.85 ± 0.1	−3.97	12.20	12.15	7.35	8.18
Styrene	−0.25 ± 0.05	−0.39	8.43	8.49	8.18	8.10
	−1.05 ± 0.1	−1.09	9.18	9.20	8.13	8.11
	−2.48 ± 0.1	−2.27	10.45	10.41	7.97	8.14
	−4.67 ± 0.1	−4.21	12.30[d]	12.39	7.63	8.18

[a] The theoretical values were obtained from the semiempirical method of Younkin, Smith, and Compton (ref 14). We have readjusted the empirical relationship between the energies of the occupied orbitals and the IP's to obtain somewhat better agreement with experiment. [b] Ethylene (ref 11), benzene (ref 12), styrene (ref 13). [c] Reference 5. [d] It has not been unambiguously demonstrated that the 12.30 eV IP corresponds to ejection of a π electron.