

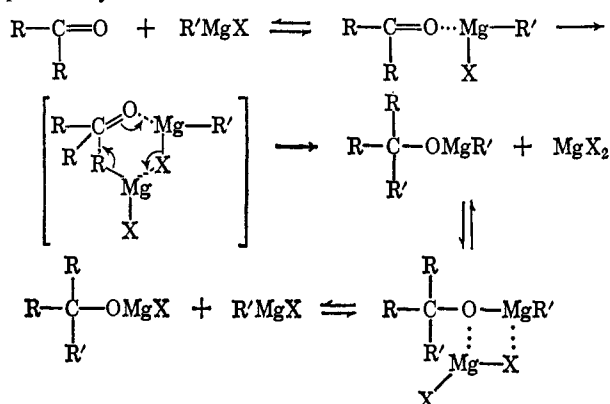
The mechanism suggested by Mosher<sup>5</sup> and Becker<sup>6</sup> is similar to the one suggested here, but it brings the components together in a somewhat different manner.



In this case  $k_{\text{obsd}} = k_3 k_g [G]^2 / (1 + K_g K [G]^2) = k_3 K' [G]^2 / (1 + K' [G]^2)$  for conditions such that the concentration of dimer  $G_2$  is small with respect to that of monomer  $G$ . The test of the mechanism is whether a plot of  $k_{\text{obsd}}$  vs.  $k_{\text{obsd}}/[G]_0$  is linear. The plot is not linear.

The ultimate test of the mechanism proposed here is whether the rate behavior in solutions where Grignard and ketone are in comparable concentration is consistent with the numerical values of  $K$  and  $k_2$  obtained under pseudo-first-order conditions. Such experiments are currently in progress and indicate already that this is the case.

The fact that at low Grignard:ketone ratios the rate of reaction decreases markedly after 50% of the available R groups are utilized<sup>6</sup> can be readily explained by assuming that the product (eq 4) does not readily regenerate the active Grignard species as originally proposed by Swain.



Calculations of our kinetic data at low Grignard:ketone ratios have produced agreement with this concept.<sup>7</sup>

(5) J. Miller, G. Gregoriou, and H. S. Mosher, *J. Am. Chem. Soc.*, **83**, 3966 (1961).

(6) N. M. Bikales and E. I. Becker, *Can. J. Chem.*, **41**, 1329 (1962).

(7) It should be noted that the conclusion drawn here is compatible with the existence of the Schlenk equilibrium, but that the data cannot indicate which of the species ( $RMgX$ ,  $MgX_2$ , or  $R_2Mg$ ) may be involved in the mechanism, if specificity indeed occurs.

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### The Homoaromatic 1-Hydroxyhomotropylium Cation<sup>1,2</sup>

Sir:

Known homotropylium cationic species include the parent  $C_8H_9^+$  cation<sup>3,4a</sup> I and its  $Mo(CO)_3$  complex,<sup>3a</sup>

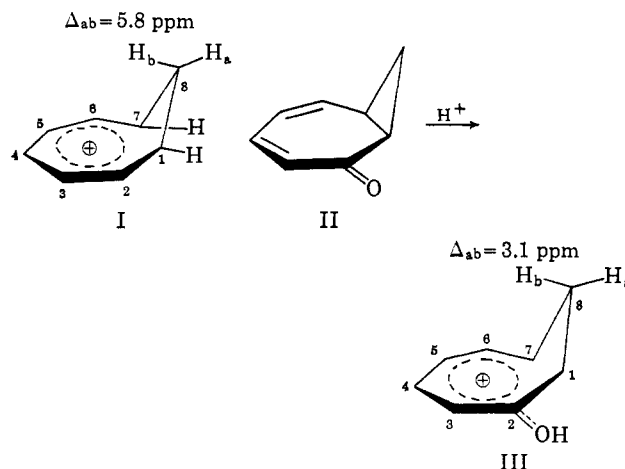
(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(2) Reported in part at The Chemical Society International Symposium on Aromaticity, Sheffield, England, July 6-8, 1966.

(3) (a) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *J. Am. Chem. Soc.*, **87**, 3267 (1965); (b) S. Winstein, C. G. Kreiter, and J. I. Brauman, *ibid.*, **88**, 2047 (1966).

as well as the 1-methylhomotropylium ion<sup>4b</sup> and its 1-phenyl analog.<sup>4b</sup> Another instructive case is the conjugate acid<sup>4c</sup> of the bicyclic ketone II (monohomotropone), whose nmr spectrum, especially the big chemical shift ( $\Delta_{ab}$ ) between inside  $H_b$  and outside  $H_a$  protons, is indicative of a nonclassical 2-hydroxyhomotropylium structure III. Even with the hydroxyl substituent on the cationic system, the nonclassical homoconjugative involvement of the cyclopropane ring in the cyclic electron delocalization is very substantial. The fact that a relatively high energy cyclopropane ring is present in the parent ketone II favors nonclassical character in species III; thus, an even more instructive monohomotropylium species which we report in the present communication is the 1-hydroxy isomer V, the conjugate acid of cyclooctatrienone (IV).

As reported recently by Roberts and his co-workers,<sup>5</sup> cyclooctatrienone displays a temperature-dependent nmr spectrum in  $CS_2$  solvent. The high-temperature spectrum ( $35^\circ$ ) contains a doublet signal at  $\tau$  7.0 for the  $C_8$  methylene protons, a quartet at  $\tau$  4.23 for the  $C_7$  proton, and a complex multiplet between  $\tau$  3.4 and 3.9 for the other five protons. In the low-temperature spectrum, e.g., at  $-73^\circ$ , the signal for  $H_a$  and  $H_b$  is that of the AB part of the ABX spectrum with the chemical shift ( $\Delta_{ab}$ ) between inside  $H_b$  and outside  $H_a$  being 0.42 ppm. We observe similar temperature dependence of the nmr spectrum of cyclooctatrienone in other solvents. In none of them is there any indication of pronounced monohomotropylium oxide character in IV.



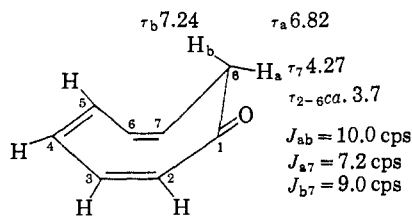
In strongly acidic media, such as  $SO_2-FSO_3H$  or  $SO_2-FSO_3H-SbF_5$ , however, the nmr spectrum of the conjugate acid of IV does correspond to a homoaromatic homotropylium species V. Using  $CH_2Cl_2$  as a secondary standard ( $\tau$  4.70), the signal for the inside  $H_b$  appears as a triplet at  $\tau$  8.68, considerably upfield from the  $H_b$  signal in the neutral parent ketone, while the signal for the outside  $H_a$  appears as a quartet of doublets at  $\tau$  5.60, downfield from the position of  $H_a$  in IV. Thus the chemical shift between  $H_a$  and  $H_b$  ( $\Delta_{ab}$ ) is now 3.1 ppm. The signal for  $H_7$  appears as a quartet at  $\tau$  4.05,<sup>6</sup> while the signals for the protons

(4) (a) J. L. Rosenberg, J. E. Mahler, and R. Pettit, *ibid.*, **84**, 2842 (1962); (b) C. E. Keller and R. Pettit, *ibid.*, **88**, 604 (1966); (c) J. D. Holmes and R. Pettit, *ibid.*, **85**, 2531 (1963).

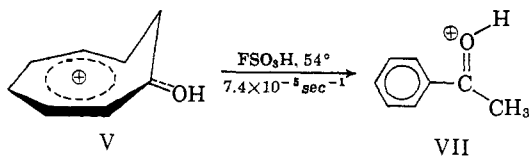
(5) C. Ganter, S. M. Pokras, and J. D. Roberts, *ibid.*, **88**, 4235 (1966).

(6) In  $SO_2-FSO_3H$  at  $-26^\circ$  the signal for  $H_1$  and  $H_7$  in the monohomotropylium ion I appears as a quartet at  $\tau$  3.52. The signal for  $H_b$  appears as a doublet of triplets at  $\tau$  10.73, that for  $H_a$  as a quartet at  $\tau$  4.87, and those for  $H_{2-6}$  as a multiplet centered at  $\tau$  1.50. Coupling

on C<sub>2</sub> to C<sub>6</sub> occur as a two-proton multiplet centered at  $\tau$  1.85 and a three-proton multiplet centered at  $\tau$  2.55. Coupling constants are 10.8 cps for the geminal  $J_{ab}$ , 9.2 cps for the *trans*  $J_{b7}$ , and 7.7 cps for the *cis*  $J_{a7}$ .



Solutions of V are stable almost indefinitely at low temperatures, and the parent ketone IV may be recovered in high yield. However, at ordinary temperatures, a slow irreversible rearrangement occurs to a species showing a three-proton singlet at  $\tau$  6.65 and a five-proton complex multiplet at  $\tau$  1.83. The nmr spectrum of the rearrangement product is identical with that of protonated acetophenone<sup>7a,b</sup> (VII), and authentic acetophenone may indeed be isolated in high yield from solutions of cyclooctatrienone in FSO<sub>3</sub>H after rearrangement. At elevated temperatures rearrangement is naturally much faster.<sup>8</sup> Even at 80°, the rearrangement is not rapid enough to interfere with good observation of the nmr spectrum of V, and it is significant that the proton signals for H<sub>b</sub> and H<sub>a</sub> are still very sharp at this temperature.



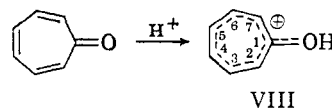
The various features of the nmr spectrum of V strongly support a homoaromatic 1-hydroxyhomotropylium ion structure. While the chemical shift between inside and outside protons in V is less than in

constants are 6.5 cps for  $J_{ab}$ , 9.8 cps for *trans*  $J_{b1}$  and 6.5 cps for *cis*  $J_{a1}$ . In SO<sub>2</sub>, we observe the signal for tropylium fluoroborate at  $\tau$  0.76.

(7) (a) M. Brookhart, G. C. Levy, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 1735 (1967); (b) T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **43**, 1045 (1965); (c) H. G. Richey and R. K. Lustgarten, *J. Am. Chem. Soc.*, **88**, 3136 (1966).

(8) The rearrangement appears to be more rapid in concentrated H<sub>2</sub>SO<sub>4</sub> solvent. The nmr spectra of rearranging solutions of V give no evidence for appreciable concentrations of intermediates between V and VII.

the parent homotropylium ion I ( $\Delta_{ab}$  = 5.9 ppm),<sup>3,6</sup> it is still large ( $\Delta_{ab}$  = 3.1 ppm), and this points to a substantial aromatic ring current<sup>3b</sup> in V. Comparing further with I,<sup>3,6</sup> we see that the chemical shift of H<sub>7</sub> in V is similar to that of H<sub>7</sub> in I and that the *cis* and *trans* coupling constants  $J_{a7}$  and  $J_{b7}$  are nearly identical in V and I. The geminal coupling constant at C<sub>8</sub> in V ( $J_{ab}$  = 10.8 cps) is larger than in I ( $J_{ab}$  = 6.5 cps) or its 1-methyl analog<sup>4b</sup> ( $J_{ab}$  = 8.0 cps). This is probably at least partly due to a widened C<sub>1</sub>-C<sub>8</sub>-C<sub>7</sub> angle. Just as it was instructive to compare the parent monohomotropylium ion I with tropylium ion itself as regards nmr and ultraviolet spectra,<sup>3b</sup> it is here interesting to compare the 1-hydroxyhomotropylium ion V with tropone conjugate acid VIII (hydroxytropylium ion).<sup>9</sup> As shown in Table I, the nmr and ultraviolet relationships between V and VIII are very similar to those observed<sup>3b,6</sup> between homotropylium ion I and tropylium ion.



It is evident that the powerfully electron-releasing 1-hydroxyl substituent does not convert the nonclassical homoaromatic homotropylium ion to a classical species. Similarly, a 7-hydroxyl substituent<sup>7a,c</sup> does not convert the *anti*-7-norbornenyl ion to a classical species. On

**Table I.** Comparison of 1-Hydroxytropylium (VIII) and 1-Hydroxyhomotropylium (V) Cations

	H <sub>2-6</sub> , $\tau$ (SO <sub>2</sub> -FSO <sub>3</sub> H)	$\lambda_{max}$ , m $\mu$ (H <sub>2</sub> SO <sub>4</sub> )	log $\epsilon$
VIII <sup>a</sup>	2.28 <sup>b</sup>	229	4.64
		306	4.04
		311 (sh)	4.03
V	2.27 <sup>c</sup>	231	4.40
		350	3.74

<sup>a</sup> The data on ultraviolet absorption of VIII are essentially identical with those of Dauben and Harmon.<sup>9</sup> <sup>b</sup> Complex multiplet. <sup>c</sup> Weighted average.

the other hand, the 2-norbornyl cation, with a smaller energy gap between nonclassical and classical structures, is rendered essentially classical by a 2-methoxy substituent.<sup>10</sup> While the present work does not provide a definite figure for the size of the barrier to ring inversion in V, we can estimate a lower limit from the sharpness of the H<sub>b</sub> and H<sub>a</sub> signals even at 80°. This leads to an upper limit of 3 sec<sup>-1</sup> for the rate constant for exchange of magnetic environments between H<sub>a</sub> and H<sub>b</sub> (ring inversion) at 80° and thus a lower limit of 20 kcal/mole<sup>11</sup> for  $\Delta F^\ddagger$ . On this basis, homoaromatic V is more stable than a classical planar ion VI by at least 20 kcal/mole.

(9) H. J. Dauben and K. M. Harmon, unpublished work; K. M. Harmon, Ph.D. Thesis, University of Washington, 1958.

(10) T. G. Traylor and C. L. Perrin, *J. Am. Chem. Soc.*, **88**, 4934 (1966).

(11) This value is substantially higher than the  $\Delta F^\ddagger$  value of 11 kcal/mole for ring inversion of IV.<sup>5</sup>

(12) National Institutes of Health Predoctoral Fellow, 1965-1967.

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