

THE THERMAL REARRANGEMENT AND RING INVERSION OF THE 1-METHOXYHOMOTROPYLIUM CATION

Maurice S. Brookhart and Mary Ann Monroe Atwater
Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27514

(Received in USA 7 September 1972; received in UK for publication 22 September 1972)

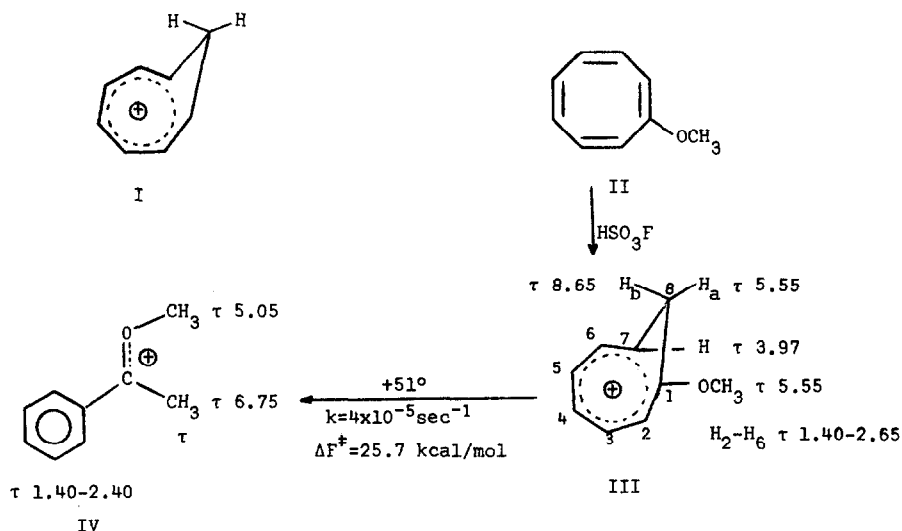
Since the report of the first direct observation of the nonclassical monohomotropylum ion, I, by Pettit¹, considerable attention has been given to the structure and direct observation of the homotropylum ion and its derivatives.² However, relatively little information is available concerning the thermal rearrangements of homotropylum ions. Winstein³ has reported the direct observation of the 1-hydroxyhomotropylum and its remarkable thermal rearrangement to protonated acetophenone, but no mechanism for this rearrangement has been proposed.

We wish to report the direct observation of the 1-methoxyhomotropylum ion and a study of its subsequent ring inversion and thermal rearrangement. The data obtained provides considerable insight into the mechanism for thermal rearrangement of homotropylum ions and the effect of 1-substituents on the rate of ring inversion.

Extraction of methoxycyclooctatetraene, II, from CD_2Cl_2 into fluorosulfonic acid at $-78^\circ C$ yields cleanly the 1-methoxyhomotropylum ion, III. The pmr spectrum⁴ of III at $25^\circ C$ is summarized below and shows signals at τ 1.40-2.65 (multiplet, H_2-H_6), τ 3.97 (H_7), τ 5.55 (methoxyl singlet overlapping H_{8a} multiplet) and τ 8.65 (H_{8b}). Coupling constants evaluated from the spectrum were $J_{8a,8b}=10.5$ Hz, $J_{8b,7}=9.8$ Hz and $J_{8a,7}=7.5$ Hz. The chemical shifts and coupling constants obtained for III are, as expected, very similar to those obtained for the 1-hydroxyhomotropylum ion.³

Extraction of methoxycyclooctatetraene into deuteriofluorosulfonic acid at $-78^\circ C$ yielded the monodeuterated ion whose pmr spectrum at $-54^\circ C$ indicated ca. 75% of the deuterium in the 9-endo (inside) position and ca. 25% in the 9-exo (outside) position.⁵ This observed 75:25 ratio of endo:exo deuteration is similar to the stereospecificities previously reported for the deuteration of cyclooctatetraene^{6,7} and methylcyclooctatetraene.⁸ The rate of ring inversion of III

could be estimated by observing at higher temperatures the equilibration of protium between the exo and endo positions. At -18°C the first-order rate constant for ring inversion was estimated as $1 \times 10^{-4} \text{ sec}^{-1}$ corresponding to $\Delta F^{\ddagger} = 19.6 \text{ kcal/mol}$.

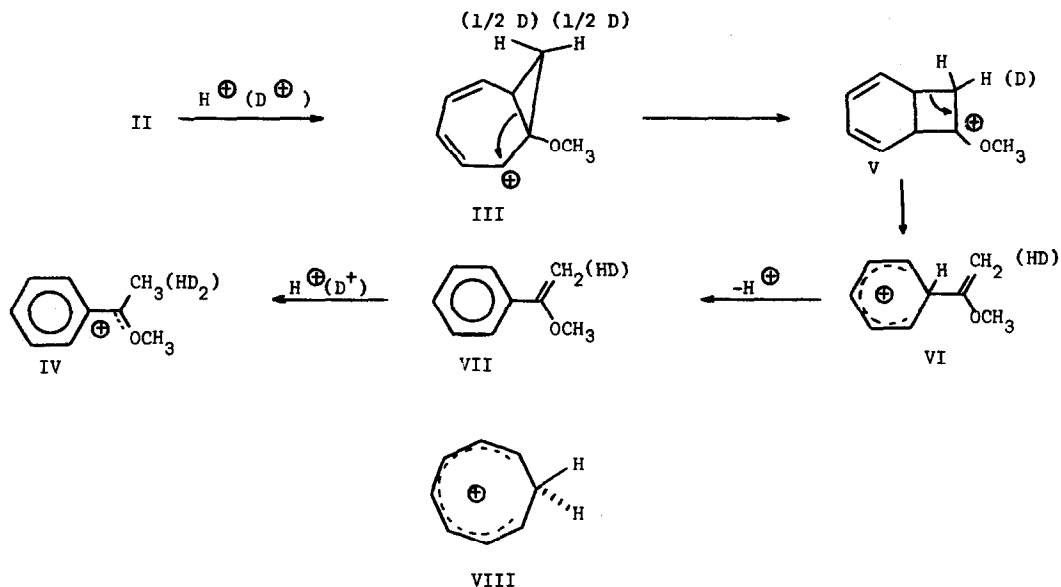


Upon warming, ion III rearranges to yield the phenylmethoxycarbonium ion, IV, whose pmr spectrum shows a five-proton multiplet at τ 1.40-2.40 (aromatic hydrogens), a three-proton singlet at τ 5.05 (methoxyl protons) and a three proton singlet at τ 6.75 (methyl protons). The first-order rate constant for this isomerization at 51° was measured as $4 \times 10^{-5} \text{ sec}^{-1}$ ($\Delta F^{\ddagger} = 25.7 \text{ kcal/mol}$). During the course of the rearrangement, singlets of minor intensity appear at τ 6.62 and τ 5.60 and increase in intensity with concomitant decrease of the τ 5.05 and τ 6.75 signals upon further heating at 51° or higher temperatures. These signals have been identified as those of the methyl group of protonated acetophenone⁹ (τ 6.62) and methyl fluorosulfonate (τ 5.60). These species apparently form from nucleophilic attack of the fluorosulfonate anion on IV.

When the generation and rearrangement of III is carried out in DSO_3F , the substituted benzyl ion IV formed shows signals of relative intensity 5.0:3.0:1.1 for the aromatic, methoxyl and methyl protons,¹⁰ respectively. This ratio indicates the incorporation of two solvent deuterons into the methyl group during isomerization.

A reasonable mechanism for the thermal rearrangement of III consistent with the deuteration

results is outlined below and involves ring contraction to the α -methoxy ion V followed by ring opening to the benzenonium ion VI from which loss of a proton yields the vinyl ether VII. Protonation (deuteration) of the vinyl ether gives rise to the observed product IV.



The free energy of activation for ring inversion of **III** (19.6 kcal/mol) is somewhat less than the free energy of activation for ring inversion in the unsubstituted homotropylium of 22.3 kcal/mol. This observation is best explained by considering qualitatively the effect of a 1-methoxyl substituent on the relative energies of the homotropylium ion and its transition state for ring inversion the planar, classical cyclooctatrienyl cation **VIII**.⁶

Upon distortion of **I** to the planar **VIII** the net positive charge must increase at C_1 while the hybridization at C_1 must change from a value between sp^3 and sp^2 to a hybridization close to sp^2 . On this basis then the electron donating methoxyl substituent should stabilize the transition state **VIII** to a greater degree than **I** and thus lower the barrier to ring inversion as is observed. A similar argument has been used to explain why electron donating 7-substituents reduce the activation energy for bridge-flipping in 7-norbornadienyl cations.¹¹

Acknowledgement: We thank Mr. Edward R. Davis for help in the synthesis of 1-methoxycyclooctatetraene.

References

1. J. L. Rosenberg, J. E. Mahler, and R. Pettit, J. Am. Chem. Soc., 84, 2842 (1962).
2. For summaries see:
 - a. S. Winstein, Chem. Soc. Spec. Publ., No. 21, 5 (1967);
 - b. S. Winstein, Quart. Rev., Chem. Soc., 23, 141 (1969); and
 - c. R. F. Childs, M. A. Brown, F. A. L. Anet and S. Winstein, J. Am. Chem. Soc., 94, 2175 (1972).
3. M. Brookhart, M. Ogliaruso, and S. Winstein, ibid., 89, 1965 (1967).
4. Chemical shifts are in τ relative to internal CH_2Cl_2 taken as τ 4.70.
5. A small amount of diprotio species (ca. 5%) was evident as a triplet at τ 8.65. This could be detected since the exo-d species exhibits a doublet at τ 8.65 each line of which falls between two lines of the triplet. This much diprotio species probably arises as a result of a deuterium isotope effect on protonation and therefore use of ca. 98% DSO_3F generates more than ca. 2% diprotio species. The percentage of diprotio species produced would be expected to vary with the percentage deuterated acid used and the temperature of protonation but this point was not investigated.
6. S. Winstein, C. G. Kreiter and J. I. Brauman, ibid., 88, 2047 (1966).
7. R. Huisgen, G. Boche, and H. Huber, ibid., 89, 3345 (1967).
8. C. E. Keller and R. Pettit, ibid., 88, 604 (1966).
9. T. Birchall and R. J. Gillespie, Can. J. Chem., 43, 1045 (1965).
10. The integration for the dideuterated methyl group is somewhat high for 1.0 proton. This is no doubt due to introduction of proportionately more protium than is present in the acid medium (ca. 2%) as a result of a deuterium isotope effect on the initial protonation (see footnote 5) and the subsequent protonation of VII.
11. a. M. Brookhart, R. K. Lustgarten and S. Winstein, J. Am. Chem. Soc., 89, 6352 (1967);
b. R. K. Lustgarten, M. Brookhart and S. Winstein, ibid., 94, 2347 (1972).