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# A NEW ROUTE TO [3.5.3]ARMILENIUM ION

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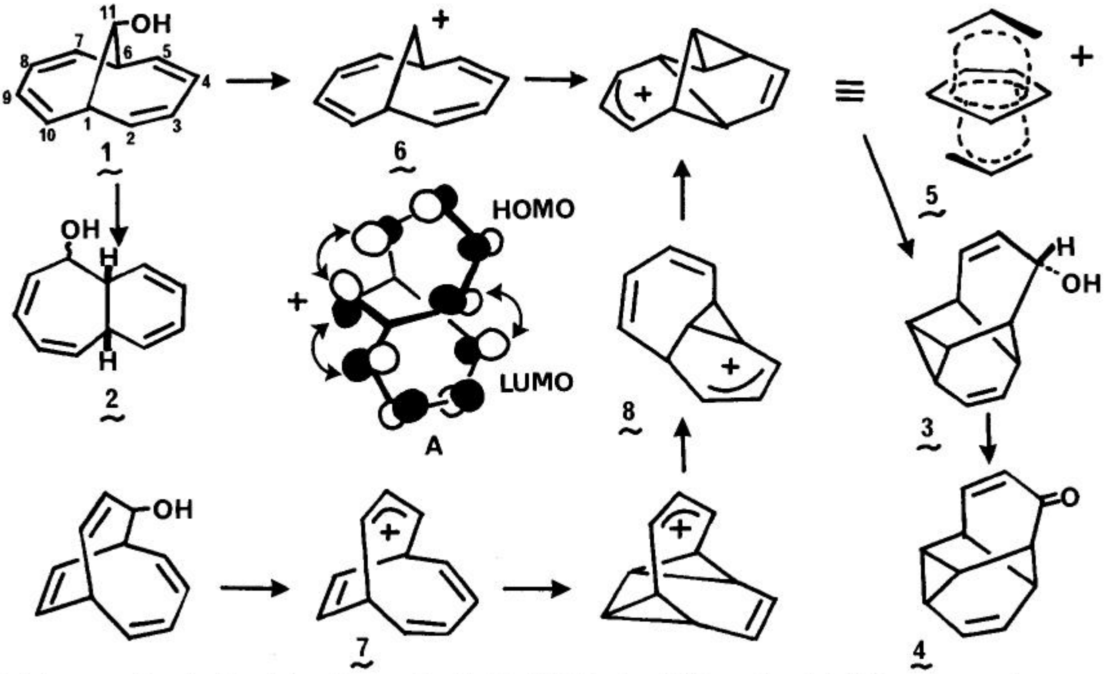
Abstract: Treatment of bicyclo[4.4.1]undeca-2,4,7,9-tetraen-11-ol with $FSO_3H-SO_2-CH_2Cl_2$ at -70° resulted in the formation of [3.5.3]armilenium ion. The general pathway to the ion is proposed.

The concept of three dimensional bicycloaromaticity introduced by Goldstein and Hoffmann[1] has received much attention in aromatic chemistry and many experimental supports[2,3,4], as well as the theoretical rationalization[5] have appeared. We have recently prepared bicyclo[4.4.1]undeca-2,4,7,9-tetraen-11-ol (1) as the precursor of bicyclic ions and reported its facile thermal rearrangement to bicyclo[5.4.0]undeca-3,5,8,10-tetraen-2-ols (2)[6]. This paper deals with the fate of the corresponding cation, the presumably destabilized[7] and yet unexplored $(CH)_{11}$ cationic species.

When $CH_2Cl_2$ solution of 1 was added to a mixture of $FSO_3H$ and $SO_2$ at -70° under $N_2$, vermilion color developed in the solution. Aqueous alkaline quenching (-70°) yielded the liquid alcohol 3[8] in 18% yield after repeated $SiO_2$-chromatography (hexane : ether = 10 : 3). $MnO_2$ oxidation of 3 afforded the corresponding ketone 4 in 83% yield. The structures of these compounds were established as shown by the comparison of their spectra with those of the authentic specimens[2,8]. For the identification of the intervening cation, the colored solution was subjected to PMR measurement (-100°C, in $CD_2Cl_2$-$SO_2ClF$). Three major signals observed at 2.73 (s), 7.57 (t, J=6.0), 8.00 ppm (d, J=6.0) were identical with those of the [3.5.3]armilenium ion (5)[2]. The observation of 5 seems to prove that the ion 6 which can directly be formed by ionization of 1 is not stabilized and rearranges at low temperature to the more stable 5[9]. Assuming the ion 6 be a discrete species, the reaction sequence can be depicted as is shown in the next page.

The rearrangement of 6 to 5 is likely a concerted process as shown in the orbital interaction A, an expression based on the three system interaction theory[5]. The interaction can be justified because 1) molecular mechanics calculations clearly indicate that the twisted ($C_2$) form, in which C-2 is facing C-7 in the distance of 3.15 Å, is the most stable conformation and their interaction is observed in its UV spectrum[6], and 2) the ion 6 corresponding to 1 is also likely to be twisted because no significant strain release and/or the longicyclic stabilization to overcome the strain are expected in the planer ($C_s$) conformation.

It is interesting that the mechanism suggested by Groves[3] for the Goldstein's original conversion of the ion 7 to 5[2] involves the ion 8 which is very similar to 6 both in geometry and electronic interaction.



The orbital expression A, involving three antarafacial (Möbius type) interaction of "ribbons" may also contribute to the stability of 5.

We are deeply indebted to Professor M.J. Goldstein for the spectra of various armilene derivatives.

## References and Notes

1) M.J. Goldstein and R. Hoffmann, J. Amer. Chem. Soc., 93, 6193 (1971).

2) M.J. Goldstein and S.A. Kline, ibid., 95, 935 (1973).

3) K.W. Ma and J.T. Groves, Tetrahedron Letters, 1141 (1975).

4) Inter al. R.K. Lustgarten, M. Brookhart and S. Winstein, J. Amer. Chem. Soc., 89, 6350 (1967). J.B. Grutzner and S. Winstein, ibid., 92, 3186 (1970), 94, 2200 (1972). M.J. Goldstein, S. Tomoda and G. Whittaker, ibid., 96, 3676 (1974). M.J. Goldstein, S. Tomoda, S-I. Murahashi, K. Hino and I. Moritani, ibid., 97, 3847 (1975). M.J. Goldstein, Y. Nomura, Y. Takeuchi and S. Tomoda, ibid., 100, 4899 (1978). M.J. Goldstein and D.P. Warren, ibid., 100, 6539, 6541 (1978).

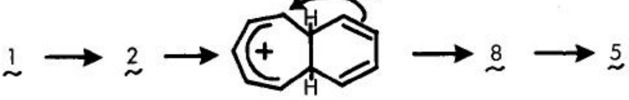
5) S. Inagaki, H. Fujimoto and K. Fukui, J. Amer. Chem. Soc., 98, 4693 (1976).

6) T. Sato and S. Itô, Tetrahedron Letters, 1051 (1979).

7) The cation belongs to the Goldstein's (0,0,0) system[1] and Fukui's electron-localizing system[5].

8) 3: m/e 160 ($M^+$); $\nu^{CCl_4}$ 3615, 3030, 2925, 1623, 1389, 1047, 1008, 952, 703 $cm^{-1}$; $\delta^{CCl_4}$ 1.10 (1H, td, J=9.0, 1.7), 1.2~1.6 (4H, m), 1.80 (1H, td, J=9.0, 4.2), 2.35 (1H, br.d, J=6.5), 4.25 (1H, br.dd, J=3.8, 1.7), 5.45 (1H, br.dd, J=9.3, 3.8), 5.90 (2H, m), 6.25 ppm (1H, dd, J=9.3, 6.0).

9) Another path, the thermal rearrangement of 1 to 2 and the subsequent ionization shown below, is unlikely because of the energy requirement ($\Delta H^{\ddagger}_{20}$=21.3 kcal/mol)[6] in the first process.



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