

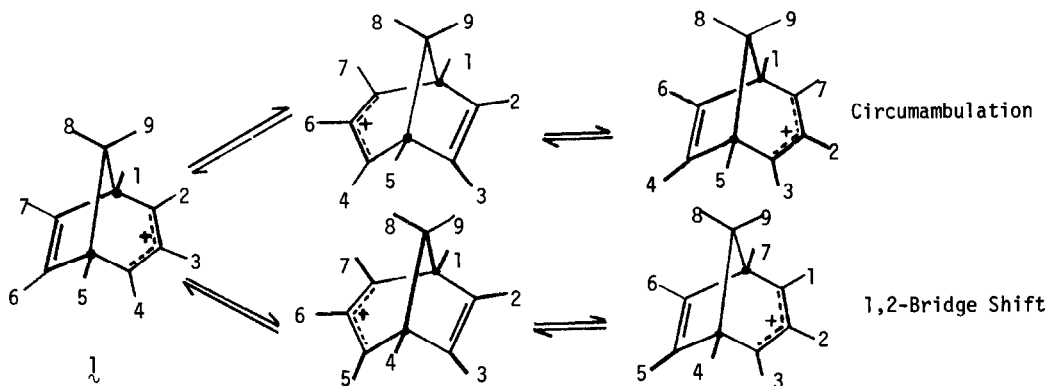
MECHANISM OF THE REARRANGEMENT OF BICYCLO[3.2.1]OCTADIEN-2-YL  
CATIONS TO BICYCLO[3.3.0]OCTADIEN-2-YL CATIONS

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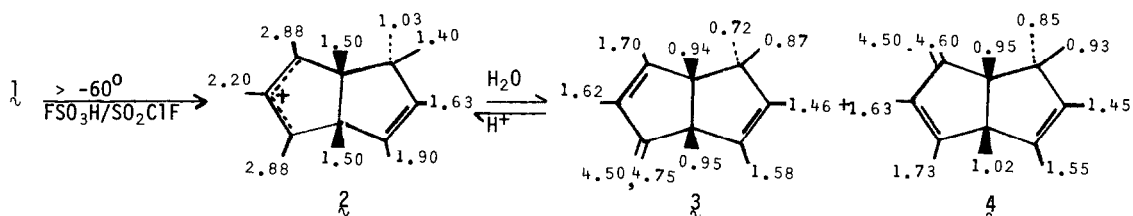
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Below  $-60^{\circ}$  in  $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$  the nonamethyl bicyclo[3.2.1]octadien-2-yl cation **1** undergoes two degenerate rearrangements, circumambulation<sup>1</sup> and a 1,2-shift of the methano bridge.<sup>2</sup> The first of these processes is much faster than the second, and is nmr-observable,<sup>1</sup> whereas the second process was detected only by labeling studies.<sup>2</sup> When solutions of **1** in  $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$



were maintained at or above  $-60^{\circ}$  for an extended time, an irreversible rearrangement to a new cation occurred, and it is the mechanism of this process we wish to discuss here.

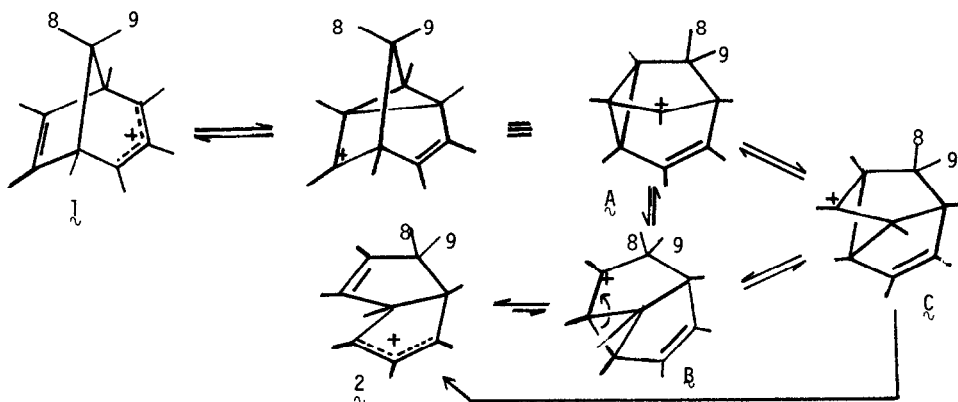
At  $-52^{\circ}$  the nmr spectrum of **1** consists of a sharp singlet at  $\delta 1.27$  (equilibrating methyls 8 and 9), a sharp singlet at  $\delta 1.52$  (methyls 1 and 5) and a broad singlet at  $\delta 2.20$  (equilibrating methyls 2,3,4,6 and 7).<sup>1,3</sup> Gradually this spectrum is replaced by one with seven peaks. The process, which was conveniently followed kinetically by the decay of the peak at  $\delta 1.27$  and by the appearance of the peaks at  $\delta 1.03$  and  $\delta 2.88$ , has a first order rate constant of  $1.9 \pm 0.2 \times 10^{-4} \text{sec}^{-1}$ . We assign the product ion structure **2**, with two pairs of methyls that should be unique having coincidentally the same chemical shifts.<sup>4</sup>



When quenched,  $\mathbf{2}$  gave two isomeric hydrocarbons  $\mathbf{3}$  and  $\mathbf{4}$ <sup>5</sup> in a ratio which varied between 1:1 and 1:2 depending on the quenching technique. Dissolution of either  $\mathbf{3}$  or  $\mathbf{4}$  in  $\text{FSO}_3\text{H}$  or in trifluoroacetic acid (TFA) regenerated  $\mathbf{2}$ , which was stable in TFA up to  $+50^\circ$ .

When  $\mathbf{1}$  containing 3/7 deuterium label<sup>2</sup> in methyls 1-7 but no deuterium in methyls 8 and 9 was allowed to rearrange to  $\mathbf{2}$  in  $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$ , the product showed no reduction in the areas of the two high-field singlets assigned to the gem-dimethyl protons. Consequently mechanisms which involve a 1,2-shift of one of these methyl groups can be eliminated.<sup>6</sup>

We propose the following scheme to rationalize the labeling result:<sup>7</sup>



The cyclopropylcarbanyl cation  $\mathbf{A}$  may rearrange directly to cyclopropylcarbanyl cation  $\mathbf{B}$  which can collapse to  $\mathbf{2}$ .  $\mathbf{A}$  may rearrange to  $\mathbf{B}$  via  $\mathbf{C}$  ('inch-worm' mechanism involving successive 1,2-shifts). Finally, if  $\mathbf{C}$  is an intermediate it could collapse directly to  $\mathbf{2}$ . At present there are no data which permit a distinction among these paths.

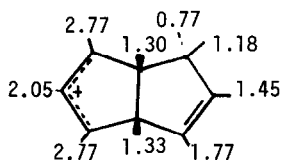
The rate of isomerization of  $\mathbf{1} \rightarrow \mathbf{2}$  was measured at eight temperatures<sup>8</sup> between  $-36$  and  $-55^\circ$  and furnished the following activation parameters:  $\Delta F^\ddagger$  ( $-45^\circ$ ) 16.6 Kcal/mol,  $\Delta S^\ddagger$   $+3.5$  eu/mol,  $\Delta H^\ddagger$  17.4 Kcal/mol. The corresponding values for the circumambulatory process were  $\Delta F^\ddagger$  ( $-80^\circ$ ) 10.2 Kcal/mol,  $\Delta S^\ddagger$   $-6.6$  eu/mol,  $\Delta H^\ddagger$  7.0 K cal/mol. Presumably the 1,2-bridge shift has an activation enthalpy between those of the other two processes.

Although ions  $\lambda$  and  $\xi$  are both allylic cations,  $\lambda$  is a pericyclic cation of the ( $2^+$ ,  $2^0$ ) mode.<sup>9</sup> It is therefore destabilized (or incipiently bis-homo antiaromatic) relative to  $\xi$ , which must be regarded only as an allylic cation since the free double bond is out of the ribbon segment. This difference, as well as relief of strain, may contribute to the driving force for the facile isomerization of  $\lambda \rightarrow \xi$ .

Acknowledgement. We are indebted to the National Science Foundation for a grant in support of this research.

#### REFERENCES

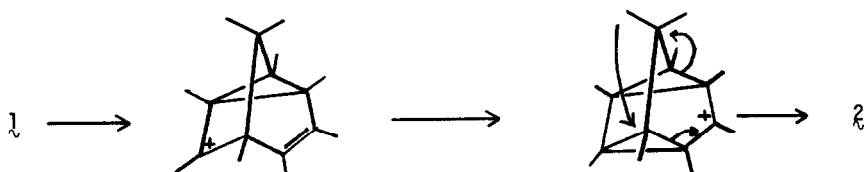
1. H. Hart and M. Kuzuya, J. Amer. Chem. Soc., **95**, 4096 (1973).
2. M. Kuzuya and H. Hart, Tetrahedron Lett., preceding paper.
3. The reference was  $(\text{CH}_3)_4\text{N}^+\text{BF}_4^-$ ,  $\delta$ 3.13.
4. The signals at  $\delta$ 2.88 and 2.20 are expected for methyls at the terminus and middle, respectively, of a cyclopentenyl cation [see N. C. Deno in "Carbonium Ions," Ed. by G. A. Olah and P. von R. Schleyer, Wiley-Interscience, New York, Vol II, p. 796 (1970)]. The uv spectrum ( $\lambda_{\text{max}}^{\text{H}_2\text{SO}_4}$  326 nm,  $\epsilon$ 4600) also supports the structure. In TFA the nmr spectrum was shifted as shown, and the ring juncture methyls became unique (their assignment is arbitrary)



In TFA-d at room temperature the peak at  $\delta$ 2.77 washed out in less than 1 min. The peak at  $\delta$ 1.45 exchanged after several hours, presumably as a consequence of some return from  $\xi$  to ion  $\beta$ . Further deuterium exchange of  $\xi$  on longer standing in TFA-d, and its mechanistic implications, will be discussed in the full paper.

5. Anal. Calcd for  $\text{C}_{17}\text{H}_{26}$ : C, 88.62; H, 11.38. Found: C, 88.68; H, 11.27. Analysis was done on the mixture since a mass spectrum showed that  $\xi$  and  $\eta$  (separated by vpc using a 10 ft x 1/4 in column, 20% FFAP on Chromosorb W,  $160^\circ$ , 100 ml/min He) were isomers. The structures are supported by nmr, ir, uv and mass spectra, and deuterium labeling experiments to be described in a full paper.

6. One such mechanism which at first seemed attractive is:



7. For a similar mechanism which rationalizes the intramolecular interconversion of the two cations obtained by protonating hexamethyl dewarbenzene, see H. Hogeveen and H. C. Volger, Rec. Trav. Chim., 88, 353 (1969).
8. Each rate constant was the average of at least four runs, with the experimental error within  $\pm 10\%$ .
9. M. J. Goldstein and R. Hoffmann, J. Amer. Chem. Soc., 93, 6193 (1971).