

ON THE QUESTION OF 1,2-BRIDGE SHIFTS IN BICYCLO[3.2.1]OCTADIEN-2-YL CATIONS, AND A CAUTIONARY NOTE ON RAPID PROCESSES CONCEALED FROM NMR DETECTION

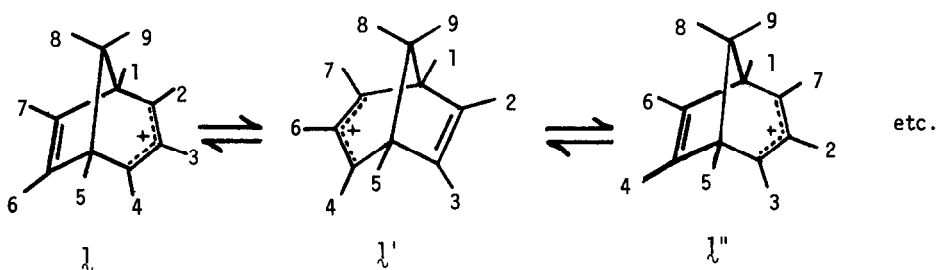
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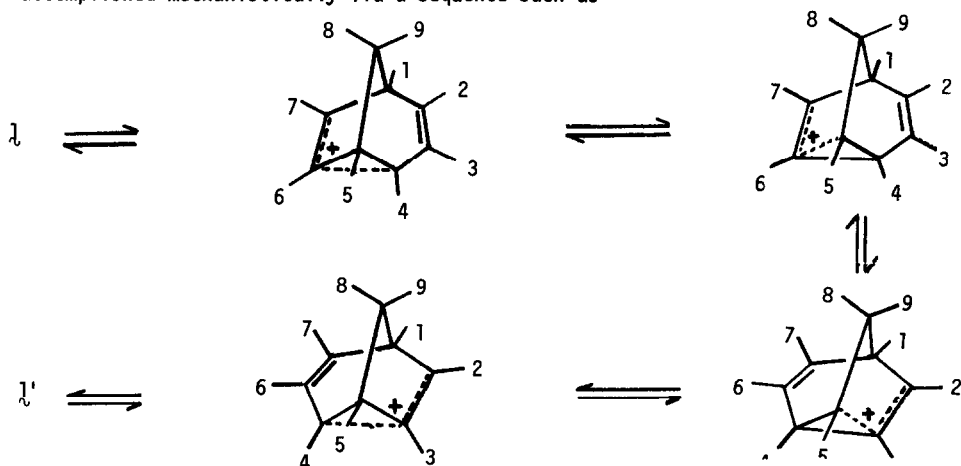
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In  $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$  at  $-50$  to  $-100^\circ$  the nonamethylbicyclo[3.2.1]octadien-2-yl cation  $\lambda$  undergoes an nmr-observable reversible exchange process which equilibrates methyls 2,3,4,6 and 7 and methyls 8 and 9, but leaves the bridgehead methyls (1 and 5) unique.<sup>1</sup>

CIRCUMAMBULATION



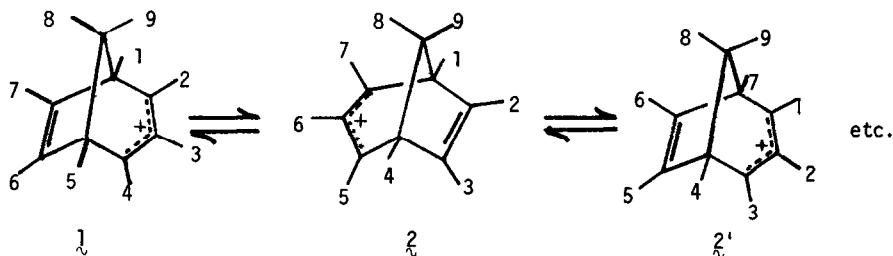
This observation was rationalized by a circumambulatory process ( $\lambda \rightleftharpoons \lambda' \rightleftharpoons \lambda''$ , etc.) which may be accomplished mechanistically via a sequence such as



Solutions of  $\lambda$  in  $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$  maintained at  $-50$  to  $-60^\circ$  underwent an irreversible change which could be followed kinetically by nmr and which converted  $\lambda$  to a bicyclo[3.3.0]octadien-2-yl cation (see accompanying paper for details). No other processes are observable by nmr.

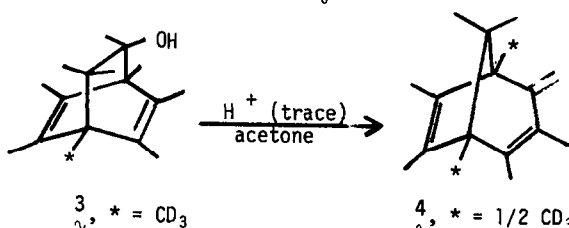
It seemed unusual that, as far as one could discern from nmr studies, ion  $\lambda$  did not appear to undergo a 1,2-shift of the methano bridge ( $\lambda \rightleftharpoons \xi \rightleftharpoons \xi'$ , etc.). This process, which might be expected to have a low activation energy, would equilibrate methyls 1-7 and methyls 8 and 9.

#### BRIDGE SHIFT

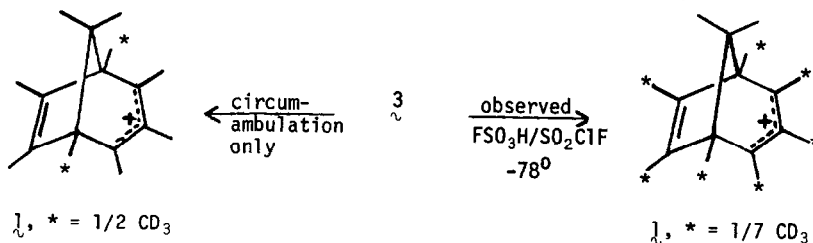


To test for this possibility, two types of labeling experiments were performed.

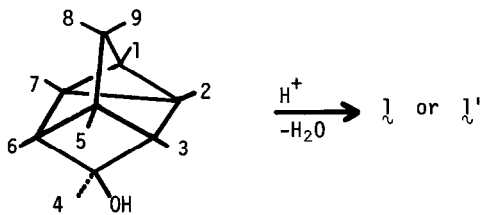
In alcohol  $\xi^2$ , the  $\text{CD}_3$  group is located so that it must become a bridgehead methyl in ion  $\lambda$ . If only circumambulation occurred, one would expect the nmr singlet due to methyls (1 + 5) to be reduced 50% in area relative to the singlets from methyls (2 + 4) and (6 + 7). This area reduction should have been readily observable. Indeed, when  $\xi$  was treated with a trace of acid (0.1% HCl in acetone, room temperature, 15 min) hydrocarbon  $\lambda$  (the sole quenching product<sup>1</sup> of  $\lambda$ ) was obtained half-labeled at each bridgehead position. Under these conditions,  $\lambda$  loses a proton before equilibration can occur. However, when  $\xi$  was treated with  $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$  at  $-78^\circ$ , the



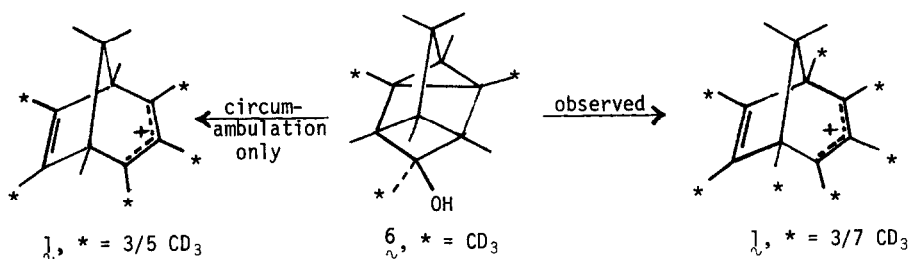
resulting  $\lambda$  had an nmr spectrum which was barely distinguishable from that of unlabeled  $\lambda$ , because the three deuteriums were equally distributed amongst the 21 hydrogens of methyls 1-7.



Ion  $\lambda$  was first prepared<sup>1</sup> from  $\xi$ , which ionizes in acid with contraction of the cyclobutane ring:



Alcohol  $\xi$  has  $\text{CD}_3$  groups in positions which become methyls 2, 4 and 7 in ion  $\lambda$  (or  $\lambda'$ ). If only circumambulation occurred, one would expect the nmr singlet due to methyls (1 + 5) to remain at full intensity. In fact, when  $\xi$  was treated at  $-78^\circ$  with  $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$ , the signal due to methyls (1 + 5) had the same intensity as the singlets due to methyls (2 + 4) and (6 + 7). The observed nmr (see table) indicated that the label was equally distributed amongst methyls 1-7.



#### Process

#### Expected Areas of Proton Nmr Signals in $\lambda$ Derived from $\xi$

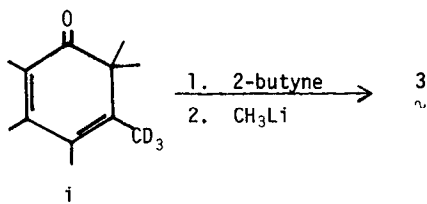
	(1 + 5)	(2 + 4)	(6 + 7)	(3)	(8)	(9)
Circumambulation	6	2.4	2.4	1.2	3	3
Observed	2.6	2.6	2.6	1.3	3	3

We conclude that  $\lambda$  undergoes 1,2-methano bridge shifts in strong acid at a rate which is rapid relative to the irreversible isomerization to a bicyclo[3.3.0]octadien-2-yl cation but slow relative to circumambulation. The bridge shift is concealed from nmr detection, however, since before the temperature where it would be observable is attained,  $\lambda$  rearranges irreversibly.

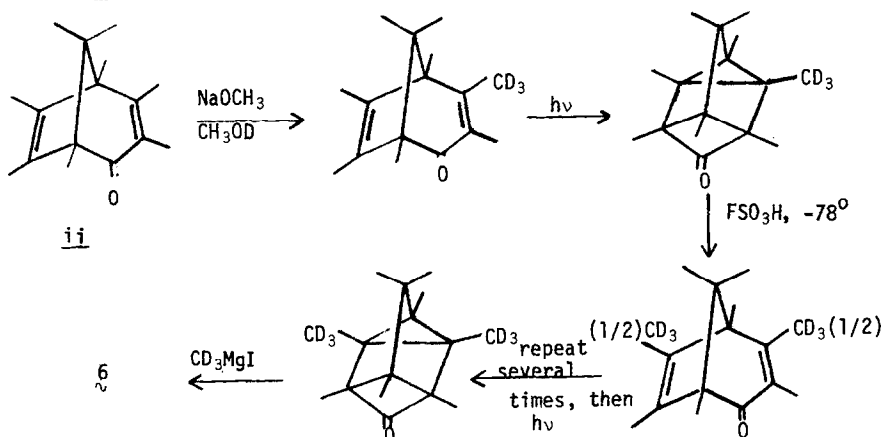
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## REFERENCES

- H. Hart and M. Kuzuya, *J. Amer. Chem. Soc.*, 95, 4096 (1973). Irradiation (100 MHz,  $-80^{\circ}$ ) of any one of the signals due to methyls (2 + 4), (3), or (6 + 7) in ion 1 caused a reduction in the areas of the other two but had no effect on the signal due to methyls (1 + 5).
- Prepared from 1<sup>3</sup>.



- H. Hart, P. M. Collins and A. J. Waring, *J. Amer. Chem. Soc.*, 88, 1005 (1966).
- Prepared from 1<sup>5</sup> by the sequence:



- H. Hart and G. M. Love, *J. Amer. Chem. Soc.*, 93, 6266 (1971).