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A DEUTERIUM TRACER STUDY OF 6,1,2-HYDRIDE SHIFT IN SUBSTITUTED NORBORNYL CATIONS*

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One of the important but unanswered questions concerning the reaction of nitrous acid with primary aliphatic amines[1,2] has been[3] whether the classical ions originally formed on loss of nitrogen can survive several Wagner-Meerwein rearrangements or hydride shifts. *We now have evidence that they can.* We previously reported[4] that a classical, secondary norbornyl cation survives a Wagner-Meerwein rearrangement, since the rearranged cation was attacked from the endo-direction to produce 1.8% of endo-product. Hückel and Kern[5] have demonstrated that both exo- and endo-fenchylamines produce exo- and endo-isomers of α-fenchene hydrate, thus showing that a tertiary classical cation can survive Wagner-Meerwein rearrangement to yield endo-products.

In the deaminations (in acetic acid—sodium acetate) of 1[6] and 2[7] (Chart I) the yields of 3 and 4 (as the monoacetates)[8] are in the same ratio (1.6-1.7) from both reactants, and this ratio is roughly the same as the ratio of 3:4 (1.4) observed upon the hydrolyses[9] of the secondary tosylates of 3 and of 4. Thus B and C *might mistakenly be interpreted as a nonclassical* ion particularly

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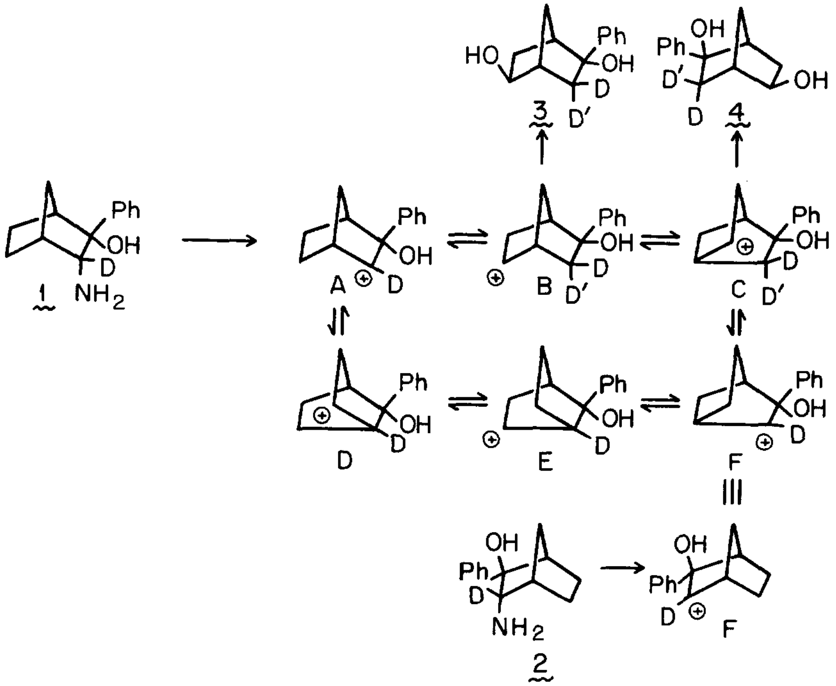

CHART I

since the two *exo*-amines corresponding to the two ions B and C yield the acetates of **3** and **4**, on deamination, in the ratios of 2.2:1 and 1:1.7 respectively.[10]

If both **1** and **2**, however, should prefer the same clockwise pathway and approach B ⇌ C from the "B-side," then deaminations both of **1** and **2** should result in **3**:**4** > 1, even if B and C are classical. That both reactants approach the equilibrium B ⇌ C through clockwise pathways (as the intermediates are oriented in the chart) was demonstrated by means of deuterium labeling. The positions in **3** and **4** designated "D" denote where the deuterium goes *via* the clockwise pathways, whereas "D′" denotes the fate of deuterium when **3** and **4** result from counterclockwise pathways. The results are given in Table I, and show that both reactants yield **3** and **4** by predominant (77-89%) clockwise routes. The yields of **3** and **4** as determined by the isotope dilution method,[11] are also given in Table I. These data thus show that a comparison of the product ratios **3**:**4** from the two reactants **1** and **2** is not of itself a sufficient criterion for nonclassical character of the ions $B \rightleftharpoons C$.

Another important conclusion can be drawn from Chart I and Table I: If $B \rightleftharpoons C$ were in fact a single nonclassical ion then 3 and 4 from a given, single reactant should exhibit identical deuterium distributions in D and D′. That these distributions are significantly different means that even after two Wagner-Meerwein rearrangements and a hydride shift, ions B and C are best formulated as unbridged, classical ions, *which have not reached equilibrium*.

Table I

Yields and Deuterium Distributions in 3 and 4 from Deaminations of 1 and 2

Reactant	Product 3		Product 4	
	Yield, %[a]	D′[b]	Yield, %[a]	D′[b]
1	4.25 ± .01	0.11 ± .025	2.7 ± .01	0.175 ± .016
2	6.3 ± .02	0.145 ± .025	3.7 ± .02	0.23 ± .016

[a] The ± values are the reproducibilities of the carbon-14 assays.

[b] Standard error.

In 4 containing no D, the signals for 2H at C_3 are centered at $\delta = 2.07$ ppm (pyridine), and overlap the multiplet for the *anti*-C_7H (intensity 3.00 ± .02). In 4 from either 1 or 2 the intensity is 2.00 ± .03. There was no loss of deuterium in the other products[7,8] of deamination of 1 and 2. Conversion of 4 to the 2-*exo*-5-*endo*-diol[7] allowed isolation of the signal ($\delta = 3.25$ ppm) for *endo*-H at C_3. Diol 3 (no D) exhibits a quartet ($\delta = 2.4$ ppm, pyridine) for *exo*-H at C_3, and is overlapped by H at C_4 (intensity, 2.00 ± .03). Integration of this signal for 3 (with D) gave the fraction of *exo*-H at C_3. On oxidation of 3 to the ketone,[4] the signal for *exo*-H at C_3 is at $\delta = 2.6$ ppm (pyridine) and is also overlapped by H at C_4.

References

1. H. Söll, in Houben Weil "Methoden der organischen Chemie," E. Müller, Ed., Georg Thieme Verlag, Stuttgart XI/2, 133-181 (1958).
2. J. H. Ridd, *Quarterly Reviews (London)*, **15**, 418 (1961).
3. P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, New York, N. Y., page 65 (1965).
4. B. M. Benjamin and C. J. Collins, *J. Amer. Chem. Soc.* **92**, 3183 (1970).
5. W. Hückel and H.-J. Kern, *Ann* **738**, 49 (1969).
6. C. J. Collins, B. M. Benjamin, V. F. Raaen, I. T. Glover, and M. D. Eckart, *Justus Liebig's Annalen der Chemie* **739**, (1970).
7. C. J. Collins, V. F. Raaen, and M. D. Eckart, *J. Amer. Chem. Soc.* **92**, 1787 (1970).
8. The products of the deaminations of **1** and **2** have all been described before [see ref. 7, and C. J. Collins and B. M. Benjamin, *ibid.*, **89**, 1652 (1967)].
9. B. M. Benjamin, B. S. Benjaminov, and V. F. Raaen, unpublished work.
10. C. J. Collins and B. M. Benjamin, *J. Amer. Chem. Soc.* **92**, 3182 (1970).
11. V. F. Raaen, G. A. Ropp, and H. P. Raaen, "Carbon-14," McGraw-Hill, New York, N. Y., 1968, Chapter 2.