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SECONDARY ISOTOPE EFFECTS IN THE SOLVOLYSIS OF exo-NORBORNYL BROMIDE

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Secondary isotope effects have provided a subtle but powerful tool for diagnosing intimate details of solvolysis reactions (1); we wish to report the results of an application of this technique to the solvolysis of exo-norbornyl bromide. Optically active exo-norbornanol (2) was oxidized to norcamphor (3) and reduced to the endo alcohols with lithium aluminum hydride (4). Reaction of this alcohol with triphenylphosphine and bromide (5) gave optically active exo-norbornyl bromide (1). Repetition of these experiments with optically active norcamphor-3,3-d_2 produced optically active exo-norbornyl bromide-3,3-d_2 (2). All of the above reactions were shown to proceed without any detectable racemization. The solvolysis rates of the bromides were measured polarimetrically (k_α) and titrametrically (k_t) (using a Modified Volhard Procedure) in acetic acid (4 M in water, 0.6 M in sodium acetate, 51.25°) and our results

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are summarized in Table 1. Rate constants were calculated using a least squares procedure and the deviations reported indicate the range of values observed for several runs. Several features of these data are significant.

Table 1

Solvolysis of exo-Norbornyl Bromides

Compound	k_α(x 10^3 min.$^{-1}$)	k_t(x 10^3 min.$^{-1}$)	$(k_H/k_D)_\alpha$	$(k_H/k_D)_t$
1	2.142 ± .001	0.2516 ± .0006	1.087 ± .005	1.038 ± .011
2	1.971 ± .007	0.2425 ± .0020		

The solvolysis of 11-chloro-11-methyl-9,10-dihydro-9,10-ethanoanthracene-12,12-d_2 (3) is limiting and since the stereochemical relationship of the halogen and adjacent methylene groups is almost identical to that of C_2 and C_3 in the norbornyl skeleton, this compound can serve as a useful model for comparison. Before a quantitative assessment of our data can be attempted, however, it is necessary to evaluate the effects of comparing (1) a limiting solvolysis in a secondary and tertiary system, (2) chloride versus bromide as a leaving group and (3) solvolysis in acetic acid (4 M in water) versus 60% ethanol-water.

From the extensive data in the literature (1) it is now apparent that once geometrical factors have been allowed for, the magnitude of a secondary isotope effect in a solvolysis reaction is a function of the electron deficiency at the reacting carbon atom in the transition state.

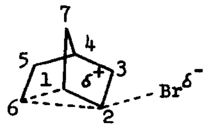
Since there are more possibilities for charge delocalization in tertiary carbinyl systems than in comparable secondary carbinyl systems, a greater secondary isotope effect (per D) would be expected from a limiting solvolysis in the latter system.

The magnitude of a secondary isotope effect is also a sensitive function of the nature of the leaving group (exiphile)** and increases as the exiphilicity of the group increases in non-limiting solvolysis. On this basis, the secondary isotope effect observed during the solvolysis of a bromide should always be slightly *greater than* that of an analogous chloride, but this difference is probably negligible for limiting solvolysis.

Lastly, secondary isotope effects observed in limiting solvolysis are insensitive to wide variations in electrophilic and nucleophilic properties of solvents at constant Y values (6). Although no comparable studies concerning the effect of varying Y values have been published, fragmentary data indicate that variation of Y over a range of 2-3 log units causes *less than* 0.5% variation if k_H/k_D (per D) (6,7). On these grounds we have concluded that the differences in solvent used in the present study and in the model system which we have chosen (8) will not seriously effect our interpretation.

When the solvolysis rates of **1** and **2** were measured polarimetrically, a secondary isotope effect $(k_H/k_D)_\alpha$ of 1.087 was found. This value is about 40% less than the value which is predicted by our model (1.14) (8) (**3**) and provides further evidence that the transition state for the solvolysis of *exo*-norbornyl derivatives is stabilized by delocalization of the C_1-C_6 sigma bond (9). Since this conclusion requires that in the transition state for solvolysis (**4**) the electron deficiency on carbon is borne by both C_1 and C_2

** We propose that the word *exiphile* be used to denote a leaving group. Extensions to exiphilicity (e.g. leaving tendancy) are obvious, descriptive and concise.



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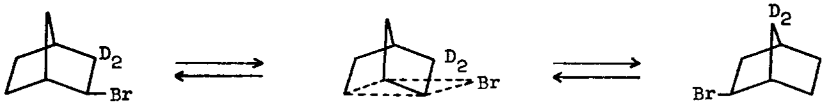
it became apparent that a study of the solvolysis of *exo*-norbornyl bromide-7,7-d_2 (5) would be profitable and reveal considerable additional detail about the geometry of the transition state.

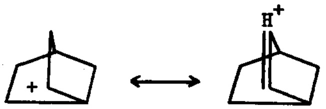
Internal return in the norbornyl system results in the interchange



2 **5**

of the C_3 and C_7 methylene groups (10) and if solvolysis conditions are chosen such that internal return is significant enough to allow equilibration of **2** and **5** a comparison of the secondary isotope effects measured polarimetrically for **2** can provide an estimate of the value of $(k_H/k_D)_\alpha$ for **5** (11). Although the experimental uncertainty in the value of $(k_H/k_D)_t$ is about twice as large as for $(k_H/k_D)_\alpha$, it is apparent that $(k_H/k_D)_\alpha$ for **5** must be very small and probably approaches 1.00.

For a resonance form such as **6** to be important, carbon atoms 1, 2, 4, and 7 must be nearly coplanar. Since this would require a considerable molecular reorganization as progress is made from the starting material to



the transition state for solvolysis, the small value of $(k_H/k_D)_\alpha$ for 5 indicates that the geometry of the nuclei of the norbornyl framework has not changed significantly in the transition state.

An alternative explanation for the absence of a secondary isotope effect in the solvolysis of 5 which should also be considered is that there is no electron deficiency at C_1 in the transition state; several experimental facts argue against this interpretation. Substituents attached to C_1 will be restricted in their electronic interactions with the transition state by similar geometrical requirements for resonance as those discussed above for the C_7 methylene group and therefore, substituent effects at C_1 should follow primarily an inductive order rather than a resonance-inductive order. Schleyer (13) has reported that the relative rate promoting factors of 1-methyl, 1-ethyl, and 1-phenyl substituents are 50, 82, and 3.9 respectively for the solvolysis of exo-norbornyl tosylates which is consistent with these expectations. These data, coupled with our own findings, provide strong supporting evidence that the formation of the transition state in the solvolysis of *exo*-norbornyl derivatives is anchimerically assisted (9,10) but that the geometry of the carbon skeleton is approximately that of the starting material.

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References

1. E.A. Halevi, "Progress in Physical Organic Chemistry", Vol. 1, Interscience Publishers, New York, N.Y., 1963, p. 109.

2. H.C. Brown and G. Zweifel, J. Am. Chem. Soc., 83, 486 (1961).

3. D.C. Kleinfelter and P. von R. Schleyer, J. Org. Chem., 26, 3740 (1961).

4. C.F. Wilcox, M. Sexton, and M.F. Wilcox, J. Org. Chem., 28, 1079 (1963).

5. G.A. Wiley, R.L. Hershkowitz, B.M. Rein, and B.C. Chung, J. Am. Chem. Soc., 86, 964 (1964).

6. G.J. Frisone and E.R. Thornton, J. Am. Chem. Soc., 86, 1900 (1964).

7. A.H. Fainberg and S. Winstein, J. Am. Chem. Soc., 78, 2770 (1956).

8. V.J. Shiner, Jr. and J.S. Humphrey, J. Am. Chem. Soc., 85, 2416 (1963).

9. S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, J. Am. Chem. Soc., 87, 376 (1965) and references cited therein.

10. S. Winstein and D. Trifan, J. Am. Chem. Soc., 74, 1154 (1952).

11. The possibility exists that further scrambling can occur via 1,3-hydride shifts. However, Roberts[12] has found that in the solvolysis reaction this occurs only to the extent of 45% for the overall reaction and it seems likely that it will occur to a much lesser extent in the intimate ion pair.

12. J.D. Roberts, C.C. Lee, and W.H. Saunders, Jr., J. Am. Chem. Soc., 76, 4501 (1954).

13. P. von R. Schleyer, M.M. Donaldson, and W.E. Watts, J. Am. Chem. Soc., 87, 375 (1965). P. von R. Schleyer and D.C. Kleinfelter, Abstracts of Papers, 138th National Meeting of the American Chemical Society, New York, N.Y., Sept. 1960, p. 43.