Secondary Deuterium Isotope Effects on the Solvolysis of *exo*-8- and *endo*-8-Tetracyclo[4,3,0,$0^{2,4}$,$0^{3,7}$]nonyl ("Deltacyclyl") Brosylates

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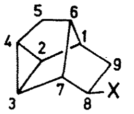
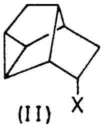
Summary Secondary β-deuterium isotope effects measured for acetolysis of *exo*-9-deuterio-*exo*-8-deltacyclyl brosylate (VI) and *exo*-9-deuterio-*endo*-8-deltacyclyl brosylate (VIII) support the direct generation of a delocalized intermediate (III) from *exo*-brosylate (I-OBs) and a localized ion (IV) from *endo*-brosylate (II-OBs).

OUR recent research on the stereochemistry of solvolysis of *exo*-8- and *endo*-8-deltacyclyl[1] substrates (I) and (II), the deuterium scrambling pattern for acetolysis of labelled (I-OBs) and (II-OBs), the rates of acetolysis of (I-OBs) and (II-OBs), and the acetolysis of optically active (I-OBs) and (II-OBs) has encouraged us to suggest that ionization of (I) generates the non-norbornonium-delocalized cation (III) directly, while ionization of (II) initially produces a classical ion (IV).[2] We now find that an analysis of secondary β-deuterium isotope effects for the solvolyses of labelled (I-OBs) and (II-OBs) provides significant insight into the reaction pathways followed during the solvolyses of substrates (I) and (II).

exo-9-Deuterio-*exo*-8-deltacyclyl brosylate (VI) was synthesized from the corresponding alcohol, which was prepared by deuterioboration of deltacyclene (V)[1,3] followed by oxidation. *exo*-9-Deuterio-*endo*-8-deltacyclyl brosylate (VIII) was constructed by allowing 8-deltacyclanone (VII) to undergo base-catalysed exchange with deuterium oxide and then reducing the labelled ketone (17·5% d_0, 78.5% d_1, 4% d_2) with lithium aluminium hydride and converting the 88 : 12 *endo* : *exo*-mixture of alcohols into *endo*-brosylate (VIII) by treatment with brosyl chloride and pyridine, followed by recrystallization.



(I)



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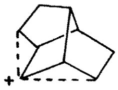
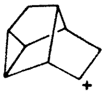
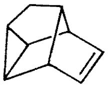


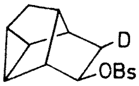
(III)



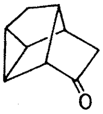
(IV)



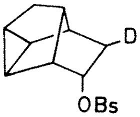
(V)



(VI)



(VII)



(VIII)

The large isotope effect found for the *endo*-brosylate (VIII), $k_H/k_D = 1{\cdot}26$, and the reduced isotope effect found for *exo*-brosylate (VI), $k_H/k_D = 1{\cdot}14$ (see Table), provide a similar pattern to that for secondary β-deuterium isotope effects in 2-norbornyl systems.[4,5] A consideration of the range of possible dihedral angles between the β-C–D bond and the developing *p*-orbital for the transition states for ionization of brosylates (VI) and (VIII) reveals that any differences in this angle would only serve to increase the k_H/k_D ratio for (VI) over that for (VIII).[6] Since the reverse order is the case, the present evidence clearly supports a reduced hyperconjugative demand[7] in the transition state for ionization of *exo*-substrates (I) due to delocalization and the direct generation of a classical intermediate for solvolytic reactions of *endo*-substrates (II). The extent of delocalization and/or bridging appears to be less well developed in the transition state for (I) than in the *exo*-2-norbornyl case.

First order rate constants for the acetolysis of (I-OBs), (II-OBs), (VI), and (VIII) at 25·68°

Brosylate	k (sec.$^{-1}$)[a]	k_H/k_D	k_H/k_D per D
(I-OBs)	$2{\cdot}61 \pm 0{\cdot}09 \times 10^{-4}$		
(VI)	$2{\cdot}29 \pm 0{\cdot}01 \times 10^{-4}$	$1{\cdot}14 \pm 0{\cdot}04$	$1{\cdot}14 \pm 0{\cdot}04$
(II-OBs)	$4{\cdot}62 \pm 0{\cdot}06 \times 10^{-6}$		
(VIII)	$3{\cdot}75 \pm 0{\cdot}001 \times 10^{-6}$	$1{\cdot}23 \pm 0{\cdot}02$	$1{\cdot}26 \pm 0{\cdot}02$

[a] Average and average deviation based on two runs except for the rate constant for (I-OBs) which is based on three runs.

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[1] The name deltacyclane has been suggested for tetracyclo[4,3,0,0^{2,4},0^{3,7}]nonane and deltacyclene for the related olefin, tetracyclo-[4,3,0,0^{2,4},0^{3,7}]non-8-ene (V) by A. Nickon, G. D. Pandit, and R. O. Williams, *Tetrahedron Letters*, 1967, 2851, and H. R. Kwasnik, Ph.D. Thesis, Johns Hopkins University, Baltimore, 1966.

[2] P. K. Freeman and D. M. Balls, *Tetrahedron Letters*, 1967, 437; P. K. Freeman, D. M. Balls, and J. N. Blazevich, submitted for publication in *J. Amer. Chem. Soc.*

[3] P. K. Freeman and D. M. Balls, *J. Org. Chem.*, 1967, **32**, 2354.

[4] J. P. Schaefer, M. J. Dagani, and D. S. Weinberg, *J. Amer. Chem. Soc.*, 1967, **89**, 6938; J. P. Schaefer and D. S. Weinberg, *Tetrahedron Letters*, 1965, 2491; J. P. Schaefer, J. P. Foster, M. J. Dagani, and L. M. Honig, *J. Amer. Chem. Soc.*, 1968, **90**, 4497.

[5] J. M. Jerkunica, S. Borčić, and D. E. Sunko, *Chem. Comm.*, 1968, 1488.

[6] V. J. Shiner, jun., B. L. Murr, and G. Heinemann, *J. Amer. Chem. Soc.*, 1963, **85**, 2413; V. J. Shiner, jun., and J. S. Humphrey, jun., *ibid.*, 2416.

[7] V. J. Shiner, jun., W. E. Buddenbaum, B. L. Murr, and G. Lamaty, *J. Amer. Chem. Soc.*, 1968, **90**, 418.