

## $\sigma$ -Participation and Secondary Deuterium Isotope Effects: the Norbornyl Case

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THE interesting, but still controversial proposal, of carbon-carbon  $\sigma$ -bond participation in the solvolysis of *exo*-2-norbornyl derivatives as opposed to a nonparticipating path for the *endo*-isomer, stimulated the study of secondary kinetic isotope effects in specifically deuterated 2-norbornyl derivatives. Thus, a significant  $\gamma$ -isotope effect was observed in the *exo*-2,6-dideuterio-series, while

such an effect was absent in the *endo*-2,6-dideuterio-series.<sup>1</sup>

In a previous paper<sup>2</sup> the hypothesis was advanced that charge delocalization results in a reduced hyperconjugative electron release from neighbouring CH<sub>3</sub> and CD<sub>3</sub> groups, and that secondary  $\beta$ -deuterium isotope effects might become a useful probe for neighbouring group participation. A

TABLE 1

*Acetolysis rates of 2-norbornyl p-bromobenzenesulphonates*

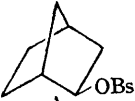
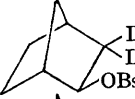
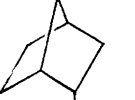
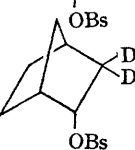
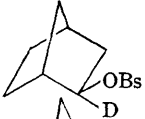
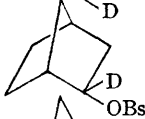
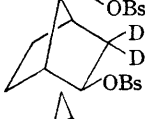
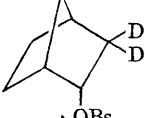
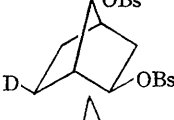
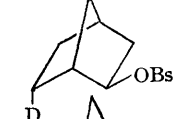
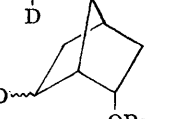
Compound	Temp. (°C)	$k \times 10^5 \text{ sec.}^{-1}$	$k_{\text{H}}/k_{\text{D}}$
	44.3	$97.2 \pm 1.3$	—
	44.3	$95.8 \pm 1.4$	$1.014 \pm 0.018$
	65.0	$5.63 \pm 0.03$	—
	65.0	$4.47 \pm 0.08$	$1.26 \pm 0.009$

TABLE 2

*Secondary deuterium isotope effects in the acetolysis of 2-norbornyl p-bromobenzenesulphonates*

Reactant	Transition state	Expected $k_{\text{H}}/k_{\text{D}}$	Observed	Reference
	classical bridged	1.15–1.20 1.10	1.10	6
	classical	1.15–1.20	1.20	6
	classical bridged	1.30 1.10	1.014	this work
	classical	1.30	1.26	this work
	classical bridged	1.00 1.10	1.09–1.15	1
	classical bridged	1.00 1.10	1.10–1.11	1
	classical	1.00	0.98–1.02	1

subsequent systematic investigation<sup>3</sup> revealed a linear relationship between  $\alpha$ -methyl substituent effects and CD<sub>3</sub> isotope effects. This, however, did not invalidate the original hypothesis but merely demonstrated the mostly hyperconjugative origin of methyl group rate effects.

In the 2-norbornyl system, the hydrogen atoms on the methylene group, adjacent to the reacting centre, form a dihedral angle of 0–120° with the leaving group. Therefore, by replacing both hydrogens on C-3 with deuterium, the isotope effect should be the same regardless of the stereochemistry at C-2 (*exo* or *endo*). However, if bridging in the transition state is sufficiently advanced<sup>4</sup> and present only in the solvolysis of *exo*-2-norbornyl derivatives, deuteration in the 3-position should have only a small effect on the rate, while the corresponding *endo*-derivative should show a  $\beta$ -effect of normal magnitude.

The *exo*-3,3-dideuterio-2-norbornyl bromide was already solvolysed by Schaefer and Weinberg,<sup>5</sup> who reported a drastically reduced  $\beta$ -effect, but no data were presented for the *endo*-compound. We have now determined the  $\beta$ -isotope effect in

the two isomeric norbornyl derivatives under conditions comparable to the one used with the 6-deuterio-compounds.<sup>1b</sup> Thus, *exo*- and *endo*-3,3-dideuterio-2-norbornyl *p*-bromobenzenesulphonates were prepared and solvolysed in glacial acetic acid. The rate of the reaction was followed automatically using a Radiometer Copenhagen TTT-11 titrigraph and the results are presented in Table I.‡

As predicted, only the *exo-p*-bromobenzenesulphonate showed a significantly reduced  $\beta$ -effect, while the rate retardation in the *endo*-compound was of the expected magnitude for unassisted solvolysis.

The relevance of this result, as well as of similar studies,<sup>1,6</sup> to the non-classical ion problem may be questioned by opponents of bridged, electron-deficient intermediates, but the direct comparison of isotope effects in specifically deuterated norbornyl derivatives undoubtedly shows an exceptional behaviour of the *exo*-isomer (Table 2), for which some explanation should be made.

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‡ The position of the label in the epimeric 3,3-dideuterionorborneols was checked by n.m.r. The deuterium content was better than 92% for 2 deuteriums. The possibility of a complicating internal return can be ruled out on the grounds identical to the ones discussed for the 6-deuterio-compounds (see ref. 1).

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<sup>3</sup> K. L. Servis, S. Borčić, and D. E. Sunko, *Tetrahedron*, 1967, **23**, in the press.

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<sup>5</sup> J. P. Schaefer and D. S. Weinberg, *Tetrahedron Letters*, 1965, 2491.

<sup>6</sup> C. C. Lee and E. W. C. Wong, *J. Amer. Chem. Soc.*, 1964, **86**, 2752.