

## Swamping of Norbornyl Nonclassical Participation by Allyl Participation

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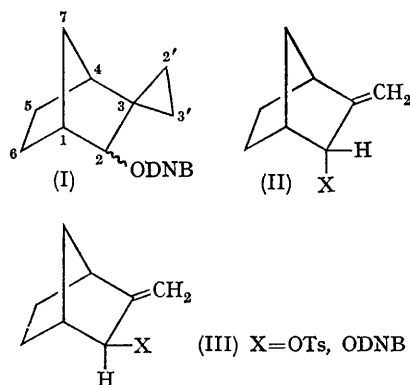
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THE solvolyses of the spiro-cyclopropyl norbornyl 3,5-dinitrobenzoates (I) in acetone-water show a marked decrease in the *exo/endo*-rate ratio commonly associated with norbornyl systems.<sup>1,2</sup> This result was interpreted to mean that the normally large *exo/endo*-rate ratio due to nonclassical participation could be swamped by the strongly rate-enhancing cyclopropyl group. However, a number of objections could be made to this interpretation.<sup>1</sup> Notably, the participation of the cyclopropyl group could involve nuclear displacement of C-2' so as to favour the *endo*-solvolysis for steric reasons. Also, the difference in leaving group and solvent from other norbornyl solvolyses might cause complications.

We report here the solvolysis (in both 70% acetone-H<sub>2</sub>O and acetic acid) of the allyl compounds (II) and (III), which like the previously reported cyclopropyl compounds are substituted at the 3-position.

If the explanation suggested for the cyclopropyl compounds is correct one would expect a similarly small *exo/endo*-ratio for the allyl system. The

alternate steric interpretation should lead to the usual large ratio of 280—1000. The observed kinetic data, recorded in the Table, show a small ratio that is nearly identical to that observed in the cyclopropyl case. The fact that the solvolysis



TABLE

Compound	T(°C)	k(sec. <sup>-1</sup> )	k <sub>exo/endo</sub>
<i>exo</i> -OTs (HOAc)	25.00	1.02 × 10 <sup>-4</sup>	3.9
<i>endo</i> -OTs (HOAc)	25.00	2.62 × 10 <sup>-5</sup>	
<i>exo</i> -ODNB(acetone-H <sub>2</sub> O)	124.9	3.1 × 10 <sup>-6</sup>	3.1 (125°)
<i>endo</i> -ODNB(acetone-H <sub>2</sub> O)	127.3	1.3 × 10 <sup>-6</sup>	
<i>exo</i> -norbornyl-OTs(HOAc)	25.00	2.36 × 10 <sup>-5</sup> (ref. 4)	280
<i>endo</i> -norbornyl-OTs(HOAc)	25.00	8.28 × 10 <sup>-8</sup> (ref. 4)	

rate of (III) is not enhanced much over the *exo*-norbornyl rate could be explained by the decrease of angle at the solvolytic centre.<sup>3</sup>

These results provide additional evidence that the large *exo*-/*endo*-rate ratio commonly observed in the solvolysis of norbornyl derivatives does not have a

primarily steric origin. The results do not, however, reveal the degree of distortion of the C-1-C-6 bond or the nuclear displacement of C-6 in the norbornyl transition state.

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<sup>1</sup> C. F. Wilcox, jun., and R. G. Jesaitis, *Tetrahedron Letters*, 1967, 2567.

<sup>2</sup> G. D. Sargent, *Quart. Rev.*, 1966, 20, 301.

<sup>3</sup> The Schleyer-Foote correlation (P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1964, 86, 1946, 1854) may be used to estimate that this factor causes a decrease of *ca.* 1000 in the rates by noting that the difference in the C=O stretch between norcamphor and methylenenorcamphor is only 13 cm.<sup>-1</sup>. Conjugation with a double bond usually produces a shift of *ca.* 40 cm.<sup>-1</sup>.

<sup>4</sup> P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Amer. Chem. Soc.*, 1965, 87, 375.