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EXAMINATION FOR σ PARTICIPATION IN SECONDARY 2-NORBORNYL DERIVATIVES INVOLVING INDUCTIVELY ENHANCED ELECTRON DEMAND

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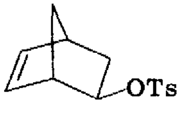
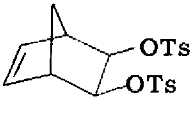
The question of the existence of σ participation in the solvolysis of 2-norbornyl systems has been given an almost unseemly scrutiny, yet chemists have still not reached a consensus.[1] Recent work has taken two principal directions: examination of the cation by spectroscopic methods (XPS, NMR, Raman) under conditions of long life[2] and use of tertiary systems that electronically resemble the secondary system through increased electron demand at the cationic center.[3] Proponents of the first experiments must demonstrate that the conditions of long-lived carbonium ions are relevant to the solvolytic problem, and those of the second experiments must demonstrate that tertiary systems are legitimate models for the actual cynosure: the 2-norbornyl system. We wish to report solvolytic experiments on secondary systems that suffer from neither of these limitations. The results do not support participation by the 6, 1 σ electrons in the transition state to solvolysis of 2-norbornyl tosylates.

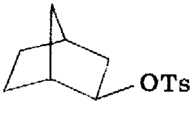
Previously, we demonstrated that the very weak double bond participation in the acetolysis of *exo*-2-norborn-5-enyl tosylate (*exo*-1) can be considerably enhanced by



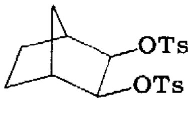
exo-1



cis-*exo*-2



exo-3



cis-*exo*-4

placement of a strongly electron-withdrawing group at the 3 position, as in cis-exo-2 (also in trans-2 and in the analogous cis-exo acetoxy tosylate).[4] Thus, the exo/endo rate ratio at 25° for 1 is 2900[5] (430 at 100°) but the cis-exo/cis-endo ratio for 2 is 140,000 (29,000 at 100°). Furthermore, the unsaturated/saturated ratio at 25° for the exo monotosylates (exo-1/exo-3) is 0.3, but for the ditosylates (cis-exo-2/cis-exo-4) it is 504.[4] Thus by both the exo/endo and the unsaturated/saturated criteria, double bond participation is much stronger in the ditosylate than in the monotosylate. The double bond in cis-exo-2 removes positive charge from the vicinity of the remaining electronegative group (tosylate or acetate). There is greater need for double bond participation in 2 than in 1 because of increased electron demand at the original site of positive charge development. Thus, homoallylic double bond participation is "inductively enhanced."

Whereas Brown used increased electron demand to make tertiary systems resemble secondary systems, we use increased electron demand through introduction of a 3-tosyloxy group (4) to create a new secondary system capable of stronger σ participation than 2-norbornyl (3). The exo/endo ratio in the 2-norbornyl system (3) originally served as a criterion for σ participation, although the absolute magnitude (280 at 25°[6]) can no longer be considered meaningful, since many tertiary systems that clearly lack σ participation have similar exo/endo ratios.[3] Nonetheless, if σ participation is at all viable, an electron-withdrawing group, as in 4, should accelerate the departure of an adjacent exo tosylate group over that of an endo tosylate. As in the homoallylic case (2), increased electron demand caused by the adjacent tosylate group in 4 should enhance participation by 6,1 σ electrons. The homoallylic system (2) is a legitimate model for the behavior expected for σ participation (4), since the perturbing 3 substituent is the same number of bonds removed from the positive charge in the delocalized models (5 position for π delocalization in 2, 1 position for σ delocalization in 4). By the same token, use of a 3 substituent for enhancement of participation does not significantly alter the electronic nature of the participating bond (5,6 double bond in 2, 6,1 single bond in 4) by direct substitution.[7] An exo substituent at the 3 position cannot exert a steric effect at the 5 position of 2 or the 1 position of 4. Thus the sole function of the 3 substituent is to increase electron demand at the secondary 2 position and thereby induce greater participation of the π bond of 2 or the σ bond of 4.

Consequently, we have prepared the cis-exo- (4) and cis-endo-2,3-norbornylene ditosylates and measured their titrimetric acetolysis rates (Table I). Full product studies have also been completed but shed no particular light on the mechanism. At 25°, the exo/endo ratio for the ditosylates (**4**) is 48, compared to 280 for the monotosylates[6] (**3**). At 100° (closer to the temperatures of measurement),[8] the ditosylate ratio is 17, compared to 73 for the monotosylates.[6] The 3-acetoxy-2-norbornyl tosylates were also examined, and the cis-exo/cis-endo ratio at 100° was 8.2 (250 at 25°). Thus in the σ systems (**3**,**4**), neither tosyloxy nor acetoxy invokes an enhanced reactivity of the adjacent exo leaving group. In contrast, the tosyloxy group in the unsaturated series (**1**,**2**) increases the exo/endo ratio by a factor of 67 at 100°. These results are illustrated graphically in Figure 1, in which our data considerably extend those obtained earlier by Brown *et al.*[3] Most significantly, our data extend the points from their tertiary systems past the parent secondary 2-norbornyl (2-norbornenyl) case to the new secondary systems of even greater demand (**2**,**4**), as measured (*x* axis) by the solvolysis rate of the endo isomer. π Participation is enhanced enormously by the presence of an adjacent electron-withdrawing group (Figure 1, upper curve), but the σ systems elicits no such response (lower curve). σ Participation therefore cannot be an important factor in the acetolytic reactivity of *exo*-2-norbornyl tosylate. These experiments offer no information concerning σ bridging in the 2-norbornyl cation itself, but they leave no doubt that there is no σ bridging in the transition state leading to the cationic intermediate.

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REFERENCES AND NOTES

1. See, as representatives of the opposing views, (a) G. D. Sargent, in "Carbonium Ions," G. A. Olah and P. v. R. Schleyer, ed., John Wiley, New York, N.Y., 1972, Chapter 24; and (b) H. C. Brown, *Acc. Chem. Res.*, **6**, 377 (1973).
2. G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lin, *J. Amer. Chem. Soc.*, **92**, 4627 (1970).
3. H. C. Brown, E. N. Peters, and M. Ravindranathan, *J. Amer. Chem. Soc.*, **97**, 2900 (1975).
4. J. B. Lambert and A. G. Holcomb, *J. Amer. Chem. Soc.*, **93**, 2994 (1971).
5. The oft-quoted value of 8000 is not in fact based on a direct measurement; see footnote *a* to Table IV of S. Winstein and M. Shatavsky, *J. Amer. Chem. Soc.*, **78**, 592 (1956).
6. P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Amer. Chem. Soc.*, **87**, 375 (1965).
7. For studies involving 1 or 6 substitution, see D. Lenoir, *Chem. Ber.*, **108**, 2055 (1975); G. H. Hartman and T. G. Traylor, *J. Amer. Chem. Soc.*, **97**, 6147 (1975).
8. It should be emphasized that the extrapolation from 150-200° down to 25° involves considerable systematic error, so that the ratios at 100° are probably more representative. If real, the small decrease in the exo/endo rate ratio on introduction of the 3-tosyloxy group may result from an increase in the k_s component.

TABLE I. Rate Constants for Acetolysis of 2,3-Norbornyl Ditosylates[a]

Stereochem	Temp, °C	*k*, sec^{-1}
cis-exo	25.0	(6.62×10^{-12})[b]
	100.0	(4.11×10^{-7})[b]
	141.0	3.22×10^{-5}
	150.0	7.26×10^{-5}
	160.0	1.82×10^{-4}
cis-endo	25.0	(1.39×10^{-13})[b]
	100.0	(2.35×10^{-8})[b]
	180.4	1.10×10^{-4}
	190.3	2.87×10^{-4}
	200.3	5.74×10^{-4}

[a] Anhydrous acetic acid containing 1% acetic anhydride and 1.1 equiv of KOAc. [b] Calculated from the Arrhenius parameters.

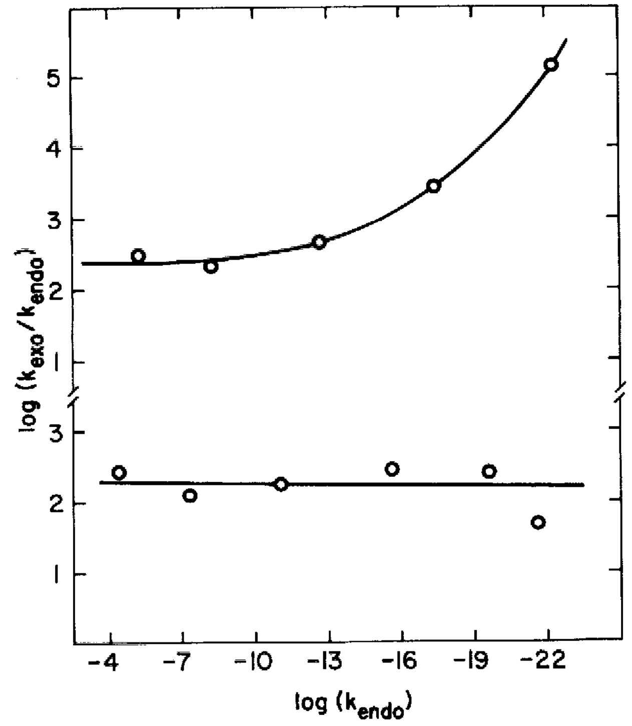

FIGURE 1. The exo/endo rate ratio (25°) as a function of electron demand (80% aqueous acetone k_{endo} for the *p*-nitrobenzoate leaving group). The upper curve is for the 2-norbornenyl series, the lower for the 2-norbornyl series. In each curve, the first three points from the left correspond to Brown's tertiary systems: 2-*p*-methoxyphenyl, 2-phenyl, and 2-*m*,*m*-bistrifluoromethylphenyl (ref. 3). The fourth points from the left are the parent secondary systems (1 and 3). The last points on the right are the 3-tosyloxy systems (2 and 4). The 3-acetoxy system provides the next-to-the-right point for the norbornyl series but is not available for the norbornenyl series.