into account in any case could well obscure the mechanistic interpretation of similar data for even fairly simple nonenzymatic reactions.

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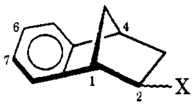
Bridgehead Oxygen Substitution as a Potent Probing Tool for Evaluating Exo/Endo Rate Ratios and σ–π Participation. Acetolysis of the Epimeric Benzo-7-oxabicyclo[2.2.1]hepten-2-yl Brosylates[1]

Sir:

Solvolysis reactions of benzobicyclo[2.2.1]heptene derivatives, rich as they are in important mechanistic information, remain as continuing sources of controversy. In this connection, the acetolysis of the epimeric benzo-7-oxabicyclo[2.2.1]hepten-2-yl brosylates (**4**) has now been examined and the observed exo/endo rate ratio at 25° (5700) has been shown to be of the same order of magnitude as that derived for the parent system (15,000).[2] Since the O-7 atom provides a sensitive probe for the delocalization of charge to the 1 position, it is concluded that the rate-determining ionization of *exo*-**4** cannot proceed through σ-delocalized cation **7**, corresponding to the related ion **3** proposed for the parent system.[3,4]



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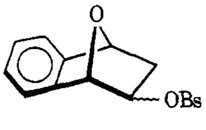
The benzo-7-oxabicyclo[2.2.1]hepten-2-yl system (**4**) offers a unique opportunity to evaluate the importance and nature (σ or π) of carbon participation (if any) in a *secondary* derivative free of added steric encumbrances. Anchimeric assistance to ionization in *endo*-**4** by direct oxygen involvement is not anticipated by analogy to the behavior of *endo*-**5**.[5] However, if significant buildup of positive charge on C_1 were to operate during rate-determining ionization of *exo*-**4**, an appreciable increase in the exo/endo rate ratio might be expected based upon **6** as an extraannular model (–OBs, 9800;[6a] –OTs, 6200[6b]), providing that here, as in other strained heterobicyclics, Bredt's rule considerations do not apply.[7]



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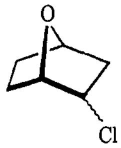

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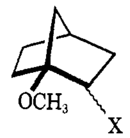

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On the basis of a high exo/endo rate ratio (15,000 at 25°) and clean retention of stereochemistry during acetolysis of *exo*-**1**-OBs, Bartlett and Giddings originally proposed intervention of the unsymmetrical π-delocalized homobenzylic cation **2**.[2] The subsequent finding that acetolysis of optically active *exo*-**1**-OBs gives racemic *exo*-**1**-OAc led to acceptance of the symmetrical σ-delocalized intermediate **3** as the species most compatible with the data.[3] 6-Methoxyl substitution of *exo*-**1**-OBs eventuates in a 178-fold rate acceleration at 77.6° (exo/endo = 310,000[8]), whereas the 7-CH_3O derivative ionizes somewhat more slowly ($k_{\text{rel}}^{77.6°}$ = 0.72, exo/endo = 2800[8]) but still with full retention of stereochemistry.[9] In contrast, the *exo*-6,7-$(NO_2)_2$ derivative is strongly deactivated ($k_{\text{rel}}^{77.6°}$ = 1.1×10^{-5}) and reacts to a significant extent by SN2 displacement at C_2 (exo/endo = 3.7).[9d,e]

Although Winstein[9a] and Tanida[9b,d,e] have cited such evidence as supportive of intermediate **3**, Brown has advanced an alternative steric explanation[9c,10] in which the space-filling requirements of the aromatic ring presumably effect destabilization of the endo transition state by impeding departure of the leaving group. Support for the steric argument was gained by examining the exo/endo rate ratios of tertiary systems such as the 2-methyl- (65),[11a] 2-phenyl- (4300),[11a] and 2-*p*-anisyl-2-OPNB's (3000).[11b] If it is granted that participation is not operative in the last derivative, then the exo/endo ratio for **1** could result from a factor of up to 20 attributable to participation and 3000 due to steric effects.

Reaction of benzo-7-oxabicyclo[2.2.1]heptadiene[12] with *m*-chloroperbenzoic acid in buffered (Na_2CO_3) methylene chloride proceeded stereoselectively to afford only exo epoxide (70–77%), which proved unusually resistant to lithium aluminum hydride reduction (large excess of $LiAlH_4$, refluxing THF, 5 days, 81%). The resulting alcohol was converted directly to *exo*-**4** and also oxidized to the corresponding ketone with dipyridinechromium(VI) oxide[13] in dichloromethane (65%). Hydride reduction and reaction with *p*-bromobenzenesulfonyl chloride in pyridine completed the sequence to *endo*-**4**.[14]

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[1] Stereochemical Aspects of Ether Oxygen Participation. IX. For part VIII, see L. A. Paquette, I. R. Dunkin, J. P. Freeman, and P. C. Storm, *J. Amer. Chem. Soc.*, **94**, 8124 (1972).

[2] P. D. Bartlett and W. P. Giddings, *ibid.*, **82**, 1240 (1960). The original $k_{\text{exo}}/k_{\text{endo}}$ value has been corrected from 7500 to 15,000: H. Tanida, K. Tori, and K. Kitahonoki, *ibid.*, **89**, 3212 (1967), ref 27.

[3] W. P. Giddings and J. Dirlam, *ibid.*, **85**, 3900 (1963).

[4] J. P. Dirlam, A. Diaz, S. Winstein, W. P. Giddings, and G. C. Hanson, *Tetrahedron Lett.*, 3133 (1969).

[5] J. C. Martin and P. D. Bartlett, *J. Amer. Chem. Soc.*, **79**, 2533 (1957).

[6] (a) Y. Lin and A. Nickon, *ibid.*, **92**, 3496 (1970); (b) P. v. R. Schleyer, P. J. Stang, and D. J. Raber, *ibid.*, **92**, 4725 (1970). The values should be compared to that of norbornyl brosylate (Table I).

[7] H. Stetter, P. Tacke, and J. Gartner, *Chem. Ber.*, **97**, 3480 (1964); C. A. Grob and A. Sieber, *Helv. Chim. Acta*, **50**, 2531 (1967); R. D. Fisher, T. D. Bogard, and P. Kovacic, *J. Amer. Chem. Soc.*, **94**, 7599 (1972); P. G. Gassman, R. L. Cryberg, and K. Shudo, *ibid.*, **94**, 7600 (1972).

[8] Uncorrected for internal return and compares to a value of 4600 for the parent system under these conditions.

[9] (a) D. V. Braddon, G. A. Wiley, J. Dirlam, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 1901 (1968); (b) H. Tanida, H. Ishitobi, and T. Irie, *ibid.*, **90**, 2688 (1968); (c) H. C. Brown and G. L. Tritle, *ibid.*, **90**, 2689 (1968); (d) H. Tanida, H. Ishitobi, T. Irie, and T. Tsushima, *ibid.*, **91**, 4512 (1969); (e) H. Tanida, T. Irie, and T. Tshushima, *ibid.*, **92**, 3404 (1970).

[10] H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1972, Part III.

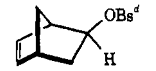
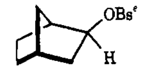
[11] (a) H. C. Brown and G. L. Tritle, *J. Amer. Chem. Soc.*, **88**, 1320 (1966); (b) H. C. Brown, personal communication.

[12] L. F. Fieser, private communication; G. Wittig and L. Pohmer, *Chem. Ber.*, **89**, 1334 (1956); E. Wolthuis, *J. Org. Chem.*, **26**, 2215 (1961); R. Gompper, G. Seybold, and B. Schmolke, *Angew. Chem., Int. Ed. Engl.*, **7**, 389 (1965); G. R. Ziegler, *J. Amer. Chem. Soc.*, **91**, 446 (1969).

[13] J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, 3363 (1968).

[14] Analytical and spectral data for all new compounds were fully compatible with the given assignments.

Table I. Kinetic Data for Solvolysis in Buffered (NaOAc) Acetic Acid

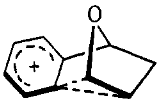
Compd	T, °C	k, sec^{-1}	k(exo)^a/k(endo)	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k_{rel}^{a}
exo-**4**	25	1.6×10^{-9} [b]	5,700	28.9	−1.9	5.7×10^3
	79.91	3.79×10^{-6}				
	100.05	3.67×10^{-5}				
	109.95	1.04×10^{-4}				
endo-**4**	25	2.8×10^{-13} [b]	5,700	33.6	−3.3	1
	142.85	3.62×10^{-6}				
	158.95	1.60×10^{-5}				
	173.25	6.22×10^{-5}				
exo-**1**[c]	25.03	7.47×10^{-6}	15,000	24.1	−1.2	2.7×10^7
endo-**1**[c]	25	5.1×10^{-10}	15,000	27.85	−7.0	1.8×10^3
	25.00	4.5×10^{-5}	8,000			1.6×10^8
	24.98	1.22×10^{-4}	350[f]			4.4×10^8

[a] At 25°. [b] Data obtained by extrapolation using the activation parameters. [c] Taken from ref 2. [d] S. Winstein, H. M. Walborsky, and K. C. Schreiber, *J. Amer. Chem. Soc.*, **72**, 5795 (1950); S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956). [e] S. Winstein and D. Trifan, *ibid.*, **74**, 1154 (1952). [f] S. Winstein, E. Clippinger, A. H. Fainberg, and G. C. Robinson, *Chem. Ind.* (*London*), 664 (1954).

Measured first-order rate constants for acetolysis of **4** are summarized in Table I along with additional relevant data. Because the acetolysis mixtures were found to be sensitive to air at the requisite elevated temperatures, the reactions were performed under an atmosphere of nitrogen. Despite this precaution, the formation of a dark precipitate in the late stages of the solvolysis of *endo*-**4** did occur and the resulting sample inhomogeneity necessitated the use of calculated infinity titers for the rate constant calculations.

The kinetic data reveal clearly that the oxygen bridge in *exo*- and *endo*-**4** exerts a very large decelerative effect when compared to the respective carbocyclic congeners (**1**). Calculated rate retardations at 25° are 4.7×10^3 and 1.8×10^3, respectively, for the two epimers. These values compare very closely to that calculated for the inductive deceleration caused by the heteroatom in **5** ($2\text{–}6 \times 10^3$);[5] consequently, the purely inductive contribution of the oxygen is a constant affecting the exo and endo derivatives about equally.

Also, the exo/endo reactivity ratio of **4** is of the same order of magnitude as that observed for **1** (2.5-fold difference) and the simpler norbornenyl brosylate (Table I). The absence of a significant increase in σ participation for *exo*-**4** which one might have predicted from the behavior of **6** can be attributed in part to the presence of an extra driving force in **6** provided by ionization to a stabilized tertiary species. The 7-oxa derivatives **4** and **5** do not possess this additional driving force.[15] More importantly, the results reveal that charge delocalization to the 1 position in the exo isomer does not gain significance since resonance interaction with the heteroatom is not operative. Nor is it possible that σ-delocalized intermediates intervene without n orbital involvement from the oxygen, for on this basis marked rate retardation in exo solvolyses should result from adverse inductive effects and these are not encountered. In our opinion, the development of positive charge at C_1 would have been readily detected due to the well-aligned stereoelectronic overlap of the nonbonding electrons on oxygen with the developing p orbital at the 1 position and the apparent inapplicability of Bredt's rule restrictions.



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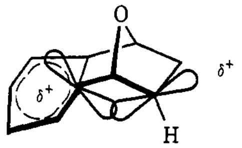

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Consequently, it may be concluded that *exo*-**4** and, by analogy, *exo*-**1** do not experience initial ionization *via* anchimeric assistance by σ participation with charge dispersal to the bridgehead position. Although the data are inconsistent with the involvement of the σ-delocalized cation **7** during rate-determining ionization of *exo*-**4**, it is entirely possible that p–π participation (*cf.* **8**) operates since delocalization of positive charge into the aromatic ring by this mechanism seemingly would not affect the electronic character of C_1 to an extent sufficiently large to be detected. Dissection of the exo/endo rate ratio of **4** into its p–π and steric components is not yet possible.

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1-Lithiocyclopropyl Phenyl Sulfide. A New Spiroannelating Reagent

Sir:

We recently reported a facile method for synthesizing oxaspiropentanes and cyclobutanones employing di-

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[15] The acetolysis of *exo*- and *endo*-**4** is accompanied by structural rearrangement. Although the acetates of retained structure were stable to the reaction conditions up to at least 110°, the rearranged products underwent polymerization and full characterization was thereby precluded. Additional evidence that rearrangement *via* an oxonium ion follows upon generation of a carbonium ion at C_2 in this ring system is afforded by the recent studies of Sasaki, *et al.*, wherein the oxonium ion was trapped intramolecularly upon addition of certain uniparticulate electrophiles to benzo-7-oxabicyclo[2.2.1]heptadiene.[16]

[16] T. Sasaki, K. Kanematsu, and M. Uchide, *Tetrahedron Lett.*, 4855 (1971).