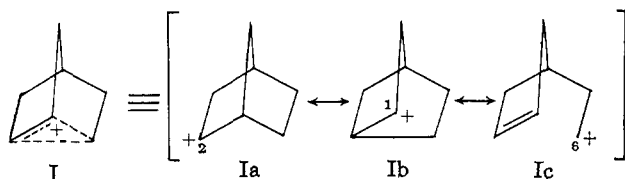# Communications to the Editor

Substituent Effects on 2-Norbornyl Solvolysis Rates. The 6,6-Dimethyl Group[1]

Sir:

Nonclassical structure I has been proposed for the norbornyl cation, implying simultaneous positive charge delocalization to C-2 (Ia), C-1 (Ib), and C-6 (Ic).[2,3] The

transition state of a reaction leading to a carbonium ion is thought to resemble the structure of the carbonium ion itself, provided the geometry of the precursor is suitable.[3b] 2-*exo*-Norbornyl derivatives (II) are said to possess this optimum geometry[2,3]; their solvolysis
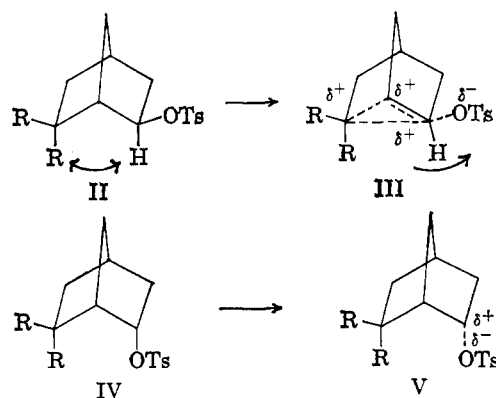
This theory leads to the prediction that substituents attached to norbornyl carbons C-1 and C-6 should differ significantly in their electronic influence on the solvolysis of 2-*endo*- and 2-*exo*-norbornyl derivatives.[3] For example, a 6-*gem*-dimethyl group should *enhance*

Table I. Acetolysis Rates of Norbornyl *p*-Toluenesulfonates

Tosylate	Temp., °C.	k_1, sec.$^{-1}$	Rel. rate 25°	Rel. rate 75°	ΔH, kcal.	ΔS, e.u., 25°
2-*endo*-Norbornyl	25.0[a]	8.28×10^{-8}	1.00	1.00	25.8[b]	−4.4[b]
(IV, R = H)[e]	49.84	$2.52 \pm 0.05 \times 10^{-6}$				
	74.84	$5.09 \pm 0.05 \times 10^{-5}$				
	99.7	$6.33 \pm 0.05 \times 10^{-4}$				
6,6-Dimethyl-2-*endo*-norbornyl	25.0[a]	4.47×10^{-9}	0.05	0.10	28.5	−1.1
(IV, R = CH₃)[d]	74.84	$5.14 \pm 0.17 \times 10^{-6}$				
	99.7	$8.61 \pm 0.47 \times 10^{-5}$				
2-*exo*-Norbornyl	25.0[a]	2.33×10^{-5}	280[f]	100	21.6	−7.2
(II, R = H)[e]	25.24	$2.40 \pm 0.19 \times 10^{-5}$				
	49.84	$4.67 \pm 0.09 \times 10^{-4}$				
	74.84	$5.19 \pm 0.31 \times 10^{-3}$				
6,6-Dimethyl-2-*exo*-norbornyl	25.0[a]	9.20×10^{-7}	11	7	24.0	−5.6
(II, R = CH₃)[g]	49.84	$2.24 \pm 0.26 \times 10^{-5}$				
	74.84	$3.65 \pm 0.14 \times 10^{-4}$				
	99.7	$3.86 \pm 0.18 \times 10^{-3}$				

[a] Calculated rates. [b] Compare $\Delta H^* = 26.0$ kcal. and $\Delta S^* = -1.5$ e.u. (50°) for 2-*endo*-norbornyl brosylate.[2] [c] M.p. 27.2–28.0°, lit. m.p. 28.1–29.2°.[2] [d] M.p. 30.0–31.0°. [e] M.p. 53.7–54.6°, lit. m.p. 53–54°.[5] [f] Compare with the ratio of 350 for the corresponding brosylates at 25°.[2] [g] M.p. 53.4–54.6°.

rates are enhanced[4] due to participation; therefore, charge is believed to be distributed in the transition state to C-1 and C-6 as well as to C-2 (III). 2-*endo*-Norbornyl derivatives (IV) do not have leaving group geometry suitable for participation[2,3]; their solvolysis rates are normal[4] and the solvolysis transition states are those of "classical" carbonium ions, with positive charge localized chiefly on a single carbon (C-2) (V).

the rate of 2-*exo*-norbornyl tosylate solvolysis (II, R = CH₃ *vs.* II, R = H), but a 6,6-dimethyl, barring some steric factor, should have little effect on the rates in the *endo* series (IV, R = CH₃ *vs.* IV, R = H).

We have tested these predictions (Table I),[5] but we find that the results in no way verify these simple expectations. In the *exo* series, instead of an *increase* the 6,6-dimethyl group (II, R = CH₃) produces a sharp rate *decrease*.[9] This result means: (a) all

(1) For additional details, see M. M. Donaldson, Ph.D. Thesis, Princeton University, 1958 (*Dissertation Abstr.*, **22**, 738 (1961)).

(2) S. Winstein and D. S. Trifan, *J. Am. Chem. Soc.*, **74**, 1147, 1154 (1952); S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *ibid.*, **74**, 1127 (1952).

(3) For reviews, see (a) P. von R. Schleyer, Ph.D. Thesis, Harvard University, 1956; (b) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; (c) J. A. Berson in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3, p. 111 ff.

(4) P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1854, 1856 (1964); (1964); C. S. Foote, *ibid.*, **86**, 1853 (1964).

(5) The key step in the preparative sequence used here was the highly stereoselective reduction of 2,3-*exo*-epoxy-5,5-dimethylnorbornane by LiAlH₄ in refluxing N-methylmorpholine.[6-8] This gave 6,6-dimethyl-2-*exo*-norbornanol[6] in 96% purity, and oxidation to the ketone followed by LiAlH₄ reduction gave the *endo* alcohol.[1]

(6) *Cf.* H. Kwart and T. Takeshita, *J. Org. Chem.*, **28**, 670 (1963).

(7) *Cf.* J. Meinwald and B. C. Cadoff, *ibid.*, **27**, 1539 (1962).

(8) D. E. McGreer, *Can. J. Chem.*, **40**, 1554 (1962).

(9) Only titrimetric rates are compared here. Polarimetric rates on optically active materials[2] would give a measure of internal return, but there is no reason to believe that II (R = CH₃ or H) should differ markedly in this respect.

2-*exo*-norbornyl solvolysis transition states are essentially classical in nature, or (b) the transition states are nonclassical, but are nòt satisfactorily represented by III since structures such as Ic make no appreciable contribution to the resonance hybrid, or (c) structures such as Ic do make a contribution, but the effect this produces is being overwhelmed by some rate-retarding influence not considered by the simple theory.

The results do not appear to support possibility a. A 6-*endo*-methyl group (II, R = CH_3) would introduce a steric interaction with the *endo*-hydrogen at C-2. If the 2-*exo*-norbornyl transition state were classical, then the 2-*endo*-hydrogen should bend away from the 6-*endo* substituent during solvolysis. On this basis, the solvolysis of II (R = CH_3) should be accelerated roughly 10-fold over II (R = H) due to relief of steric strain. In fact, a 25-fold rate *decrease* is observed at 25° (Table I). Using the scheme for estimating anchimeric assistance which we have proposed,[4] an acceleration of less than 10^1 for II (R = CH_3) is calculated, compared to $10^{3.3}$ for II (R = H).[9] Solvolysis of II (R = CH_3), but not II (R = H), is largely unassisted and may be proceeding through a transition state very nearly classical.

Of the remaining possibilites, we favor (b) on the basis of greater simplicity. There appears to be no positive evidence from the literature[3] to support the idea of contributions from structures such as Ic. The acetolysis products from both II and IV (R = CH_3) support this contention. In both cases we have been able to detect by capillary gas chromatography only the acetate of 6,6-dimethyl-2-*exo*-norbornanol. Neither attack at C-6, fragmentation, nor 6,2-methyl shift[10] takes place under these conditions.

Perhaps the rate-depressing effect of the *gem*-dimethyl in II is due to unfavorable methyl group steric interactions with both C-*1* and C-2 in a nonclassical transition state (III, R = CH_3). Models indicate that these interactions *increase* in going from II to III (R = CH_3). The rate enhancement in 2-*exo*-norbornyl solvolyses[4] is due, largely, to partial relief of strain in proceeding to the transition state, and not just to charge delocalization.[2,3] Hence, an unfavorable transition-state steric interaction (as III, R = CH_3) should remove much of the driving force for participation.

Acetolysis of 6,6-dimethyl-2-*endo*-norbornyl tosylate (III, R = CH_3) is also slower than that of the parent compound III (R = H). In the *endo* series there is no question of participation, so that a steric effect must be responsible. We believe the observed rate decrease, a factor of 19 at 25°, to be the first significant case of "steric deceleration" (transition state more crowded than the ground state)[4,11] in a unimolecular solvolysis reaction.[12]

The *exo/endo* rate ratio for the 6,6-dimethyl compounds (206 at 25°) is nearly as large as the ratio for the parent norbornyl derivatives (280 at 25°, Table I).

We regard this agreement to be fortuitous, and we agree with Brown, Chloupek, and Rei[11] that a large *exo/endo* rate ratio is not sufficient evidence upon which to base an assignment of nonclassical structure for a carbonium ion. In the present instance, we feel that steric factors contribute more to the rate difference between II and IV (R = CH_3) than does nonclassical electronic influence.

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The Nonclassical Norbornyl Cation[1]

Sir:

Some 15 years ago[2a] we extended our studies of neighboring group participation to neighboring saturated carbon and reported on the reactivity and stereochemistry in solvolysis of the *exo*- and *endo*-norbornyl *p*-bromobenzenesulfonates[2] (I-OBs and II-OBs). We considered equilibrating classical ion intermediates,[2d] but decided in favor of anchimerically assisted ionization of I-OBs leading to an internally compensated bridged or nonclassical three-center carbonium ion species A which gives rise to racemic *exo* product. On the other hand, *endo*-II-OBs was presumed to undergo anchimerically unassisted ionization to a classical carbonium ion species[2c] B. The latter was presumed to leak extensively into nonclassical A, while the remainder collapsed to inverted *exo* product.

Although he apparently subscribed to this interpretation at first,[3a] Brown has now for some years been questioning it and urging consideration of another interpretation of the facts involving only classical carbonium ions. Most recently he has referred to the norbornyl cation in his Transition State Symposium paper[3b] and in a series of communications in this journal.[3c,d] It seems appropriate to report further new evidence regarding solvolysis of norbornyl bromobenzenesulfonates and to consider all the evidence in the light of Brown's proposals.

Solvolysis of ROBs produces some hydrocarbon accompanying the substitution product. For example, from acetolysis of *exo*-I-OBs at 25°, 4% of elimination product is observed. Significantly, the hydrocarbon composition is 98% nortricyclene, 2%

(10) P. Yates and S. Danishefsky, *J. Am. Chem. Soc.*, 84, 879 (1962).
(11) H. C. Brown in "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, p. 155; H. C. Brown, F. J. Chloupek, and M.-H. Rei, *J. Am. Chem. Soc.*, 86, 1248 (1964).
(12) A similar 1,3-type CH_3···OTs axial–axial interaction in the cyclohexyl series does not produce steric deceleration, presumably because of greater flexibility. See H. P. Fischer, C. A. Grob, and W. Schwarz, *Tetrahedron Letters*, No. 1, 25 (1962); C. A. Grob, W. Schwarz, and H. P. Fischer, *Helv. Chim. Acta*, in press; S. Nishida, *J. Am. Chem. Soc.*, 82, 4290 (1960).

(1) (a) Research supported by the National Science Foundation. (b) Research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.
(2) S. Winstein, *et al.*, *J. Am. Chem. Soc.*: (a) 71, 2953 (1949); (b) 74, 1127 (1952); (c) 74, 1147 (1952); (d) 74, 1154 (1952); (e) 83, 4485 (1961); (f) 84, 4993 (1963).
(3) H. C. Brown, *et al.*: (a) *J. Am. Chem. Soc.*, 74, 1894 (1952); (b) Special Publication No. 16, The Chemical Society, London, 1962, pp. 140–157, 176–178; (c) *J. Am. Chem. Soc.*, 85, 2322 (1963); (d) *ibid.*, 86, 1246, 5008 (1964)