nitric acid in acetic acid and acetic anhydride at *ca.* 5° yielded a mixture of *homo-para* and *homo-meta* nitroacetates,[10a] mp 109–112°. Hydrolysis of the acetate mixture with dilute hydrochloric acid in methanol led to the *exo* alcohols, a yellow liquid with a methyl singlet at τ 8.97, *p*-nitrobenzoate (*exo*-VI-OPNB)[10b] mp 192–196° dec.

The *p*-nitrobenzoates of the tertiary alcohols were solvolyzed in 50% aqueous acetone. The data are summarized in Table I. The products and yields are summarized in Table II.

Table II. Products and Yields[a]

Compd	% *exo* alcohol in ROH[b]	% exocyclic olefin	% unknown compd
exo-III-OPNB	>99.6	29	<0.3
exo-IV-OPNB	>99.9	5	<0.3
exo-V-OPNB	>99.5	42	<0.3
exo-VI-OPNB	95.3[c]	51	13

[a] The compounds were solvolyzed at 125° in 50% aqueous acetone (ROPNB 0.011 *M*) containing 0.017 *M* NaOAc. [b] Control experiments showed the *endo* alcohols to be fully stable under these conditions. [c] An authentic sample of the *endo* alcohol was not available. A glpc peak was assigned the *endo* alcohol on the basis of relative retention times found for the other *endo* alcohols.

Theory and previous experience with the secondary 2-benzonorbornenyl system[4] lead one to expect rate enhancement by a *homo-p*-methoxy and slight rate retardation by a *homo-m*-methoxy group in the anchimerically assisted solvolysis (k_Δ). Substantial rate retardation would be expected for deactivating substituents, such as the nitro group. On the other hand, such substituent effects should be very small for anchimerically unassisted solvolysis. As is clear from Table I, the *homo-p*-methoxy group is substantially accelerating, *homo-m*-methoxy is slightly retarding, while *homo-p-* and *homo-m*-nitro are substantially retarding in solvolysis of the tertiary *exo* derivatives.

The factor of 16 at 125° (extrapolated value 25 at 25°), by which the *homo-p*-methoxy group accelerates the tertiary *exo* system, compares favorably with the factor of 150 at 25°, which was previously found in the secondary derivative.[4a] The nitro group retards the tertiary *exo* system by a factor of 40 at 125°. A plot of the present rate data against σ^+ is shown in Figure 1, where a ρ of -1.9 is obtained[11] at 125°. As can be expected, the ρ is smaller in magnitude than it is for the secondary *exo*-I system. However, it is much too large for k_s, and it shows that anchimerically assisted ionization (k_Δ) is very dominant in solvolysis of the tertiary *exo* system.

While the addition of the 2-methyl substituent must be decreasing the k_Δ/k_s ratio in solvolysis of the tertiary *exo* derivatives, it is obvious that this decrease is only moderate. It certainly is not sufficient to render anchimerically unassisted solvolysis (k_s) dominant, as is sometimes assumed, *a priori*. The effect of a 2-phenyl substituent in the 2-benzonorbornenyl system is reported in a following communication.[12]

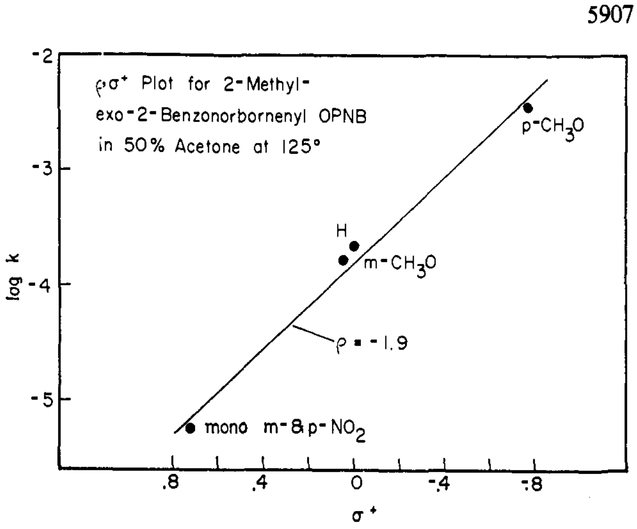

Figure 1. Methoxy and nitro substituent effects and anchimeric assistance in solvolysis of 2-methyl-2-benzonorbornenyl *p*-nitrobenzoates.

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[10] (a) The nmr spectrum showed that two protons in the aromatic region were appreciably more deshielded than the third proton, in agreement with the introduction of the nitro group β to the norbornyl ring fusion; (b) although the two *exo* isomers could not be separated, this was not felt to be a very serious problem, since a *p*-NO_2 and *m*-NO_2 group have similar σ^+ values, $+0.777$ and $+0.662$, respectively.

[11] An even better linear free-energy correlation exists between log *k* for the tertiary *exo* derivatives and log *k* for neophyl OTs[5c] in AcOH at 75°. The slope of the least-squares line is 0.55, this line reproducing four points with a mean deviation of 0.06 log unit.

[12] J. P. Dirlam and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 5907 (1969).

[13] National Science Foundation Trainee, 1965–1969.

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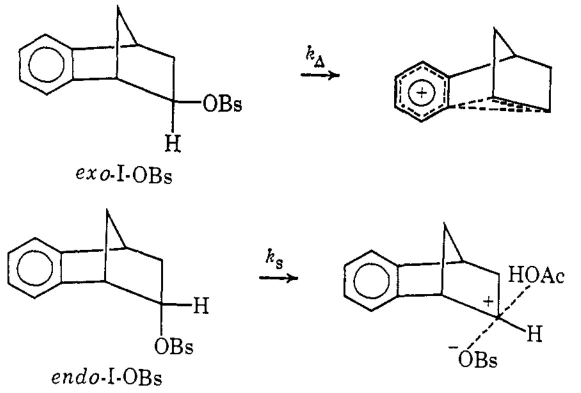
Methoxy Substituent Effects in Solvolysis of 2-Phenyl-2-benzonorbornenyl *p*-Nitrobenzoates[1,2]

Sir:

In solvolysis of *exo*-2-benzonorbornenyl bromobenzenesulfonate (*exo*-I-OBs) ionization is strongly anchimerically assisted (k_Δ), whereas ionization of the *endo* epimer (*endo*-I-OBs) is anchimerically unassisted (k_s).[3a,b] Substituent effects in the benzo group of the



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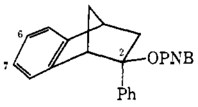
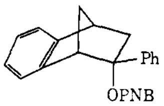
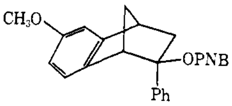
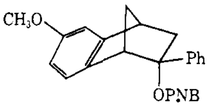
[1] Supported in part by the National Science Foundation.

[2] Reported by S. Winstein at the 21st National Organic Chemistry Symposium of the American Chemical Society, Salt Lake City, Utah, June 15–19, 1969.

[3] (a) P. D. Bartlett and W. P. Giddings, *J. Amer. Chem. Soc.*, **82**, 1240 (1960); (b) W. P. Giddings and J. Dirlam, *ibid.*, **85**, 3900 (1963); (c) H. Tanida, K. Tori, and K. Kitahonoki, *ibid.*, **89**, 3212 (1967), ref 27. The *exo*/*endo* rate ratio in the acetolysis of 2-benzonorbornenyl brosylates is corrected from 7500 to 15,000.

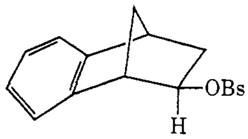
Table I. Summary of Solvolysis Rates in 80% Aqueous Acetone

Compd	Structure	Temp, °C	10^6k, sec^{-1} [a]	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Relative rates *exo*	Relative rates *endo*	Rate ratio *exo/endo* at 25.0°
exo-III-OPNB		100.0 75.0 25.0[c]	1320 ± 40[b] 124 ± 3[b] 0.312	23.8 ± 1.3	−8.4 ± 3.7	1		3,200
endo-III-OPNB		125.0 100.0 25.0[c]	26.4 ± 0.6[b] 2.16 ± 0.05[b] 9.78×10^{-5}	28.8 ± 1.1	−7.8 ± 3.0		1	
exo-IV-OPNB		75.0 50.0 25.0[c]	587 ± 6 36.7 ± 0.4 1.45	24.1 ± 0.6	−4.4 ± 1.8	4.7		11,000
endo-IV-OPNB		125.0 100.0 25.0[c]	34.4 ± 0.6 2.85 ± 0.02 1.38×10^{-4}	28.6 ± 0.8	−7.6 ± 2.3		1.3	

[a] Mean value of two determinations. [b] Similar values were previously reported by Brown and Tritle.[5] [c] Calculated from data at other temperatures.

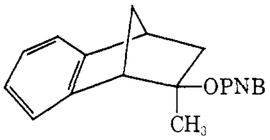
exo epimer are substantial,[4] the ρ in a $\rho\sigma^+$ fit of rates of acetolysis being −3.3 at 77.6°.[4d] It is of considerable interest to investigate the shift from anchimerically assisted to unassisted ionization as a 2-R group is added to the 2-benzonorbornenyl system and made increasingly more electron releasing.[5] In the previous communication[6] we reported that in solvolysis of the tertiary 2-methyl-*exo*-2-benzonorbornenyl *p*-nitrobenzoate (*exo*-II-OPNB), a *homo-para*-methoxy group is substantially accelerating while a *homo-para*-nitro group is substantially retarding. The ρ in a $\rho\sigma^+$ fit of the data for this tertiary system is −1.9 at 125°. Thus, while a 2-methyl group decreases the degree of participation by the neighboring benzo group, anchimerically assisted ionization (k_Δ) is still very dominant. In order to compare the effect of a 2-phenyl group with that of a 2-methyl, we have investigated the effect of a *homo-para*-methoxy substituent in the solvolysis of the 2-phenyl-2-benzonorbornenyl system (III-OPNB). The results are reported and discussed in this communication.

exo-I-OBs



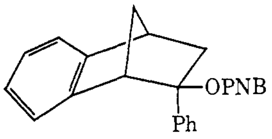
exo/*endo* rate ratio; 25° 7,500[3a] 15,000[3c] 62,000[7]

exo-II-OPNB



6500[5]
6500[5]

exo-III-OPNB



4300[5]
3200

Table II. Products and Yields[a]

Compd	% *exo* alcohol in ROH[b]	% *exo* acetate	% unknown compound
exo-IV-OPNB	>99.9	10	1
endo-IV-OPNB	>99.7	2	<0.3

[a] The *exo* and *endo* compounds were solvolyzed at 100° and 125°, respectively, in 80% aqueous acetone (ROPNB 0.011 *M*) containing 0.017 *M* NaOAc. [b] Control experiments showed the *endo* alcohol to be fully stable under these conditions.

Addition of phenylmagnesium bromide to 2-benzonorbornenone[3a] produced 2-phenyl-*endo*-2-benzonorbornenol, mp 84–85° (lit.[5] 85.2–86.5°), and *p*-nitrobenzoate (*endo*-III-OPNB), mp 122–124° (lit.[5] 124.5–126.0°). Solvolysis of *endo*-III-OPNB on a preparative scale in 80% aqueous acetone containing sodium acetate gave the tertiary *exo* alcohol, mp 110–112° (lit.[5] 112.8–113.4°), and *p*-nitrobenzoate (*exo*-III-OPNB), mp 183–186° dec (lit.[5] 186–188° dec). Addition of phenylmagnesium bromide to 6-methoxy-2-benzonorbornenone[4a] led to the *homo-para endo* alcohol, mp 92–93°, and *p*-nitrobenzoate[8] (*endo*-IV-OPNB), mp 158.5–160°. Solvolysis of *endo*-IV-OPNB on a preparative scale in 80% aqueous acetone containing sodium acetate

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(4) (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).

(5) H. C. Brown and G. L. Tritle, *ibid.*, 88, 1320 (1966).

(6) J. P. Dirlam and S. Winstein, *ibid.*, 91, 5905 (1969).

(7) For *exo*-I-OBs the polarimetric: titrimetric ratio is 4.2 in AcOH at 25°. This ratio is 1.0 for *endo*-I-OBs in AcOH at 100° (J. Dirlam, A. Diaz, S. Winstein, W. Giddings, and G. Hanson, *Tetrahedron Lett.*, 3133 (1969). The *exo*/*endo* polarimetric rate ratio becomes 4.2 × 15,000[3c] for the 2 benzonorbornenyl system.

(8) Satisfactory carbon and hydrogen analyses were obtained for the new compounds mentioned.

Table III. ρ_Δ Values for Three Sets of Relative Contributions of k_Δ and k_s to the Titrimetric Rate Constants (k_t) of *exo*-III-OPNB and *exo*-IV-OPNB

Compd	k_t	k_s	k_Δ	ρ_Δ	k_s	k_Δ	ρ_Δ	k_s	k_Δ	ρ_Δ
exo-IV-OPNB	4.7	*Ca.* 0	4.7	−0.9	0.65	4.05	−1.2	1.10	3.60	−1.8
exo-III-OPNB	1	*Ca.* 0	1		0.5	0.5		0.85	0.15	

yielded the *homo-para* tertiary *exo* alcohol, mp 64–65.5°, and *p*-nitrobenzoate[8] (*exo*-IV-OPNB), mp 151–152°. The *p*-nitrobenzoates of the tertiary alcohols were solvolyzed in 80% aqueous acetone, and the data are summarized in Table I. Products and yields are summarized in Table II.

The *homo-p*-methoxy group accelerates the *exo*-III-OPNB system 4.7-fold, a factor somewhat smaller than the factor of 16 observed with the tertiary 2-methyl system (*exo*-II-OPNB).[6] To compare with the value of 4.7, the factor is only 1.3 for the anchimerically unassisted *endo* epimer. The factor of 4.7 in the *exo* system corresponds to ρ of −0.9 in a $\rho\sigma^+$ fit; this is big enough to show at least a substantial fraction of the solvolysis rate is due to k_Δ. The line of reasoning may be illustrated, as in Table III, by considering three sets of relative contributions of k_Δ and k_s to the titrimetric rate constant (k_t) of the *exo* epimers, assuming that k_s is accelerated by a *homo-p*-methoxy group by a factor of 1.3, the same as that observed in the *endo* cases.[8a] For each assumed dissection of k_t into k_Δ and k_s portions, the corresponding ρ_Δ, in a $\rho\sigma^+$ fit, may be calculated for the effect of the methoxy group on k_Δ. For example, if k_Δ were contributing only 15% to the rate of the unsubstituted tertiary 2-phenyl derivative (*exo*-III-OPNB), ρ_Δ becomes −1.8, just as large as for the tertiary 2-methyl system (*exo*-II-OPNB). Since ρ_Δ decreases in magnitude from −3.3 to −1.9 on introduction of a 2-methyl group and we would expect a further substantial reduction on changing from a 2-methyl to a 2-phenyl substituent, it is obvious that k_Δ contributes substantially more than 15% in solvolysis of *exo*-III-OPNB. An estimate of 50% leads to a ρ_Δ of −1.2, and a figure of *ca.* 100% corresponds to the already quoted value of −0.9 for ρ_Δ. A contribution of k_Δ higher than 50% and possibly near 100% seems most likely for the contribution of anchimerically assisted ionization (k_Δ) in solvolysis of *exo*-III-OPNB.

It is now evident that changing from 2-hydrogen to 2-methyl to 2-phenyl in the benzonorbornenyl system does decrease the degree of participation, but this decrease is gradual and moderate. Neither a 2-methyl nor a 2-phenyl substituent completely suppresses the benzo participation, as is sometimes assumed *a priori*.[8b] The benzo substituent results reported in this and the preceding communication,[6] along with the previously reported substituent effects in the secondary system,[4] show how treacherous is Brown's *exo/endo* rate ratio criterion for participation in the secondary derivatives.[5] The expected rapid attenuation of the *exo/endo* rate ratio as a 2-substituent is added, and then made increasingly more electron releasing, is based on the reasonable supposition that an electron-releasing group will be more rate enhancing for the anchimerically unassisted *endo* derivative than the anchimerically assisted *exo* epimer. However, steric effects obviously bolster the *exo* rate relative to the *endo*, helping to mask the otherwise expected decrease. As regards the actual titrimetric *exo/endo* rate ratios for the secondary (I), tertiary 2-methyl (II), and tertiary 2-phenyl (III) systems, respectively, Brown[5] had listed the sequence of values as 7500:6500:4300. Our present values are 15,000, 6500, and 3200. If one employs the available polarimetric rate ratio for the I system,[7] the sequence of values becomes 62,000:6500:3200. The breakdown of these ratios into components due to participation in the *exo* epimer, and due to extraneous steric effects, on the other hand, is still not clear.

The *exo/endo* rate ratio criterion has been applied extensively by Brown[9] to the 2-norbornyl systems, and here it fails as well. All the direct solvolytic evidence supports anchimerically assisted ionization of the *exo* epimer in the secondary 2-norbornyl system.[10] Very recently, proton and C^{13} nmr studies by Olah on the "frozen" 2-norbornyl cation and on the 2-methylnorbornyl cation have shown conclusively that these species are nonclassical in super acid media.[11]

[8a] Note Added in Proof. In view of a referee's comment, it may be worthwhile to clarify the terms k_Δ and k_s. As we have been using these terms for some years [*e.g.*, S. Winstein, E. Allred, R. Heck, and R. Glick, *Tetrahedron*, 1 (1958)], k_Δ denotes the rate constant for anchimerically assisted ionization, while k_s denotes, in general, the rate constant for anchimerically unassisted ionization, but assisted by whatever nucleophilic solvent participation is appropriate for the substrate structure involved and the solvent being employed. For the right substrate structure and solvent, as presumably in the present case, k_s becomes equal to k_c, a rate constant involving neither anchimeric assistance nor assistance from nucleophilic solvent participation. In a number of *primary* and *secondary* cases involving phenyl participation, considerable success is achieved in treating k_Δ and k_s as discrete, separate processes. It is not clear that k_Δ and k_s can be so successfully treated in the present *tertiary* cases.

[8b] Note Added in Proof. From the data reported in accompanying communications by H. C. Brown and coworkers, not even a 2-*p*-anisyl group completely suppresses the benzo participation: H. C. Brown and K. T. Liu, *J. Amer. Chem. Soc.*, **91**, 5909 (1969); H. C. Brown, S. Ikegami, and K. T. Liu, *ibid.*, **91**, 5911 (1969).

(9) H. C. Brown, *Chem. Brit.*, 199 (1966); *Chem. Eng. News*, **45**, No. 7, 87 (1967).

(10) Reference 4a, footnote 13.

(11) G. A. Olah, 21st National Organic Chemistry Symposium of the American Chemical Society, Salt Lake City, Utah, June 15–19, 1969.

(12) National Science Foundation Trainee, 1965–1969.

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Solvolysis of 2-Aryl-6-methoxybenzonorbornen-2-yl *p*-Nitrobenzoates Containing Representative Substituents in the 2-Aryl Group. Variation in the *exo/endo* Rate Ratio with the Electron Demand of the 2-Aryl Group

Sir:

The *exo/endo* rate ratio in the solvolysis of the 2-aryl-6-methoxybenzonorbornen-2-yl *p*-nitrobenzoates (**1**, **2**) increases with increasing electron demand of the 2-aryl substituents. This observation supports the presence of π participation in the solvolysis of the 2-aryl-6-