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		0.65	4.05		1.10	3.60	
				-0.9			-1.2			-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]

(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.

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]

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-

Table I. Rates of Solvolysis of 2-Aryl-6-methoxybenzonorbornen-2-yl p-Nitrobenzoates in 80% Aqueous Acetone

| Substituent in 2-aryl | Isomer (OPNB) | Temp, °C | $10^6 k_1$,[a] sec^{-1} | $\Delta H^{\ddagger}$, kcal/mol | $\Delta S^{\ddagger}$, eu | Relative rates at 25° | | 6-OMe/6-H[b] | 6-OMe/6-H[b] | exo/endo |
						exo	endo	exo	endo	6-OMe
p-OCH$_3$	exo	25.0	2190[c]			1610		2.0		7,000
	endo[e]	75.0	159							
		50.0	8.95							
		25.0	0.311[f]	25.2	−4.0		3330		1.0	
p-H	exo[g]	50.0	37.1							
		25.0	1.36	24.7	−2.4	1.00		4.9		14,500
	endo[h]	125.0	19.1							
		100.0	1.66							
		25.0	9.33×10^{-6} [f]	28.3	−9.1		1.00		1.0	
p-CF$_3$	exo[i]	100.0	171							
		75.0	12.1							
		25.0	0.016[f]	26.8	−4.5	0.0118		34		25,000
	endo[j]	150.0	6.97							
		125.0	0.615							
		25.0	6.34×10^{-7} [f]	31.9	−7.3		0.0068		3.7	
m,m'-(CF$_3$)$_2$	exo[k]	125.0	110							
		100.0	8.57							
		25.0	3.07×10^{-4} [f]	29.6	−2.8	2.3×10^{-4}		40		34,000
	endo	25.0	9×10^{-9} [l]				(9.6×10^{-3})		(3.0)	

[a] Computer calculated using least-squares program. [b] Reference 9. [c] Estimated from $k_{OPNB} = k_{OBz} \times 20.8$. [d] Benzoate ester, mp 118.5–119°, $k_1{}^{25°}$ 1.055 × 10^{-4} sec^{-1}. [d] Reference 2. [e] Mp 118–119°. [f] Calculated from data at other temperature. [g] Mp 146–147°. [h] Mp 160–161°. [i] Mp 157–158°. [j] Mp 133–134°. [k] Mp 214–215° dec. [l] Estimated by extrapolation of the log k–σ^+ plot for other derivatives

methoxy-exo-benzonorbornenyl derivatives,[1] as well as the efficacy of this tool as a test for participation in the norbornyl system.[2,3]

1

2
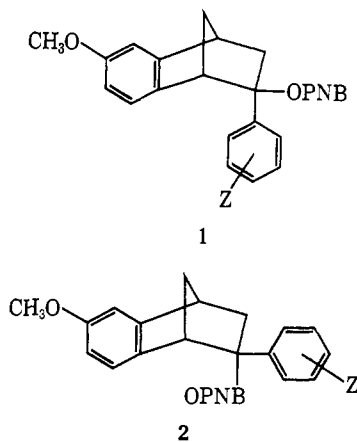
Originally, we attempted to obtain confirmatory evidence for the oft-postulated σ participation as a factor in the high exo/endo rate and product ratios of norbornyl derivatives[4] by examining the behavior of the 2-H, 2-Me, and 2-Ph derivatives.[5] Indeed, the remarkable similarity in the exo/endo rate and product ratios in

(1) The solvolysis of the secondary derivatives has been subjected to detailed examination: (a) P. D. Bartlett and W. P. Giddings, J. Amer. Chem. Soc., 82, 1240 (1960); (b) D. V. Braddon, G. A. Wiley, J. Dirlam, and S. Winstein, ibid., 90, 1901 (1968); (c) H. Tanida, W. Ishitobi, and T. Irie, ibid., 90, 2688 (1968); (d) H. C. Brown and G. L. Tritle, ibid., 90, 2689 (1968).

(2) H. C. Brown and K. Takeuchi, ibid., 90, 2691, 2693, 5268, 5270 (1968).

(3) This experimental approach rests on the proposal that the magnitude of participation by a neighboring group should decrease with increasing stability of the carbonium ion center: S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, ibid., 74, 1113 (1952).

(4) For a review with pertinent references, see H. C. Brown, Chem. Brit., 2, 199 (1966).

(5) H. C. Brown, F. J. Chloupek, and M.-H. Rei, J. Amer. Chem. Soc., 86, 1248 (1964); M.-H. Rei and H. C. Brown, ibid., 88, 5335 (1966).

these secondary and tertiary norbornyl derivatives suggested that σ participation could not be a major factor in these ratios.[4] However, the possible influence of differences in the ground-state energies of secondary and tertiary norbornyl derivatives has led some authors to consider such evidence to be unreliable.[6]

More recently we have utilized the well-tested Hammett approach to vary the electron demand while maintaining steric effects constant. The results consistently indicate the absence of any observable change in the exo/endo rate and product ratio with increasing electron demand at the 2 position.[2] However, the reliability of this approach has also been questioned.[7] Consequently, it appeared desirable to subject this approach to a critical test by ascertaining whether it would detect participation in a system where it should exist.[8]

A 6-methoxy substituent in the secondary exo-benzonorbornenyl derivative increases the rate of solvolysis by a factor of 150–210[1] and increases the exo/endo rate ratio from 15,000 for the parent compound to 830,000.[1b] Consequently, the 6-methoxy substituent increases the exo/endo rate ratio by a factor of 55, attributable to π participation.[1b–d] It appeared, therefore, that this system might provide a satisfactory test for the ability of 2-aryl substituents to detect the presence of participation of this order of magnitude (∼55).

The 2-aryl derivatives of the parent benzonorbornen-2-yl system were also examined for comparison.[9]

(6) "However, such substituent effects can be treacherous, since substituents can introduce steric problems." [1b]

(7) H. Tanida, Accounts Chem. Res., 1, 239 (1968). However, see rebuttal in B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms—1967," Interscience Publishers, New York, N. Y., 1968, p 31.

(8) This tool has been recently utilized to demonstrate that the importance of π participation in 7-aryl-7-norbornenyl derivatives does indeed vary inversely with the stability of the developing carbonium ion center: P. G. Gassman and A. F. Fentiman, Jr., J. Amer. Chem. Soc., 91, 1545 (1969). However, π participation is so enormous in this system, 10^{11}, that it might be argued that the results cannot be extrapolated to support applicability of the technique to systems where the extent of participation can only be much smaller, of the order of 10^2 to 10^3.

Hydrochlorination of 6-methoxybenzonorbornadiene[10] in methylene chloride at 0° yielded a 95:5 mixture[11] of 6- and 7-methoxy-*exo*-benzonorbornenyl chlorides.[10] Selective hydrolysis gave 6-methoxy-*exo*-benzonorborneol, converted to the ketone by an Oppenauer oxidation. Addition of the appropriate arylmagnesium bromide yielded the tertiary *endo* alcohols. These were converted to the chlorides which were hydrolyzed to the *exo* alcohols. The alcohols were converted into the *p*-nitrobenzoate and benzoate esters *via* the lithium alkoxides.[5,12]

The esters were subjected to solvolysis in 80% aqueous acetone. The results are summarized in Table I. The data reveal excellent linear correlations with the σ^+ constants yielding ρ −3.72 (correlation coefficient 0.999) for the *exo* series (1) and −4.05 (correlation coefficient 0.991) for the *endo* series (2).

As in the related secondary system,[1] the 6-methoxy substituent exerts little effect on the rates of the 2-aryl-*endo* derivatives. However, in the *exo* series the rate enhancement ($k_{6\text{-OMe}}/k_{6\text{-H}}$) increases from 2.0 for *p*-anisyl, to 4.9 for phenyl, to 34 for *p*-trifluoromethylphenyl, to 40 for *m,m'*-bis(trifluoromethyl)phenyl. This compares with the observed value of 150 for acetolysis of the corresponding secondary brosylates.[1b]

The *endo* derivative has long been utilized as a standard of reference for the rate to be anticipated for the *exo* isomer in the absence of participation. Consequently, we should anticipate that the *exo*/*endo* rate ratio should increase with increasing electron demand of the 2-aryl group. Indeed, the *exo*/*endo* rate ratio rises from 7000 for *p*-anisyl, to 14,500 for phenyl, to 25,000 for *p*-trifluoromethylphenyl, to 34,000 for *m,m'*-bis-(trifluoromethyl)phenyl.[13]

In the present study the Hammett approach was utilized to maintain the steric effects constant while the electron demand was varied at the 2 position of the benzonorbornenyl system. The results unambiguously confirm the presence of additional π participation arising from the presence of the activating methoxy substituent at the 6 position (*homo-para*).

It is important to note that the present approach tests only for the increase in π participation attributable to the 6-methoxy substituent over that present in the parent system. (However, the results indicate the absence of significant π participation in the parent 2-aryl derivatives[9].) This increase in the *exo*/*endo* rate ratio in the secondary derivative, × 55, is even less than the *exo*/*endo* rate ratio in norbornyl itself (× 300), usually attributed to σ participation. Yet the same methods applied to 2-norbornyl and 2-camphenilyl fail to reveal

(9) H. C. Brown, S. Ikegami, and K.-T. Liu, *J. Amer. Chem. Soc.*, 91, 5911 (1969).

(10) Both 6-methoxybenzonorbornadiene and 7-methoxy-*exo*-benzonorbornenyl chloride were kindly made available by Dr. H. Tanida.

(11) Analysis by glpc using a Perkin-Elmer Model No. 226 instrument with 150 ft × 0.01 in. silicone DC 550 column. Previously, the purity was estimated as 97% from solvolytic data.[1d]

(12) All new compounds exhibited sharp melting points, satisfactory elemental analyses, and spectral data consistent with the proposed structure.

(13) Unexpectedly, the 6-methoxy substituent results in an appreciable rate enhancement in the secondary *endo* isomer (× 2.5)[1b] and in the tertiary *endo* isomers containing the more electron-demanding substituents (× 3.7) (Table I). The precise source of this rate enhancement is of considerable interest and we hope to explore its origin. However, its effect is to reduce the observed *exo*/*endo* rate ratios for both the secondary and the more electron-demanding tertiary derivatives over the values that would have been predicted from the observed rate enhancements in the *exo* isomers.

any increase whatsoever in the *exo*/*endo* rate ratio with increasing electron demand by the 2-aryl substituent. We can only conclude that the high *exo*/*endo* rate and product ratios exhibited by the 2-arylnorbornyl and 2-arylcamphenilyl systems must arise from causes other than σ participation.[14]

The importance of π participation in the parent 2-arylbenzonorbornen-2-yl system is explored in the following communication.[9]

(14) A detailed pmr study of the 2-phenylnorbornyl cation led the authors to conclude that there is no detectable charge delocalization from the 2 to the neighboring 1 position: D. G. Farnum and G. Mehta, *J. Amer. Chem. Soc.*, 91, 3256 (1969).

(15) Postdoctorate research associate on a grant (GP 6492 X) supported by the National Science Foundation.

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Solvolysis of 2-Arylbenzonorbornen-2-yl *p*-Nitrobenzoates Containing Representative Substituents in the 2-Aryl Group. Constancy in the *exo*/*endo* Rate Ratio with Increasing Electron Demand by the 2-Aryl Group

Sir:

The *exo*/*endo* rate ratio in the solvolysis of the 2-arylbenzonorbornen-2-yl *p*-nitrobenzoates (1, 2) remains
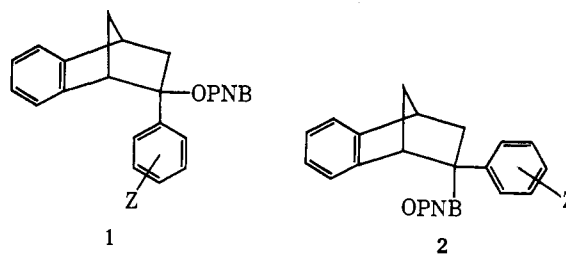
sensibly constant at ∼3000 as the electron demand of the 2-aryl substituent is varied over a major range in reactivity (>10^8). This observation indicates the absence of π participation as a significant factor in the high *exo*/*endo* rate ratio (∼3000) observed in these 2-arylbenzonorbornen-2-yl derivatives.

The near-constancy of the *exo*/*endo* rate ratios in the benzonorbornen-2-yl derivatives (2-H, 15,000; 2-Me, 6500; 2-Ph, 2900) originally led to the conclusion that π participation could not be a major factor in these high rate ratios.[1] It has long been accepted that participation by a neighboring group should decrease with increasing stability of the electron-deficient center.[2,3] The observation that a 6-methoxy group enhanced the *exo*/*endo* rate ratio by a factor of 55[4] was not inconsistent with this conclusion. However, the observation that a nitro group at the 6 or 7 position decreased the *exo*/*endo* rate ratio to approximately 100[4d] did appear to

(1) H. C. Brown and G. L. Tritle, *J. Amer. Chem. Soc.*, 88, 1320 (1966). The values are slightly modified from those originally used to take advantage of later, more precise measurements.

(2) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, 74, 1113 (1952).

(3) For example, the rate factor of 10^{11} for the participation in *anti*-7-norbornenyl is decreased drastically to a factor of less than 10^2 by a 7-phenyl substituent: P. G. Gassman and A. F. Fentiman, Jr., *ibid.*, 91, 1545 (1969).

(4) (a) P. D. Bartlett and W. P. Giddings, *ibid.*, 82, 1240 (1960); (b) D. V. Braddon, G. A. Wiley, J. Dirlam, and S. Winstein, *ibid.*, 90, 1901 (1968); (c) H. Tanida, H. Ishitobi, and T. Irie, *ibid.*, 90, 2688 (1968); (d) H. C. Brown and G. L. Tritle, *ibid.*, 90, 2689 (1969).