sults indicated that the *exo* hydrogen isomer, *endo*-2-*p*-anisylnorbornane, was formed predominantly, ≥98%.

Consequently, the highly stabilized 2-*p*-anisylnorbornyl system, which cannot involve significant σ participation, exhibits both a high *exo*:*endo* rate ratio and the predominant *exo* substitution of the norbornyl cation. Clearly we must reexamine the position that these characteristics require σ participation and a nonclassical structure for the norbornyl cation.

Unfortunately, the two isomers could not be separated by capillary glpc. However, they exhibited highly characteristic pmr spectra: *endo*, a broad multiplet centered at 3.09 ppm (J = 5 cps); *exo*, a triplet centered at 2.62 ppm (J = 7 cps). Tests revealed that small amounts of the *exo* isomer in the *endo* could be determined to ±1-2%.

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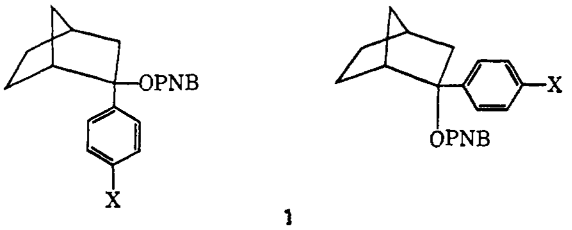
Solvolysis of 2-Aryl-2-norbornyl *p*-Nitrobenzoates Containing Deactivating Substituents in the Aromatic Ring. A New Technique for Evaluating the Importance of σ Participation in the Solvolysis of Norbornyl Derivatives

Sir:

The *exo*:*endo* rate ratios and predominant *exo* substitution remain sensibly constant as various substituents are introduced into the aromatic ring of the 2-aryl-2-norbornyl *p*-nitrobenzoates. It must be concluded that over the range of substituents examined (X = *p*-OCH_3, *p*-H, *p*-CF_3, *p*-NO_2), with a range of 3.6×10^6 in reactivity, σ participation is not a factor in the observed high *exo*:*endo* rate ratio and predominant *exo* substitution (**1**).



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The enormous stabilizing effect of the *p*-anisyl substituent is indicated by the rate enhancement of 5×10^{11} that it brings to the solvolysis of *exo*-norbornyl chloride[1] and by the loss of nearly 10^{11} in participation that it causes in the *anti*-7-dehydronorbornyl system.[2] It follows that the *exo*:*endo* rate ratio of 284 and the predominant *exo* substitution observed in the solvolysis of 2-*p*-anisyl-2-norbornyl esters[3] cannot be attributed to σ participation. It is probable that steric effects,[4] with contributions from torsional factors,[5] are responsible for these characteristics.

These factors must also be present in the parent norbornyl system and must therefore contribute to the high *exo*:*endo* rate ratio observed (280) and the predominant *exo* substitution. However, it is presently not possible to conclude that σ participation may not also contribute in the parent secondary derivative, even though it cannot be a significant factor in the 2-*p*-anisyl system.[6] The problem is how to bridge the gap between the highly stabilized 2-anisyl-2-norbornyl and the corresponding secondary 2-norbornyl system without introducing uncertain corrections for the differences in the ground-state energies.

The Hammett relationship offers a promising solution. By introducing appropriate substituents into the aromatic ring of 2-aryl-2-norbornyl, it is possible to vary the reactivity over a wide range, ultimately approaching or even exceeding the inertness of 2-norbornyl itself.[7] By restricting these substituents to the *meta* and *para* positions, changes in the steric factor can be avoided.

Consequently, as the aromatic ring is deactivated, increasing the electron demand from the carbonium ion center, we should observe increasing contributions from σ participation and increasing *exo*:*endo* rate ratios, providing such σ participation is a significant factor.

Accordingly, we synthesized various 2-aryl-*exo*- and -*endo*-norbornyl *p*-nitrobenzoates and determined their

Table I. Rates of Solvolysis of 2-Arylnorbornyl *p*-Nitrobenzoates

		First-order rate constant, $k_1 \times 10^6$ sec^{-1} (80% acetone)						*exo*:*endo*
Substituent[a]	Isomer	125.0°	100.0°	75.0°	50.0°	25.0°	0.0°	rate ratio (25°)
p-CH_3O	*exo*					11,400[h]		284
	endo[b]					40.2[h]	1.17[h]	
p-H	*exo*[c]				179[i]	7.56[i]		143
	endo[d]		364[i]	30.2[i]		0.0530[j]		
p-CF_3	*exo*[e]		400	29.4		0.0427[j]		188
	endo[f]	70.1	5.62			0.000227[j]		
p-NO_2	*exo*[g]		106	6.49		0.00597[j]		(114)[k]
	endo					0.0000524[k]		

[a] All new compounds gave spectral and microanalytical data consistent with the proposed structure. [b] Mp 115°. [c] Mp 107.5°. [d] Mp 137°. [e] Mp 127.5–128.0°. [f] Mp 135.0–135.5°. [g] Mp 178.0–178.5°. [h] Reference 3. [i] D. L. Vander Jagt, Ph.D. Thesis, Purdue University, 1967. [j] Calculated from data at other temperatures. [k] Because of synthetic difficulties, the rate of the *endo* isomer was obtained by extrapolation of the log k–σ^+ plot for the other derivatives (Figure 1).

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(1) H. C. Brown and K. Takeuchi, *J. Am. Chem. Soc.*, **88**, 5336 (1966).

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(3) H. C. Brown and K. Takeuchi, *J. Am. Chem. Soc.*, **90**, 2691 (1968).

(4) H. C. Brown, W. J. Hammer, J. H. Kawakami, I. Rothberg, and D. L. Vander Jagt, *ibid.*, **89**, 6381 (1967).

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(6) Indeed, E. M. Kosower, "An Introduction to Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1968, has estimated that only half of the observed effect in norbornyl arises from σ participation.

(7) See Figure 1 of ref 3.

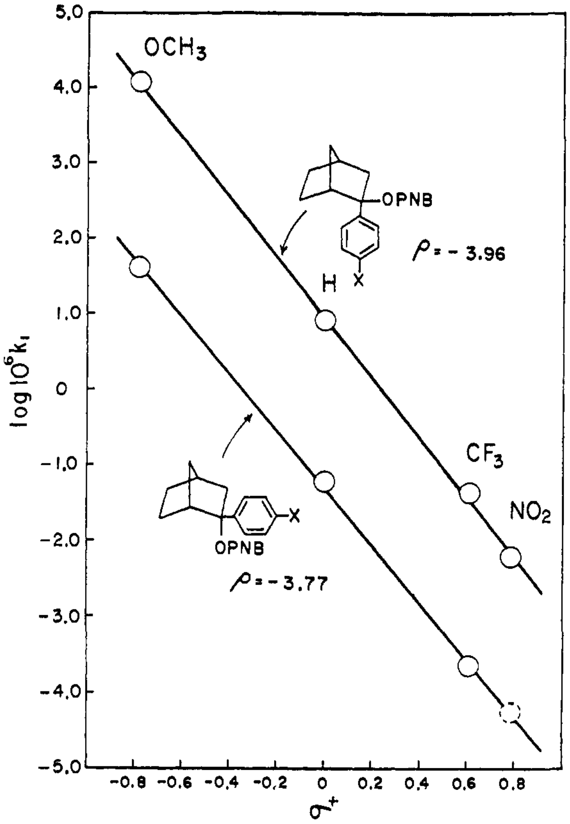

Figure 1. Correlation with σ^+ constants of the rates of solvolysis in 80% aqueous acetone at 25° of 2-aryl-*exo*- and -*endo*-norbornyl *p*-nitrobenzoates.

solvolysis rates in 80% acetone. The results are summarized in Table I. The data give excellent σ^+ plots (Figure 1).

We also carried out trapping experiments on the corresponding chlorides.[8] As indicated by the data in Table II, all compounds consistently gave predominant *exo* attack of borohydride.

Table II. Trapping of the Carbonium Ion by Sodium Borohydride in the Solvolysis of the Substituted 2-Aryl-*exo*-norbornyl Chlorides in 70% Diglyme at 25°

Substituent	Yield of 2-arylnorbornane, %[a]	2-Arylnorbornane, %[b] *exo*-H	*endo*-H
p-CH_3O	68	≥98	≤2
p-H	82	≥98	≤2
p-CF_3[c]	32	≥97	≤3
p-NO_2	59	≥97	≤3

[a] Glpc analysis. [b] Analysis for isomers by pmr. [c] Mp 51.0–51.5°.

It is evident that there is no observable increase in the *exo–endo* rate ratios as electron-withdrawing substituents are introduced into the aromatic ring over the range examined. Consequently, it is quite clear that σ participation cannot be a significant factor in the high *exo*:*endo* rate ratios and the predominant *exo* substitution of these derivatives.

Conflicting opinions have been expressed as to whether the 2-methyl-2-norbornyl cation is classical[9] or nonclassical.[10] However, the reactivity of 2-*p*-nitrophenyl-2-norbornyl is practically identical with that of 2-methyl-2-norbornyl.[7] Electron demand at the electron-deficient center of these two systems should be essentially identical. Since the present results support the conclusion that σ participation is not a factor in the 2-*p*-nitrophenyl derivative, it cannot be a factor in the 2-methyl structure, supporting the view that the 2-methyl-2-norbornyl cation must be essentially classical.[9]

The present data do not permit a definitive answer to the question of whether σ participation is present in norbornyl itself. Even with the least reactive derivative we have studied, 2-*p*-nitrophenyl-2-norbornyl, we have progressed only 60% of the reactivity range from 2-*p*-anisyl-2-norbornyl to 2-norbornyl.[7] However, the present results clearly imply that if such σ participation is present, it cannot be large. This conclusion is based on the observation that the *exo*:*endo* rate ratios in the present 2-aryl derivatives are of the same order of magnitude as that observed in norbornyl itself, and equilibration studies[11] do not permit any large contribution from the differences in ground-state energies.

It follows that even in norbornyl, a major if not the only important contribution to the *exo–endo* rate ratio must be a blend of steric[4] and torsional[5] effects.

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Occurrence and Timing of the Rearrangement of Benzyl Ions to Tropylium Ions in the Mass Spectra of Substituted Benzyl Phenyl Ethers

Sir:

Among the most challenging current problems in mass spectrometry is the assignment of ion structures and the detailed elucidation of fragmentation pathways. We report here application of the elegant techniques of kinetic substituent effects[1–3] and metastable ion characteristics[4,5] recently developed by McLafferty and coworkers to the general question of ion structure in the decomposition of substituted benzyl derivatives I. The results obtained with substituted benzyl phenyl ethers (I, Y = OC_6H_5) suggest that in the ionizing electron energy range 20–70 eV benzyl-type ions II can be precursors to rearranged tropylium ions III and are interpreted most simply in terms of the following stepwise scheme.

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[2] M. M. Bursey and F. W. McLafferty, *ibid.*, **89**, 1 (1967).

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