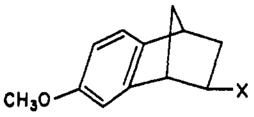
are appreciably more deshielded than the third proton, in agreement with the introduction of the nitro group β to the norbornyl ring fusion (III-OAc). The mixture[9] of the two isomeric acetates was hydrolyzed to the *exo* alcohols (III-OH, III-OBs mp 116–117°), oxidized to the ketones,[1] and reduced with tetrahydrofuran–borane to the *endo* alcohols (VI-OH, VI-OBs mp 140–146°).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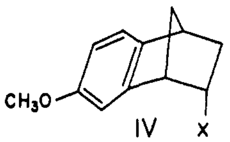
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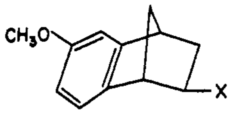
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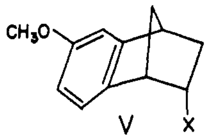
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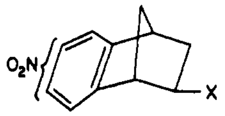
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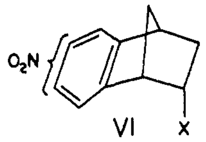
VI

Because of the great reactivity of II-OH, the rate of solvolysis of II-Cl in 80% aqueous acetone was determined and compared with that of the parent chloride. The rate data are summarized in Table I.

First, a methoxy group in the 7 position ("*homo-meta*"[4b]) has little effect on the rate of solvolysis. In the 6 position ("*homo-para*") the methoxy substituent increases the rate by a factor of 210. It is noteworthy that this is the largest rate acceleration yet observed for a neighboring "*p*-anisyl" group.[10]

The point of major interest for the present objective is the *exo*:*endo* rate ratio for the nitro derivative. A value of 94 was observed. (This value may be low, since the acetolysis of 2-d_1-*endo*-benzonorbornadienyl brosylate revealed that 28% of the reaction involved an inversion at the 2 position, without scrambling of the tag. If this is the result of an SN2 component, the *exo*:*endo* ratio rises to 130.) A nitro substituent has an enormous deactivating effect on the aromatic ring.[11] For example, 3-*p*-nitrophenyl-2-butyl tosylate fails to exhibit any evidence of the unique properties of the parent structure.[12] Similarly, a nitro substituent causes the *anti*:*syn* rate ratio to decrease from 1200 for the parent benzonorbornan-9-yl brosylates to 4.4 for the 6-nitro derivatives.[3b] If the nitro substituent in III-OBs effectively cancels out π participation from the aromatic ring, then the 15,000 *exo*:*endo* ratio involves a factor of 160 for π participation and a factor of 94 for steric and torsional contributions. (Corrected for the possible SN2 component, the factor would be 115 for π participation and 130 for steric and torsional contributions.) Unfortunately, the possibility that there may not be some residual π participation, even in the presence of this highly deactivating group, cannot now be excluded. Only by making a systematic study of a series of compounds with deactivating substituents will it be possible to state whether one approaches a plateau value for the *exo*:*endo* rate ratio or whether the value diminishes to unity.

These results indicate that π participation makes an important contribution to the *exo*:*endo* rate ratio of the secondary benzonorbornen-2-yl derivatives. But what can we say about the behavior of the tertiary derivatives? It has recently been reported that a *p*-anisyl group in the 7 position of dehydronorbornyl causes the loss of nearly all of the 10^{11} of π participation in the parent secondary compound.[13] Consequently, the close similarity in the *exo*:*endo* rate ratio for the tertiary 2-methyl and 2-phenyl derivatives is not consistent with a large contribution of π participation to the observed high *exo*:*endo* ratio in these tertiary derivatives. This indicates that the high *exo*:*endo* rate ratios in these tertiary derivatives must arise primarily from steric and torsional contributions. We hope to make tertiary benzonorbornen-2-yl derivatives containing deactivating substituents in the aromatic ring to test this indication.

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[9] Since the σ^+ values of *m*-NO$_2$ and *p*-NO$_2$ are not greatly different, +0.674 and +0.790, it did not appear important for the purposes of this study to separate the isomers.

[10] For example, rate accelerations in the range from 26 to 78 are observed for the acetolysis and formolysis of β-anisylethyl and 3-anisyl-2-butyl derivatives. See Table V of H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *J. Am. Chem. Soc.*, **89**, 370 (1967).

[11] It is of interest that the effect of the nitro substituent (0.044) on the rate of the *endo* isomer, VI-OBs, is almost identical with its effect on the rate of the *syn* isomer[3b] (0.037).

[12] D. J. Cram and J. A. Thompson, *J. Am. Chem. Soc.*, **89**, 6766 (1967).

[13] P. G. Gassman, J. Zeller, and J. T. Lumb, *Chem. Commun.*, 69 (1968).

[14] Purdue Research Foundation Fellow, 1964–1966.

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High *exo*:*endo* Rate Ratio and Predominant *exo* Substitution in the Solvolysis of 2-*p*-Anisylnorbornyl Derivatives. The Characteristics of a Highly Stabilized, Classical Norbornyl Cation

Sir:

The rate of ethanolysis of 2-*p*-anisyl-*exo*-norbornyl chloride is greater than that of *exo*-norbornyl chloride by the enormous factor of 500,000,000,000[1] (Figure 1). Clearly the *p*-anisyl group must provide major stabilization of the incipient cation in the transition state.

It has been generally accepted that the more stable the carbonium ion center, the less demand that center will make upon neighboring groups for additional stabilization through participation.[2] The remarkable ability of the *p*-anisyl group to cause such participation to vanish is elegantly indicated by the recent study of Gassman and his coworkers.[3] They observed that the 10^{11} acceleration arising from participation of the double bond in the solvolysis of *anti*-7-dehydronorbornyl derivatives[4] essentially vanishes in the corresponding 7-*p*-anisyl derivatives[3] (**1**).

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

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

[3] P. G. Gassman, J. Zeller, and J. T. Lumb, *Chem. Commun.*, 69 (1968).

[4] S. Winstein, M. Shatevsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955).

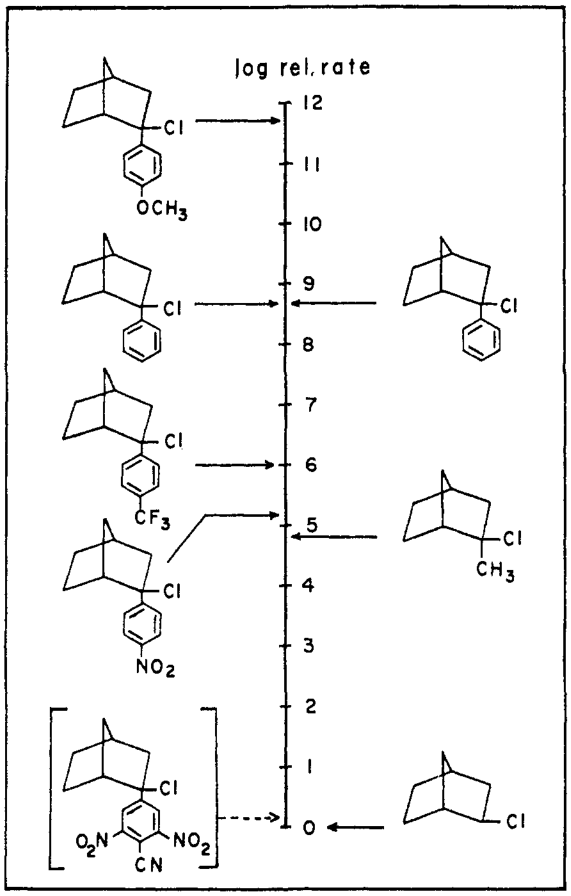
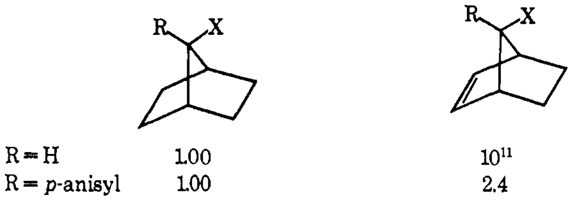


Figure 1. Relative rates of ethanolysis of 2-norbornyl derivatives (relative to *exo*-norbornyl chloride = 1.00).

The *exo*:*endo* rate ratio in the acetolysis of norbornyl tosylate is 280,[5] long attributed to σ participation in the *exo* isomer and its absence in the *endo*.[6]



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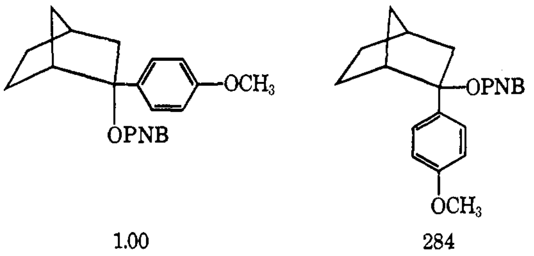
If the *p*-anisyl substituent can cause the truly enormous participation ($\times 10^{11}$) observed in *anti*-7-dehydronorbornyl essentially to vanish, surely it should also cause the much smaller σ participation ($\times 280$) proposed for *exo*-norbornyl to vanish.[7]

However, we have observed that the *exo*:*endo* rate ratio in the solvolysis of 2-*p*-anisylnorbornyl *p*-nitrobenzoates[8] to be 284 (**2**).

Table I. Rates of Solvolysis of the Tertiary 2-Phenyl and 2-*p*-Anisyl *p*-Nitrobenzoates and Benzoates of the Norbornane System

Compound[a]	First-order rate constants, $k_1 \times 10^6$ sec^{-1} (80% acetone)				*exo*:*endo* rate ratio
	75.0°	50.0°	25.0°	0.0°	25°
2-Phenyl-*exo*-OBz[b]	202	11.1	0.378[e]		
2-Phenyl-*exo*-OPNB		179[f]	7.56[f] 7.86		
2-*p*-Anisyl-*exo*-OBz[c]			548	18.7	
2-*p*-Anisyl-*exo*-OPNB			11,400[g]		
2-*p*-Anisyl-*endo*-OPNB[d]			40.2	1.17	284

[a] All new compounds gave spectral and microanalytical data consistent with the proposed structure. [b] Mp 99.5–100°. [c] Mp 91.0–91.5°. [d] Mp 115° dec. [e] Extrapolated from data at other temperatures. [f] D. L. Vander Jagt, Ph.D. Thesis, Purdue University, 1967. [g] Estimated by multiplying the rate constant for the benzoate by the factor 20.8 (from k_{OPNB}/k_{OBz} for the 2-phenyl-*exo*-norbornyl esters).



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The data are summarized in Table I.

Clearly the *exo*:*endo* rate ratio does not vanish here with the introduction of the *p*-anisyl group in the manner that the huge participation factor essentially vanishes in the corresponding 7-*p*-anisyldehydronorbornyl derivatives (**1**). We can only conclude that the high *exo*:*endo* rate ratio here observed for the 2-*p*-anisylnorbornyl derivatives may be the result of steric effects[9] and/or torsional effects[10] but cannot be the result of σ participation.[11]

exo substitution in the cation has likewise been accepted as a supporting argument for σ bridging. Consequently, it was of interest to examine the behavior of the highly stable 2-*p*-anisylnorbornyl cation. Accordingly, 2-*p*-anisyl-*exo*-norbornyl chloride was solvolyzed in the presence of sodium borohydride[12] and the product, 2-*p*-anisylnorbornane, examined by pmr for the presence of *exo* and *endo* isomers.[13] The re-

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[5] P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Am. Chem. Soc.*, **87**, 375 (1965). Since data are not available for the contribution of internal return in any of these systems, other than norbornyl itself, we restrict this discussion to the observed titrimetric rate constants.

[6] S. Winstein and D. Trifan, *ibid.*, **74**, 1147, 1154 (1952).

[7] It should be pointed out that it was previously concluded, both from reactivity data and direct pmr observation on the cation, that the 1,2-di-*p*-anisylnorbornyl cation exists as a rapidly equilibrating pair of ions, rather than as a symmetrically bridged species: P. von R. Schleyer, D. C. Kleinfelter, and H. G. Richey, Jr., *J. Am. Chem. Soc.*, **85**, 479 (1963). We have been informed that a more intensive pmr study of the ion over a range of temperature has confirmed the original conclusion (private communication from P. von R. Schleyer).

[8] Actually, the *exo* isomer proved to be highly unstable, so the benzoate was prepared and run, and the rate for the *p*-nitrobenzoate (OPNB) was calculated from that of the benzoate (OBz) by using the factor of 20.8 obtained from the corresponding 2-phenyl derivatives.

[9] H. C. Brown, W. J. Hammar, J. H. Kawakami, I. Rothberg, and D. L. Vander Jagt, *J. Am. Chem. Soc.*, **89**, 6381 (1967).

[10] P. von R. Schleyer, *ibid.*, **89**, 701 (1967).

[11] The fact that we conclude that σ participation cannot be a significant factor in the observed high *exo*:*endo* rate ratio in the present system should not be extrapolated to the position that σ participation cannot be a factor in the *exo*:*endo* rate ratio in the parent norbornyl system. This point is considered in more detail in the following communication: K. Takeuchi and H. C. Brown, *ibid.*, **90**, 2693 (1968).

[12] H. M. Bell and H. C. Brown, *ibid.*, **88**, 1473 (1966).

[13] Authentic *exo*-*p*-anisylnorbornane (n^{20}D 1.5475) was prepared by the alkylation of anisole with norbornene under the influence of sulfuric acid. The *para* isomer was separated from the *ortho* and *meta* derivatives by preparative gas chromatography. The *endo* isomer (n^{20}D 1.5498) was prepared by hydrogenation of 2-*p*-anisylnorbornene.

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

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%.

(14) Research assistant on grants (G 19878 and GP 6492X) supported by the National Science Foundation.

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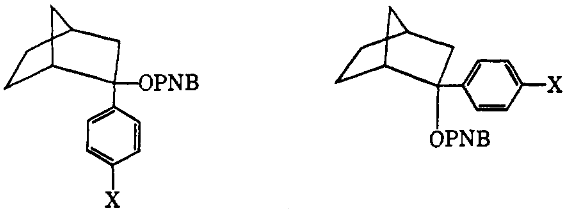
Solvolysis of 2-Aryl-2-norbornyl *p*-Nitrobenzoates Containing Deactivating Substituents in the Aromatic Ring. A New Technique for Evaluating the Importance of σ Participation in the Solvolysis of Norbornyl Derivatives

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.

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

Substituent[a]	Isomer	First-order rate constant, $k_1 \times 10^6$ sec^{-1} (80% acetone) 125.0°	100.0°	75.0°	50.0°	25.0°	0.0°	*exo*:*endo* 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).

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

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

(2) P. G. Gassman, J. Zeller, and J. T. Lumb, *Chem. Commun.*, 69 (1968).

(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).

(5) P. von R. Schleyer, *ibid.*, **89**, 701 (1967).

(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.