Table I. Summary of Rates in Solvolysis

Compd[a]	Solvent[b]	Temp, °C	k_1, sec^{-1}	Calcd at 77.6° k_1, sec^{-1}	Calcd at 77.6° Rel reactivity	*exo*:*endo* rate ratio
I-Cl (*homo-para*)	70% aqueous acetone	75.0	2.64×10^{-4}	3.36×10^{-4}	178	3.2×10^{5}
		50.0	2.16×10^{-5}			
II-Cl (*homo-meta*)	70% aqueous acetone	145.0	3.17×10^{-4}	7.63×10^{-7}	0.40	1600
		120.4	4.46×10^{-5}			
V-OBs (*homo-para*)	Acetic acid	120.5	1.93×10^{-4}	2.18×10^{-6}	5.6×10^{-4}	
		77.6	2.18×10^{-6}			
VI-OBs (*homo-meta*)	Acetic acid	120.5	8.75×10^{-5}	9.57×10^{-7}	2.5×10^{-4}	
		77.6	9.57×10^{-7}			
exo-2-Benzonorbornenyl chloride	70% aqueous acetone	145.0	5.36×10^{-4}	1.89×10^{-6}	1	4200
		120.0	8.27×10^{-5}			
exo-2-Benzonorbornenyl brosylate	Acetic acid	50.0	1.88×10^{-4} [c]	3.87×10^{-3}		
		25.0	7.47×10^{-6} [c]			
endo-2-Benzonorbornenyl brosylate	Acetic acid	114.8	5.49×10^{-5} [c]	9.35×10^{-7}	2.4×10^{-4}	
		95.8	7.60×10^{-6} [c]			

[a] In the present runs, [RX] = 0.019 *M*. [b] The aqueous acetone is volume per cent and the acetic acid contained 0.02 *M* NaOAc and 1% acetic anhydride. [c] P. D. Bartlett and W. P. Giddings, *J. Am. Chem. Soc.*, **82**, 1240 (1960).

duction of III and IV led to the respective *endo*-alcohols V-OH, mp 54.5-55°, brosylate mp 97–98°, and VI-OH, mp 63–63.5°, brosylate mp 111–112°. Rates of solvolysis of the chlorides and brosylates and their conditions are summarized in Table I.

In the *exo* series, the *homo-para*-methoxy substituent increases the rate by a factor of 178 and the *homo-meta*-methoxy depresses it slightly (0.4). The small increasing effect (2.3) is noted in the rate of the *homo-para endo*, while almost no effect on the *homo-meta endo* is noted. The results in the *exo* series are those to be expected on the basis of the methoxy substituent effects on electrophilic aromatic reactions and also, consistent with our previous suggestion, the rates at the *homo-para* position would be correlated with σ_p^+ and those at the *homo-meta* position with σ_m^+ (formula A).[1a] The high *exo*:*endo* rate ratio exhibited by 2-benzonorbornenyl brosylate, with the high stereospecificity in product, was originally attributed by Bartlett and Giddings[8] to the ability of the benzene ring to assist ionization. An alternative explanation based on the unusual steric requirements of the rigid bicyclic system has been proposed.[9] In accord with the former proposal, the present results indicate that the amount of participation and the magnitude of the *exo*:*endo* rate ratio increase greatly by introducing an activating substituent, while maintaining the steric requirements constant. In acetolyses of 9-benzonorbornenyl brosylates, we have found a linear Hammett correlation for the *anti*:*syn* rate ratio and that introduction of a nitro group reduces the ratio near unity and two nitro groups reverse the *anti* and the *syn* rates.[1d] Increments of the *exo*:*endo* rate ratio in the present system from 4200 (at 77.6°) for the unsubstituted to 3.2×10^5 for the *homo-para* methoxyl correspond to a ρ of -2.4 in a $\rho\sigma^+$ treatment. Therefore, if introduction of a deactivating substituent(s) having σ^+ of >1.5 results in equality of both the *exo* and *endo* rates (or reverses them), it becomes clear that the steric requirements have no effect on the *exo*:*endo* rate ratio.[10]

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(8) See Table I, footnote *c*.

(9) H. C. Brown and G. L. Tritle, *J. Am. Chem. Soc.*, **88**, 1320 (1966).

(10) Note Added in Proof. After submitting this communication, we were informed by Professors Winstein and Brown of similar independent results on the same topics. We thank them for showing us their communications: D. V. Braddon, G. A. Wiley, J. Dirlam, and S. Winstein, *J. Am Chem. Soc.*, **90**, 1901 (1968); H. C. Brown and G. Tritle, *ibid.*, **90**, 2689 (1968).

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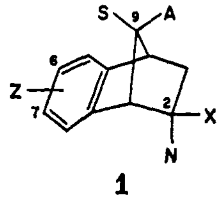
π Participation and *exo*:*endo* Rate Ratios in the Solvolysis of Methoxy- and Nitro-Substituted Benzonorbornen-2-yl Derivatives

Sir:

The benzonorbornadiene system **1** offers many advantages for the study of the importance of π participation in a rigid system.[1] It is possible to introduce both activating[2] and deactivating substituents into the aromatic ring and observe the effect on the *anti*:*syn* rate ratio at the 9 position[3] or the *exo*:*endo* rate ratio



1

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(1) P. D. Bartlett and W. P. Giddings, *J. Am. Chem. Soc.*, **82**, 1240 (1960).

(2) The first application of this technique appears to have been made by G. A. Wiley for the 5,8-dimethoxy derivative, as reported in A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1961, pp 389-391.

(3) (a) H. Tanida, T. Tsuji, and H. Ishitobi, *J. Am. Chem. Soc.*, **86**, 4904 (1964); (b) H. Tanida, Y. Hata, S. Ikegami, and H. Ishitobi, *ibid.*, **89**, 2928 (1967).

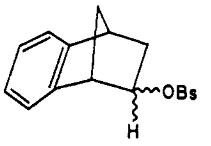
Table I. Rates of Solvolysis of the 6- and 7-Substituted Benzonorbornen-2-yl Derivatives

Substituent								
Z	X	N	Solvent	Temp, °C	$k \times 10^6$, sec^{-1}	$\Delta H^{\ddagger}$ kcal mole^{-1}	$\Delta S^{\ddagger}$, eu	*exo*:*endo* rate ratio at 25°
H	OBs	H	HOAc	25.0	7.47	24.1	−1.2	15,000[a]
				50.0	188			
H	H	OBs	HOAc	25.0	5.1×10^{-4} [a,b]	28.9	−3.9	
				95.75	7.60			
				114.8	54.9			
7-CH_3O	OBs	H	HOAc	25.0	6.70	22.8	−5.8	4,350
				50.0	143			
(6,7)-CH_3O[c]	H	OBs	HOAc	25.0	1.54×10^{-3} [b]	27.0	−8.8	
				100.0	17.7			
				125.0	183			
H	Cl	H	80% Me_2CO	25.0	1.57×10^{-3} [b]	27.8	−25	
				100.0	3.34			
				125.0	22.6			
6-CH_3O	Cl	H	80% Me_2CO	25.0	0.332[b]	22.6	−12.0	3.2×10^6 [d]
				50.0	6.89			
				75.0	92.5			
6-CH_3O	H	OBs	HOAc	25.0	6.07×10^{-4} [b]	30.8	2.7	
				100.0	25.7			
				125.0	368			
(6,7)-NO_2	OBs	H	HOAc	25.0	2.11×10^{-3} [b]	28.8	−1.4	94
				100.0	46.5			
				125.0	564			
(6,7)-NO_2	H	OBs	HOAc	25.0	2.25×10^{-5} [b]	30.0	−6.4	
				125.0	9.92			
				150.0	97.9			

[a] Bartlett and Giddings[1] reported an *exo*:*endo* rate ratio of 5000. However, the ratio of their rate constants at 25° gave the value 7500, and this value was used in the earlier publication.[5] Recalculation has revealed a further error in their extrapolation to obtain the constants at 25°, so that the correct value is actually 15,000.[4a] [b] Extrapolated value. [c] The rate was originally run on the mixture, before we had developed the preparation of the pure isomers. Since the rates of 6- and 7-methoxy *endo* derivatives are so similar, we did not attempt to repeat the synthesis and rate. [d] Estimated from the accelerating effect of the 6-methoxy group in the chloride, 210, and the *exo*:*endo* rate ratio of 15,000 in the parent compound.

at the 2 position.[4] Alternatively, it is possible to introduce stabilizing substituents at the 9 position[3b] or at the 2 position[5] and observe the effects of decreased electron demand at the reaction center on these rate ratios.[6]

The *exo*:*endo* rate ratio in the secondary and tertiary derivatives examined exhibited a surprisingly small change in the ratio with increasing stability of the carbonium ion center.[5]



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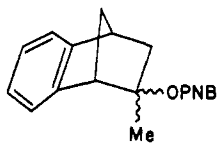

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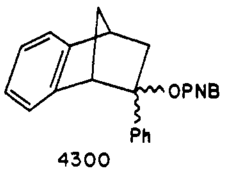

4300

Although the small decrease in the observed *exo*:*endo* rate ratios with increasing stability of the carbonium ion center did not appear to be compatible with π participation as the sole contributor to this ratio, there were disturbing features which led us to reserve judgment[5] until we could examine a benznorbornen-2-yl derivative containing a strongly deactivating substituent, such as nitro, in the aromatic ring. We also decided to examine derivatives with a methoxy substituent in the 6 and 7 positions, although the earlier work on the 5,8-dimethoxy derivative[2] had already established that such activating substituents would increase the *exo* rate and the *exo*:*endo* rate ratio through π participation.

Hydroboration–oxidation of 6-methoxybenzonorbornadiene[7] gave two isomeric *exo* alcohols (I-OH and II-OH), present in a 60:40 ratio by glpc analysis of the acetate. The 40% isomer was exceedingly reactive and was assigned the structure II-OH. The less reactive 60% isomer was assigned I-OH. The brosylate, obtained in 44% yield, mp 106–107°, was apparently a single isomer, I-OBs, since it solvolyzed in acetic acid to give the 60% acetate, I-OAc. Addition of hydrogen chloride to 6-methoxybenzonorbornadiene in the automatic hydrochlorinator at 0° gave predominantly a single chloride (~97%)[8] which was solvolyzed in aqueous acetone to give the reactive alcohol, II-OH, oxidized to the ketone,[1] and reduced to V-OH, brosylate mp 93–94.5°.

exo-Benzonorbornen-2-yl acetate, 45 g, was dissolved in 135 ml each of acetic acid and acetic anhydride, and nitration was achieved by the addition of 34.2 ml of fuming nitric acid in 30 ml of acetic acid at 4–8°. There was obtained 50.4 g (91%) of the acetate, bp 146–148° (0.3 mm), $n^{20}D$ 1.5660. The pmr spectra reveal that two protons in the aromatic region

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(4) (a) H. Tanida, T. Tsuji, and S. Teratake, *J. Org. Chem.*, **32**, 4121 (1967); (b) H. Tanida, H. Ishitobi, and T. Irie, *J. Am. Chem. Soc.*, **90**, 2688 (1968).

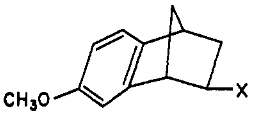
(5) H. C. Brown and G. L. Tritle, *ibid.*, **88**, 1320 (1966).

(6) It has long been an accepted position that the magnitude of the participation by a neighboring group varies inversely with the stability of the developing carbonium ion center: S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, **74**, 1113 (1952).

(7) We are indebted to H. Tanida for making this material available to us.

(8) However, compare ref 4b.

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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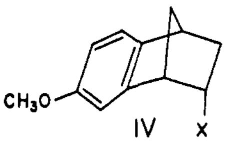
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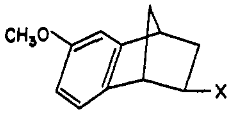
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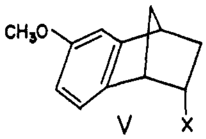
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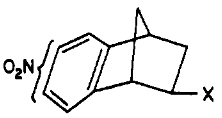
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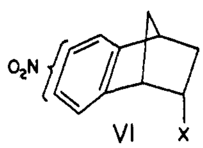
VI

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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Received March 14, 1968

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).