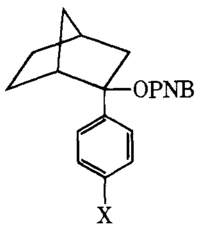
Solvolysis of the 2-[3,5-Bis(trifluoromethyl)phenyl]-2-norbornyl *p*-Nitrobenzoates and the 1-Arylcyclopentyl *p*-Nitrobenzoates. Failure of a Further Increase in Electron Demand to Alter the Exo:Endo Rate Ratio

Sir:

The epimeric 2-[3,5-bis(trifluoromethyl)phenyl]-*exo*- and -*endo*-norbornyl *p*-nitrobenzoates were synthesized and their rates of solvolysis in 80% aqueous acetone determined. However, the exo:endo rate ratio, 176, reveals that even this highly electron demanding substituent fails to alter the exo:endo rate ratio, pointing to the absence of σ-participation as a factor in the high exo:endo rate ratios in the 2-aryl-2-norbornyl derivatives. The rates of solvolysis of substituted 1-arylcyclopentyl *p*-nitrobenzoates provide $\rho^+ = -3.82$. This is in excellent agreement with ρ^+ for *endo*-2-norbornyl, −3.75, and ρ^+ for *exo*-2-norbornyl, −3.83.

The tool of increasing electron demand has revealed the presence of π-participation in the *anti*-7-norbornenyl system,[1] the 6-methoxybenzonorbornenyl system,[2] and in the 5-methyl-2-norbornenyl system.[3] Similarly, σ-contributions to the electron deficient center have been revealed by this tool in the cyclopropylcarbinyl system.[4] However, previous attempts to confirm the oft postulated σ-participation in the 2-norbornyl system[5,6] by the use of this tool have failed.[7,8]

For example, although the rates vary over a factor of 10^6, the exo:endo rate ratio remains essentially constant[7] (**1**, **2**).



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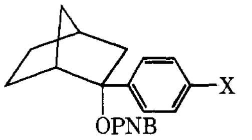

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substituent	relative rate exo:endo
p-OCH$_3$	284
p-H	127
p-CF$_3$	187

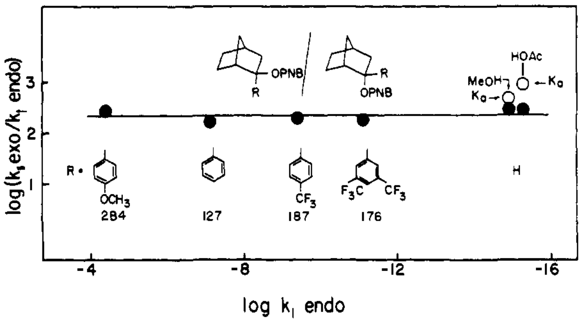
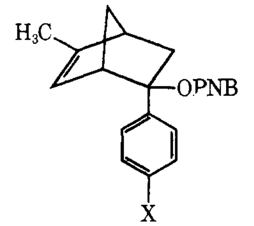


Figure 1. Exo:endo rate ratio as a function of increasing electron demand in the 2-norbornyl system.

Over the same range of electron demand other systems reveal major changes in the exo:endo rate ratio[3] (**3**, **4**).



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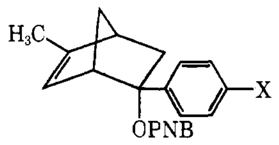

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substituent	relative rate exo:endo
p-OCH$_3$	354
p-H	1260
p-CF$_3$	(6700)

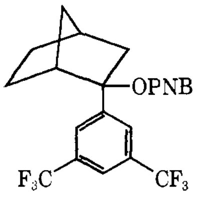
From a detailed ^{1}H NMR examination of the 2-aryl-2-norbornyl cations in superacid media, Farnum and coworkers have recently concluded that the 2-phenyl-2-norbornyl cation is a classical ion with no evidence for σ-bridging.[8] However, they report that they do observe the onset of C(1)–C(6) σ-bond delocalization in those 2-aryl-2-norbornyl cations involving more electron demanding aryl groups.[9] This development encouraged us to extend our solvolytic study to the 3,5-(CF$_3$)$_2$ derivatives (**5**, **6**) to see if the onset of σ-participation could be detected under solvolytic conditions.

We also synthesized 1-arylcyclopentyl derivatives with

Table I. Rates of Solvolysis of 2-[3,5-Bis(trifluoromethyl)phenyl]-2-norbornyl *p*-Nitrobenzoates and the 1-Arylcyclopentyl *p*-Nitrobenzoates in 80% Acetone

OPNB[a]	Rate constant (10^6k_1, sec^{-1}) t_2	t_1	25°[b]	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, eu
5[c]	368 (125°)	29.3 (100°)	0.0012	29.2	−1.5
6[d]	49.2 (150°)	4.63 (125°)	6.88×10^{-6}	31.1	−5.4
1-(p-Methoxyphenyl)-cyclopentyl[e]			3980[f]		
1-Phenylcyclopentyl[g]	926 (75°)	61.6 (50°)	2.6	23.7	−4.8
1-(p-Trifluoromethylphenyl)-cyclopentyl[h]	98.1 (100°)	7.54 (75°)	0.012	25.9	−7.9
1-[3,5-(Bistrifluoromethyl)-phenyl] cyclopentyl[i]	76.2 (125°)	7.02 (100°)	5×10^{-4}	27.6	−8.2

[a] All new compounds gave spectral and microanalytical data consistent with the proposed structure. [b] Values calculated from data at other temperatures. [c] ROPNB mp 150.5–151°; ROH mp 74–75° (lit.[9] mp 75–76.5°). [d] ROPNB mp 136–136.5°, ROH mp 71–72°. [e] Benzoate mp 70–71.5°, $k_1^{25°} = 1.91 \times 10^{-4}$ sec^{-1}. [f] Rate constant for *p*-nitrobenzoate estimated by multiplying the rate constant for the benzoate by the factor 20.8.[7] [g] ROPNB mp 82–82.5°; ROH bp 84° (1.0 mm). [h] ROPNB mp 94–94.5°; ROH bp 76–78° (2.0 mm). [i] ROPNB mp 85.7–86.8°, ROH mp 80.6–81.5°.



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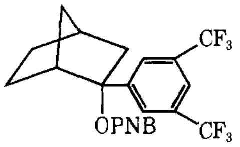

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the full range of substituents (p-OCH$_3$, p-H, p-CF$_3$, 3,5-(CF$_3$)$_2$) in order to see if the ρ^+ values provided evidence for some unusual electronic contributions from the *exo*- and *endo*-norbornyl systems as compared to the cyclopentyl system. The compounds were solvolyzed in 80% acetone and the rates compared at 25° (Table I).

The exo:endo rate ratio at 25° for the solvolysis of 2[3,5-bis(trifluoromethyl)phenyl]-2-norbornyl p-nitrobenzoates is 176, comparable with the exo:endo rate ratios for the less demanding substituents previously studied (**1, 2**). Indeed, extrapolation of the data to the corresponding secondary derivatives[10] reveals no significant change (Figure 1). Only k_α in acetic acid reveals a modest increase ($\sim$4) which might be associated with the proposed σ-participation. However, even this small factor is rendered doubtful by the remarkable constancy of the exo:endo rate ratio for the parent 2-norbornyl system in a remarkably wide range of solvents.[11]

The data for the 2-aryl-2-norbornyl derivatives follow the ρ^+ relationship[12] very closely. The exo derivatives yield $\rho^+ = -3.83$ (correlation coefficient 0.999); the endo derivatives yield $\rho^+ = -3.75$ (correlation coefficient 1.000). Finally, the 1-arylcyclopentyl derivatives yield $\rho^+ = -3.82$ (correlation coefficient 0.999). The results again support the conclusion that there are no significant electronic contributions in these derivatives from *exo*-norbornyl or *endo*-norbornyl that are not present in the cyclopentyl. The data do not support the oft-postulated[5,6] importance of σ-participation as a factor in the exo:endo rate ratio.

In superacid media the 2-aryl-2-norbornyl cations containing deactivating substituents (p-CF$_3$, 3,5-(CF$_3$)$_2$) in the aryl group exhibit changes in the ^{1}H NMR spectra interpreted as involving electronic redistributions in the norbornyl structure.[9] Whatever might be the origin of these electronic effects—inductive, field, hyperconjugative, or σ-bridging—they are clearly not effective in altering the exo:endo rate ratio in the solvolysis of the related norbornyl derivatives. This result points to the need for caution in extrapolating data from superacid media to solvolytic media.[13]

References and Notes

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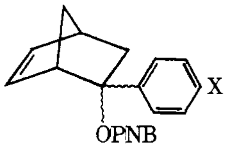
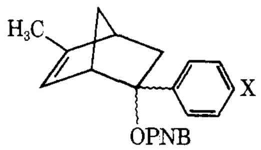
Rates and Products of Solvolysis of 2-Methyl-2-norbornenyl and 2,5-Dimethyl-2-norbornenyl *p*-Nitrobenzoates. Evidence for Increasing π-Participation with Increasing Electron Demand

Sir:

The exo:endo rate ratio in the solvolysis of the 2-methyl-2-norbornenyl p-nitrobenzoates (895) reveals no significant increase over the corresponding saturated derivatives (885). On the other hand, the exo:endo rate ratio of the parent 2-norbornenyl derivatives (7000) does reveal an appreciable increase. Consequently, it is concluded that π-participation is not important under the high electron demand of the tertiary methyl cationic center, but becomes important under the even higher electron demand of the secondary system. On the other hand, a greatly increased exo:endo rate ratio, 112,000, is observed in the solvolysis of the 2,5-dimethyl-2-norbornenyl p-nitrobenzoates. This increase is attributed to the activation of the double bond by the 5-methyl substituent facilitating π-participation. The interpretation in terms of major π-participation is consistent with the formation of 1,3-dimethyl-3-nortricyclanol as the predominant product (98%). The increase in the value of the exo:endo rate ratio over that realized in the solvolysis of the corresponding 2-phenyl-5-methyl-2-norbornenyl derivatives, 1260, is attributed to the much higher electron demand of the tertiary 2-methyl cationic center, as contrasted to the less demanding tertiary 2-phenyl cationic center. This result confirms the position that the tool of increasing electron demand can detect participation where such participation is significant.

The solvolysis of the 2-aryl-2-norbornenyl derivatives (**1**) fails to reveal any significant increase in the exo:endo rate ratio with increasing electron demand over the usual range of substituents.[1]





	1	**2**
	exo: endo	exo: endo
p-OCH$_3$	312	354
p-H	202	1260
p-CF$_3$	283	(6700)

Only with the major increase in electron demand provided by the secondary derivative (2-H) is there observed a major increase in the exo:endo rate ratio to a value of 7000.[2] Consequently, it was concluded that π-participation cannot be a significant factor in the high exo:endo rate ratios observed in the tertiary derivatives **1**.

It was desired to increase the electronic demand by utilizing the 2-[3,5-bis(trifluoromethyl)phenyl] derivatives in