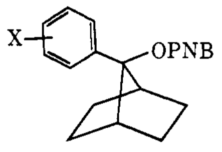

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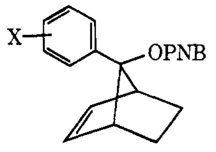
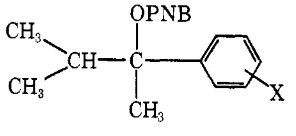


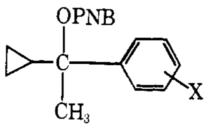
I

X	II	I
p-CH_3O	1.0	3.4
p-H	1.0	41.5
p-CF_3	1.0	34,500
m,m'-$(CF_3)_2$	1.0	255,000

2-aryl-3-methyl-2-butyl (III) and 1-aryl-1-cyclopropyl-1-ethyl p-nitrobenzoates (IV) in 80% acetone. It was observed that with increasing electron demand at the cationic center the rate of solvolysis of the cyclopropyl derivative (IV) increases enormously, as compared to the isopropyl derivative (III).[3,4] Thus, the postulate is



III



IV

X	III	IV
p-CH_3O	1.0	505
p-H	1.0	25,300
p-CF_3	1.0	285,000
m,m'-$(CF_3)_2$	1.0	1,210,000

valid for electron supply from the carbon–carbon bonds of the cyclopropane ring. The data are summarized in Table I.

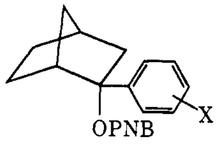
Table I. Rates of Solvolysis of 1-Aryl-1-cyclopropyl-1-ethyl and 2-Aryl-3-methyl-2-butyl p-Nitrobenzoates in 80% Acetone at 25.0°

Substituent[a]	System[b]	$k_1 \times 10^6$,[c] sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
p-CH_3O	III[d]	65.3[e]		
	IV[f]	33,000[g]		
p-H	III[h]	9.51×10^{-3}	26.7	−5.7
	IV[i]	241[e]	20.8	−5.5
p-CF_3	III[j]	1.36×10^{-5}	31.4	−2.8
	IV[k]	3.88	22.9	−6.4
m,m'-$(CF_3)_2$	III[l]	2.61×10^{-7}	34.8	0.4
	IV[m]	0.315	23.6	−9.1

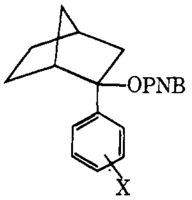
[a] All new compounds gave spectral and microanalytical data consistent with the proposed structure. [b] III, 2-aryl-3-methyl-2-butyl; IV, 1-aryl-1-cyclopropyl-1-ethyl. [c] Calculated from rates at higher temperatures, except where otherwise indicated. [d] Mp 90.4–91.0° dec. [e] Rate constant measured at 25°. [f] This ester was too unstable to isolate. [g] Because of synthetic difficulties, this rate constant was obtained by extrapolation of the log k-σ^+ plot from the other derivatives. [h] Mp 75.0–76.2°. [i] Mp 76.5° dec. [j] Mp 122.7–123.6°. [k] Mp 115.8–116.1°. [l] Mp 95.6–96.3°. [m] Mp 71.3–72.3°.

The data reveal excellent linear correlations with σ^+ constants. III yields a ρ value of −4.65 (correlation coefficient 0.999), while IV yields one of −2.78 (correlation coefficient 0.999).[7] Thus, the stabilizing effect of the cyclopropyl group is a linear function of the electron demand of the incipient carbonium ion over the range of reactivity examined.

It is of major importance that application of the same tool to the evaluation of participation by the 1,6 carbon–carbon bond in 2-aryl-2-*exo*-norbornyl p-nitrobenzoates (VI) reveals that the relative rates with respect to the



V



VI

X	V	VI
p-CH_3O	1.0	284
p-H	1.0	143
p-CF_3	1.0	188

corresponding endo isomer (V) remain essentially constant as the electron demand of the cationic center is increased over the same range.[10]

Clearly, application of this tool reveals π participation in the 7-aryl-7-*anti*-norbornenyl system and stabilization by carbon–carbon bonds in the 1-aryl-1-cyclopropyl-1-ethyl derivatives (IV) but no participation by the 1,6 carbon–carbon bonds in the tertiary aryl norbornyl derivatives (VI).

In conclusion, neighboring group stabilization by carbon–carbon bonds in the 1-aryl-1-cyclopropyl-1-ethyl system (IV) is a linear function of the electron demand of the carbonium ion center. However, significant σ participation in the 2-aryl-2-norbornyl system is absent. Consequently, the high exo:endo rate ratio in the solvolysis of tertiary 2-norbornyl derivatives must be due to some factor other than σ participation. Steric hindrance to ionization has been suggested as an alternative explanation.[10]

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(3) Rate enhancements of 100–1000 have been reported for the substitution of one cyclopropyl group for an isopropyl group: H. Hart and J. M. Sandri, *J. Amer. Chem. Soc.*, **81**, 320 (1959); H. Hart and P. A. Law, *ibid.*, **84**, 2462 (1962).

(4) The 10^6 rate enhancement for IV (X = m,m'-$(CF_3)_2$) is similar to the value, 5×10^5, estimated for a secondary cyclopropylcarbinyl cation.[5] From the relative reactivities of a bis(3,5-trifluoromethyl)phenyl and a hydrogen adjacent to a carbonium ion center,[6] a rate enhancement of about 10^9 would appear to be more appropriate for secondary cyclopropylcarbinyl systems.

(5) J. E. Baldwin and W. D. Foglesong, *J. Amer. Chem. Soc.*, **90**, 4303 (1968); also see T. Tsuji, I. Moritani, and S. Nishida, *Bull. Chem. Soc. Jap.*, **40**, 2338 (1967).

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

(7) The ρ value for IV is lower than the ρ value of −4.2 for the benzhydryl system[8] and is close to the ρ value of −2.5 for the triarylmethyl system.[9] Thus, it appears that the cyclopropyl group in IV stabilizes the cation more than an additional phenyl group would. H. C. Brown and E. N. Peters, *J. Amer. Chem. Soc.*, **95**, 2398 (1973).

(8) S. Nishida, *J. Org. Chem.*, **32**, 2692 (1967); also see ref 9.

(9) N. C. Deno and W. L. Evans, *J. Amer. Chem. Soc.*, **79**, 5804 (1957).

(10) (a) K. Takeuchi and H. C. Brown, *ibid.*, **90**, 2693 (1968); (b) H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1972, Chapters 9, 10, and 11.

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Solvolysis of the 2-Aryl-2-norbornenyl p-Nitrobenzoates. Constant Exo:Endo Rate Ratio with Increasing Electron Demand by the 2-Aryl Group

Sir:

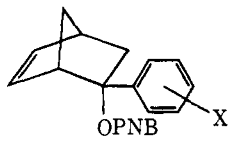
The exo:endo rate ratio in the solvolysis of the 2-aryl-2-norbornenyl p-nitrobenzoates remains essentially constant (~300) as the electron demand of the 2-aryl

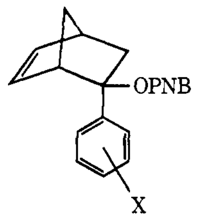
Table I. Rates of Solvolysis of 2-Aryl-2-norbornenyl *p*-Nitrobenzoates in 80% Acetone at 25.0°

Substituent in 2-aryl[a]	Isomer (OPNB)	$k_1 \times 10^{-6}$, sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	Exo:endo rate ratio
p-CH_3O[b]	Exo	2520			312
	Endo	8.08	22.7	−5.6	
p-H[c]	Exo	1.22[d]	24.7	−2.7	202
	Endo	0.00603[d]	26.3	−7.9	
p-CF_3	Exo[e]	0.00360[d]	26.8	−7.4	283
	Endo[f]	1.27×10^{-5}[d]	30.4	−6.6	

[a] All new compounds gave spectral and microanalytical data consistent with the proposed structure. [b] Reference 6. [c] Reference 7. [d] Calculated from data at other temperatures. [e] Mp 130.4–131.2°, ROH mp 98.5–99.4°, $k^{100} = 38.6 \times 10^{-6}$ sec^{-1}, $k^{75} = 2.73 \times 10^{-6}$ sec^{-1}. [f] Mp 115.1–116.4°, ROH mp 58.8–59.0°, $k^{150} = 63.8 \times 10^{-6}$ sec^{-1}, $k^{125} = 6.33 \times 10^{-6}$ sec^{-1}.

substituent is varied over a wide range in reactivity. This observation indicates the absence of π participation as a significant factor in the high exo:endo rate ratio observed in these derivatives.



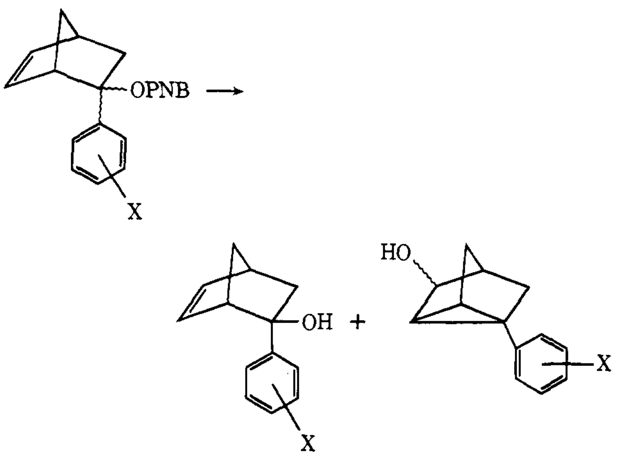


A basic tenet of neighboring group effects is that the more stable the carbonium ion center, the less demand that center will make on neighboring groups for addition stabilization.[1] Recently we established that this postulate is valid even for stabilization by neighboring carbon–carbon σ bonds.[2] Thus, in the 1-aryl-1-cyclopropyl-1-ethyl system, stabilization varies linearly with the electron demand of the carbonium ion center. However, the exo:endo rate ratio remained essentially constant in a similar test for σ participation in the 2-aryl-2-norbornyl system.[3] It was concluded that the high exo:endo rate ratio in these derivatives cannot be due to σ participation.

Gassman and Fentiman have demonstrated that this tool can be used to test for π participation.[4] They observed that the ability of the π electrons in 7-aryl-7-*anti*-norbornenyl *p*-nitrobenzoates to stabilize the developing carbonium ion center increased with the electron demand at that center.[5]

We undertook to apply this tool to evaluate the importance of π participation in the 2-aryl-2-norbornenyl system. If π participation is a significant factor in the exo:endo rate ratios, then one should observe increasing neighboring group participation accompanied by increasing exo:endo rate ratios, as the electron demand of the carbonium ion center is increased. However, this does not occur. The exo:endo rate ratio remains essentially constant (~300) over the range of reactivity studied. The results are summarized in Table I. The data give excellent $\rho\sigma^+$ plots. The exo isomers yield a ρ value of −4.21 (correlation coefficient 1.000). The endo isomers yield a ρ value of −4.17 (correlating coefficient 1.000). Therefore, there is no significant amount of π participation in the solvolysis of the 2-aryl-2-norbornenyl derivatives over the range of reactivity studied.[6,7]

The products of solvolysis of 2-aryl-2-norbornenyl *p*-nitrobenzoates were determined in buffered 80% acetone at 100.0°.[8] The predominant product is the corresponding 2-aryl-2-*exo*-norbornenol.



X (exo or endo)		
p-CH_3O	>99%	
p-H	95%	5%
p-CF_3	88%	12%

The amount of rearranged product, 1-aryl-3-nortricyclanol, increases as the stability of the carbonium ion center decreases. Hence, the involvement of the π electrons of the double bond may be increasing in the product determining step as the stability of the cation decreases.

Since the rate data establish that π participation must be absent, some other factor, presumably steric effects, must be primarily responsible for the constant exo:endo rate ratio of 300 for the 2-aryl-2-norbornenyl derivatives.[3,6,7,9]

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(1) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Amer. Chem. Soc.*, **74**, 1113 (1952).

(2) E. N. Peters and H. C. Brown, *ibid.*, **95**, 2397 (1973).

(3) K. Takeuchi and H. C. Brown, *ibid.*, **90**, 2693 (1968).

(4) P. G. Gassman and A. F. Fentiman, Jr., *ibid.*, **91**, 1545 (1969).

(5) 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 this technique to systems where the extent of participation can only be much smaller (on the order of 10^2). However, application of this tool to the 2-aryl-6-methoxybenzonorbornen-2-yl system revealed that a factor of 55 was attributable to π participation. H. C. Brown and K.-T. Liu, *ibid.*, **91**, 5909 (1969).

(6) E. N. Peters and H. C. Brown, *ibid.*, **94**, 5899 (1972).

(7) E. N. Peters and H. C. Brown, *ibid.*, **94**, 7920 (1972).

(8) Carried out in 10 mol % excess sodium acetate and analyzed by nmr spectroscopy. For 2-*p*-anisyl-2-*exo*-norbornenyl the benzoate ester was used. The products of solvolysis of 2-*p*-trifluoromethylphenyl-2-*endo*-norbornenyl *p*-nitrobenzoate were determined in 50% aqueous acetone at 100°.

(9) H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1972, Chapter 11.

(10) Procter and Gamble Fellow in Chemistry, 1970–1971.

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