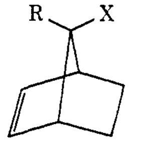
High Exo:Endo Rate Ratio and Predominant Exo Substitution in the Solvolysis of 2-*p*-Anisyl-2-norbornenyl Derivatives. Evidence for a High Exo:Endo Rate Ratio in a 2-Norbornenyl Derivative Solvolyzing without Significant π Participation

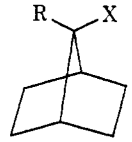
Sir:

We wish to report that the rates of solvolysis of 2-*p*-anisyl-2-norbornenyl *p*-nitrobenzoates reveal a high exo:endo ratio of 312. Moreover, both esters yield the pure exo alcohol in essentially quantitative yield, with no indication of the tricyclic compound to be expected if π participation were a factor. Consequently, we are left with the conclusion that the high exo:endo rate ratio in these highly stabilized 2-*p*-anisyl derivatives cannot be the result of any significant amount of π participation.

The more stable the carbonium ion center, the less demand that center should make upon neighboring groups for additional stabilization.[1] For example, the rate enhancement of 10^{11} observed in the acetolysis of *anti*-7-norbornenyl tosylate (Ia) relative to its saturated analog (IIa) is attributed to stabilization of the transition state by participation of the double bond.[2] Gassman and coworkers have reported that the introduction of a 7-*p*-anisyl group (Ib) essentially "levels" such participation of the double bond.[3] Indeed, the 7-*p*-anisyl derivative Ib solvolyzes at essentially the same rate as the corresponding saturated derivative, IIb.



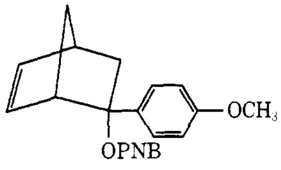
Ia, R = H
Ib, R = *p*-anisyl



IIa, R = H
IIb, R = *p*-anisyl

The high exo:endo rate ratio of 7000 in the acetolysis of norborn-5-en-2-yl brosylates has been attributed to π participation in the exo isomer.[4] If the *p*-anisyl group can cause the rate difference of 10^{11} observed in *anti*-7-norbornenyl essentially to vanish, then the much smaller factor of 7000 observed for *exo*-norbornenyl should also vanish. However, we have observed that the exo:endo rate ratio in the solvolysis of 2-*p*-anisyl-2-norbornenyl *p*-nitrobenzoates (III and IV) does not vanish, but exhibits a value of 312, comparable to the value of 284 exhibited by the corresponding saturated derivatives.[5] Clearly the exo:endo rate ratio does not diminish with the introduction of the *p*-anisyl group in the manner that a *p*-anisyl group causes participation effectively to vanish in 7-*p*-anisylnorbornenyl (Ib).

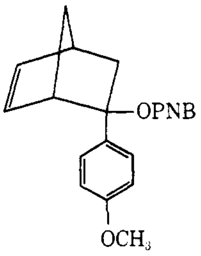
The data are summarized in Table I.



III

1.0

$k_{\rm rel}$



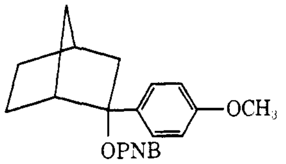
IV

312

Table I. Rates of Solvolysis of 2-*p*-Anisyl-2-norbornenyl and 2-*p*-Anisyl-2-norbornyl Derivatives in 80% Acetone

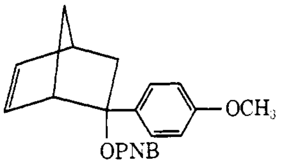
Compound[a]	*T*, °C	$k_1 \times 10^6$, sec^{-1}	(Relative rate at 25°)$_{\rm OPNB}$ Exo	Endo	Exo/endo
III[b]	50.0	170			
	25.0	8.08		1.0/5.0	
VII[c]	25.0	121			
IV[d]	25.0	2,520	1.0/4.5		312
V[e]	25.0	40.2		1.00	
VI[e]	25.0	11,400	1.0		284

[a] All new compounds gave spectral and microanalytical data consistent with the proposed structures. [b] Mp 106.0° dec. [c] Mp 100.7–101.9°. [d] Because of synthetic difficulties, this rate constant was estimated by multiplying the rate constant for the benzoate by the factor 20.8; reference 5. [e] See reference 5.



V

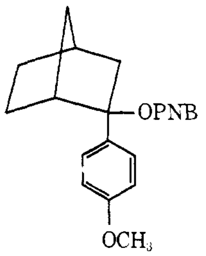
$k_{\rm rel}$ 1.0



III

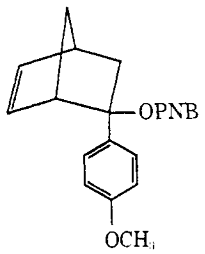
1.0/5.0

2-*p*-Anisyl-2-*endo*-norbornenyl *p*-nitrobenzoate (III) reacts five times slower than 2-*p*-anisyl-2-*endo*-norbornyl *p*-nitrobenzoate (V). This rate decrease is probably due to the inductive effect of the double bond. This is the expected behavior in the absence of π participation. However, 2-*p*-anisyl-2-*exo*-norbornenyl *p*-nitrobenzoate (IV) also reacts slower than its saturated analog, 2-*p*-anisyl-2-*exo*-norbornyl *p*-nitrobenzoate (VI) by the similar factor of 4.5. Clearly the homoallylic double bond exerts no significant amount of anchimeric assistance in the solvolysis of IV.



VI

$k_{\rm rel}$ 1.0



IV

1.0/4.5

Products of solvolysis of 2-*p*-anisyl-2-*endo*-norbornenyl *p*-nitrobenzoate (III) and 2-*p*-anisyl-2-*exo*-nor-

---

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

(2) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, **77**, 4183 (1955).

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

(4) S. Winstein, H. Walborsky, and K. C. Schreiber, *J. Amer. Chem. Soc.*, **72**, 5795 (1950).

(5) H. C. Brown and K. Takeuchi, *ibid.*, **90**, 2791, 2693 (1968).

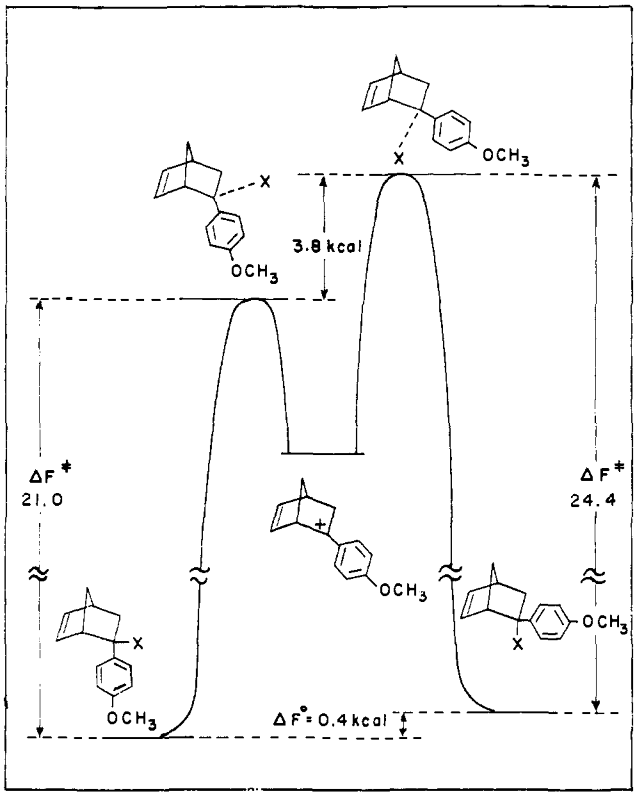


Figure 1. Goering–Schewene diagram for the solvolysis of 2-*p*-anisyl-2-norbornenyl *p*-nitrobenzoates in 80% acetone at 25.0° (X = OPNB or OH).

bornenyl benzoate (VII) in 80% acetone (containing a 10 mol % excess of sodium acetate) at 25.0° were analyzed by nmr. No products with the structure corresponding to π participation, 1-*p*-anisyl-3-nortricyclanol, were observed. Both esters gave only 2-*p*-anisyl-2-*exo*-norbornenol.[6]

These results clearly establish that π participation is not significant in the solvolysis of these 2-*p*-anisyl-2-norbornenyl derivatives. Consequently, the high exo:endo rate ratio must be due to some other factor. Possibly this factor is steric hindrance to ionization, such as has been proposed previously to account for the behavior of the 2-arylnorbornyl compounds.[5,7] If this interpretation is valid, it would mean that the π cloud of the double bond in the rigid bicyclic system resists the departure of the anion in the same manner as the endo 6 hydrogen in the saturated derivative.[7a,8,9]

The Goering–Schewene diagram for the 2-*p*-anisyl-2-norbornenyl system (Figure 1) was constructed assuming the differences in the ground-state free energy of III and IV is the same as the difference in ground-state free energy for the 2-phenyl-2-norbornyl system.[10] This diagram makes it clear that the cation formed reacts preferentially with the solvent (or anion) to give predominantly the exo product.

Clearly the Goering–Schewene diagram shows that the factors responsible for the difference in energy between the exo and endo transition states in the 2-*p*-anisyl-2-norbornenyl system must likewise be responsible for the stereoselectivity leading to the almost exclusive formation of the exo product in this system. Since π participation is evidently absent, some other factor, presumably steric effects, must be making a major contribution to the exo:endo rate ratio in the stabilized 2-*p*-anisyl-2-norbornenyl system. It follows that this factor must also be contributing at least in part to the higher exo:endo rate ratio in the parent secondary 2-norbornenyl system.[11]

---

[6] 2-*p*-Anisyl-2-*endo*-norbornenol, bp 110.5° (0.15 mm); 2-*p*-anisyl-2-*exo*-norbornenol, mp 65.4–66.5°.

[7] (a) H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N. Y., in press (Chapters 9–11); (b) H. C. Brown and K.-T. Liu, *J, Amer. Chem. Soc.*, **91**, 5909 (1969); (c) H. C. Brown, S. Ikegami, and K.-T. Liu, *ibid.*, **91**, 5911 (1969).

[8] It has been shown that attack of borohydride ion on norcamphor and dehydronorcamphor is 86% exo and 95% exo, respectively: H. C. Brown and J. Muzzio, *ibid.*, **88**, 2811 (1966).

[9] H. C. Brown, F. J. Chloupek, and M.-H. Rei, *ibid.*, **86**, 1248 (1964).

[10] Determined from the equilibration of 2-phenyl-2-norbornanol: M.-H. Rei and H. C. Brown, *ibid.*, **88**, 5335 (1966).

[11] Our conclusion that π participation cannot be a significant factor in the high exo:endo rate ratio in the 2-*p*-anisyl-2-norbornenyl system should not be extrapolated to the position that π participation cannot be a factor in the large exo:endo rate ratio, 7000, in the parent 2-norbornenyl system. If we assume that the present factor of 312, attributed to steric effects, is present in the secondary system, this leaves a factor of approximately 20 attributable to π participation in this system.

[12] Proctor and Gamble Fellow in Chemistry, 1970–1971.

Edward N. Peters,[12] Herbert C. Brown*
Richard B. Wetherill Laboratory, Purdue University
Lafayette, Indiana 47907

Received March 13, 1972

Influence of Lone-Pair Electrons on Carbon-13–Phosphorus-31 Nuclear Spin Couplings in Aromatic Phosphines

Sir:

In recent years there has been an increasing interest in the effect of the orientation of lone-pair electrons on two-bond nuclear spin–spin coupling constants with special attention being paid to the effect on $^2J(^1H-^{15}N)$ and $^2J(^{13}C-^{15}N)$.[1-6] In phosphines it has previously been shown that the $^2J(^1H-^{31}P)$ coupling exhibits a dihedral dependence,[7] and recently a similar stereospecificity was also noted for the two-bond $^{13}C-^{31}P$ couplings, $^2J(^{13}C-C-^{31}P)$, in some four-membered cyclic phosphines (methyl-substituted phosphetans).[8] We wish to report on the observation of an extraordinarily large influence of ortho substituents on some of the $^{13}C-^{31}P$ couplings in triarylphosphines. The results have been interpreted in terms of a lone-pair effect on the $^{13}C-^{31}P$ couplings. This appears to be the first observation of its kind in ^{13}C nmr of nonrigid structures.

The magnitudes and, in most cases, the signs of the $^{13}C-^{31}P$ couplings for some ortho methyl and ortho bromo substituted trithienylphosphines (**1**, **3**, and **4**)

---

[1] J. P. Kintzinger and J. M. Lehn, *Chem. Commun.*, 660 (1967).

[2] D. Crepaux and J. M. Lehn, *Mol. Phys.*, **14**, 547 (1968).

[3] T. Yonezawa, I. Morishima, K. Fukuta, and Y. Ohmori, *J. Mol. Spectrosc.*, 31, 341 (1969).

[4] M. S. Gopinathan and P. T. Narasimhan, *Mol. Phys.*, **22**, 473 (1971).

[5] R. L. Lichter and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 5218 (1971).

[6] P. S. Pregosin, E. W., Randall, and A. I. White, *J. Chem. Soc., Perkin Trans. 2*, 1 (1972).

[7] J.-P. Albrand, D. Gagniare, J. Martin, and J.-B. Robert, *Bull. Soc. Chim. Fr.*, 40 (1969).

[8] G. A. Gray and S. E. Cremer, *J. Chem. Soc., Chem. Commun.*, 367 (1972).