Structural Effects in Solvolytic Reactions. 20. Solvolysis of 2-*p*-Anisyl-2-norbornyl and 2-*p*-Anisyl-2-camphenilyl *p*-Nitrobenzoates. Evidence for the Unimportance of σ-Participation as a Factor in the High Exo:Endo Rate and Product Ratios Realized in the Solvolysis of Highly Stabilized Tertiary 2-Norbornyl Derivatives[1]

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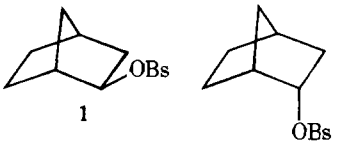
Abstract: The solvolyses of *exo*- and *endo*-2-*p*-anisyl-2-norbornyl and *exo*- and *endo*-2-*p*-anisyl-2-camphenilyl *p*-nitrobenzoates in 80% aqueous acetone reveal high exo:endo rate ratios, 284 in the case of the 2-*p*-anisylnorbornyl and 44 000 in the case of the 2-*p*-anisylcamphenilyl derivatives. The solvolysis of 2-*p*-anisyl-*exo*-norbornyl chloride in the presence of sodium borohydride affords *endo*-2-*p*-anisylnorbornane arising from the capture of the hydride from the exo direction (≥98%). Both *exo*- and *endo*-2-*p*-anisyl-2-camphenilyl derivatives yield ≥99.5% exo-substituted alcohols. Therefore, these highly stabilized norbornyl derivatives show high exo:endo rate ratios and high exo:endo product ratios, at one time considered to be the essential criteria required to postulate σ-participation with formation of a σ-bridged intermediate. Yet σ-participation cannot be a factor in the solvolysis of these highly stabilized tertiary norbornyl derivatives. It is concluded that steric effects must make a major contribution to the high exo:endo rate and product ratios observed in these stabilized tertiary norbornyl derivatives.

The high exo:endo rate ratio and predominant exo substitution observed in the solvolysis of secondary 2-norbornyl derivatives were considered to be the distinguishing features of the σ-bridged 2-norbornyl cation.[3] The acetolyses of *exo*- and *endo*-norbornyl brosylates (**1, 2**) yield an exo:endo rate ratio of 350 (1).[3] Moreover, both yield 99.98% exo alcohol.[3,4] It was

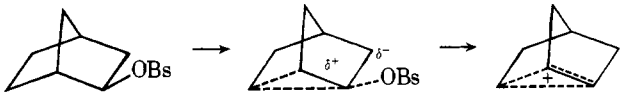


(1)

1 **2**

exo:endo (25°C)	350	1.00

postulated that the 1,6-bonding pair is in ideal position to participate in the displacement of the exo brosylate group, but it is in an unfavorable position to assist the ionization of the endo isomer (2).[3]

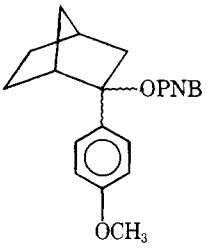


1 OBs^- (2)

It has been proposed that the importance of neighboring group participation should diminish as the incipient carbonium ion center is stabilized by substitution.[5] The postulate has received general acceptance.[6] Consequently, we undertook to synthesize *exo*- and *endo*-2-*p*-anisyl-2-norbornyl and 2-*p*-anisyl-2-camphenilyl *p*-nitrobenzoates (**3, 4**) in order to establish the effect of the stabilization produced by the *p*-anisyl group at the cationic center on the exo:endo rate and product ratios.

Results

Synthesis. Addition of *p*-anisylmagnesium bromide to 2-norbornanone (**5**) yielded 2-*p*-anisyl-*endo*-norbornanol (**6**). Treatment with hydrogen chloride gave the exo chloride (**8**).



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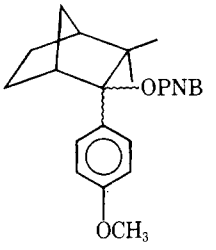

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Hydrolysis then yielded the 2-*p*-anisyl-*exo*-norbornanol (**9**). The endo alcohol (**6**) was converted into the *p*-nitrobenzoate (**7**) by treating with *n*-butyllithium, followed by *p*-nitrobenzoyl chloride.[7] The exo *p*-nitrobenzoate was too unstable to be isolated and hence the benzoate was synthesized for solvolytic studies. 2-*p*-Anisylcamphenilyl derivatives were also synthesized by similar procedures (see Experimental Section).

Rate Studies. The rates of solvolysis of 2-*p*-anisylnorbornyl (**7, 10**) and 2-*p*-anisylcamphenilyl derivatives were measured in 80% aqueous acetone following the standard titrimetric procedures.[7] The rate constant for the solvolysis of 2-*p*-anisyl-*exo*-norbornyl *p*-nitrobenzoate was determined by multiplying the rate of the benzoate by the factor 20.8. This factor was obtained from the corresponding 2-phenyl derivatives. Similarly, the rate of solvolysis of 2-*p*-anisyl-*exo*-camphenilyl *p*-nitrobenzoate was calculated from that of the benzoate by using $k_{OPNB}/k_{OBz} = 23.5$, determined for the phenyl derivatives. The pertinent rate data are summarized in Table I.

Solvolytic Products. 2-*p*-Anisyl-*exo*-norbornyl chloride (**8**) was solvolyzed in diglyme–water mixture in the presence of sodium borohydride.[8] Analysis by ^1H NMR revealed more than 98% attack from the exo side. Both *exo*- and *endo*-2-*p*-anisylcamphenilyl derivatives were solvolyzed in buffered 80% aqueous acetone. ^1H NMR analysis of the product indicated more than 99.5% exo alcohol.

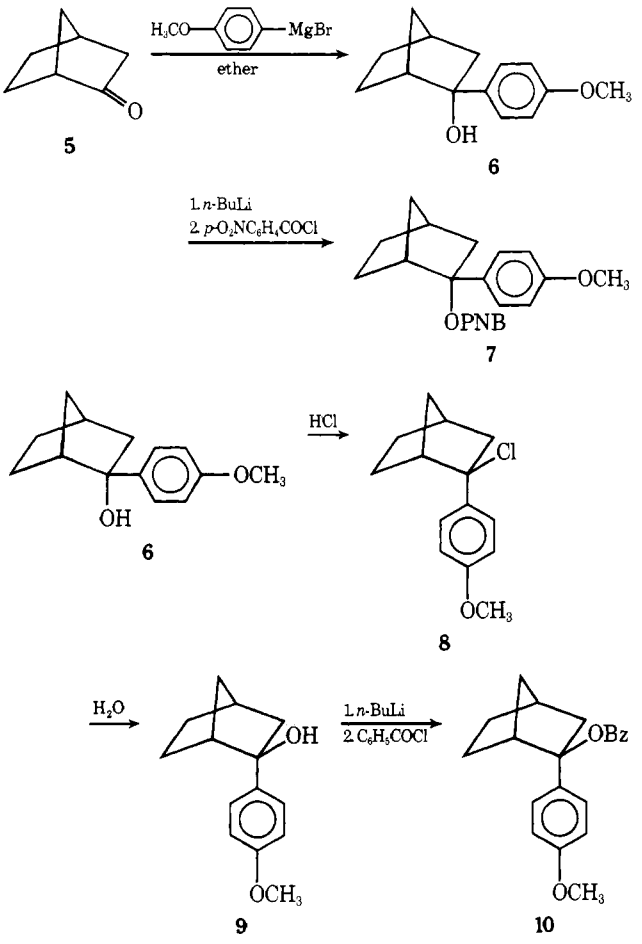
Discussion

The rate of ethanolysis of 2-*p*-anisyl-*exo*-norbornyl chloride is greater than that of *exo*-norbornyl chloride by an enormous

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

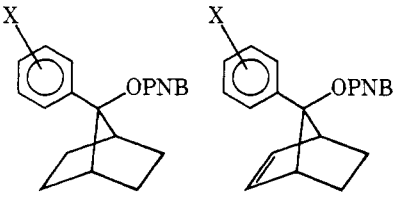
System	Isomer	Derivative	Rate constant, $k_1 \times 10^6$, s^{-1} T_2, °C	T_1, °C	25 °C	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	Exo:endo at 25 °C
2-Norbornyl	Exo	OBz		18.7 (0)	548	21.3	−2.1	
		OPNB			11 400[a]			284
	Endo	OPNB		1.17 (0)	40.2	22.3	−3.8	
2-Camphenilyl	Exo	OBz		15.7 (0)	514	22.0	0.2	
		OPNB			12 100[b]			44 000
	Endo	OPNB	171 (75)	8.77 (50)	0.273	26.0	−1.6	

[a] Calculated by multiplying the rate of the benzoate by the factor of 20.8. [b] Calculated by multiplying the rate of the benzoate by the factor of 23.5.



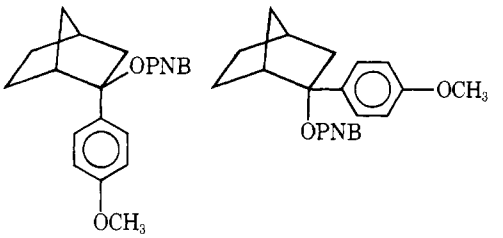
factor of 5×10^{11}.[9] Clearly the *p*-anisyl group must provide major stabilization of the incipient carbonium ion in the transition state. Hence a carbonium ion stabilized by a *p*-anisyl group should make relatively little demand on neighboring groups for further stabilization through participation. The remarkable stabilizing effect of the *p*-anisyl group causing neighboring group participation to vanish was elegantly demonstrated by Gassman and co-workers.[10] They observed that the rate enhancement of 10^{11} in the secondary 7-norbornenyl derivatives[11] decreases with the introduction of stabilizing groups at the 7 position and effectively vanishes with the *p*-anisyl group (3). If the *p*-anisyl group can cause the truly enormous π-participation ($\times 10^{11}$) observed in *anti*-7-norbornenyl to vanish, it should surely cause the much smaller σ-participation ($\times$ 350) proposed for *exo*-norbornyl to vanish.

Exo:Endo Rate Ratio in 2-*p*-Anisyl-2-norbornyl. Solvolysis of 2-*p*-anisylnorbornyl derivatives (**7, 10**) in 80% aqueous acetone reveals an exo:endo rate ratio of 284 (**4**). This compares with a value of 350 for the parent 2-norbornyl brosylates[3] and 284 for the corresponding tosylates.[12] Consequently, we do not observe a significant decrease in the exo:endo rate ratio in spite of the high stability of the cationic center, which should make σ-bridging insignificant.



(3)

	11	**12**
X = 7H	1.00	10^{11}
3,5-$(CF_3)_2$	1.00	225 000
p-CF_3	1.00	34 000
p-H	1.00	41.5
p-CH_3O	1.00	3.4

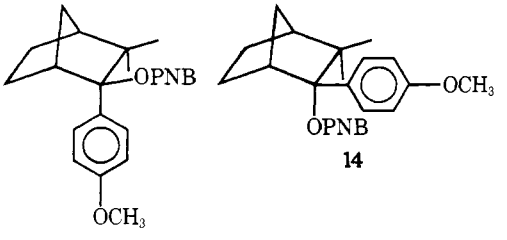


(4)

exo:endo 284 1.00

A ^1H NMR study of the 2-phenyl-2-norbornyl cation has revealed no evidence for charge delocalization from the 2 to the 1 and 6 positions.[13] If the 2-phenyl-2-norbornyl cation is classical, there surely cannot be argument about the more stable 2-anisyl derivative. Clearly the results do not support the interpretation that the high exo:endo ratios in the 2-norbornyl system must be the result of σ-participation, even in tertiary derivatives.[14]

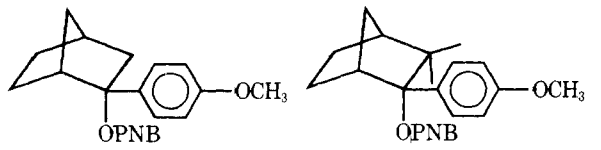
Exo:Endo Rate Ratio in 2-*p*-Anisyl-2-camphenilyl. The exo:endo rate ratio in 2-*p*-anisyl-2-camphenilyl derivatives (**13, 14**) is still higher, 44 000 (5). An examination of the individual



(5)

exo:endo
(25°C) 44 000 1.00

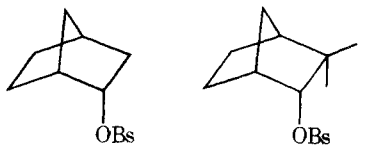
rate constants (Table I) reveals that the rates of the exo isomers are quite similar. The high exo:endo rate ratio results largely from a considerable decrease in rate of the endo isomer (6). A



(6)

relative reactivity (25°C)	1.00	1/147

comparison of the rates of acetolysis of *endo*-camphenilyl brosylate (**15**) with *endo*-norbornyl brosylate also reveals a decrease for the camphenilyl derivative,[15] albeit somewhat smaller (7). These decreases are consistent with the proposal



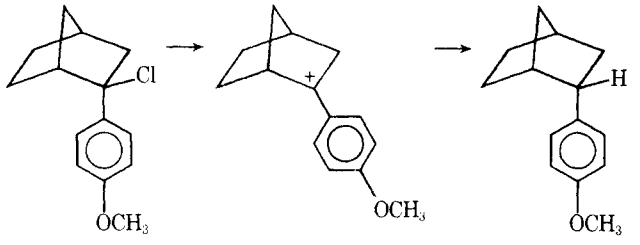
(7)

relative reactivity (25°C)	2	15
	1.00	1/10

that the rate of ionization of the endo isomer is retarded by steric difficulties in the solvation of the incipient anion and its departure. The *gem*-dimethyl group in the 3 position and the twisting of the aromatic ring must produce a more effective cage for the incipient anion than does the parent norbornyl structure.

Exo:Endo Product Ratios in 2-*p*-Anisyl-2-norbornyl and 2-*p*-Anisyl-2-camphenilyl. The predominant exo substitution (≥99.98%) observed in the solvolysis of 2-norbornyl brosylate has been considered to be a major support for σ-bridging. Consequently, it was of interest to examine the products of solvolysis of these highly stabilized norbornyl derivatives.

The solvolysis of 2-*p*-anisylnorbornyl chloride (**8**) yields 2-*p*-anisyl-*exo*-norbornanol (**9**). Unfortunately, the product is highly unstable and difficult to analyze quantitatively. Solvolysis of the chloride in the presence of sodium borohydride[8] gave a more stable product, the hydrogen derivative (**16**) (8). Analysis by ^{1}H NMR revealed attack by the borohydride from the exo direction ≥98%.



8 16

(8)

The presence of the *gem*-dimethyl substituents in 2-*p*-anisyl-2-camphenilyl greatly stabilizes the alcohols. As was pointed out earlier, solvolysis of either isomer in 80% acetone proceeds to give ≥99.5% of the exo alcohol (9). Therefore, even these highly stabilized derivatives exhibit predominant substitution from the exo side.

Free Energy Diagrams. The foregoing discussion makes it clear that these highly stabilized 2-norbornyl derivatives exhibit the high exo:endo rate and product ratios previously considered to represent a major argument favoring the σ-bridged formulation. If we accept both the theoretical and experimental evidence that highly stabilized cations, such as 2-*p*-anisyl-2-norbornyl, cannot involve σ-bridging, it follows that high exo:endo rate and product ratios do not constitute evidence for such bridging. More logically, there must be some characteristic feature of the norbornyl structure other than σ-bridging for the observed high exo:endo rate and product ratios.

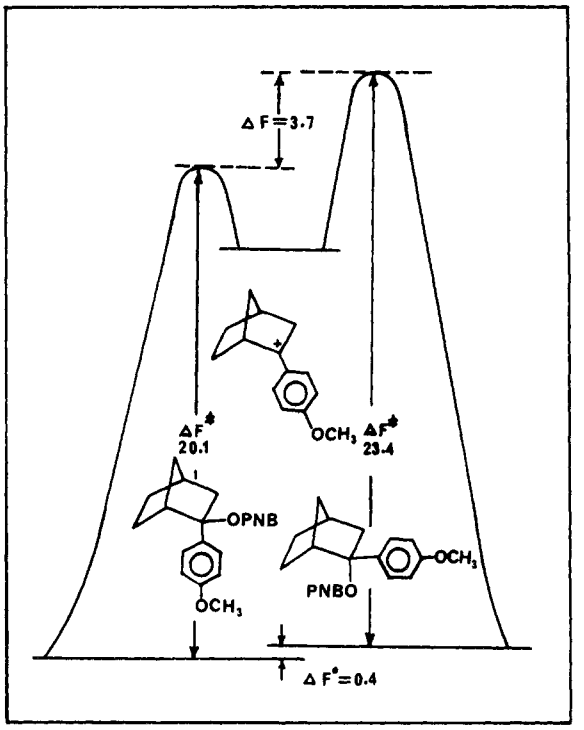
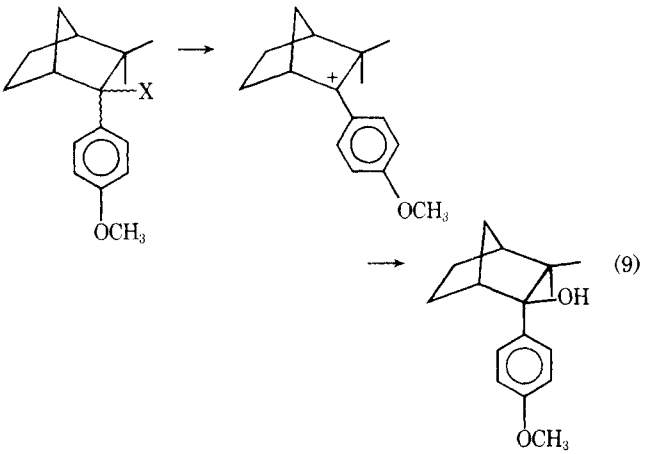


Figure 1. Free-energy diagram for the solvolysis of the 2-*p*-anisyl-2-norbornyl *p*-nitrobenzoates in 80% aqueous acetone at 25 °C.



(9)

It is of interest to construct the Goering–Schewene diagrams for the 2-*p*-anisyl-2-norbornyl and 2-*p*-anisyl-2-camphenilyl systems for comparison with the diagram for the parent system.[4]

The free energy of activation for the solvolysis of 2-*p*-anisyl-*exo*-norbornyl *p*-nitrobenzoate in 80% aqueous acetone is 20.1 kcal mol^{-1}. The corresponding value for the endo isomer is 23.4 kcal mol^{-1}. Both isomers yield the same intermediate. Equilibration of the two epimeric alcohols in the case of the phenyl derivatives established that they are of comparable stabilities with the ground state of the endo isomer being higher in energy by a relatively small factor of 0.4 kcal mol^{-1}.[16] Finally, the available evidence indicates that there is no significant difference in the steric requirements of the acyloxy and hydroxyl groups in the norbornyl system.

With these approximations in mind, it is possible to construct a free-energy diagram for the solvolysis of the exo:endo pair (Figure 1). The diagram reveals a difference in energy of the two transition states of 3.7 kcal mol^{-1}.

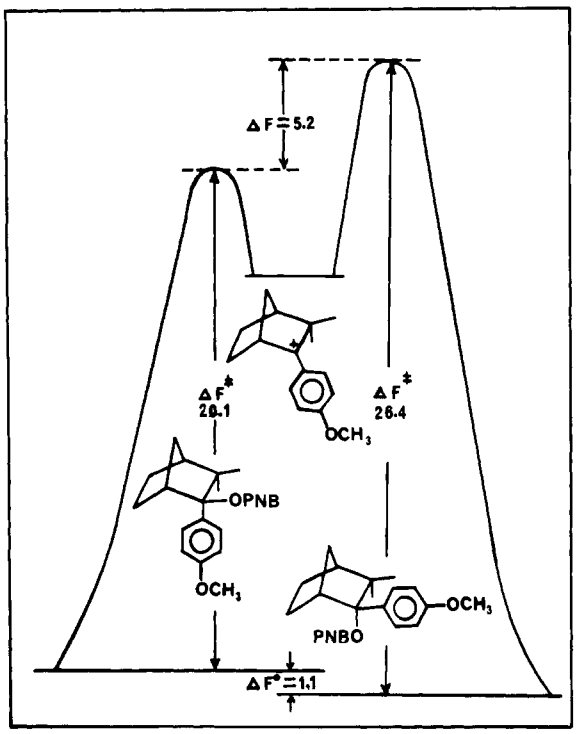


Figure 2. Free-energy diagram for the solvolysis of the 2-*p*-anisyl-2-camphenilyl *p*-nitrobenzoates in 80% aqueous acetone at 25 °C.

It is clear that the cation once formed will react with the anion (or the solvent) to give the two epimeric derivatives in a ratio determined by the difference in energy of the respective transition states. The reaction will evidently proceed in the case of both isomers to give the exo isomer predominantly.

The essential problem is that of accounting for the major difference in energy of the two transition states. Is the endo transition state normal with the exo transition state stabilized by σ-participation or is the exo transition state normal with the endo transition state destabilized by some factor?

In the case of the parent 2-norbornyl system, it has been customary to argue that the exo transition state must be stabilized by σ-bridging over the corresponding endo transition state. However, this explanation cannot be utilized for the two 2-*p*-anisyl derivatives. There appears to be considerable experimental evidence and general agreement that a cationic center highly stabilized by a 2-*p*-anisyl group cannot engage in such σ-bridging.[5,6] This leaves us with the possibility that the exo transition state must be considered normal, with the endo transition state destabilized by some factor.

The free energy of activation for the solvolysis of 2-*p*-anisyl-*exo*-camphenilyl derivative is the same, 20.1 kcal mol^{-1}, as for the corresponding 2-norbornyl derivative. However, the free energy of activation for the endo isomer is 26.4 kcal mol^{-1}, considerably larger than the value for the corresponding 2-norbornyl derivative. Consequently, as pointed out earlier, the major increase in the exo:endo rate observed for 2-*p*-anisyl-2-camphenilyl derivatives (44 000) as compared with the 2-*p*-anisylnorbornyl derivative comes about primarily because of a major decrease in the rate of solvolysis of the endo isomer of the camphenilyl system. Construction of the free-energy diagram reveals a difference in the energy of the two transition states of 5.2 kcal mol^{-1}, considerably larger than in the related 2-*p*-anisyl-2-norbornyl system (Figure 2). It is evident that the partition of the cationic intermediate between the exo and the endo product should be more stereoselective for exo in the case of the camphenilyl derivative than in the case of the corresponding norbornyl derivatives.

Exo:Endo Rate Ratios as a Steric Phenomenon. At the time the high exo:endo rate and product ratios for the solvolysis of 2-norbornyl derivatives were observed, little was known about the remarkable steric characteristics of the norbornane structure. The highly stabilized 2-*p*-anisyl-2-norbornyl and 2-*p*-anisyl-2-camphenilyl derivatives exhibit equally high exo:endo rate and product ratios. Therefore, explanations other than σ-bridging have to be explored to account for these characteristics. The marked preference for reaction from the exo over reaction from the endo direction appears to be in the rigid U-shaped structure of the norbornane system.[17] The high exo:endo rate ratios are presumably the result of decreased rates of reaction in the sterically hindered endo direction of the U-shaped structure.[17] Consequently, it appeared appropriate to consider that the high exo:endo rate ratio in the solvolysis of the tertiary 2-*p*-anisyl-2-norbornyl and the parent secondary 2-norbornyl derivatives may actually be the result of a normal exo rate combined with a very slow endo rate.

Conclusion

The solvolysis of the 2-*p*-anisyl-2-norbornyl and the 2-*p*-anisyl-2-camphenilyl *p*-nitrobenzoates proceeds through classical cations without σ bridges. Yet these two systems reveal high exo:endo rate and product ratios comparable to those in norbornyl itself. The two systems (**3, 4**) yield free-energy diagrams (Figures 1 and 2) which are remarkably similar to the parent secondary system.[4,17] The behavior of such tertiary 2-norbornyl derivatives can be clearly understood in terms of the steric interactions with a high order of consistency. The conclusion that σ-participation is not a factor in these stabilized tertiary derivatives should not be extrapolated to the position that σ-participation may not contribute to the high exo:endo rate ratios and product ratios observed in the secondary norbornyl derivatives. However if steric effects make a major contribution to the exo:endo rate and product ratios in these stabilized tertiary norbornyl derivatives, it is difficult to see why such steric destabilization of the endo transition state will not also make a significant contribution to these ratios in the secondary norbornyl derivatives.

Experimental Section

2-*p*-Anisyl-*endo*-norbornanol (6). This alcohol was prepared by the addition of *p*-anisylmagnesium bromide to norcamphor, bp 135–138 °C (2 mm) [lit.[18] bp 160–170 °C (2–2.5 mm)].

2-*p*-Anisyl-*exo*-norbornanol (9). The exo alcohol was converted to the chloride by treating with dry HCl gas in methylene chloride at 0 °C in an automatic hydrochlorinator.[19] The solvent was pumped off and the chloride was hydrolyzed in 60% acetone at 0 °C in the presence of 100% excess sodium bicarbonate. The solvent was evaporated, alcohol extracted with ether, and dried over anhydrous magnesium sulfate. Removal of solvent gave the exo alcohol; this alcohol was used for the benzoate preparation without further purification.

2-*p*-Anisyl-*endo*-norbornyl *p*-Nitrobenzoate (7). This compound was prepared by treating the alcohol with *n*-butyllithium and *p*-nitrobenzoyl chloride in the usual manner,[7] mp 115 °C dec.

Anal. Calcd for $C_{21}H_{21}NO_5$: C, 68.65; H, 5.76; N, 3.81. Found: C, 68.59; H, 5.67; N, 4.04.

2-*p*-Anisyl-*exo*-norbornyl Benzoate (10). This benzoate was prepared by treating the lithium salt of the alcohol with benzoyl chloride in THF, mp 91–91.5 °C.

Anal. Calcd for $C_{21}H_{19}O_3$: C, 78.18; H, 6.79. Found: C, 78.23; H, 6.88.

2-*p*-Anisyl-*endo*-camphenilol. Camphenilone (from Shawnee Chemicals, 41.4 g, 0.3 mol) was treated with *p*-anisylmagnesium bromide prepared from *p*-bromoanisole (60 g, 0.321 mol) and magnesium turnings (7.8 g, 0.321 mol) in ether. The reaction mixture was worked up in the usual manner.[20] Crystallization from ethanol gave 34.0 g (41.5%) of the endo alcohol, mp 113.5–114 °C (lit.[21] mp 115.5–116 °C). On GLC analysis, the alcohol decomposed to give *p*-anisylapocyclene.

2-*p*-Anisyl-*exo*-camphenilol. 2-*p*-Anisyl-*endo*-camphenilol (5 g) was dissolved in 50 mL of 96% sulfuric acid. After 10 min, the reaction mixture was poured into 400 g of ice. Extraction with ether and recrystallization from *n*-pentane afforded 3.7 g (74%) of 2-*p*-anisyl-*exo*-camphenilol, mp 77.5–78 °C (lit.[21] mp 76–78 °C). On GLC analysis, this was detected as *p*-anisylapocyclene.

2-*p*-Anisyl-*endo*-camphenilyl *p*-Nitrobenzoate (14). This *p*-nitrobenzoate was obtained by treating the lithium salt of the alcohol with *p*-nitrobenzoyl chloride in 41% yield, mp 133.8–134.8 °C (lit.[21] mp 129.5–135 °C).

2-*p*-Anisyl-*exo*-camphenilyl Benzoate. This compound was prepared by treating the alcohol with *n*-butyllithium and benzoyl chloride in 54% yield, mp 127.5–128 °C.

Anal. Calcd for $C_{23}H_{26}O_3$: C, 78.83; H, 7.48. Found: C, 78.58; H, 7.58.

Trapping of 2-*p*-Anisylnorbornyl Cation by Sodium Borohydride. In a typical experiment, sodium borohydride (8.5 g, 0.225 mol) was dissolved in a mixture of diglyme (80 mL) and water (37.5 mL). A solution of 2-*p*-anisyl-*exo*-norbornyl chloride (1.18 g, 5 mmol) in diglyme (7.5 mL) was added at 25 °C. This results in 1.8 M in sodium borohydride and 0.04 M in chloride. The reaction mixture became foamy. After 10 min, 80 mL of pentane was added. The pentane layer was washed with four portions of 50 mL of water to wash out diglyme and dried over anhydrous magnesium sulfate. The solvent was evaporated and 2-*p*-anisylnorbornanes were separated from the olefin by preparative GLC (6-ft FFAP column at 150 °C) in 68% yield. The exo:endo ratio of the trapping material was determined by ^{1}H NMR by measuring the peak area exhibited by the C_2 protons in CCl_4 solution (30%). The C_2 proton of the exo isomer appeared as a triplet at δ 2.62 (J = 6.5 Hz) and of the endo isomer as a multiplet at δ 3.15 (J = 5 Hz). Analysis revealed that 2-*p*-anisylnorbornanes obtained in the trapping experiment consisted of $\geq$98% exo and $\leq$2% endo.

Product Study of the Solvolysis of 2-*p*-Anisylcamphenilyl Derivatives. One millimole of *p*-nitrobenzoate or benzoate was dissolved in 25 mL of 0.08 M sodium acetate in 80% acetone. After keeping the solution for 10 half-lives, acetone was evaporated with a rotary evaporator and then 20 mL of 10% sodium carbonate was added. The ether extract was washed with water and dried over anhydrous magnesium sulfate. After evaporation of ether the residue was subjected to ^{1}H NMR analysis. Analysis was carried out by comparing the heights of methyl signals appearing at δ 0.44–0.48 (endo OH) and 0.74–0.80 (exo OH). Both exo and endo derivatives gave 99.5% exo alcohol and $\leq$0.5% endo alcohol.

Equilibration of 2-*p*-Anisylcamphenilols. The alcohol (2 g) (exo or endo) was dissolved in 8 mL of chloroform. The solution was stirred with 10 mL of 4 N sulfuric acid on a magnetic stirrer at room temperature. Aliquots were taken and examined by ^{1}H NMR (Varian A-60A). The amount of each alcohol was determined by measuring the peak heights at δ 0.5 (endo OH) and 0.78 (exo OH). In the case of both exo and endo alcohols, the equilibrium mixture consisted of 86.4% endo and 13.6% exo.

Kinetic Measurements. The method used for determining the rate constants of the *p*-nitrobenzoates and benzoates is essentially the same as described earlier.[7]

References and Notes

(1) Preliminary accounts of portions of this study were published earlier: H. C. Brown and K. Takeuchi, *J. Am. Chem. Soc.*, **90**, 2691, 2693, 5268, 5270 (1968).
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