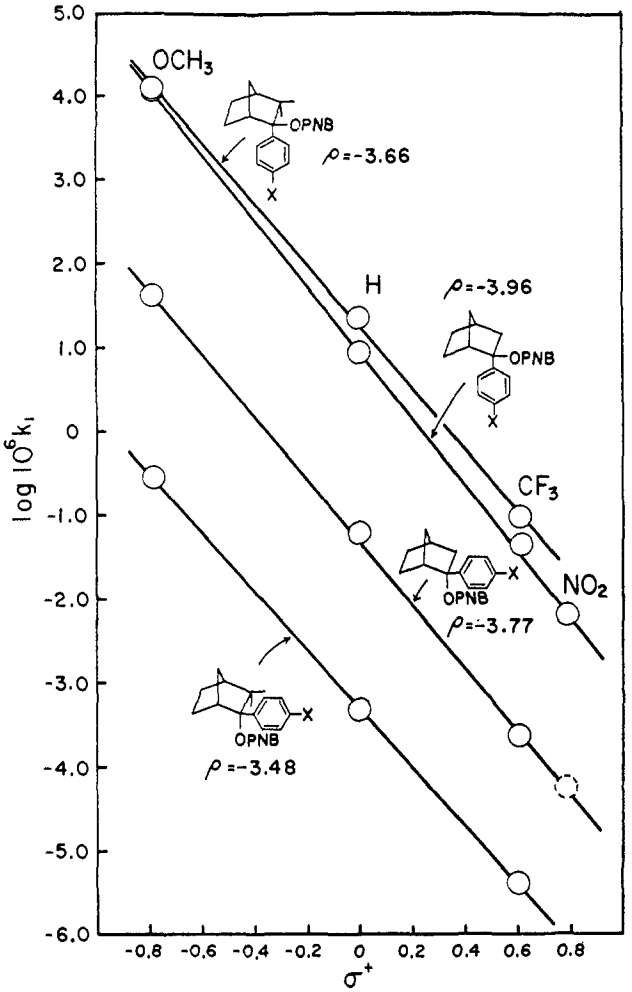

Figure 1. Correlations of the rate constants for the solvolysis of the *p*-nitrobenzoates at 25° in 80% acetone with σ^+.

An examination of the data (Table I, Figure 1) indicates that the higher *exo*:*endo* rate ratio in the camphenilyl as compared to the norbornyl system arises primarily because of greatly decreased rates for the *endo* derivatives. This is consistent with the proposal that the rate of ionization of the *endo* isomer is retarded by steric difficulties in the solvation of the incipient anion and its departure.[10] An examination of molecular models reveals that the *gem*-dimethyl group in the 3 position and the twisting of the aromatic ring that it must produce provides a more effective "cage" for the incipient anion than does the parent norbornyl structure.

Recent evidence clearly implies that steric effects must be an important contributing factor in the *exo*:*endo* rate ratios observed for such tertiary bicyclic systems.[11] Whether such steric effects constitute the sole important factor remains to be decided.[12]

It has long been customary to interpret high *exo*:*endo* rate ratios in bicyclic systems in terms of σ participation leading to the formation of σ-bridged norbornyl cations.[8] Yet it appears clear that σ participation cannot be a significant factor in the large *exo*:*endo* rate ratios observed in these stabilized tertiary systems. The present results therefore support the earlier conclusion[13] "that a high *exo*:*endo* rate ratio in a norbornyl derivative does not provide a unique basis for concluding that the derivative undergoes ionization with participation of the 1,6-bonding pair to form a nonclassical norbornyl cation."

(10) H. C. Brown, *Chem. Brit.*, 2, 199 (1966).
(11) H. C. Brown, W. J. Hammar, J. H. Kawakami, I. Rothberg, and D. L. Vander Jagt, *J. Am. Chem. Soc.*, 89, 6381 (1967).
(12) P. von R. Schleyer, *ibid.*, 89, 701 (1967).
(13) H. C. Brown, F. J. Chloupek, and M.-H. Rei, *ibid.*, 86, 1248 (1964).
(14) Research assistant on grants (G 19878 and GP 6492 X) supported by the National Science Foundation.

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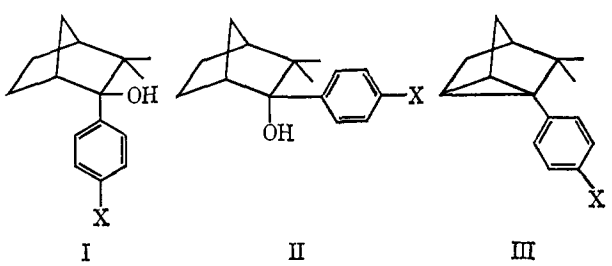
Predominant *exo* Substitution in the Products from the Solvolysis of 2-*p*-Anisylcamphenilyl and Related Compounds. Further Evidence for Steric Effects as a Major Factor in the *exo*:*endo* Product Ratios from Tertiary Norbornyl Derivatives

Sir:

It has been commonly postulated that a classical norbornyl cation would undergo substitution to give considerable amounts of *endo* products.[1] An anisyl group in the 7 position of dehydronorbornyl effectively destroys the 10^{11} participation observed in the parent system.[2] Consequently, it appears safe to conclude that σ participation cannot be significant in norbornyl derivatives containing an anisyl group in the 2 position.[3] Yet the 2-arylcamphenilyl *p*-nitrobenzoates previously described[3b] undergo solvolysis in 80% aqueous acetone to give the *exo* alcohols I only. The formation of the *endo* alcohols II was insignificant, less than the experimental uncertainty (<0.5%). In the case of the *p*-trifluoromethyl derivative, the apocyclene III constituted an appreciable fraction of the product.



I II III

The results are summarized in Table I.

The high yield of the apocyclene derivative in the solvolysis of 2-*p*-trifluoromethylphenyl-*endo*-camphenilyl *p*-nitrobenzoate is unexpected. It suggests the possibility that approximately one-half of the solvolysis of this inert derivative may proceed *via* a γ-elimination reaction. If so, this would halve the observed rate to give the true rate for the conversion to carbonium ion, the true SN1 process, and would increase the *exo*:*endo* rate ratio from the observed value of 24,000 to a value of 48,000, in much closer agreement with the value observed for the other derivatives.

(1) P. G. Gassman and J. L. Marshall, *J. Am. Chem. Soc.*, 88, 2822 (1966).
(2) P. G. Gassman, J. Zeller, and J. T. Lumb, *Chem. Commun.*, 69 (1968).
(3) (a) H. C. Brown and K. Takeuchi, *J. Am. Chem. Soc.*, 90, 2691 (1968); (b) K. Takeuchi and H. C. Brown, *ibid.*, 90, 2693 (1968); (c) H. C. Brown and K. Takeuchi, *ibid.*, 90, 5268 (1968).

Table I. Product Distribution in the Solvolysis of Substituted 2-Arylcamphenilyl *p*-Nitrobenzoates in 80% Aqueous Acetone

Substituent	Isomer	Product distribution, %[a]			Crude product, mp, °C
		exo-OH (I)	*endo*-OH (II)	Apocyclene (III)	
p-CH_3O	*exo*[b,c]	≥99.5	≤0.5	0.0	79.0–80.0[k]
	endo[d]	≥99.5	≤0.5	0.0	76.0–77.0[k]
p-H	*exo*[e]	≥99.5	≤0.5	0.0	51–54[l]
	endo[f]	≥99.5	≤0.5	0.0	54–55[l]
p-CF_3	*exo*[g,i]	87	≤0.4	13	*m*
	endo[h,j]	41	≤1	58	*m*

[a] Analysis by pmr. [b] Benzoate. The *p*-nitrobenzoate was unstable and could not be isolated. [c] 220 min at 25°. [d] 540 min at 75°. [e] 200 min at 50°. [f] 720 min at 125°. [g] 1440 min at 75°. [h] 3000 min at 150°. [i] Glpc analysis showed 85% *exo*-OH and 13% apocyclene derivative, with 2% unidentified product (secondary OH?). [j] Glpc analysis indicated 45% *exo*-OH and 55% apocyclene derivative. [k] Authentic *exo*-OH mp 79.6–80.0°; *endo*-OH mp 113.5–114.0°. [l] Authentic *exo*-OH mp 56.5–57.5°; *endo*-OH liquid $n^{20}D$ 1.5509. [m] Authentic *exo*-OH mp 54.4–55.0°; *endo*-OH liquid $n^{20}D$ 1.5020.

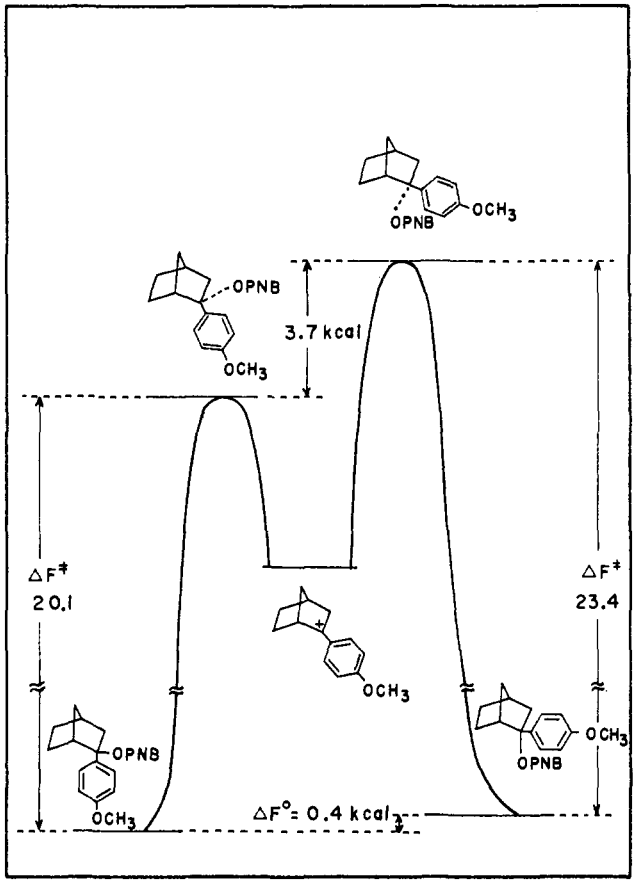


Figure 1. Free-energy diagram for the solvolysis of 2-*p*-anisyl-2-norbornyl *p*-nitrobenzoates in 80% aqueous acetone at 25°.

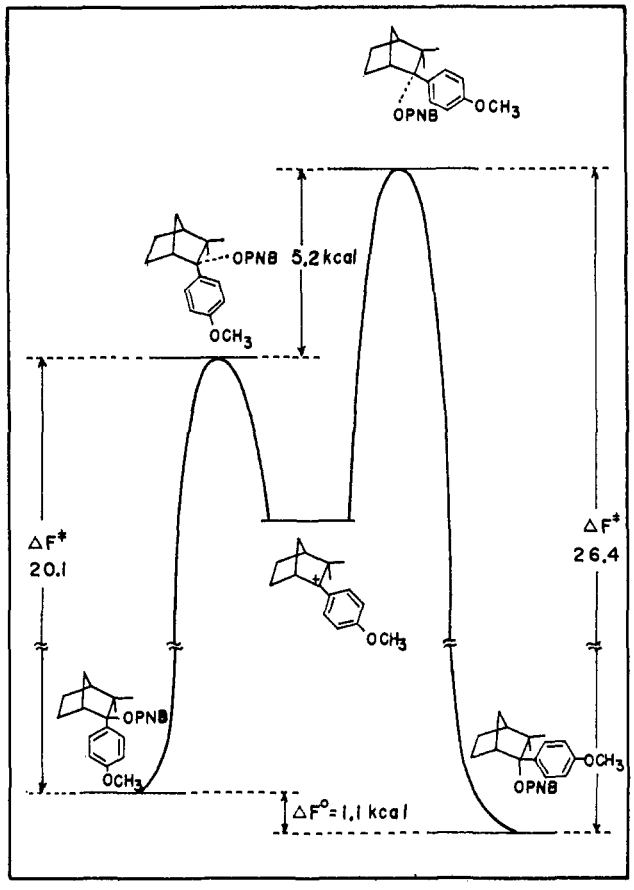


Figure 2. Free-energy diagram for the solvolysis of 2-*p*-anisyl-camphenilyl *p*-nitrobenzoates in 80% aqueous acetone at 25°.

It has been reported that 2-*p*-anisyl-*endo*-camphenilol is more stable than the *exo* isomer.[4] However, it appeared desirable to have quantitative data on the equilibrium between the two isomers. Solutions of each alcohol in chloroform were stirred with 4 *N* sulfuric acid and aliquots were removed and examined by pmr. The results indicated the presence of 13.6% *exo*-OH at equilibrium (25°), an *exo*:*endo* product ratio of 1:6.4. Thus the *endo* alcohol is more stable than the *exo* alcohol by 1.1 kcal/mol.

The available evidence indicates there is no significant difference in the steric requirements of the acyloxy and hydroxy groups in the norbornyl system.[5] Accordingly, we undertook to construct Goering–Schewene diagrams[6] for 2-*p*-anisylnorbornyl (Figure 1) and the 2-*p*-anisylcamphenilyl (Figure 2) systems.

The diagrams make it clear that the cation, once formed, will react preferentially with the anion or solvent (of essentially the same steric requirements) to give the *exo* product predominantly. Indeed, the difference in the free energies of formation of the two transition states, 3.7 kcal/mol for 2-*p*-anisylnorbornyl and 5.2 kcal/mol for 2-*p*-anisylcamphenilyl, are of the same order of magnitude as that estimated for the corresponding norbornyl system, 4.4 kcal/mol.

(4) P. D. Bartlett, E. R. Webster, C. E. Dills, and H. G. Richey, Jr., *Ann.*, **623**, 217 (1959).

(5) M.-H. Rei and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 5335 (1966).

(6) H. L. Goering and C. B. Schewene, *ibid.*, **87**, 3516 (1965). We utilized the free energies of activation at 25° and the difference in the free energies of formation of the ground states in these diagrams because it appeared to us that this would provide the difference in the free energies of the respective transition states that would define the relative rates at which the ion would be transformed into *exo* and *endo* products.

The Goering–Schewene diagram makes it clear that the factor or factors responsible for the difference in energy between the *exo* and *endo* transition states in norbornyl systems must likewise be responsible for the stereoselectivity leading to the almost exclusive formation of the *exo* products in these systems. It was pointed out that several possibilities exist:[7] (1) the *exo* transition state is stabilized by nonclassical resonance, with the *endo* transition state being normal; (2) the *endo* transition state is destabilized by steric effects, the *exo* transition state being normal; (3) a combination of 1 and 2; or (4) some new factor not now recognized by current theory.[8]

The available evidence indicates that σ participation cannot be a significant factor in the behavior of these stabilized tertiary derivatives. Consequently, we are left only with the possibilities that the *endo* transition state is destabilized by steric strain or that there is some factor not now recognized by current theory.

We wish to caution the reader again that this 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 *exo*:*endo* rate ratios and *exo*:*endo* product ratios observed in secondary norbornyl derivatives.[3b] 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 these steric effects will not also make a major contribution to these ratios in the secondary norbornyl derivatives.

(7) H. C. Brown, I. Rothberg, P. von R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Natl. Acad. Sci. U.S.*, **56**, 1653 (1966).

(8) Torsional effects might be such a factor, but it evidently can make only a minor contribution to the present reactions: P. von R. Schleyer, *J. Am. Chem. Soc.*, **89**, 699, 701 (1967).

(9) Research assistant on grants (G 19878 and GP 6492 X) from the National Science Foundation.

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A New Route to Cyclic Azomethine Imides[1]

Sir:

Azomethine imides were first prepared in 1960 through the reaction of diazoalkanes with aromatic azocyanides,[2] and later by utilization of azocarbonyl compounds.[3] More recently, the condensation of 3-pyrazolidones with ketones has been shown to lead to unusually stable azomethine imides.[4]

We report a simple new method for the preparation in good yield of stable cyclic azomethine imides possessing structure II. Thus, treatment of benzophenone chloroacetylhydrazone (Ia) with sodium hydride or potassium *t*-butoxide gave a colorless, crystalline solid, mp 199–200°. Microanalysis and mass spectroscopy (*m/e* 236) confirmed the molecular formula $C_{15}H_{12}N_2O$.

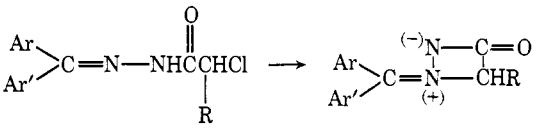
(1) This work was supported by a grant (CA-02551) to Princeton University from the National Cancer Institute, National Institutes of Health, Public Health Service.

(2) R. Huisgen, R. Fleischmann, and A. Eckell, *Tetrahedron Letters*, **No. 12**, 1 (1960).

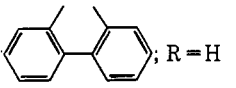
(3) G. F. Bettinetti and L. Capretti, *Gazz. Chim. Ital.*, **95**, 33 (1965).

(4) H. Dorn and A. Otto, *Angew. Chem. Intern. Ed. Engl.*, 7, 214 (1968).

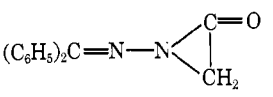
Its uv spectrum ($\lambda_{max}^{C_2H_5OH}$ 245 mμ (ε 17,000), 325 mμ (ε 26,200)) indicated the introduction of a new and potent



I II

a, Ar = Ar′ = C_6H_5; R = H
b, Ar = C_6H_5; Ar′ = C_6H_4Br-*p*; R = H
c, Ar = Ar′ = R = C_6H_5
d, Ar = C_6H_4Br-*p*; Ar′ = C_6H_5; R = H
e, Ar = Ar′ =  ; R = H

chromophore as compared with the starting hydrazone ($\lambda_{max}^{C_2H_5OH}$ 287 mμ (ε 19,850)). Its ir spectrum revealed the absence of an N–H proton and the presence of two strong bands in the carbonyl region at 1740 and 1775 cm^{-1} (*cf.* the starting hydrazone Ia: 3175 (N–H), 1700 cm^{-1} (C=O)). The high carbonyl absorption suggested the presence of a four-membered cyclic lactam. The nmr spectrum showed a singlet methylene group at δ 5.31, a complex eight-proton aromatic multiplet at 7.41, and a downfield two-proton aromatic multiplet at 7.92. These data are consistent only with formulation of the cyclization product as 1-(diphenylmethylene)-3-oxo-1,2-diazetidinium inner salt (IIa) and exclude other isomeric structures such as i, ii, and iii, all of which may formally be derived from Ia by reasonable



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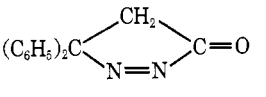
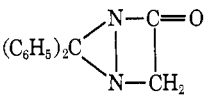


ii



iii

mechanistic pathways. Structure IIa has been confirmed by X-ray analysis[5] of the mono-*p*-bromophenyl derivative IId (*vide infra*) and by chemical transformations of IIa which are summarized in the accompanying communication.[6]

We suggest that azomethine imide IIa is formed by the route outlined in Scheme I; the following observations support this suggestion.

(1) The chloroacetylhydrazone Ia is completely stable in the absence of base. Nucleophilic bases such as pyridine bring about displacement of Cl^- to give quaternary salts. Azomethine imide formation therefore requires preliminary proton abstraction by a strong nonnucleophilic base.

(2) Treatment of the α-chloro-α-phenylacetylhydrazone Ic with sodium hydride gave azomethine imide IIc and diphenyldiazomethane. On the other hand, the α,α-diphenyl-α-chloroacetylhydrazone of benzophenone gave no azomethine imide; instead a viscous red gum was obtained whose ir spectrum indicated the presence of diphenyldiazomethane (2075 cm^{-1}). On standing

(5) C. J. Fritchie, Jr., and J. L. Wells, *Chem. Commun.*, 917 (1968).

(6) R. B. Greenwald and E. C. Taylor, *J. Am. Chem. Soc.*, **90**, 5273 (1968).