Table I. Thermal Decomposition of RCO_3-*t*-Bu

R	Temp, °C	$k \times 10^5$, sec^{-1} [a]	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Rel rate	Cor rel rate[b]
$(CH_3)_3C$	65	4.53	25.5	−2.9	1.0	1.0
	55	1.73				
	45	0.353				
$(CH_3CH_2)_3C$	65	14.6	24.7	−1.8	3.2	
	55	4.92				
	45	1.23				
$CH_3CH_2CH_2C(CH_3)_2$	65[c]	7.76[c]	25.2	−3.2	1.67	
	55	2.15				
	45	0.62				
1-Adamantyl	65	7.40	27.6	+3.7	1.63	0.36–0.47
	55	2.05				
	45	0.515				
1-Bicyclo[2.2.2]octyl	65	0.75	28.5	+2.2	0.16	~0.05
	75	2.82				
	85	8.47				
1-Bicyclo[2.2.1]heptyl	65[c]	0.00574	37.1	17.5	1.26×10^{-3}	$\sim 0.4 \times 10^{-3}$
	85	0.116				
	100	1.02				
	110	3.76				

[a] ±5%. [b] See text for explanation. [c] Extrapolated.

rather higher than the average for radical reactions[17] but is not out of line.[18,19] Thus, in the absence of destabilization from other sources, *all* of the bridged radicals should be more stable than *t*-butyl, by virtue of the inductive effect of their "extra" carbons. Since we are dealing with saturated carbocyclic systems, the destabilizing factor can be identified reasonably as geometry.[2]

A crude correction for induction in the bridged molecules may be attempted, utilizing the linear free-energy relationship developed above. It is possible to sort out the skeleton of each bridged molecule (in several ways) into simple alkyl groups, and then use the linear free-energy plot to predict roughly the rate expected for a given compound were it not constrained geometrically. In this way, for example, we find that on an inductive basis adamantyl should be faster than *t*-butyl by a factor of the order of 3.5–4.6. Division of the observed relative rate by this quantity gives the corrected relative rate shown in the last column of Table I. The stability order obtained by similar treatment of the other bridged systems parallels the order for the corresponding carbonium ions.

A reasonable tentative conclusion at this point would be that carbon free radicals prefer a planar geometry, as do carbonium ions, but that the force constants for distortion of the radicals are, as expected,[2] much smaller than those for distortion of the cations. However, there is evidence that the transition state for the decomposition of some *t*-butyl peresters[18–20] (and for other radical reactions[17]) may have some polar character, at least when a stable carbonium ion (benzyl, tropylium) can be formed. In this event, of course, the corrected rate data would parallel carbonium ion data because some measure of positive charge is developing at the bridgehead in the transition state. Studies are under way to clarify this point.

The stability obtained in this study for the 1-bicyclo[2.2.2]octyl radical is about a power of ten less than that found by Applequist and Kaplan[4] and is more in line with the suggestion of Stock[21] based on the Hunsdiecker reaction of the acid. Pyrolytic generation of the radical[22] from bicyclooctylmethyl nitrite leads to ring-opened species, likewise indicating a surprising instability. (Recall that *no* ring-opened products were found in this work.) Further studies are being carried out on this system.

Finally, it would seem evident that there is nothing unusual about the 1-adamantyl radical; it is an ordinary tertiary radical with slight geometrical destabilization.

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[17] W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966.

[18] P. D. Bartlett and C. Ruchardt, *J. Am. Chem. Soc.*, **82**, 1756 (1960).

[19] R. E. Pearson and J. C. Martin, *ibid.*, **85**, 3142 (1963).

[20] C. Rüchardt and H. Schwartzer, *Ber.*, **99**, 1861, 1878 (1966).

[21] F. W. Baker, H. D. Holtz, and L. M. Stock, *J. Org. Chem.*, **28**, 514 (1963).

[22] T. McAllister, Z. Dolesek, F. P. Lossing, R. Gleiter, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **89**, 5982 (1967).

[23] Support of this work through a Kent State University faculty research fellowship is gratefully acknowledged.

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Unusually High *exo*:*endo* Rate Ratios in the Solvolysis of 2-*p*-Anisylcamphenilyl and Related Compounds. Further Evidence for Steric Effects as a Major Factor in the *exo*:*endo* Rate Ratios of Tertiary Norbornyl Derivatives

Sir:

The *exo*:*endo* rate ratio in the solvolysis of 2-*p*-anisylcamphenilyl *p*-nitrobenzoates is 44,000, as compared to a value of 284 observed in the parent system, 2-*p*-anisylnorbornyl.[1] Moreover, it remains sensibly constant as the 2-aryl substituent is made less and less electron supplying:[2] 2-phenyl, 49,000; 2-*p*-trifluoromethylphenyl, 24,000. A comparison of the rate data

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[1] H. C. Brown and K. Takeuchi, *J. Am. Chem. Soc.*, **90**, 2691 (1968).

[2] K. Takeuchi and H. C. Brown, *ibid.*, **90**, 2693 (1968).

Table I. Rates of Solvolysis of 2-Arylnorbornyl and 2-Arylcamphenilyl *p*-Nitrobenzoates

Substituent[a]	System[b]	Isomer	First-order rate constant (80% acetone), $k_1 \times 10^6$ sec^{-1} 150.0°	125.0°	100.0°	75.0°	50.0°	25.0°	*exo*:*endo* rate ratio 25°	Rel rate C:N 25°
p-CH_3O	C	*exo*[e]						12,100[m]	44,000	1.06
	C	*endo*[f]				171	8.77	0.273[l]		1:147
	N[c]	*exo*						11,400		
	N[c]	*endo*						40.2	284	
p-H	C	*exo*[g,h]					595	22.9	49,000	3.03
	C	*endo*[i]		162	12.7			0.00047[l]		1:113
	N[d]	*exo*						7.56	143	
	N[d]	*endo*						0.0530		
p-CF_3	C	*exo*[j]				81.5	3.67	0.0982[l]	24,000	2.30
	C	*endo*[k]	46.2	4.07				4.17×10^{-6}[l]		1:55
	N[d]	*exo*						0.0427	188	
	N[d]	*endo*						0.000227		

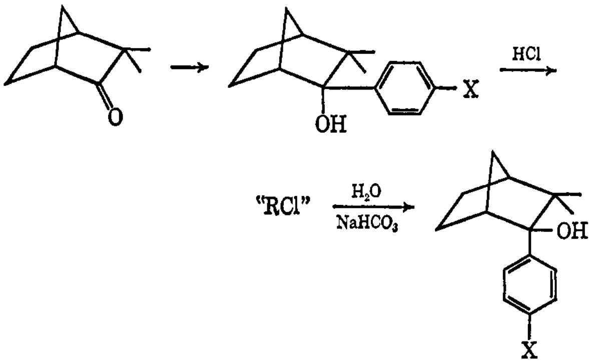
[a] All new compounds gave spectral and microanalytical data consistent with the proposed structure. [b] C: 2-arylcamphenilyl; N: 2-arylnorbornyl. [c] Reference 1. [d] Reference 2. [e] *exo-p*-Nitrobenzoate was unstable. Benzoate mp 127.5–128.5°, 10^6k_1 = 514 (25°), 15.7 (0°). [f] Mp 128–130° dec, lit.[4] mp 129.5–135°. [g] Mp 132° dec. [h] Benzoate, oil, 10^6k_1 = 547 (75°), 29.5 (50°), 0.975 (25°, extrapolated). [i] Mp 144.8–145.3°. [j] Mp 156.5–157.0°. [k] Mp 137.8–138.5°. [l] Calculated from data at other temperatures. [m] Calculated from the benzoate by using k_{OPNB}/k_{OBz} = 23.5 from the 2-phenyl derivatives.

for the two systems indicates that the unusually high *exo*:*endo* rate ratio in the camphenilyl system arises from greatly reduced rates in the *endo* derivatives. It is suggested that both the presence of the methyl groups in the 3 position and the twisting of the aryl group in the 2 position provide a greater steric barrier to the ionization of the *endo-p*-nitrobenzoate group than is present in the parent norbornyl system.

In our earlier study of 2-*p*-anisylnorbornyl derivatives[1,2] the great instability of the parent alcohols made it impossible to obtain accurate determinations of the solvolysis products. Consequently, we relied on the trapping of the cations with sodium borohydride[3] and analyzed the resulting 2-arylnorbornanes by pmr.

However, it still appeared desirable to establish the nature of the products realized in the reaction of stabilized norbornyl cations with solvent. For this purpose the corresponding camphenilyl derivatives offered promise. For example, the synthesis and reactions of the 2-*p*-anisylcamphenilols have been described,[4] and they exhibit markedly greater stability than the parent compounds. Presumably the absence of hydrogen in the 3 position makes impossible the fast dehydration to olefin which is characteristic of the norbornyl derivatives. Accordingly, we undertook the synthesis and study of the solvolysis of the appropriate camphenilyl derivatives.

The *endo* alcohols were prepared by treating camphenilone with the appropriate Grignard reagent. These were converted by hydrogen chloride to a mixture (tertiary and secondary) of chlorides which solvolyzed under neutral or alkaline conditions to the corresponding *exo* alcohol (1).



(1)

p-Nitrobenzoates were prepared in the usual manner and the rates of solvolysis in 80% aqueous acetone were determined. The results are summarized in Table I, together with earlier results for the corresponding norbornyl derivatives.

The data give excellent correlations with the σ^+ constants (Figure 1) with the following values of ρ^+: *exo*-norbornyl, −3.96; *exo*-camphenilyl, −3.66; *endo*-norbornyl, −3.77; *endo*-camphenilyl, −3.48.

The most surprising development is the enormous value observed for the *exo*:*endo* rate ratio in 2-*p*-anisylcamphenilyl, 44,000. This compares with the much smaller value of 284 observed in the corresponding norbornyl derivatives.[1]

A *p*-anisyl group has a major stabilizing effect on a cationic center, as illustrated by the fact that the rate of ethanolysis of 2-*p*-anisyl-*exo*-norbornyl chloride is greater than that of *exo*-norbornyl chloride by the enormous factor of 500,000,000,000.[5] Such a highly stabilized center should make little demand upon neighboring groups for further stabilization.[6] Indeed, it has recently been reported that the 10^{11} acceleration arising from participation of the double bond in the solvolysis of *anti*-7-dehydronorbornyl derivatives virtually vanishes in the corresponding 7-*p*-anisyl derivatives.[7] Consequently, it does not appear possible to account for this unusually high *exo*:*endo* rate ratio in terms of the usually postulated σ participation.[8] Moreover, the failure to observe a sharp rise in the *exo*:*endo* rate ratio as the aryl group is made less electron supplying by the introduction of appropriate substituents is likewise contrary to expectations for σ participation as a contributor to the *exo*:*endo* rate ratio.[9]

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(3) H. M. Bell and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 1473 (1966).

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

(5) H. C. Brown and K. Takeuchi, *J. Am. Chem. Soc.*, **88**, 5336 (1966).

(6) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, **74**, 1113 (1952).

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

(8) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1147, 1154 (1952).

(9) We again wish to emphasize that the conclusion that σ participation does not contribute significantly to the observed *exo*:*endo* rate ratios in these tertiary derivatives should not be extrapolated to the conclusion that σ participation also does not contribute to the observed *exo*:*endo* rate ratios in the parent secondary systems. See the discussion in ref 1 and 2.

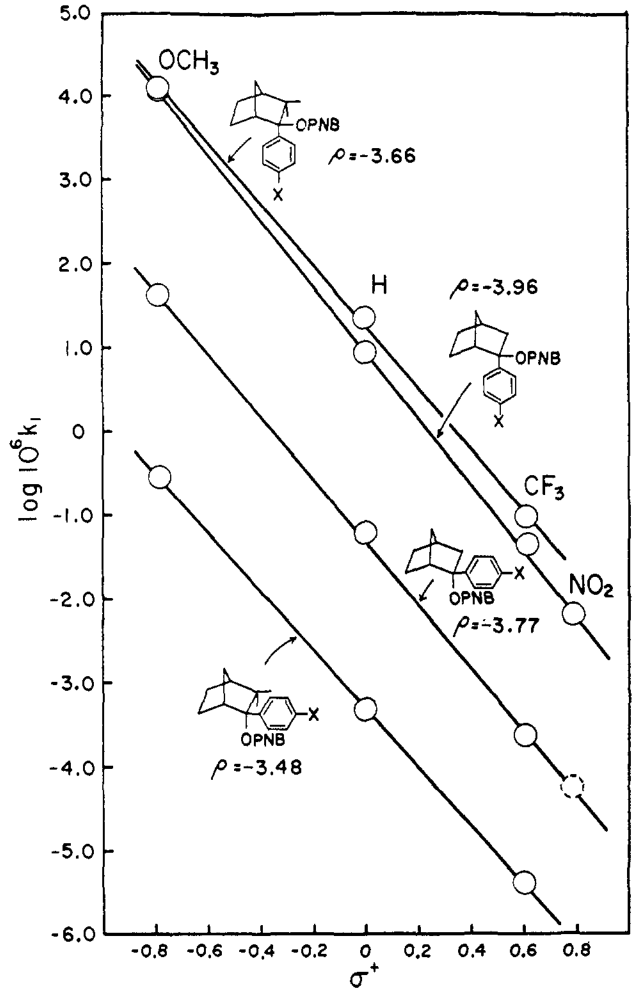

Figure 1. Correlations of the rate constants for the solvolysis of the *p*-nitrobenzoates at 25° in 80% acetone with σ^+.

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."

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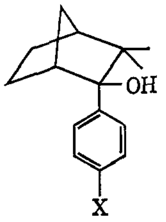
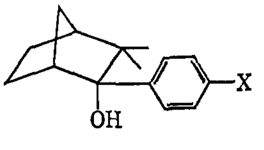
Predominant *exo* Substitution in the Products from the Solvolysis of 2-*p*-Anisylcamphenilyl and Related Compounds. Further Evidence for Steric Effects as a Major Factor in the *exo*:*endo* Product Ratios from Tertiary Norbornyl Derivatives

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



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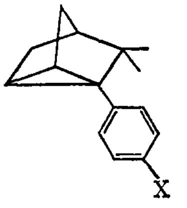

III

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.

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[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).