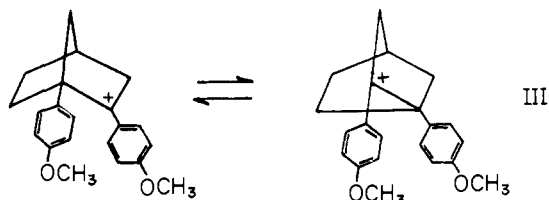
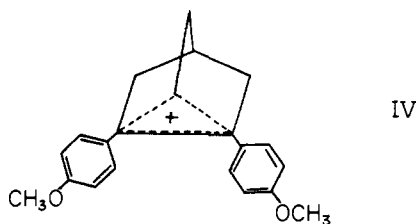


of equilibrating ions with essentially classical structures (III).



This interesting conclusion cannot be generalized to other norbornyl derivatives because of two possible difficulties. First, it has been argued that the classical structure of the 1,2-dianisylbornyl cation is the result of the great stabilization of the electron-deficient center by the anisyl group, thereby making unnecessary participation of the 1,6-bonding pair to stabilize the structure.⁴ Second, it is possible that the failure of the second anisyl group to contribute to the stabilization of the cation may be due to steric difficulties in achieving ideal orientations for both anisyl groups (IV).



It appeared that the 1-anisyl-2-methylnorbornyl system would provide a more energetic carbonium ion with much smaller steric difficulties.⁵ Accordingly, we undertook to synthesize such a derivative and to determine its rate of solvolysis in order to establish whether carbon participation would be a factor in the rate. Fortunately, the synthesis of 2-(*p*-anisyl)borneol, 2-(*p*-anisyl)bornylene, and 1-(*p*-anisyl)camphene have recently been described and the structures of the products established both by independent unambiguous syntheses and critical n.m.r. examination.⁶ Consequently, we decided to work in this series.

Hydrogen chloride was added at -5 to -10° to 10 g. of 2-(*p*-anisyl)bornylene in 50 ml. of methylene chloride until absorption was complete. The solution was concentrated by rotary evaporation and the white solid was recrystallized from dichloromethane. There was obtained 10.0 g. (87% yield) of a white solid, m.p. 113.5 – 114.5° . *Anal.* Calcd. for $C_{17}H_{23}ClO$: C, 73.21; H, 8.31; Cl, 12.72. Found: C, 72.95; H, 8.50; Cl, 12.98.

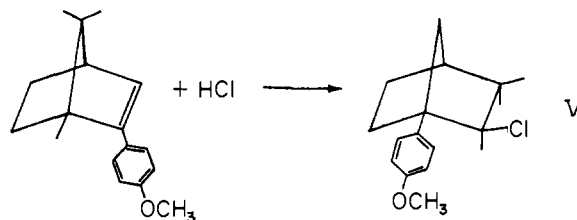
The n.m.r. spectrum exhibited methyl proton absorption at 1.05, 1.25, and 1.50 p.p.m., and a doublet at 2.73 p.p.m. ($J = 9$ c.p.s.) amounting to one proton. The three methyl groups of bornyl or isobornyl derivatives exhibit absorptions below 1.0 p.p.m., closely bunched,⁶ whereas the observed shifts are consistent

(4) S. Winstein, Reaction Mechanisms Conference at Brookhaven National Laboratory, Upton, N. Y., Sept. 5, 1962.

(5) The remarkable stability of the 2-(*p*-anisyl)camphenyl cation suggests that the ability of the *p*-anisyl group to conjugate with the carbonium center is not significantly affected by the presence of the two methyl substituents in the adjacent 3-position: P. D. Bartlett, E. R. Webster, C. E. Dills, and H. G. Richey, Jr., *Ann.*, **623**, 217 (1959). Consequently, significant steric difficulties in a 1-anisyl-2-methylnorbornyl cation would not be anticipated.

(6) W. F. Erman and T. J. Flautt, *J. Org. Chem.*, **27**, 1526 (1962).

with those anticipated for the methyl groups in a camphene hydrochloride structure. The doublet at 2.73 p.p.m. is assigned to the hydrogen of the 7-methylene group *syn* to the chlorine substituent. Both its position and the magnitude of the splitting are consistent with the assigned structure.⁷ Therefore, addition of hydrogen chloride to 2-(*p*-anisyl)bornylene proceeds with Wagner–Meerwein rearrangement to yield 1-(*p*-anisyl)camphene hydrochloride⁸ (V).



Solvolysis of 1-(*p*-anisyl)camphene hydrochloride in ethanol exhibits simple first-order kinetics for over 90% of the reaction. The observed rate constant at 25.0° , $686 \times 10^{-6} \text{ sec.}^{-1}$, compares with the value $1160 \times 10^{-6} \text{ sec.}^{-1}$ observed for camphene hydrochloride itself. Thus the 1-*p*-anisyl substituent results, not in an increase, but in an actual decrease in the rate constant. It follows that participation by the 6-carbon atom cannot be a significant factor in the transition state for the solvolysis.

The failure of the 1-anisyl substituent to facilitate the rate of solvolysis of camphene hydrochloride would appear to support the conclusion that such tertiary norbornyl derivatives undergo solvolysis *via* cations that are essentially classical in nature.⁹

(7) Private communications from Dr. T. J. Flautt and Professor P. von R. Schleyer.

(8) Treatment of 2-(*p*-anisyl)camphenilol with hydrogen chloride in ether likewise yields the Wagner–Meerwein rearranged product, 1-(*p*-anisyl)-apoisobornyl chloride (P. D. Bartlett, *et al.*, ref. 5).

(9) C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier Publishing Co., New York, N. Y., 1963, p. 62.

(10) Ethyl Corporation Fellow, 1963–1964.

R. B. WETHERILL LABORATORY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

HERBERT C. BROWN
HAROLD M. BELL¹⁰

RECEIVED JULY 24, 1964

Rates of Solvolysis of the *p*-Nitrobenzoates of 1,2-Dimethyl-*exo*- and 1,2-Dimethyl-*endo*-norborneols. Further Evidence for the Absence of Significant Carbon Participation in the Solvolysis of a Tertiary Norbornyl Derivative

Sir:

The 1-*p*-anisyl substituent fails to stabilize the 1,2-di-*p*-anisylnorbornyl cation.¹ Similarly, the 1-*p*-anisyl substituent fails to enhance the rate of solvolysis of 1-*p*-anisylcamphene hydrochloride over camphene hydrochloride itself.² These results strongly support the conclusion that tertiary norbornyl cations are essentially classical in nature.³

However, there is a possible ambiguity in the interpretation of the results. It can be argued that steric difficulties and not lack of participation are responsible

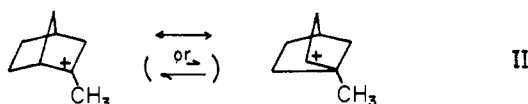
(1) P. von R. Schleyer, D. C. Kleinfelter, and H. C. Richey, Jr., *J. Am. Chem. Soc.*, **85**, 479 (1963).

(2) H. C. Brown and H. M. Bell, *ibid.*, **86**, 5003 (1964).

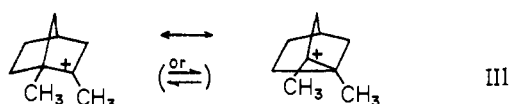
(3) C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier Publishing Co., New York, N. Y., 1963, p. 62.

for the evident failure of the anisyl substituent to provide stabilization. It appeared that the 1,2-dimethylnorbornyl system would avoid this possible ambiguity in the results. Accordingly, we undertook to study the rates of solvolysis of the *p*-nitrobenzoates of 1,2-dimethyl-*exo*-⁴ and 1,2-dimethyl-*endo*-norborneol⁴ and certain related cyclopentyl derivatives.

It has been suggested that tertiary norbornyl cations, such as 2-methylnorbornyl, should be essentially classical in structure,³ in contrast to the proposed nonclassical structure for the norbornyl cation.⁵ The latter involves the favorable requirement of resonance between two structures of identical energies (I), whereas the 2-methylnorbornyl cation involves the less favorable requirement of resonance between structures of greatly different energies (II).



The additional methyl group in the 1-position converts the cation into a symmetrical system (III).



Consequently, the 1-methyl substituent would be expected to stabilize greatly the 1,2-dimethylnorbornyl cation, and this stabilization would be expected to result in a major enhancement in the rates of solvolysis of 1,2-dimethyl-*exo*-norbornyl derivatives as compared to the corresponding 2-methyl-*exo*-norbornyl compounds.⁶ On the other hand, the effect of the 1-methyl substituent should be much smaller in the *endo* series—not appreciably different than the effect of methyl in the related cyclopentyl derivatives.

These predictions are not supported by the experimental data (Table I). A minor increase of 4.3 is observed in the case of 1,2-dimethyl-*exo*-norbornyl *p*-nitrobenzoate, with a very similar increase of 4.8 observed in the *endo* derivative. Rate enhancements of very similar order of magnitude (3.4 for *trans*, 2.3 for *cis*) are observed to accompany the introduction of a methyl group into the 2-position of 1-methylcyclopentyl *p*-nitrobenzoate.⁷

These results clearly establish that there is no significant carbon participation in the transition state for the solvolysis of 1,2-dimethyl-*exo*-norbornyl *p*-nitrobenzoate. There does not appear to be any possible manner in which this result can be ascribed to any special steric requirement of the 1-methyl substituent.

(4) H. Toivonen, *Suomen Kemistilehti*, **33B**, 66, (1960).

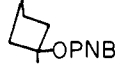

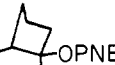




(5) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1147, 1154 (1952).

(6) The 2-methyl substituent increases the rate of solvolysis of 2-methyl-*exo*-norbornyl chloride over *exo*-norbornyl chloride by a factor of 55,000; H. C. Brown and M.-H. Rei, *ibid.*, **86**, 5008 (1964). A somewhat smaller, but still major factor would be anticipated for the second methyl group which permits the positive charge to be delocalized over two tertiary centers.

(7) These small increases are presumably the result of the combined steric and inductive influence of the methyl substituent. The slightly greater effect observed in the norbornyl derivatives may be a result of the more rigid structure which should enhance steric interactions.

TABLE I

RATES OF SOLVOLYSIS OF THE *p*-NITROBENZOATES IN 60% AQUEOUS DIOXANE

Compound	M.p., °C.	Rate constant, $k_1 \times 10^6 \text{ sec.}^{-1}$		Rel. rates, 50°	
		50°	75°	Me/H	<i>exo/endo</i>
 OPNB	82-83	0.50 ^a	9.94 ^a	1.00	
 OPNB ^b	116-117	1.16	21.3	2.3	
 OPNB ^b	99.5-100.5	1.67	25.0	3.4	
 OPNB	114-115	2.2 ^c	41.2 ^c	1.00	183
 OPNB	131-132	9.4	121	4.3	165
 OPNB	100.5-102	0.012 ^{d,e}	0.20 ^{d,e}	1.00	
 OPNB	144-145	0.057 ^d	1.1 ^d	4.8	

^a H. C. Brown, F. J. Chloupek, and M.-H. Rei, *J. Am. Chem. Soc.*, **86**, 1247 (1964). ^b Unpublished data of F. J. Chloupek. ^c Ref. 8. ^d Rate determinations were carried out under nitrogen. ^e Previous values were high because of concurrent oxidation of solvent in these slow reactions.

Consequently, it appears reasonable to conclude that the similar results previously noted for the 1,2-di-*p*-anisylnorbornyl cation¹ and for 1-*p*-anisylcamphene hydrochloride² are manifestations of the same general phenomenon and are not the result of some special steric requirement of the 1-anisyl substituent.

In spite of the fact that the results require that there be no significant carbon participation in the transition state for these tertiary norbornyl derivatives, there is observed an *exo/endo* rate ratio of 183 for the 2-methylnorbornyl, and one of 165 for the 1,2-dimethyl-norbornyl derivative. Clearly, 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.⁸

The experimental results realized with the 1,2-di-*p*-anisylnorbornyl cation,¹ the solvolysis of 1-*p*-anisylcamphene hydrochloride,² and the solvolysis of 1,2-dimethyl-*exo*-norbornyl *p*-nitrobenzoate are all consistent with the proposal that tertiary norbornyl cations are essentially classical in structure,³ with no significant delocalization of positive charge from the 2- to the 1-position.

(8) H. C. Brown, F. J. Chloupek, and M.-H. Rei, *J. Am. Chem. Soc.*, **86**, 1248 (1964).

(9) Research assistant on Grant 19878 provided by the National Science Foundation.

R. B. WETHERILL LABORATORY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

HERBERT C. BROWN
MIN-HON REI⁹

RECEIVED OCTOBER 1, 1964