

TABLE I

Products	Reaction 1	Reaction 2
<i>p</i> -Anisyltricyclene	0.3%	0.5%
2-(<i>p</i> -Anisyl)bornylene	1	1
1-(<i>p</i> -Anisyl)camphene	24	22
1-(<i>p</i> -Anisyl)isocamphene	0	0
<i>p</i> -Bornylanisole	66	64
<i>p</i> -Isobornylanisole	10	10

product with diborane to remove unsaturated materials, and isolating the saturated products by distillation. N.m.r. examination confirmed the presence of a mixture of *p*-bornyl- and *p*-isobornylanisole, with the former in large excess.

Consequently, the solvolysis of 1-(*p*-anisyl)camphene hydrochloride in the presence of borohydride produces 23% 1-(*p*-anisyl)camphene, presumably the result of the elimination of a proton from the highly hindered 1-(*p*-anisyl)hydrocamphenyl cation, 65% *p*-bornylanisole, arising from *exo* substitution of borohydride on the 2-(*p*-anisyl)bornyl cation, and 10% isobornylanisole, arising from *endo* substitution.

It follows that even this highly stabilized, presumably classical, norbornyl cation reacts to give predominantly *exo* substitution (*exo/endo* = 87:13), in spite of the steric influence of the *gem*-dimethyl substituents in the 7-position.

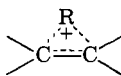
As was pointed out earlier⁷ the proposed nonclassical structure for the norbornyl cation has been justified on the basis of unusually high rates, high *exo/endo* rate ratios, and *exo* stereochemistry of substitution. On this basis a change in these characteristics would have been anticipated for tertiary norbornyl derivatives, containing substituents such as methyl, phenyl, and anisyl at the carbonium center which should form cations of increasing stability. However, no major changes in the relative rates,⁹ the *exo/endo* rate ratios,¹⁰ or the stereochemistry of substitution⁴ have been observed. It must be concluded either that these characteristics are not uniquely associated with the proposed nonclassical structure for the norbornyl cation and are characteristic of classical bicyclic cations, or that all norbornyl cations, highly stabilized or not, are nonclassical in spite of the evidence to the contrary.^{5,6}

If bicyclic cations are not resonance-stabilized species, how can we account for the marked preference for *exo* substitution? One possibility which should receive careful consideration is the proposal by Professor S. Winstein that the stereochemical behavior of a bridged ion may be simulated by an equilibrating pair of isomeric cations.¹¹ It is evident that this proposal

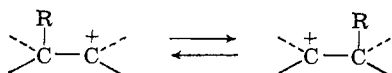
(9) H. C. Brown, F. J. Chloupek, and M.-H. Rei, *J. Am. Chem. Soc.*, **86**, 1247 (1964).

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

(11) S. Winstein and B. K. Morse, *ibid.*, **74**, 1133 (1952), footnote 13: "Just as in the case of functional neighboring groups [S. Winstein, *Bull. soc. chim. France*, **18**, 55 (1951), and S. Winstein and E. Grunwald, *J. Am. Chem. Soc.*, **70**, 828 (1948)], it must be kept in mind that the stereochemical results corresponding to formation and opening of



may, in some cases, be simulated by a dynamic pair of isomeric cations



would resolve the evident difficulty in reconciling the marked preference for *exo* substitution with the absence of any data supporting any unusual stability for norbornyl cations and the absence of any data (such as the effect of substituents) supporting the presence of electron deficiencies in the 1- and 6-positions, as required by the proposed nonclassical structure.

(12) Ethyl Corporation Fellow, 1963-1964.

RICHARD B. WETHERILL LABORATORY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

HAROLD M. BELL¹²
HERBERT C. BROWN

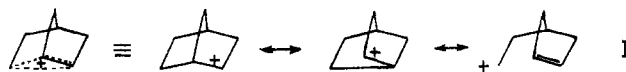
RECEIVED JULY 24, 1964

Comparison of the Effect of Substituents at the 2-Position of the Norbornyl System with Their Effect in Representative Secondary Aliphatic and Alicyclic Derivatives. Evidence for the Absence of Nonclassical Stabilization of the Norbornyl Cation

Sir:

Previous studies now appear to establish that tertiary norbornyl cations are essentially classical in nature.¹ We are left with the problem of the structure of secondary cations of the norbornyl type.²

The nonclassical formulation of the norbornyl cation requires that positive charge be delocalized to the 1- and 6-positions (I).



It has been previously demonstrated that methyl substituents in the 6-position fail to stabilize the electron-deficient transition state or intermediate.^{3,4} Similarly, in the symmetrical systems 1,2-di-*p*-anisyl-norbornyl cation and 1,2-dimethyl-*exo*-norbornyl *p*-nitrobenzoate, the substituent in the 1-position fails to stabilize the electron-deficient intermediate or transition state.^{1a,i,5} In the present study we turn our attention to an experimental test of a major consequence of the nonclassical formulation—decreased electron deficiency at the 2-position of the norbornyl cation or transition state resulting from the proposed delocalization of the charge to the 1- and 6-positions.

Methyl and phenyl groups at a carbonium center stabilize the electron-deficient species because of their ability to supply electrons to the electron-deficient center. The greater the electron deficiency, the greater

(1) (a) P. von R. Schleyer, D. C. Kleinfelter, and H. G. Richey, Jr., *J. Am. Chem. Soc.*, **85**, 479 (1963); (b) P. Beltramé, C. A. Bunton, A. Dunlop, and D. Whittaker, *J. Chem. Soc.*, 658 (1964); (c) C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier Publishing Co., New York, N. Y., 1963, p. 62; (d) H. C. Brown and F. J. Chloupek, *J. Am. Chem. Soc.*, **85**, 2322 (1963); (e) H. C. Brown, F. J. Chloupek, and M.-H. Rei, *ibid.*, **86**, 1246 (1964); (f) *ibid.*, **86**, 1247 (1964); (g) *ibid.*, **86**, 1248 (1964); (h) H. C. Brown and H. M. Bell, *ibid.*, **86**, 5003 (1964); (i) H. C. Brown and M.-H. Rei, *ibid.*, **86**, 5004 (1964); (j) H. C. Brown and H. M. Bell, *ibid.*, **86**, 5006 (1964); (k) H. M. Bell and H. C. Brown, *ibid.*, **86**, 5007 (1964).

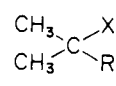
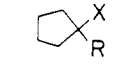
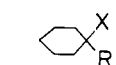
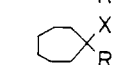
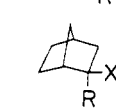
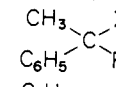
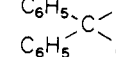
(2) S. Winstein and D. Trifan, *ibid.*, **74**, 1147, 1154 (1952).

(3) D. E. McGreer, *Can. J. Chem.*, **40**, 1554 (1962).

(4) P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Am. Chem. Soc.*, in press.

(5) Modest rate enhancements, involving factors of 3.9 and 42, respectively, are observed in the ethanolysis at 25° of 1-phenyl- and 1-methyl-*exo*-norbornyl tosylate (research in progress with M.-H. Rei). However, in these cases the solvolyses proceed with rearrangement to the more stable tertiary cations, so that the results are not applicable to the question of whether carbon participation is significant in symmetrical norbornyl systems not involving rearrangement to more stable structures.

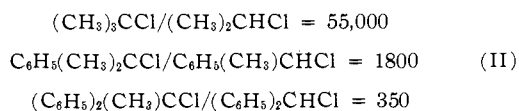
TABLE I
LIMITING SOLVOLYSIS RATES FOR REPRESENTATIVE SECONDARY AND TERTIARY DERIVATIVES

R X Solvent	First-order rate constants for solvolysis at 25°, sec. ⁻¹ × 10 ⁶					Relative rates	
	H OTs HOAc	H OTs EtOH ^a	H Cl EtOH ^b	Me Cl EtOH	Ph Cl EtOH	k ^{Me} /k ^H	k ^{Ph} /k ^{Me}
	0.081 ^c	0.0184	1.57 × 10 ⁻⁶	0.086 ⁱ	394 ^l	55,000	4580
	1.66 ^d	0.377	3.21 × 10 ⁻⁵	5.62 ^j	21,100 ⁿ	175,000	3760
	0.484 ^d	0.011	9.35 × 10 ⁻⁷	0.031 ^k	59 ^o	33,000	1900
	2.82 ^d	0.64	5.44 × 10 ⁻⁵	4.90 ^k	7,240 ^o	90,000	1480
	24.4 ^e	5.55	5.42 × 10 ⁻⁴ ^f 4.72 × 10 ⁻⁴	30.0 ^j	158,000 ⁿ	55,000 63,000	5260
			0.216 ^g	394 ^l	19,900 ^m	1,800	50
			575 ^h	19,900 ^m	578,000 ^p	346	29

^a Limiting rate of ethanolysis of the tosylate calculated by dividing the rate of acetolysis by a factor of 4.4. ^b Limiting rate of ethanolysis of the chloride by use of the factor $k_{\text{RCl}}/k_{\text{ROTs}} = 8.5 \times 10^{-5}$. ^c Calculated from the rate of acetolysis of the brosylate: S. Winstein and H. Marshall, *J. Am. Chem. Soc.*, **74**, 120 (1952). ^d Calculated from rate data at higher temperatures: H. C. Brown and G. Ham, *ibid.*, **78**, 2735 (1956). ^e D. C. Kleinfelter, Ph.D. Thesis, Princeton University. ^f Estimated from the rate constant at 25° in 80% ethanol, calculated from data at higher temperatures: J. D. Roberts and W. Bennett, *J. Am. Chem. Soc.*, **76**, 4623 (1954); W. G. Woods, R. A. Carboni, and J. D. Roberts, *ibid.*, **78**, 5653 (1956). ^g A. M. Fainberg and S. Winstein, *ibid.*, **79**, 1602 (1957). ^h A. M. Ward, *J. Chem. Soc.*, 2282 (1927). ⁱ A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2770 (1956). ^j Ref. 1d. ^k Calculated from the rate of solvolysis in 80% ethanol: H. C. Brown and M. Borkowski, *J. Am. Chem. Soc.*, **74**, 1894 (1952). ^l Y. Okamoto, T. Inukai, and H. C. Brown, *ibid.*, **80**, 4972 (1958). ^m This study: $k_1(0^\circ) 1.380 \times 10^{-6}$ sec.⁻¹, $\Delta H^\ddagger 16.9$ kcal. mole⁻¹, $\Delta S^\ddagger -9.8$ e.u. ⁿ Ref. 1e. ^o G. Baddeley, J. Chadwick, and H. T. Taylor, *J. Chem. Soc.*, 451 (1956). ^p Calculated from the rate of ethanolysis of diphenylmethylcarbinyl chloride at 25° and the relative rates of solvolysis of trityl and diphenylmethylcarbinyl chloride in aqueous acetone at 0° (corrected to 25°): H. C. Brown, Y. Okamoto, and T. Inukai, *J. Am. Chem. Soc.*, **80**, 4964 (1958).

is the contribution of the substituent. For example, *t*-butyl chloride undergoes ethanolysis at 25° at a rate that is 55,000 times greater than the limiting⁶ rate of ethanolysis of isopropyl chloride.

On the other hand, *t*-cumyl chloride undergoes ethanolysis at a rate that is only 1800 times that of α -phenylethyl chloride, whereas diphenylmethylcarbinyl chloride undergoes ethanolysis at a rate that is only 350 times that of benzhydryl chloride (II).

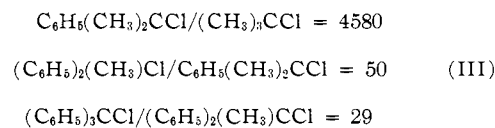


It is evident that the methyl substituent is making a much smaller contribution to the resonance-stabilized α -phenylethyl and benzhydryl transition states than to the less stable isopropyl transition state.

The same effects are evident in comparing the relative contributions of phenyl *vs.* methyl groups in stabilizing the related transition states (III). Since

(6) We utilized the rates of acetolysis of isopropyl and cycloalkyl tosylates to obtain estimates of the limiting rates of ethanolysis of the secondary derivatives, as recommended by E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948). The rates of acetolysis at 25° were divided by the average factor, 4.4, to obtain the limiting rates of ethanolysis of the tosylates at 25°. We then utilized the factor $k_{\text{RCl}}/k_{\text{ROTs}} = 8.5 \times 10^{-5}$ to obtain the rate constant for the limiting rate of ethanolysis of the secondary chloride.

these derivatives involve only tertiary derivatives, essentially limiting in character, it is possible to compare the rate constants directly.



Data for the isopropyl, cyclopentyl, cyclohexyl, and cycloheptyl derivatives are summarized in Table I. It is evident that the effect of the methyl and the phenyl substituent exhibits a remarkable constancy, approximately the same as that in the isopropyl derivative within a factor of roughly three—in all cases very much larger than the effects of these substituents in the resonance-stabilized α -phenylethyl and benzhydryl systems.

If the norbornyl cation were a resonance-stabilized species, we should anticipate that the effects of the methyl and phenyl substituents would be very similar to their effects in the α -phenylethyl and benzhydryl systems, and very much smaller than their effects in the other secondary systems. However, the effect of methyl is to produce a rate enhancement of 55,000, with phenyl bringing about a further increase of 5260. Clearly, these results do not accord with the postu-

lated presence of nonclassical resonance in the norbornyl cation or transition state.⁷

It has been suggested that the failure to observe any decreased contribution of the 2-methyl and 2-phenyl substituents in the norbornyl derivatives may be due to the fortuitous cancellation of opposing factors. On the one hand, carbon participation might decrease from norbornyl to 2-methylnorbornyl to 2-phenylnorbornyl, with steric acceleration of the solvolysis providing a compensating rate-enhancing factor.⁸ However, this possible interpretation is rendered untenable by the observation that carbon participation is not a significant factor in the solvolysis of 1,2-dimethylnorbornyl derivatives.¹¹

Another possible interpretation would postulate that the relief of steric strain in the essentially classical tertiary norbornyl derivatives counterbalances precisely the nonclassical resonance energy in the *exo*-norbornyl transition state. However, this requires the highly improbable assumptions that the steric requirements of *endo*-2-methyl and *endo*-2-phenyl are equal and that the decrease in steric strain between the initial and the transition states in these tertiary derivatives will amount to 6.0 kcal./mole.

Consequently, it does not appear possible to escape the conclusion that the norbornyl cation fails to exhibit the delocalization of the charge from the 2- to the 1- and 6-positions required by the currently proposed nonclassical structure. We have failed to find any independent experimental kinetic evidence to support the proposal that cations of the norbornyl type exist as nonclassical resonance hybrids,^{2,9} rather than as an equilibrating pair of ions^{9a,10} (IV). Moreover,



the classical tertiary norbornyl cations exhibit precisely those properties, such as enhanced rates, high *exo/endo* rate ratios, and *exo* substitution, previously considered to be characteristic of the nonclassical norbornyl structure.¹

It must be concluded that formulation of the norbornyl cation as an equilibrating pair of classical ions (IV) is in better agreement with all of the experimental data presently available.

(7) If the observed *exo/endo* rate ratio for norbornyl brosylate is the result of participation in the *exo*, but not in the *endo*, we can arrive at an estimate of the nonclassical resonance stabilization in the transition state. Correction of the *exo/endo* rate ratio of 350 for internal return results in a relative rate of ionization of 1350. This is equivalent to 5 kcal. By adding 1 kcal. to correct for the higher ground-state energy of the more strained *endo* brosylate, we arrive at a value of 6 kcal./mole for the stabilization of the transition state for *exo*-norbornyl brosylate, as compared to the presumably classical transition state for the *endo* isomer. (It is customary to assume that resonance effects are only partially developed in the transition state. Consequently, nonclassical resonance would be considerably larger in the norbornyl cation.) It should be noted that the additional resonance stabilization afforded by the phenyl group in the *t*-cumyl as compared with the *t*-butyl chloride transition state is of the same order of magnitude (Table I). It is evident that the proposed nonclassical resonance stabilization is sufficiently large so that, if really present, it should exhibit some experimentally observable effects.

(8) Private communication from Professor P. von R. Schleyer.

(9) (a) T. P. Neville, E. de Salas, and C. L. Wilson, *J. Chem. Soc.*, 1188 (1939); (b) F. Brown, E. D. Hughes, C. K. Ingold, and J. F. Smith, *Nature*, **168**, 65 (1951).

(10) H. Meerwein and K. van Emster, *Ber.*, **55**, 2500 (1922).

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

R. B. WETHERILL LABORATORY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

HERBERT C. BROWN
MIN-HON REI¹¹

RECEIVED OCTOBER 1, 1964

Racemization and Radiochloride Exchange of *p*-Chlorobenzhydryl Chloride in a Series of Solvents¹ Sir:

Ion pair return during solvolysis causes the polarimetric rate constant, k_α , for formation of racemic starting material and product from *p*-chlorobenzhydryl chloride (RCI) to exceed the titrimetric rate constant, k_t , by a substantial factor in acetic acid^{2a} and by a smaller one in 80% acetone.^{2b} Similarly, in the aprotic solvent acetone,^{2c} k_α is much larger than the first-order radiochloride exchange rate constant, k_e , with low concentrations of added labeled LiCl. Several other aprotic solvents have now been studied so that the available data provide some perspective over a considerable solvent spectrum and point up the striking solvent specificity of the (k_α/k_e) ratios.

Summarized in Table I are the k_α^0 and k_t^0 values in the solvolyzing solvents at or extrapolated to zero concentration of added salt. Also listed are k_α^0 , k_e^0 , and k_{2e} values in four aprotic solvents.³ In MeNO₂, MeCN, and HCONMe₂ (DMF), k_e values at low concentrations of labeled Bu₄NCl are fitted to eq. 1, where k_{2e} is the slope and k_e^0 is the intercept of a plot of k_e vs. [Bu₄NCl]. In all three cases k_α^0 exceeds k_e^0 by a substantial factor.

$$k_e = k_e^0 + k_{2e}[\text{Bu}_4\text{NCl}] \quad (1)$$

$$\log k_\alpha^0 = 4.22 + 2.02 \log k_1 \quad (2)$$

As regards mechanisms associated with k_α^0 , k_e^0 , and k_{2e} , it is clear that k_α^0 is associated with ionization² of RCI. This conclusion is supported by the variation

TABLE I

POLARIMETRIC (k_α^0), TITRIMETRIC (k_t^0), AND EXCHANGE (k_e^0 AND k_{2e}) RATE CONSTANTS FOR *p*-CHLOROBENZHYDRYL CHLORIDE AT 75.0°

Solvent	10 ⁶ k, sec. ⁻¹			10 ³ k _{2e} , M ⁻¹ sec. ⁻¹
	k _α ⁰	k _t ⁰	k _e ⁰	
AcOH ^{2a}	68 ^{a,c} (21,300) ^b	1.8 ^{a,c}		
80% Me ₂ CO ^{2b}	60 ^a (11,650) ^b	23.1 ^a		
MeNO ₂	145		3.25	1.03
MeCN	60.7		0.2	1.23
HCONMe ₂	18.9		5.0	2.00
Me ₂ CO ^{2c}	1.38		<0.03	1.90

^a 25.0°. ^b Extrapolated from values at 25.0°. ^c From data with either LiOAc or Bu₄NOAc; erroneously high k values previously reported^{2a} for Bu₄NOAc.

of k_α^0 over a range of 4.2 powers of ten as solvent ionizing power varies. In fact, $\log k_\alpha^0$ in all six solvents at 75° is linear in $\log k_1$ for *p*-methoxyneophyl toluenesulfonate,⁴ the slope of the plot being 2.0 (eq. 2). Further, k_α^0 in MeNO₂ shows an appropriate α -deuterium isotope effect, k_H/k_D being 1.05.

The k_{2e} values for the slopes of the plots of k_e vs. [Bu₄NCl] are nearly identical in the four aprotic

(1) Research sponsored by the National Science Foundation.

(2) (a) S. Winstein, J. S. Gall, M. Hojo, and S. Smith, *J. Am. Chem. Soc.*, **82**, 1010 (1960); (b) S. Winstein, M. Hojo, and S. Smith, *Tetrahedron Letters*, **No. 22**, 12 (1960); (c) S. Winstein, A. Ledwith, and M. Hojo, *ibid.*, **No. 10**, 341 (1961).

(3) In all four aprotic solvents, RCI is sufficiently stable for attainment of the calculated statistical distribution of radiochloride in the exchanges.

(4) S. Smith, A. Fainberg, and S. Winstein, *J. Am. Chem. Soc.*, **83**, 618 (1961).