that the anisyl group at the 2-position stabilizes the carbonium ion so strongly that participation of the 1,6-bonding pair is not required.[5] Indeed, Bunton has suggested that even a simple 2-methyl substituent converts the nonclassical norbornyl cation into an essentially classical 2-methylnorbornyl cation.[6]

In view of the difficulties which appear to prevent the direct physical observation of the parent norbornyl cation, we have undertaken an alternative approach to the problem. We are examining the rates, the *exo–endo* rate ratios, and the stereochemistry of substitution of stabilized tertiary norbornyl cations. It is evident that if the above characteristics are uniquely associated with the nonclassical structure of the norbornyl cation, then essentially classical tertiary norbornyl cations should not exhibit these characteristics.[7]

Alternatively, if these essentially classical tertiary ions exhibit these unique characteristics, then these properties cannot be used as the primary justification for the proposed existence of the norbornyl cation as a nonclassical structure.

The present communication reports our observations on the relative rates of reaction of norbornyl[8] and cyclopentyl derivatives. The following communication reports our results on the *exo–endo* ratio.[9] A subsequent communication will report our studies of the stereochemistry of substitution.[10]

The reactivities of norbornyl derivatives are frequently compared with those of the corresponding cyclohexane compounds.[3] However, the norbornane system, with its opposed bonds, would appear to resemble cyclopentane more closely than the strain-free cyclohexane system.[11] Accordingly, data comparing the norbornyl compounds with the corresponding cyclopentyl derivatives are summarized in Table I.

2-Phenyl-*exo*-norbornyl chloride undergoes ethanolysis at a rate that is 7.5 times that of 1-phenylcyclopentyl chloride. Similarly, 2-methyl-*exo*-norbornyl chloride undergoes ethanolysis at a rate 5.3 times that of the cyclopentyl derivative. The corresponding factors for the solvolysis of the corresponding *p*-nitrobenzoates are slightly smaller.

exo-Norbornyl brosylate undergoes solvolysis at a rate approximately 350–444 times that of the *endo* isomer (Table I). If this factor is the result of participation, which should be essentially absent in the 2-phenyl and 2-methyl tertiary derivatives, we should expect to find an increase in the *exo*-norbornyl to cyclopentyl brosylate rate ratio to a value in the neighborhood of 2000 (∼5 × 400). However, the observed factor, *exo*-norbornyl to cyclopentyl derivative, is of the

(5) S. Winstein, Reaction Mechanisms Conference at Brookhaven, Sept. 5, 1962.

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

(7) In this discussion we are adopting Bunton's conclusion (ref. 6) that the tertiary norbornyl cations are essentially classical. However, this position is not essential to our study. It is adequate to postulate that with increasing stability of the cationic center, such as is encountered in the series 2-norbornyl, 2-methylnorbornyl, 2-phenylnorbornyl, and 2-anisylnorbornyl, there will be decreasing participation of the 1,6-bonding pair with a resulting decrease in the magnitude of the nonclassical contribution to the structure of the cation. Under this condition, the characteristics now associated with the nonclassical structure of the norbornyl cation should reveal a marked decrease with the increasing classical nature of the cation, vanishing in a truly classical norbornyl cation derivative.

(8) See also H. C. Brown, F. J. Chloupek, and M.-H. Rei, *J. Am. Chem. Soc.*, **86**, 1246 (1964).

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

(10) Research in progress with H. M. Bell.

(11) For a discussion of the relative merits of cyclohexyl and cyclopentyl derivatives as models for the norbornyl system, see S. Winstein, *et al.*, *J. Am. Chem. Soc.*, **74**, 1127 (1952). However, the similarities in the observed magnitude of the carbonyl group stretching vibration (cyclopentanone, 1750 cm.⁻¹; cyclohexanone, 1717; norcamphor, 1751) support a preference for the cyclopentyl system as an appropriate model.

same order of magnitude as observed with the tertiary derivatives: 3.9 for methanolysis, 3.6 for ethanolysis, and 14 for acetolysis.[12]

All in all, the remarkable similarity in the rates of reaction of a given norbornyl derivative with its related cyclopentyl derivative, a similarity which is independent of major differences in the stabilities of the ions examined, argues strongly for the position that there is no major factor influencing the solvolysis of the secondary norbornyl derivative that is not present in the highly stabilized tertiary norbornyl cations. The data appear difficult to reconcile with the postulated formation of a highly stabilized nonclassical structure for the norbornyl cation, with classical or essentially classical structures for the tertiary norbornyl cations.

(12) A possible difficulty with this argument should be pointed out. The observed rate of solvolysis of cyclopentyl brosylate may be enhanced by solvent participation, which is absent or negligible in the tertiary derivatives. However, it has been concluded that the rates of solvolysis of secondary sulfonates are only slightly dependent upon the nucleophilicity of the solvent [S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2700 (1951)].

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Rates of Solvolysis of the *p*-Nitrobenzoates of *exo–endo* Tertiary Norborneols.   A Critical Examination of the *exo–endo* Rate Ratio as a Basis for the Postulated Nonclassical Structure of the Norbornyl Cation

Sir:

We wish to report that the rates of solvolysis of the *p*-nitrobenzoates of several isomeric tertiary norborneols exhibit high *exo–endo* ratios of the same order of magnitude as those observed in the solvolysis of representative secondary norbornyl derivatives. Since it is now believed that these tertiary norbornyl derivatives undergo ionization to classical tertiary cations,[1,2] it would appear that a high *exo–endo* ratio does not provide a unique basis for concluding that a given system undergoes ionization to a nonclassical norbornyl cation.

exo-Norbornyl brosylate undergoes acetolysis at a rate some 350 times greater than that of the *endo* isomer.[3] This is a phenomenon of some generality, with the observed *exo–endo* ratio varying from a low of 13 for the *exo*-trimethylene-2-norbornyltosylates[4] to a high of 1230 for the 3,3-dimethyl-2-norbornyl brosylates.[5–7]

The greater rate of the *exo* isomer has been attributed to its more favorable geometry for participation of the 1,6-bonding pair in the ionization stage (eq. 1).

In the *endo* isomer the 1,6-electron pair is not in position to participate (eq. 2).

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

(2) See discussion in preceding communication: H. C. Brown, F. J. Chloupek, and M.-H. Rei, *J. Am. Chem. Soc.*, **86**, 1247 (1964).

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

(4) P. Schleyer, Ph.D. Thesis, Harvard University, 1956.

(5) A. Colter, Ph.D. Thesis, University of California at Los Angeles, 1956.

(6) For a summary of the data, see J. A. Berson, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, Chapter 3.

(7) This discussion is necessarily restricted to the titrimetric rate ratios, since polarimetric rate data (ref. 3) are not generally available.

$$\text{(1)}$$

$$\text{(2)}$$
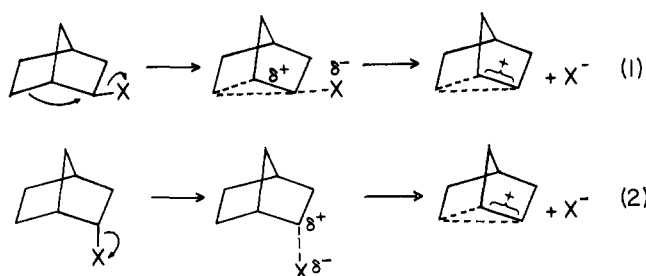
According to this interpretation, high *exo–endo* rate ratios should not be observed in tertiary norbornyl derivatives, where participation of the 1,6-electron pair should be much less important than in the secondary norbornyl cation.[1,2,8,9]

Accordingly, we synthesized the *p*-nitrobenzoates of *exo*- and *endo*-2-methyl- and -2-phenylnorbornreols, and of camphene hydrate and methylcamphenilol, and determined their rates of solvolysis in 60% aqueous dioxane at two temperatures.

The *p*-nitrobenzoates were synthesized by treating the tertiary carbinol in hexane solution with 1 equiv. of a standardized solution of *n*-butyllithium in hexane. The lithium alkoxide, soluble in hexane, was treated with 1 equiv. of *p*-nitrobenzoyl chloride. The solution was separated from the precipitated lithium chloride and the product recovered and recrystallized from hexane to constant melting point.

The experimental results are summarized in Table I.

TABLE I

REPRESENTATIVE *exo–endo* RATE RATIOS IN SECONDARY AND TERTIARY NORBORNYL DERIVATIVES

Compound[a]	Isomer	M.p., °C.[b]	Rate constant $k_1 \times 10^6$ sec.$^{-1}$ 50°	75°	$\dfrac{exo}{endo}$ (°C.)
[OBs]					350 (25)[c]
[OTs]					13 (68.6)[d]
[OBs]					1230 (25)[e]
[OPNB, CH₃]	exo	114.5	1.96	41.2	83 (50)
	endo	100.5	0.0237	0.434	
[OPNB, C₆H₅]	exo	107.5	946	14,100	140 (50)
	endo	137	6.74	119	
[OPNB, CH₃]	exo	101	16.5	205	593 (50)
	endo	144	0.0278	0.542	

[a] OBs = *p*-bromobenzenesulfonate, OTs = *p*-toluenesulfonate, OPNB = *p*-nitrobenzoate. [b] Recrystallized from hexane to not more than 1° range. Elementary analyses of the *p*-nitrobenzoates agreed with the calculated values to the usual accepted limits. [c] Ref. 3. [d] Ref. 4. [e] Ref. 5.

It is evident that the *exo–endo* rate ratios observed for the three tertiary pairs examined are of the same order of magnitude as those observed in the secondary norbornyl derivatives. Since participation by the 1,6-electron pair should be far less significant in these stabilized tertiary carbonium ions than in the much higher

(8) P. Schleyer, D. C. Kleinfelter, and H. G. Richey, Jr., *J. Am. Chem. Soc.*, **85**, 497 (1963).
(9) See footnote 7, ref. 2.

energy secondary cations, it follows that such participation cannot be the sole cause, or even the major cause, for the observed high *exo–endo* ratios.

If transannular participation is not responsible, what factor can be involved? One possibility which must be considered is that the rates of solvolysis of 2-methyl- and 2-phenyl-*exo*-norbornyl chlorides are strongly enhanced by the relief of steric strain accompanying the movement of the organic substituent out of the *endo* position during the solvolysis. On this basis, the strain in the corresponding *endo* derivative should result in a compensating increase in its rate, reducing the net effect on the *exo–endo* rate ratio.[10]

However, experimental data exist which strongly suggest that such relief of steric strain cannot be a major factor in the observed *exo–endo* rate ratios. The methyl and phenyl groups differ markedly in their steric requirements. If their steric requirements were a major factor in the rate of ionization of the *exo*-norbornyl derivatives, we should expect to find important differences in their relative effectiveness in the norbornyl system, as compared to acyclic and cyclic derivatives. However, the effect of phenyl *vs.* methyl substituents on the rates of ethanolysis at 25° exhibits a remarkable constancy: *t*-cumyl:*t*-butyl chloride, 4640; 1-phenylcyclopentyl:1-methylcyclopentyl chloride, 3740; and 2-phenyl-*exo*-norbornyl:2-methyl-*exo*-norbornyl chloride, 5270. One must fall back upon a fortuitous cancellation of large factors if these data include major contributions both for the relief of steric strain and for variable nonclassical participation in the tertiary norbornyl derivatives.

Previous treatments of high *exo–endo* rate ratios in norbornyl systems have assumed that these arise from enhanced *exo* rates. However, it has been suggested that the high *exo–endo* ratios which are observed may
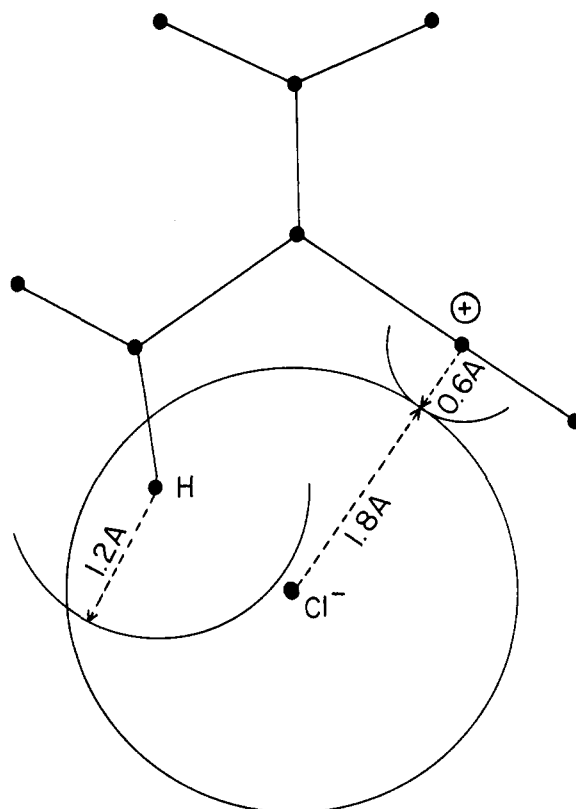
(10) It has been estimated that this steric effect may contribute a factor of 5 to the *exo–endo* ratio in 2-methylnorbornyl chloride: private communication from Professor Paul Schleyer, Princeton University.

be the result, not of an unusually high *exo* rate with a normal *endo* rate, as is commonly assumed, but of a normal *exo* rate with an unusually slow *endo* rate.[11] But what is the factor that might be responsible for the slow *endo* rate? An examination of the preferred path for the leaving group in the *endo* derivative reveals that this path brings the departing group very close to the opposite side of the rigid endocyclic system. Indeed, if one constructs an intimate ion pair with a representative anion, such as chloride, situated along the perpendicular to the face of the carbonium ion at C-2, at distances equal to the sum of the two ionic radii, the anion is observed to be severely crowded against the 5,6-bridge.[12]

It is apparent that the chloride ion must depart along some other path which is more favorable sterically, but more costly in requiring greater separation of charges in the ion pair.

In conclusion, the results clearly indicate 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 pairs to form a nonclassical norbornyl cation.

Acknowledgment.—This investigation was assisted by Project No. AT(11-1)-70, supported by the Atomic Energy Commission, and by Grant 19878, provided by the National Science Foundation.

(11) H. C. Brown, "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, pp. 140–158, 174–178.

(12) This hypothesis of steric hindrance to ionization in rigid bicyclic systems is readily susceptible to experimental test, and such tests are underway in research in progress with Dr. I. Rothberg.

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The Diamagnetic Anisotropy of a Borazine Ring. A Correction

Sir:

The importance of data on the diamagnetic anisotropy of borazines[1,2] with respect to the problem of the aromaticity of these compounds[3] renders necessary the correction of some errors made in the paper by Watanabe, Ito, and Kubo,[1] especially in the paragraph headed "Evaluation of Diamagnetic Anisotropy."

The experimental molar susceptibilities of boron compounds listed in the compilation by Foëx[4a] clearly show that Pascal's rule concerning the additivity of atomic susceptibilities, χ_A, for obtaining the molar susceptibilities, χ_M, *does not hold for boron compounds.* This might be due to the fact that Pascal calculated the χ_A values[4b] of nitrogen, oxygen, hydrogen, and chlorine from χ_M values of carbon compounds, so that these values do not reflect any effects specific to boron compounds, such as back coordination. Moreover, Pascal's value for the atomic susceptibility of boron,[5] $\chi_B = -7.2 \times 10^{-6}$, was obtained solely from the χ_M of $B(OCH_3)_3$. It remains to be proved that this value could indeed be used as such for calculating the χ_M

(1) H. Watanabe, K. Ito, and M. Kubo, *J. Am. Chem. Soc.*, **82**, 3294 (1960).

(2) K. Lonsdale and E. Toor, *Acta Cryst.*, **12**, 1048 (1959).

(3) J. C. Sheldon and B. C. Smith, *Quart. Rev.* (London), **14**, 200 (1960).

(4) (a) G. Foëx, "Tables de Constantes et Données Numériques. 7. Constantes Sélectionnées, Diamagnétisme et Paramagnétisme," Masson et Cie, Paris, 1957, pp. 28–29; (b) *ibid.*, p. 222.

(5) P. Pascal, *Compt. rend.*, **218**, 57 (1944).

values of boron compounds. It is, therefore, apparently as yet impossible to calculate the diamagnetic susceptibility of the borazine molecule, its plane parallel to the magnetic field, $\chi_|$, from $\chi = 3\chi_B + 3\chi_N + 6\chi_H$ as has been done.[1,6]

The χ_B required for calculating $\chi_|$[1] was obtained from the χ_M of BCl_3. However, the value -67.0×10^{-6} for the molar susceptibility of boron trichloride listed in this paper[1] is incorrect. According to these authors,[1] this value was taken from the compilation of Foëx,[4] who, however, does not list the -67.0×10^{-6} value, but gives only the value -59.9×10^{-6}, this being an experimental value given by Pascal.[5] The value[1] $\chi_M = -67.0 \times 10^{-6}$ is probably an approximation of the $\chi_M = -66.9 \times 10^{-6}$ *calculated* by Pascal[5] by adding the χ_A of Cl, -19.9×10^{-6}, and the χ_A of B, -7.2×10^{-6}, *i.e.*, $-(3 \times 19.9 + 7.2) \times 10^{-6} = -66.9 \times 10^{-6}$. It is very difficult to justify this procedure for obtaining χ_B,[1] which amounts to estimating χ_B from an experimentally nonexisting value for the χ_M of BCl_3, -67.0×10^{-6}.

Moreover, as a result of an arithmetical error, these authors[1] obtained $\chi_B = -3.2 \times 10^{-6}$, whereas from their values they should have obtained $\chi_B = -(67.0 - 3 \times 19.6) \times 10^{-6} = -8.2 \times 10^{-6}$. This value, $\chi_B = -8.2 \times 10^{-6}$, is the χ_B from $B(OCH_3)_3$, $\chi_B = -7.2 \times 10^{-6}$, modified by adding and subtracting different χ_A values of chlorine.

The erroneous value $\chi_B = -3.2 \times 10^{-6}$ was used by those authors[1] for calculating the $\chi_|$ of borazine

$$\chi_| = 3\chi_B + 3\chi_N + 6\chi_H$$
$$= -(3 \times 3.2 + 3 \times 3.3 + 6 \times 2.93) \times 10^{-6}$$
$$= -37.1 \times 10^{-6}$$

Had the value $\chi_B = -8.2 \times 10^{-6}$ been used, the $\chi_{||}$ would have amounted to -52.1×10^{-6}, whereas the value $\chi_B = -7.2 \times 10^{-6}$ would yield $\chi_|$, $= -49.1 \times 10^{-6}$. It must here again be stressed that the χ_N (*at least*) was chosen[1] quite arbitrarily. Thus no significance at all should be attributed to the "corrected" $\chi_|$ values -52.1×10^{-6} or -49.1×10^{-6}.

The molar susceptibility of borazine as determined,[1] $\chi_M = -49.6 \times 10^{-6}$, and the $\chi_|$ values -52.1×10^{-6} or -49.1×10^{-6}, yield the following values for the diamagnetic anisotropy, $\Delta\chi$, respectively

$$\Delta\chi = 3(\chi_M - \chi_|)$$
$$\Delta\chi = -3(49.6-52.1) \times 10^{-6} = +7.5 \times 10^{-6}$$

and

$$\Delta\chi = -3(49.6-49.1) \times 10^{-6} = -1.5 \times 10^{-6}$$

It is thus clear that the otherwise important conclusions,[1] based on the value $\Delta\chi = -36 \times 10^{-6}$,[1] are as yet unsubstantiated. On the other hand, the other values of $\Delta\chi$, $+7.5 \times 10^{-6}$ and -1.5×10^{-6}, create the impression of borazine not possessing any diamagnetic anisotropy. However, from the very moderately accurate data of Lonsdale and Toor[2] for the diamagnetic anisotropy of B-trichloroborazine, $\Delta\chi = -18 \times 10^{-6}$, it seems that borazine and its other derivatives would show some diamagnetic anisotropy. Obviously this problem requires further investigation.

(6) Neither can the $\chi_{||}$ of borazine be *assumed* to be equal to the $\chi_{||}$ of the isoelectronic benzene molecule as suggested.[1] Thus, the calculated $\chi_{||}$-values of molecules isoelectronic with benzene, such as pyridine, pyrimidine, pyrazine, and *sym*-triazine, differ appreciably from the $\chi_{||}$ of benzene.

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