A consideration of inductive effects is also pertinent. Higher degree of s character in a bond is reflected in a higher electronegativity.[8] Since the norbornyl C–H bonds presumably possess more than 25% s character, the hybridization effect results in a greater electron-withdrawing capacity relative to *i*-Pr. However, the norbornyl ring system may possess special bulk and steric factors which also contribute to the over-all inductive effect. At present, there are insufficient data to evaluate such contributions.[9]

The rates of benzoylation for a number of cycloalkylbenzenes are also under investigation. The amount of p character in the C–C bonds of various cycloalkanes is known or can be calculated from bond angles and $J_{^{13}\mathrm{C-H}}$ values.[6] It is hoped that some meaningful correlation between rates of electrophilic substitution and C–C bond p character exists.

The present work has indicated C–C hyperconjugation should be considered as a primary factor in stabilizing carbonium ions when the C–C bond(s) involved are expected to possess more than 75% p character and this is anticipated to be a general phenomenon. The importance of differential solvent effects is not manifested in the present work (*vide supra*).

exo-2-Phenylnorbornane[10] (I), 7-phenylnorbornane[11] (III), and 1-phenylnorbornane[12] (IV) were all prepared by previously reported methods. Hydrogenation of 2-phenyl-2-norbornene[12] in ethyl acetate with 10% Pd–C catalyst afforded *endo*-2-phenylnorbornane (II). All compounds were shown to be homogeneous by gas chromatographic examination and displayed nmr spectra in agreement with indicated structures. Purification of ethylene dichloride,[13] aluminum chloride,[14] and benzoyl chloride[14] for kinetic measurements has been described previously. Preparation of solutions and kinetic measurements employed are described in previous work.[13,15]

Acknowledgment. This work was supported by the National Science Foundation under Grant GP 6350X.

(8) A. D. Walsh, *Trans. Faraday Soc.*, **43**, 60 (1947); A. D. Walsh, *Discussions Faraday Soc.*, **2**, 18 (1947); A. D. Walsh, *J. Chem. Soc.*, 398 (1948).

(9) Synthesis and determination of pK_a values of a number of norbornyl-substituted benzoic acids are under investigation to clarify this point.

(10) L. Schmerling, U. S. Patent 2,480,267 (1949).

(11) P. R. Story and S. R. Fahenholtz, *J. Org. Chem.*, **28**, 1716 (1963).

(12) D. C. Kleinfelter and P. von R. Schleyer, *ibid.*, **26**, 3741 (1961).

(13) See Table I, footnote *d*.

(14) H. C. Brown and F. R. Jensen, *J. Am. Chem. Soc.*, **80**, 2291, 2296 (1958).

(15) H. C. Brown, B. Bolto, and F. R. Jensen, *J. Org. Chem.*, **23**, 414, 417 (1958).

(16) National Institutes of Health Predoctoral Fellow, 1968–1969.

Frederick R. Jensen, Bruce E. Smart[16]
Department of Chemistry, University of California
Berkeley, California

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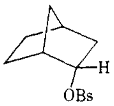
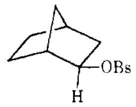
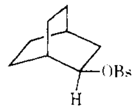
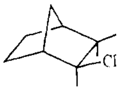
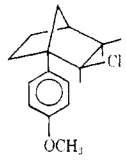
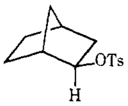
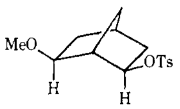
Carbon–Carbon Hyperconjugation in the Norbornyl Cation[1]

Sir:

In the preceding paper[2] it was proposed that increased hyperconjugative stabilization due to the presence of excess p character in C–C bonds in the norbornyl ring is responsible for the observed abnormally high rate of Friedel–Crafts benzoylation of the norbornylbenzenes. It is now suggested that the "extra" hyperconjugative ability of the strained C–C bonds in the norbornyl system is responsible, at least in part, for the rate acceleration observed in the formation of the *exo*-2-norbornyl cation. It is also suggested that accelerated rates of carbonium ion formation will be observed whenever the developing p bond has the proper geometry to undergo hyperconjugative stabilization by a (compressed) strained ring system.

A comparison of the solvolysis rates of the 2-bicyclo[2.2.2]octyl arenesulfonate III and the *endo*- and *exo*-norbornyl arenesulfonates I and II probably provides the best evidence for rate enhancement in the *exo*-norbornyl compound (Table I). The norbornyl system contains considerably more internal strain than the bicyclo[2.2.2]octyl system and this strain is expected to be considerably increased in forming the cations. Nevertheless, the 2-*exo*-norbornyl reacts faster than the 2-bicyclo[2.2.2]octyl compound, and this suggests the presence of a special stabilizing factor in the formation of the 2-*exo*-norbornyl cation. Although considerable evidence has been presented by Brown and coworkers[3] indicating the *exo*-2-norbornyl cation is classical, the existence of a factor producing rate acceleration appears to be present.

Table I. Relative Acetolysis Rates at 25°

			
	I	II	III
$k_{\mathrm{rel}}{}^{a}$	1	350	36
			
$k_{\mathrm{rel}}{}^{b}$	1	0.6	
			
$k_{\mathrm{rel}}{}^{c}$	1	0.014	

[a] See ref 6. [b] H. C. Brown and H. M. Bell, *J. Am. Chem. Soc.*, **86**, 5003 (1964). [c] P. J. Stang and P. von R. Schleyer, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstracts, p 192.

In the preceding paper,[2] *exo*-2-norbornylbenzene was reported to undergo acylation 4.2 times faster than *t*-butylbenzene (>90% *para* substitution). This increased rate of reaction was attributed to increased (C–C) hyperconjugative stabilization in the norbornyl system because of the greater amount of p character in norbornyl C–C bonds and the observed stabilization is equivalent to about 850 cal/mol. The developing posi-

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(1) Refers to the cation developed from heterolysis of the appropriate 2-norbornyl derivatives.

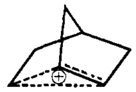
(2) See F. R. Jensen and B. E. Smart, *J. Am. Chem. Soc.*, **91**, 5686 (1969).

(3) (a) H. C. Brown, "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962; (b) H. C. Brown, *Chem. Brit.*, **2**, 199 (1966); M. Rei and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 5335 (1966).

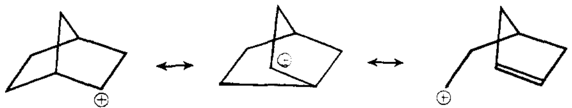
tive charge in the acylation reaction is divided between the positions *ortho* and *para* to the incoming group, and the geometry for hyperconjugation in the *para*-substituted norbornyl group is expected to be only "good." In contrast, in the solvolysis of *exo*-2-norbornyl derivatives the charge is highly localized and the developing p orbital from the *exo* leaving group is aligned parallel to the C_6–C_1 bond. This parallel configuration is optimum for stabilization through hyperconjugation.[4] Therefore, it would not be unexpected for the developing *exo*-2-norbornyl cation to receive several times the stabilization observed in the acylation reaction, *i.e.*, the norbornyl cation might receive 2–3 or more kcal/mole "extra" hyperconjugative stabilization because of the presence of more than the normal amount of p character in the C_1–C_6 bond.

Although the geomerty is optimum for hyperconjugative stabilization of the developing p orbital in the *exo*-2-norbornyl cation, the developing p orbital in the generation of the *endo*-2-norbornyl cation is in a geometrically less favorable position for C–C hyperconjugation with the C_1–C_7 bond, while overlap with the C_6–C_1 bond is virtually impossible.[5] Therefore, the *endo* compound is expected to react slower than the *exo* derivative. Similarly, the intermediate reactivity of 2-bicyclo[2.2.2]octyl derivatives is explained on the basis of normal hyperconjugative stabilization because of good geometry and small ring strain.

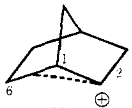
It is important to distinguish between C–C hyperconjugation and what is implied by participation in the nonclassical cationic sense. When the nonclassical intermediate IV is written, it represents a resonance hybrid of the canonical forms IVa → IVc.[6] Now valence bond theory depicts C–H hyperconjugation to an electron-deficient center as VI → VII.[4,7] By analogy, C–C hyperconjugation in the norbornyl cation would be depicted as IVa → IVc in valence bond terms. However, it is felt that these canonical forms involving σ-bond breaking are misleading when applied to hyperconjugation. Hyperconjugation should be considered as a phenomenon by which σ-bonding electrons are only partially delocalized to an electron-deficient center and these "participating" electrons formally remain in the σ bond. In other words, the movement of electrons and atoms is only slight but enough to provide stabilization at an adjacent developing electron-deficient center. Invoking the canonical forms (IVa → IVc) is not justified in the hyperconjugation model. In contrast to the nonclassical ion structure, the ion from the *exo* substrate has essentially retained its "classical" geometry. The partial σ-bond delocalization in the intermediate ion will be written as V, indicating at no time is the C_1–C_6 bond completely delocalized.



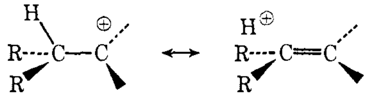
IV



IVa IVb IVc



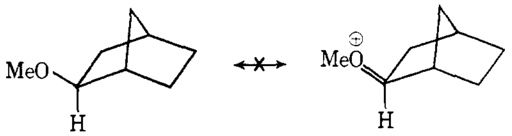
V



VI VII

Some examples of typical anomalies to the nonclassical ion picture can be seen in Table I.

The effect of a 1-anisyl or 6-methoxy substituent is incompatible with the nonclassical carbonium ion model. Both anisyl and methoxy are electron withdrawing inductively and will reduce the hyperconjunctive contribution of the C_1–C_6 bond,[8] and the decreased *exo* rate upon introduction of these substituents is predictable. It should be emphasized that the partial positive charge at position 1 or 6 in the hyperconjugation model cannot be delocalized by resonance of the type indicated in VIII. Since the hyperconjugation model assumes the bonding electrons are still formally localized on C_1 and C_6, stabilization by resonance as in VIII would effectively place ten electrons on C_6.



VIII

It is felt that the hyperconjugation model can explain much of the phenomena observed in the norbornyl system while also recognizing data anomalous to the nonclassical ion picture. Along with considerations of steric[3] and torsional[9] factors, the hyperconjugation model should be a highly predictive tool involving substituent effects.

Acknowledgment. This work was supported by the National Science Foundation under Grant GP 6350X.

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[4] For example, M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962.

[5] Electron delocalization is into the portion of the developing p orbital opposite the leaving group.

[6] G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966), and references therein.

[7] J. W. Baker, "Hyperconjugation," Oxford University Press, New York, N. Y., 1952.

[8] For the effect of substituents on hyperconjugative capacity, see, for example, J. R. Knowles and R. O. C. Norman, *J. Chem. Soc.*, 2938 (1961).

[9] P. von R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 699, 701 (1967).

[10] National Institutes of Health Predoctoral Fellow, 1968–1969.

Frederick R. Jensen, Bruce E. Smart[10]
Department of Chemistry, University of California
Berkeley, California 94720

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An Electron Paramagnetic Resonance Spectral Study of Intramolecular Reactions of Aryl Radicals

Sir:

Recently developed methods[1,2] for the generation of free alkyl and aryl radicals within the cavity of an epr

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[1] A. L. J. Beckwith and R. O. C. Norman, *J. Chem. Soc.*, *B*, 403 (1969).

[2] A. L. J. Beckwith and R. O. C. Norman, *ibid.*, 400 (1969).