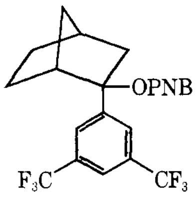
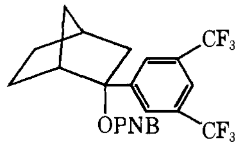


5



6

the full range of substituents (p-OCH$_3$, p-H, p-CF$_3$, 3,5-(CF$_3$)$_2$) in order to see if the ρ^+ values provided evidence for some unusual electronic contributions from the *exo*- and *endo*-norbornyl systems as compared to the cyclopentyl system. The compounds were solvolyzed in 80% acetone and the rates compared at 25° (Table I).

The exo:endo rate ratio at 25° for the solvolysis of 2[3,5-bis(trifluoromethyl)phenyl]-2-norbornyl p-nitrobenzoates is 176, comparable with the exo:endo rate ratios for the less demanding substituents previously studied (**1**, **2**). Indeed, extrapolation of the data to the corresponding secondary derivatives[10] reveals no significant change (Figure 1). Only k_α in acetic acid reveals a modest increase (~4) which might be associated with the proposed σ-participation. However, even this small factor is rendered doubtful by the remarkable constancy of the exo:endo rate ratio for the parent 2-norbornyl system in a remarkably wide range of solvents.[11]

The data for the 2-aryl-2-norbornyl derivatives follow the ρ^+ relationship[12] very closely. The exo derivatives yield $\rho^+ = -3.83$ (correlation coefficient 0.999); the endo derivatives yield $\rho^+ = -3.75$ (correlation coefficient 1.000). Finally, the 1-arylcyclopentyl derivatives yield $\rho^+ = -3.82$ (correlation coefficient 0.999). The results again support the conclusion that there are no significant electronic contributions in these derivatives from *exo*-norbornyl or *endo*-norbornyl that are not present in the cyclopentyl. The data do not support the oft-postulated[5,6] importance of σ-participation as a factor in the exo:endo rate ratio.

In superacid media the 2-aryl-2-norbornyl cations containing deactivating substituents (p-CF$_3$, 3,5-(CF$_3$)$_2$) in the aryl group exhibit changes in the ^{1}H NMR spectra interpreted as involving electronic redistributions in the norbornyl structure.[9] Whatever might be the origin of these electronic effects—inductive, field, hyperconjugative, or σ-bridging—they are clearly not effective in altering the exo:endo rate ratio in the solvolysis of the related norbornyl derivatives. This result points to the need for caution in extrapolating data from superacid media to solvolytic media.[13]

References and Notes

(1) P. G. Gassman and A. F. Fentiman, Jr., *J. Am. Chem. Soc.*, **92**, 2549 (1970).
(2) H. C. Brown and K.-T. Liu, *J. Am. Chem. Soc.*, **91**, 5909 (1969).
(3) H. C. Brown, M. Ravindranathan and E. N. Peters, *J. Am. Chem. Soc.*, **96**, 7351 (1974).
(4) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **95**, 2397 (1973).
(5) S. Winstein, *J. Am. Chem. Soc.*, **87**, 381 (1965).
(6) T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Am. Chem. Soc.*, **93**, 5715 (1971).
(7) H. C. Brown and K. Takeuchi, *J. Am. Chem. Soc.*, **90**, 2691, 2693 (1968).
(8) D. G. Farnum and G. Mehta, *J. Am. Chem. Soc.*, **91**, 3256 (1969).
(9) D. G. Farnum and A. D. Wolf, *J. Am. Chem. Soc.*, **96**, 5166 (1974).
(10) The rates for the tosylate in methanol[11] and for the tosylate in acetic acid,[11] converted with the factor ROPNB/ROTs = 3×10^{-8}.
(11) H. C. Brown, F. J. Chloupek, I. Rothberg, and M. Ravindranathan, manuscript in preparation.
(12) H. C. Brown and Y. Okamoto, *J. Org. Chem.*, **22**, 485 (1957).
(13) For example, the rate of 6:2 hydride shift for the 2-norbornyl cation in superacid was assumed to be the same in acetic acid and used to calculate a rate of Wagner–Meerwein shifts in that solvent of 6×10^{-12} sec^{-1}.[5,14] Similarly, the ESCA spectra for the ion in superacid media has been interpreted as supporting a symmetrical σ-bridged structure. This conclusion has then been extrapolated to the ion under solvolytic conditions,[15] overlooking the capture of the ion in unsymmetrical form in many reactions.[16]
(14) P. D. Bartlett, "Nonclassical Ions", W. A. Benjamin, New York, N.Y., 1965, p 526.
(15) G. A. Olah, G. Liang, G. D. Mateescu, and J. L. Reimenschneider, *J. Am. Chem. Soc.*, **95**, 8698 (1973).
(16) H. C. Brown, *Acc. Chem. Res.*, **6**, 377 (1973); H. C. Brown and K.-T. Liu, *J. Am. Chem. Soc.*, **97**, 600 (1975).

Herbert C. Brown,* M. Ravindranathan
Ken'ichi Takeuchi, Edward N. Peters
Richard B. Wetherill Laboratory, Purdue University
West Lafayette, Indiana 47907

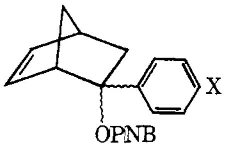
Received October 21, 1974

Rates and Products of Solvolysis of 2-Methyl-2-norbornenyl and 2,5-Dimethyl-2-norbornenyl *p*-Nitrobenzoates. Evidence for Increasing *π*-Participation with Increasing Electron Demand

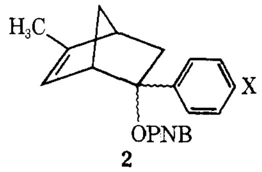
Sir:

The exo:endo rate ratio in the solvolysis of the 2-methyl-2-norbornenyl p-nitrobenzoates (895) reveals no significant increase over the corresponding saturated derivatives (885). On the other hand, the exo:endo rate ratio of the parent 2-norbornenyl derivatives (7000) does reveal an appreciable increase. Consequently, it is concluded that π-participation is not important under the high electron demand of the tertiary methyl cationic center, but becomes important under the even higher electron demand of the secondary system. On the other hand, a greatly increased exo:endo rate ratio, 112,000, is observed in the solvolysis of the 2,5-dimethyl-2-norbornenyl p-nitrobenzoates. This increase is attributed to the activation of the double bond by the 5-methyl substituent facilitating π-participation. The interpretation in terms of major π-participation is consistent with the formation of 1,3-dimethyl-3-nortricyclanol as the predominant product (98%). The increase in the value of the exo:endo rate ratio over that realized in the solvolysis of the corresponding 2-phenyl-5-methyl-2-norbornenyl derivatives, 1260, is attributed to the much higher electron demand of the tertiary 2-methyl cationic center, as contrasted to the less demanding tertiary 2-phenyl cationic center. This result confirms the position that the tool of increasing electron demand can detect participation where such participation is significant.

The solvolysis of the 2-aryl-2-norbornenyl derivatives (**1**) fails to reveal any significant increase in the exo:endo rate ratio with increasing electron demand over the usual range of substituents.[1]



1



2

	1 exo: endo	2 exo: endo
p-OCH$_3$	312	354
p-H	202	1260
p-CF$_3$	283	(6700)

Only with the major increase in electron demand provided by the secondary derivative (2-H) is there observed a major increase in the exo:endo rate ratio to a value of 7000.[2] Consequently, it was concluded that π-participation cannot be a significant factor in the high exo:endo rate ratios observed in the tertiary derivatives **1**.

It was desired to increase the electronic demand by utilizing the 2-[3,5-bis(trifluoromethyl)phenyl] derivatives in

Table I. Rates of Solvolysis of 2-Methyl-2-norbornenyl and 2,5-Dimethyl-2-norbornenyl *p*-Nitrobenzoates in 80% Acetone at 25.0°

p-Nitrobenzoate[a]	$10^6 k_1$, sec^{-1}	$\Delta H^‡$, kcal mol^{-1}	$\Delta S^‡$, eu	k_{rel}	Exo/endo
2-Methyl-*endo*-2-norbornenyl[b]	5.25×10^{-7}[c–e]			1.0	
2,5-Dimethyl-*endo*-2-norbornenyl[f]	5.13×10^{-7}[c,g,e]			0.98	
2-Methyl-*exo*-2-norbornenyl[h]	4.70×10^{-4}[e,i]	28.2	−6.8	1.0	895
2,5-Dimethyl-*exo*-2-norbornenyl[j]	5.75×10^{-2}[e,k]	24.3	−10.1	122.0	112,000

[a] All new compounds gave spectral and microanalytical data consistent with the proposed structure. [b] Mp 128.6–129.8°; G. L. Tritle, Ph.D. Thesis, Purdue University, 1966. [c] Calculated from data in other solvents using the Grunwald–Winstein relationship (ref 10). [d] In 50% acetone: $k^{25} = 1.90 \times 10^{-11}$ sec^{-1}; $\Delta H^‡ = 29.8$ kcal mol^{-1}; $\Delta S^‡ = -7.6$ eu. In 60% acetone: $k^{25} = 6.62 \times 10^{-12}$ sec^{-1}; $\Delta H^‡ = 30.6$ kcal mol^{-1}; $\Delta S^‡ = -7.1$ eu. [e] Calculated from data at higher temperatures. [f] Mp 99.8–100.5°. [g] In 50% acetone: $k^{25} = 3.59 \times 10^{-11}$ sec^{-1}; $\Delta H^‡ = 29.5$ kcal mol^{-1}; $\Delta S^‡ = -7.6$ eu. In 60% acetone: $k^{25} = 1.07 \times 10^{-11}$ sec^{-1}; $\Delta H^‡ = 30.8$ kcal mol^{-1}; $\Delta S^‡ = -5.3$ eu. [h] Mp 121.5–122.2°. [i] $k^{125} = 9.53 \times 10^{-5}$ sec^{-1}, $k^{100} = 8.24 \times 10^{-6}$ sec^{-1}. [j] Mp 133.2–133.8°. [k] $k^{100} = 2.69 \times 10^{-4}$ sec^{-1}; $k^{75} = 2.41 \times 10^{-5}$ sec^{-1}.

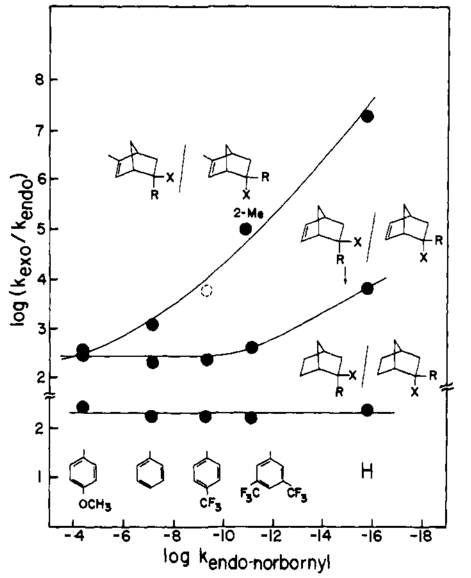
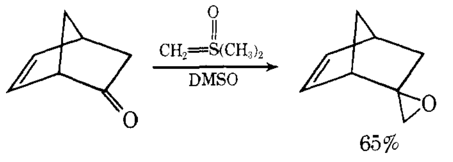


Figure 1. Effect of increasing electron demand on exo:endo rate ratio.

order to establish whether such an increase in a tertiary derivative could detect π-participation. Initially the synthesis of the exo isomer offered difficulties, so we could arrive only at an estimated rate.[3]

The introduction of a methyl group in position 5 of the norbornenyl structure (**2**) should facilitate π-participation.[4-6] Indeed, there was observed an increase in the exo:endo rate ratio from 354 for the 2-*p*-anisyl derivative to 1260 for the 2-phenyl derivative. Again the study could not be extended to aryl derivatives affording increased electronic demand because of difficulties in obtaining the exo isomer. (The value of 6700 given above for *p*-CF$_3$ was estimated, assuming the applicability of the $\rho^+\sigma^+$ relationship.[7])

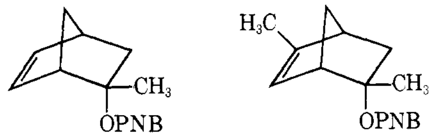
The electron demand provided by a 2-methyl group is considerably greater than that of a 2-*p*-trifluoromethylphenyl substituent and approaches that of a 2-[3,5-bis(trifluoromethyl)phenyl] substituent.[8] Accordingly, we undertook to prepare 2-methyl-2-norbornenyl and the 2,5-dimethyl-2-norbornenyl derivatives for examination. No difficulty was encountered in synthesizing the endo derivatives by the reaction of the methyl Grignard on the appropriate ketone. The discovery by Bly, Du Bose, and Konizer that dimethyloxosulfonium methylide attacks 2-norbornenone from the endo side to give the unsaturated exo oxide[9] (eq 1) provided a synthetic route to the desired exo alcohol. Accordingly, *exo*- and *endo*-2,5-dimethyl-2-norbornenyl *p*-nitrobenzoates were prepared and their rates of solvolysis determined in 80:20 (vol/vol) acetone-water. The rate for the endo isomer proved to be difficult to measure in this solvent. Consequently, these rates were determined in 50 and 60% aqueous acetone, from which the rate constant was calculated by the Grunwald-Winstein procedure.[10] The data are summarized in Table I.



(1)

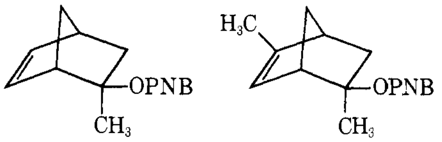
The 2-methyl-2-norbornenyl *p*-nitrobenzoates appear to undergo solvolysis without significant π-participation. On the other hand, the introduction of the 5-methyl group causes a marked increase in the exo:endo rate ratio to a value of 112,000!

The 5-methyl group has almost no effect on the rate of the endo derivative (eq 2). However, the 5-methyl group has a pronounced effect on the rate of the exo derivative[11] (eq 3).



(2)

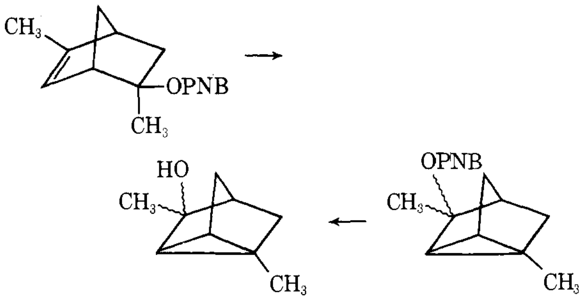
rel rate (25°) 1.00 0.98



(3)

rel rate (25°) 1.00 122

The major product of solvolysis for 2-methyl-2-norbornenyl is the exo alcohol (~80%). In the secondary 2-norbornenyl system where the involvement of the π electrons is important, the products are predominantly 3-nortricyclyl derivatives.[2,12] Both 2,5-dimethyl-2-*exo*-norbornenyl and 1,3-dimethyl-3-nortricyclyl *p*-nitrobenzoates solvolyze in buffered 80:20 acetone to give 1,3-dimethyl-3-nortricyclanol, >98% (eq 4).



(4)

Thus, the 5-methyl group in the 2,5-dimethyl-2-norbornenyl system has a dramatic effect on both the rates and products of solvolysis. It is concluded that the high exo:endo rate ratio in this system is the result of π-participation (times 120) in the exo isomer[13] and steric hindrance to ionization (times 890) in the endo isomer.

The effect of increasing electron demand in the related three systems subjected to study is revealed in Figure 1. In the 2-norbornenyl system, significant increase in the exo:endo rate ratio, reflecting π-participation, is observed only with the secondary derivative. In the 5-methyl-2-norbornenyl system, such increase in the exo:endo rate ratio is observed with much smaller electron demand, after the 2-*p*-anisyl derivative. In 2-norbornyl, no significant change in the exo:endo rate ratio is observed over the full range of electron demand explored.

References and Notes

(1) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **95**, 2398 (1973).
(2) S. Winstein, H. Walborsky, and K. C. Schreiber, *J. Am. Chem. Soc.*, **72**, 5795 (1950).
(3) Later the synthesis was successfully achieved and we realized an exo:endo rate ratio of 447 (Figure 1).
(4) R. A. Sneen, *J. Am. Chem. Soc.*, **80**, 3982 (1958).
(5) P. D. Bartlett and G. D. Sargent, *J. Am. Chem. Soc.*, **87**, 1297 (1965).
(6) P. G. Gassman and D. S. Patton, *J. Am. Chem. Soc.*, **91**, 2160 (1969).
(7) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).
(8) We adopted the rates of solvolysis of the *endo*-norbornyl derivatives as a measure of the electron demand. In the case of the 2-aryl derivatives, this is equivalent to using σ^+, but the procedure adopted permits the inclusion of the 2-Me and 2-H derivatives in the same plot (Figure 1).
(9) R. S. Bly, C. M. Du Bose, Jr., and G. B. Konizer, *J. Org. Chem.*, **33**, 2188 (1968).
(10) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948).
(11) If it is assumed that the 5-methyl group does not alter the rate of the endo isomer in the secondary derivative, the exo:endo rate ratio in that derivative is 22,000,000 (private communication from C. F. Wilcox); see Figure 1.
(12) J.D. Roberts, W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3329 (1950).
(13) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **94**, 5899 (1972).
(14) Postdoctoral Research Associate, 1972–1973, on a grant (GP 31385) provided by the National Science Foundation.
(15) Postdoctoral Research Associate, 1973–1975, on funds provided by Exxon Research and Engineering Company.

Herbert C. Brown,* Edward N. Peters[14]
M. Ravindranathan[15]
Richard B. Wetherill Laboratory, Purdue University
West Lafayette, Indiana 47907

Received December 12, 1974

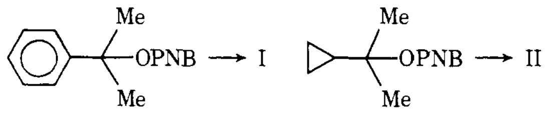
Substituent Effects on the Stability of Carbocations. The Anomalous Case of Phenyl vs. Cyclopropyl Substitution

Sir:

There have been numerous attempts made in the past decade to establish linear correlations between proton[1] and ^{19}F NMR[2] shielding constants of carbocation species and their thermodynamic stabilities in solution. That such direct relationships should indeed exist is reasonable enough.[2a] Thus, one speaks of electron donation into a carbonium center, leading to increased local shielding, as being of benefit energetically. Certainly the opposite process, withdrawal of electrons from a center which already has been largely divested of its charge, can be of little merit. Although no systematic attempt to relate ^{13}C shieldings to solution phase thermodynamic stabilities has as yet appeared in the literature, the existence of at least limited correlations here are strongly implied, by linear relationships between shieldings of different nuclei.[3]

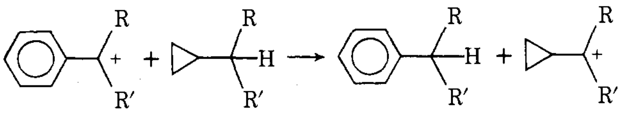
It has become increasingly evident, though, that NMR chemical shift–energy correlations are not general. For example, Olah has reported the ^{13}C shielding at the carbonium center in the *tert*-butyl cation to be shifted some 10 ppm *downfield* from that of the analogous carbon in the isopropyl system,[4] thus suggesting that the additional methyl substituent increases, not diminishes, the local positive charge. The normal relationship with energy would thus indicate an ordering of stabilities, *isopropyl* > *tert*-butyl, clearly at variance with gas phase measurements[5] and with theoretical ab initio molecular orbital calculations.[6]

There is also evidence for disparity in the electron donating and stabilizing effects of phenyl and cyclopropyl groups directly attached to a carbonium center. Olah has prepared a variety of phenyl and cyclopropyl substituted carbocations and has concluded from ^{13}C shielding measurements that the aromatic grouping is far superior to the small ring in displacing positive charge from the carbonium center.[7] For example, the observed ^{13}C shielding at the carbonium center in the dimethylbenzyl cation (I) occurs some 26 ppm upfield from that in the corresponding position in the dimethylcyclopropylcarbinyl system (II). It is more than tempting then, to suggest that the phenyl ring should be, energetically speaking, the better substituent. This stipulation is, however, at odds with Brown's measured rates of solvolysis of tertiary 2-propyl *p*-nitrobenzoate esters.[8] There are several reasonable causes for the inconsistency here. Possibly it stems from an incorrect association of NMR shielding constants and degree of charge displacement, or of thermodynamic stability and rates of solvolysis reactions. Perhaps instead, we are witnessing a breakdown in our notions of charge delocalization leading to (or accompanying) stabilization.



In this communication we describe the preliminary results of our combined experimental and theoretical efforts aimed at detailing the mechanisms by which phenyl and cyclopropyl substituents stabilize a carbonium center. Employed has been pulsed ion cyclotron resonance spectroscopy,[9] and ab initio molecular orbital theory,[10] both of which provide information on the ionic species in gas phase. Comparison of our data with those of Olah and of Brown taken in solution should provide insight into the importance of solvation.[13]

We have considered the energy of the *isodesmic*[14] hydride exchange reaction (eq 1) as a measure of the relative abilities of phenyl and cyclopropyl groups to stabilize a carbonium center. More familar processes which involve loss of a halide anion instead of H$^-$ would lead to qualitatively similar results. Experimental values of $\Delta G°$ for processes 1a and 1b have been obtained from the relative gas phase basicities α-methylstyrene–isopropenylcyclopropane (1a) and of styrene–vinylcyclopropane (1b). Low pressure ion cyclotron resonance techniques have been utilized as described previously.[15] ΔE theoretically for (eq 1) is based upon STO-3G optimized geometries for the parent benzyl and cyclopropylcarbinyl cations.[16] Details will be presented in an upcoming full report. Our data are presented in Table I, along with the NMR shift measurements of Olah and coworkers[7] and Brown's solvolysis rates.[8]



(1)

a, R = R' = Me
b, R = Me; R' = H
c, R = R' = H