(22) (a) S. J. Cristol and D. A. Beimborn, *J. Am. Chem. Soc.*, **95**, 3651 (1973); (b) S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Jurale, ibid., **84**, 3918 (1962); (c) S. J. Cristol, T. C. Morrill, and R. A. Sanchez, ibid., **88**, 3087 (1966); *J. Org. Chem.*, **31**, 2719 (1966); (d) S. J. Cristol and R. W. Gleason, ibid., **34**, 1762 (1969).

(23) Traylor recently stated [D. F. Eaton and T. G. Traylor, *J. Am. Chem. Soc.*, **96**, 1226 (1974)] that his vertical delocalization concept was only meant as an extension of Winstein's original suggestion "that hyperconjugation and bridging were description of a single delocalization phenomenon involving little or much movement of the hyperconjugated or bridging group" [cf. S. Winstein, B. K. Morse, E. Grunwald, K. C. Schneiber, and J. Corse, ibid., **74**, 1113 (1952)]. The quoted paper does not seem to contain such a statement. The closest relevant part is note 19. "Participation amounts to delocalization of the C_β–R bonding electron pairs as electron deficiency is created by ionization. Now in hyperconjugation involving β linkages, there is also delocalization. Whether, in general, hyperconjugation and participation should be considered to merge depends on the still unsettled preferred geometry in hyperconjugation."

(24) (a) T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Am. Chem. Soc.*, **93**, 5715 (1971); (b) T. G. Traylor, R. S. Brown, and N. A. Clinton, ibid., **92**, 5228 (1970); (c) T. G. Traylor, H. J. Berwin, and W. Hanstein, ibid., **92**, 829 (1970); (d) T. G. Traylor and J. C. Ware, ibid., **89**, 2304 (1967).

(25) (a) G. A. Olah, P. W. Westerman, and J. Nishimura, *J. Am. Chem. Soc.*, **96**, 3548 (1974); (b) G. A. Olah and G. Liang, ibid., in press.

(26) G. A. Olah, P. R. Clifford, and C. L. Jeuell, *J. Am. Chem. Soc.*, **92**, 5531 (1970).

(27) R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *J. Am. Chem. Soc.*, **94**, 6221, (1972).

(28) J. Meinwald, J. Crandall, and W. E. Hymans, *Org. Snyth.*, **45**, 74 (1965).

(28) (a) J. Meinwald, J. Crandall, and W. E. Hymans, *Org. Synth.*, **45**, 74 (1965). (b) E. Lippmaa, T. Pehk, and J. Paasivirta, *Org. Magn. Reson*, **5**, 277 (1973).

Solvolysis of 3-Aryl-3-nortricyclyl p-Nitrobenzoates. Evidence for Major Increases in Electron Supply by the Cyclopropyl Group with Increasing Electron Demand at the Cationic Center[1]

Herbert C. Brown* and Edward N. Peters[2]

Contribution from the Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907. Received October 17, 1974

Abstract: Increasing the electron demand at the carbonium center by varying the substituent on the aryl group results in major increases in rates of solvolysis for the p-nitrobenzoates of 3-aryl-3-nortricyclyl, as compared with the corresponding 7-aryl-7-norbornyl derivatives. The rate increases must reflect major increases in the electron supply by the cyclopropyl moiety under the increasing demand of the cationic center. This conclusion is in contrast to previous interpretations that in the rigid 3-nortricyclyl cation interaction between the cyclopropane ring and the carbonium center is relatively limited. Comparison of the ρ^+ values for solvolysis of the p-nitrobenzoates of 7-aryl-7-norbornyl (−5.27) and 7-aryl-*anti*-norbornenyl (−2.30), isopropylmethylarylcarbinyl (−4.76) and cyclopropylmethylarylcarbinyl (−2.78), 2-aryl-*endo*-norbornyl (−3.75) and 2-aryl-*exo*-norbornyl (−3.83), 2-aryl-*endo*-norbornenyl (−4.17) and 2-aryl-*exo*-norbornenyl (−4.21), and 7-aryl-7-norbornyl (−5.27) and 3-aryl-3-nortricyclyl (−3.27) reveals a consistent pattern which lends confidence in this test for participation.

In investigations of the effect of structure on reactivity, the selection of a suitable model structure is crucial. The problem is clearly revealed by the 3-nortricyclyl system, which has been compared both with 2-norbornyl and 7-norbornyl, with opposite conclusions drawn.

For example, a comparison of the relative rates for **1** and **2** led to the conclusion that the ion from **2**, containing the cyclopropylcarbinyl moiety, does not exhibit stabilization, presumably because of steric difficulties inhibiting σ bridging.[3]

	1	2
rel rate:	1.00	0.07
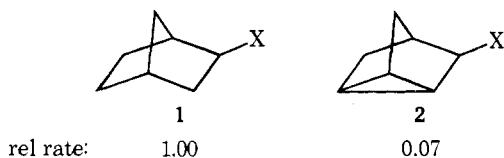
On the other hand, comparison of **3** and **4** reveals a major contribution of the cyclopropylcarbinyl moiety.[4] The fact is

	3	4
rel rate:	1.0	>10⁸
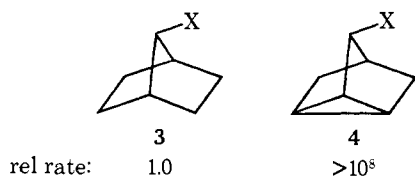
that **2** and **4** are identical. Yet opposite conclusions were reached as to the effectiveness of the cyclopropane ring in stabilizing the carbonium ion center through the particular selection of the model system.

The effect of increasing electron demand at the carbonium ion center[5] offers the hope of reducing such ambiguities. This approach has previously been utilized to compare *exo*- and *endo*-norbornyl,[6] *exo*- and *endo*-norbornenyl,[7] and cyclopropylcarbinyl with the corresponding isopropyl moiety.[8] It appeared appropriate to apply this test to the 3-nortricyclyl system.

Results and Discussion

A representative series of 3-aryl-3-nortricyclanols were synthesized by the reaction of the appropriate Grignard reagent with nortricyclanone. The products were converted to the p-nitrobenzoates, and the rates of solvolysis of the esters determined in 80:20 (v/v) acetone-water. The data are summarized in Table I.

The data follow the usual $\rho^+\sigma^+$ correlation[9] and yield a ρ^+ value of −3.27 (correlation coefficient 1.000). Irrespective of whether one utilizes 7-norbornyl or 2-norbornyl as the model, a comparison of the ρ^+ values clearly reveals resonance contributions from the cyclopropylcarbinyl moiety in the nortricyclyl system. An examination of the data now available lends confidence in this general approach.

The increase in ρ^+ from −5.27 for **5** to −2.30 for **6** reveals a large contribution resulting from π participation.[5]

Table I. Rates of Solvolysis of 3-Aryl-3-nortricyclyl
p-Nitrobenzoates in 80:20 Acetone–Water

Substituent in 3-aryl[a]	Temp, °C	$k_1 \times 10^6$, sec⁻¹	$\Delta H^{\ddagger}$, kcal mol⁻¹	$\Delta S^{\ddagger}$, eu
p-CH₃O	25.0	154		
p-H	75.0	180		
	50.0	10.3		
	25.0	0.365[b]	25.0	−4.2
p-CF₃	125.0	295		
	100.0	30.9		
	25.0	3.67×10^{-3}[b]	26.1	−9.8
m,m'-(CF₃)₂	150.0	157		
	125.0	20.2		
	25.0	1.78×10^{-4}[b]	26.9	−13.0

[a] All new compounds gave spectral and microanalytical data consistent with the proposed structure. See Experimental Section.
[b] Calculated from data at other temperatures.

5
ρ⁺: −5.27

6
−2.30   Δρ⁺ = 2.97
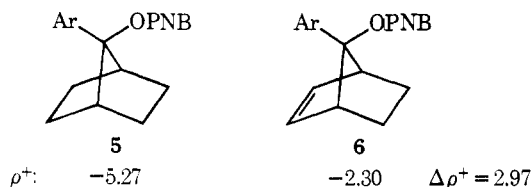
The change from −4.76 for **7** to −2.78 for **8** likewise reveals a large contribution from the cyclopropyl moiety.[8]

7
ρ⁺: −4.76

8
−2.78   Δρ⁺ = 1.98
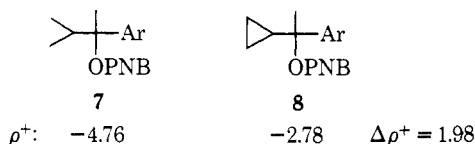
On the other hand, the ρ⁺ values for 2-aryl-*exo*- (**9**) and -*endo*-norbornyl (**10**) are essentially the same with the small change in the wrong direction for σ participation in the exo.[6]

9
ρ⁺: −3.75

10
−3.83   Δρ⁺ = −0.08
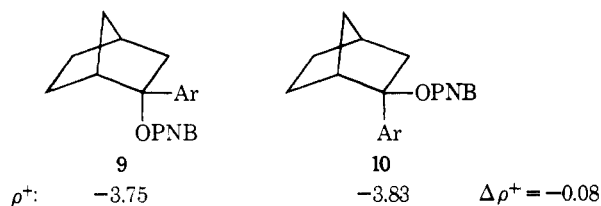
The behavior of the 2-aryl-*exo*- (**11**) and -*endo*-norbornenyl (**12**) derivatives is similar. Clearly, the large exo:endo rate ratios in these derivatives cannot be the result of participation, either π or σ.

11
ρ⁺: −4.17

12
−4.21   Δρ⁺ = −0.04
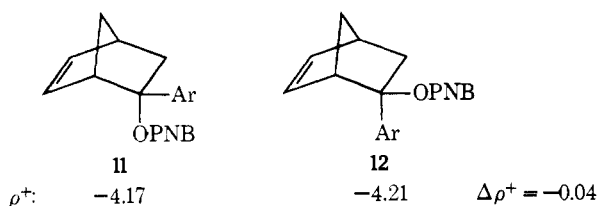
Irrespective of whether we compare 3-aryl-3-nortricyclyl (**13**) with 7-aryl-7-norbornyl (**5**) or with 2-aryl-2-norbornyl (**10**), the ρ⁺ values clearly reveal resonance contributions from the cyclopropylcarbinyl moiety.


5
ρ⁺: −5.27

10
−3.83

13
−3.27
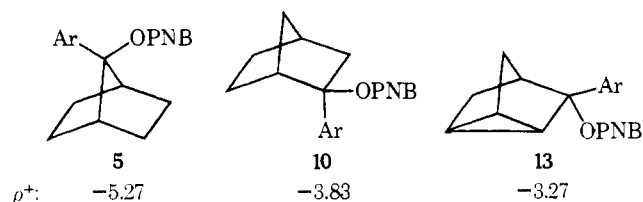
Consequently, this approach circumvents the ambiguities involved in a simple comparison of reaction rates.[10]

From a consideration of the molecular geometries, the 7-norbornyl system would appear to be a better model for comparison with 3-nortricyclyl. Bond-angle strain should be an important factor in the rates of solvolysis. Thus, nortricyclene has a C₂-C₃-C₄ bond angle of 97°,[11] in good agreement with the 96° value for the C₁-C₇-C₄ angle of norbornane,[12] but considerably smaller than the 104° value for the C₁-C₂-C₃ angle of norbornane.[12]

Comparison of the rates of solvolysis at 25° for the 3-aryl-3-nortricyclyl p-nitrobenzoates (**13**) with those for the corresponding 7-aryl-7-norbornyl derivatives (**5**) reveals major rate enhancements with increasing electron demand.

substituent in Ar	5	13
p-CH₃O:	1.0	7000
p-H:	1.0	25,000
p-CF₃:	1.0	3,010,000
m,m'-(CF₃)₂:	1.0	10,400,000

At one time, the high reactivity of cyclopropylcarbinyl derivatives in carbonium ion reactions was attributed to the formation of a stabilized species involving a σ bridge from the carbonium carbon and one or both of the far carbon atoms of the ring.[3,13] This would require the intermediate to exist in the parallel conformation to permit the p orbital of the carbonium carbon to be directed toward the ring (**14**).

14
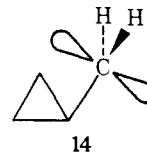
However, the rigid geometry of the 3-nortricyclyl cation forces it to exist in the bisected arrangement. It was believed that this would greatly diminish the stabilization provided by such interaction of the carbonium carbon with the cyclopropane ring.[3]

However, it should be noted that Δρ⁺ for **7** and **8** (1.98) is very similar to Δρ⁺ for **5** and **13** (2.00).[14] This indicates that the electronic contributions from the cyclopropane moiety are very similar in the two systems, in spite of the vast difference in geometries and rigidities.[15] These results confirm the conclusion that the stabilization of cyclopropylcarbinyl is not the result of σ bridging.[14,16]

Experimental Section

3-Nortricyclyl formate was prepared in improved yield and purity by a modification of the acid-catalyzed reaction of norbornadiene with formic acid.[17]

To a solution of 95 g (1.03 mol) of norbornadiene in 450 g (9.8 mol) of formic acid was added dropwise 12.5 ml of boron trifluoride etherate over a period of 15 min with rapid stirring. After 8 hr, the formic acid was removed on a roto-evaporator. The oily residue was poured into 300 ml of diethyl ether and extracted with three 100-ml portions of water, twice with 100 ml of saturated sodium bicarbonate solution, and finally with 100 ml of silver nitrate solution. The organic material was dried over anhydrous magnesium sulfate. Evaporation of solvent and distillation gave 114 g (80%) of 3-nortricyclyl formate, bp 78–80° (20 mm), n^{25}D 1.4730 [lit.[17] bp 79° (21 mm), n^{20}D 1.4758].

3-Nortricyclanol. To a stirred solution of 200 g (1.45 mol) of nortricyclyl formate in 500 ml of anhydrous methanol were added small pieces of sodium metal (5–10 g). The material was stirred and heated gently so that the resulting methyl formate was selec-

Table II. Preparation of 3-Aryl-3-nortricyclanols

Substituent in 3-aryl	% yield	Mp or bp, °C	Calcd			Found		
			C	H	F	C	H	F
p-CH$_3$O	73	87.5–88.5	77.73	7.47		77.51	7.63	
p-H	82	100 (0.5 mm)	83.88	7.52		83.65	7.58	
p-CF$_3$	52	86–86.8	66.13	5.16	22.42	66.43	5.09	22.39
m,m'-(CF$_3$)$_2$	61	104.7–105	55.91	3.75	35.37	56.19	3.99	35.30

Table III. Preparation of 3-Aryl-3-nortricyclyl p-Nitrobenzoates

Substituent in 3-aryl	% yield	Mp, °C	Calcd				Found			
			C	H	N	F	C	H	N	F
p-CH$_3$O	62	94.5–96.5	69.03	5.24	3.83		68.88	5.39	3.97	
p-H	70	127–127.8	71.63	5.11	4.18		71.38	5.23	4.02	
p-CF$_3$	76	127–127.5	62.53	4.00	3.47	14.13	62.40	4.23	3.25	14.32
m,m'-(CF$_3$)$_2$	73	140–141	56.06	3.21	2.97	24.18	56.05	3.49	2.68	24.45

tively removed by fractionation through a 30-cm Vigreux column. After warming overnight, the methanol was removed on a roto-evaporator. Recrystallization of the solid residue from pentane afforded 142 g (89%) of 3-nortricyclanol, mp 108–109.5° (lit.[17] mp 101–102°). The ir spectrum was similar to that reported for 3-nor-tricyclanol.[18]

Nortricyclanone. The conversion of the alcohol to the ketone was carried out using the convenient two-phase oxidation of Brown, Garg, and Liu.[19]

Diethyl ether (500 ml) and nortricyclanol (80 g, 0.73 mol) were placed in a 3-l. three-necked flask fitted with a stirrer, condenser, and an addition funnel. The flask was chilled in an ice bath. The chromic acid solution (50% excess), prepared from 110 g (0.368 mol) of sodium dichromate dihydrate and 61.2 ml (1.11 mol) of 97% sulfuric acid diluted to 500 ml, was added to the vigorously stirred solution over 4 hr, maintaining the temperature below 5°. After 4 additional hr of stirring, the upper ether layer was separated, and the aqueous layer was extracted with three 150-ml portions of ether. The combined ether extracts were washed with 150 ml of saturated sodium bicarbonate solution and then with 150 ml of saturated sodium chloride solution. The organic phase was dried over anhydrous magnesium sulfate. Filtration and removal of the solvent left a pale-yellow oil. Distillation yielded 67 g (85%) of nortricyclanone, bp 78.5–79.5° (24 mm), n^{25}D 1.4873 [lit.[20] bp 78–79° (24 mm), n^{25}D 1.4878].

3-Aryl-3-nortricyclanols were prepared by the addition of the corresponding arylmagnesium bromides to nortricyclanone. The melting points and analytical data are listed in Table II.

General Procedure for the Preparation of p-Nitrobenzoates. The p-nitrobenzoates were prepared from the lithium alkoxide and p-nitrobenzoyl chloride in tetrahydrofuran. In a 100-ml reaction flask, flushed with nitrogen and fitted with a sidearm with a rubber serum cap, were placed 20 mmol of the alcohol and 20 ml of tetrahydrofuran. n-Butyllithium solution (20 mmol) was added dropwise at 0°. The reaction mixture was stirred for 2 hr and then cooled to −30 to −35°. Next, 20 ml of a 1.0 M solution of p-nitrobenzoyl chloride in tetrahydrofuran was added and stirred for 15 min at −30°. The reaction mixture was allowed to warm to room temperature and stirred for an additional 3 hr. The cooled reaction mixture was then placed in a separatory funnel and washed quickly with cold 5% sodium bicarbonate solution. The tetrahydrofuran layer was dried over anhydrous magnesium sulfate. The solvent was removed, and the p-nitrobenzoates were crystallized to con-

stant melting point from hexane. The melting point and analytical data are reported in Table III.

Kinetic procedure was similar to that previously described.[21] For rate constants measured at 25 and 50°, the p-nitrobenzoate was dissolved in the thermostated solvolysis solvent (80% acetone). Five-milliliter aliquots were removed at appropriate time intervals, quenched in 20 ml of cold dry acetone, and then titrated using Bromothymol Blue indicator. The infinity titer was determined after 10 half-lives. For rate constants determined at temperatures above 50°, the solvolyses were carried in sealed ampoules charged with 5-ml aliquots of the reaction mixture.

References and Notes

(1) Structural Effects in Solvolytic Reactions. IX.
(2) Research assistant on Grants G 19878 and GP 31385 from the National Science Foundation.
(3) J. D. Roberts and R. H. Mazur, J. Am. Chem. Soc., **73**, 2509 (1951).
(4) H. G. Richey, Jr., and N. C. Buckley, J. Am. Chem. Soc., **85**, 3057 (1963); P. R. Story and S. R. Fahrenholtz, ibid., **86**, 527 (1964).
(5) P. G. Gassman and A. F. Fentiman, Jr., J. Am. Chem. Soc., **92**, 2549 (1970).
(6) K. Takeuchi and H. C. Brown, J. Am. Chem. Soc., **90**, 2693 (1968). The slightly revised values for ρ^+ are a consequence of additional data obtained by Dr. M. Ravindranathan.
(7) E. N. Peters and H. C. Brown, J. Am. Chem. Soc., **95**, 2398 (1973).
(8) E. N. Peters and H. C. Brown, J. Am. Chem. Soc., **95**, 2397 (1973).
(9) H. C. Brown and Y. Okamoto, J. Org. Chem., **22**, 485 (1957).
(10) For example, **13** (Ar = Ph) undergoes solvolysis at a slower rate ($\frac{1}{21}$) than **9** (Ar = Ph, $k_1 \times 10^6$ sec^{-1} = 7.56).[6]
(11) E. Heilbronner and V. Schomaker, Helv. Chim. Acta, **35**, 1385 (1952).
(12) J. F. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, J. Am. Chem. Soc., **90**, 3149 (1968).
(13) H. G. Richey, Jr., "Carbonium Ions", Vol. 3, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N.Y., 1972, Chapter 25.
(14) D. F. Eaton and T. G. Traylor, J. Am. Chem. Soc., **96**, 1226 (1974).
(15) G. A. Olah and G. Liang, J. Am. Chem. Soc., **95**, 3792 (1973).
(16) Although the NMR spectra of secondary and tertiary cyclopropylcarbinyl cations have been interpreted in terms of the classical bisected structures, data for the primary cyclopropyl cation have been interpreted in favor of a σ-bridged species: G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, J. Am. Chem. Soc., **94**, 146 (1972). On the other hand, W. J. Hehre and P. C. Hiberty, ibid., **96**, 302 (1974), have reported that their ab initio molecular orbital calculations favor equilibrating classical bisected cyclopropylcarbinyl cations.
(17) L. Schmerling, J. P. Luvisi, and R. E. Welsh, J. Am. Chem. Soc., **78**, 2819 (1956).
(18) J. D. Roberts, E. R. Trumbull, W. Bennett, and R. Armstrong, J. Am. Chem. Soc., **72**, 3116 (1950).
(19) H. C. Brown, C. P. Garg, and K.-T. Liu, J. Org. Chem., **36**, 387 (1971).
(20) H. K. Hall, J. Am. Chem. Soc., **82**, 1209 (1960).
(21) H. C. Brown and C. J. Kim, J. Am. Chem. Soc., **93**, 5765 (1971).