the electron-withdrawing inductive effect of the phenyl group,[2a,4a,b,10] the state of hybridization of the electron-deficient orbitals,[2a,4a,b,10] the combination of large HOMO-LUMO separations and low p coefficients for the unoccupied MO's,[13] and further delocalization of positive charge in **4a** to other positions.[15]

Acknowledgments. We wish to thank Professor H. C. Brown for exchanges of information during the course of this investigation and the A. P. Sloan Foundation and the National Institutes of Health for financial support.

References and Notes

(1) Some appropriate review and/or key leading references for substituent effects on several major types of carbonium ions are given in ref 2–5.

(2) Homoallyl- and cyclopropropylcarbinyl: (a) K. L. Servis and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 1331 (1965); (b) P. v. R. Schleyer and G. Van Dine, *ibid.*, **88**, 2321 (1966); (c) T. Shono, I. Nishiguchi, and R. Oda, *J. Org. Chem.*, **35**, 42 (1970); (d) P. v. R. Schleyer, P. J. Stang, and D. J. Raber, *J. Am. Chem. Soc.*, **92**, 4725 (1970); (e) C. F. Wilcox and H. D. Banks, *ibid.*, **94**, 8231 (1972).

(3) 7-*anti*-Norbornenyl (a) P. G. Gassman and D. S. Patton, *J. Am. Chem. Soc.*, **91**, 2160 (1969); (b) P. G. Gassman and A. F. Fentiman, Jr., *ibid.*, **92**, 2549 (1970); (c) P. G. Gassman and J. M. Pascone, *ibid.*, **95**, 7801 (1973); (d) R. K. Lustgarten, J. Lhomme, and S. Winstein, *J. Org. Chem.*, **37**, 1075 (1972).

(4) 2-Norbornyl: (a) G. D. Sargent, *Q. Rev., Chem. Soc.*, **20**, 301 (1966); (b) G. D. Sargent in "Carbonium Ions", G. A. Olah and P. v. R. Schleyer, Ed., Vol. III, Wiley-Interscience, New York, 1972, Chapter 24; (c) H. C. Brown, *Tetrahedron*, **32**, 179 (1976).

(5) Homocyclopropylcarbinyl: J. Haywood-Farmer, *Chem. Rev.*, **74**, 315 (1974).

(6) (a) R. M. Coates and J. L. Kirkpatrick, *J. Am. Chem. Soc.*, **92**, 4883 (1970); (b) R. M. Coates and E. R. Fretz, *ibid.*, **97**, 2538 (1975).

(7) P. G. Gassman and A. F. Fentiman, Jr., have reported that 8-anisyl-8-*endo,anti*-tricyclo[3.2.1.$0^{2,4}$]octyl *p*-nitrobenzoate undergoes solvolysis with exclusive cyclopropane participation: *J. Am. Chem. Soc.*, **92**, 2551 (1970).

(8) A parallel study upon the solvolysis of a series of 9-aryl pentacyclic *p*-nitrobenzoates (1-OPNB) is reported by H. C. Brown and M. Ravindranathan, *J. Am. Chem. Soc.*, following paper in this issue.

(9) Prolonged exposure to the solvolysis medium leads to increasing proportions of the more stable secondary isomers (1**b**-OH:**2b**-OH = 43:57 after 70–74 h at 100 °C; 1**c**-OH:**2c**-OH ≤ 3:97 after 49 h at 125 °C).

(10) (a) S. Winstein, E. C. Friederich, R. Baker, and Y. Lin, *Tetrahedron, Suppl.*, **8** Part II, 621 (1966); (b) Y. Lin, Ph.D. Thesis, University of California-Los Angeles, 1967; *Diss. Abstr.*, **28**, 3651-B (1968).

(11) E. J. Corey and H. Uda, *J. Am. Chem. Soc.*, **85**, 1788 (1963).

(12) (a) R. Breslow, H. Höver, and H. W. Chang, *J. Am. Chem. Soc.*, **84**, 3168 (1962); (b) R. Breslow and J. T. Groves, *ibid.*, **92**, 984 (1970); (c) J. C. Ciabattoni and E. C. Nathan, *ibid.*, **91**, 4766 (1969).

(13) C. F. Wilcox, Jr., L. M. Loew, R. G. Jesaitis, S. Belin, and J. N. C. Hsu, *J. Am. Chem. Soc.*, **96**, 4061 (1974).

(14) For example, cyclopropyl groups are considered to be relatively poor at transmitting substituent effects: C. F. Wilcox, L. M. Loew, and R. Hoffmann, *J. Am. Chem. Soc.*, **95**, 8192 (1973).

(15) MINDO/3 calculations performed by Professor W. Jorgensen (Department of Chemistry, Purdue University) indicate enhanced delocalization of the positive charge from the electron-deficient carbons to the rest of the molecule: *Tetrahedron Lett.*, 3033 (1976). We are grateful to Professor Jorgensen for preprints and discussions regarding these calculations.

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Solvolysis of 9-Aryl-9-pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonyl *p*-Nitrobenzoates. Unambiguous Evidence for the Presence of Carbon Participation by the Application of the Tool of Increasing Electron Demand

Sir:

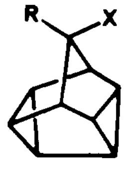
The rates of solvolysis of 9-aryl-9-pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonyl *p*-nitrobenzoates with representative substituents in the aryl ring reveal major $\pi\sigma$-participation with increasing electron demand at the cationic center. Moreover, the very low methyl/hydrogen (127) and phenyl/methyl (14) ratios realized in this system are indicative of a transition state stabilized by carbon participation resulting in little demand by the developing carbonium ion center for further stabilization by the substitutents. Thus these results establish that the Coates' cation is formed with $\pi\sigma$-participation supporting his conclusion that the intermediate is a carbon-bridged (nonclassical) cation.

Table I. Solvolysis of 9-Aryl-9-pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonyl *p*-Nitrobenzoates and Related Derivatives in 80% Aqueous Acetone

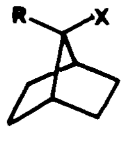
Substituent in aryl[a]	$10^6 K_1$, s^{-1} T_1	T_2	25 °C	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
p-CH_3O[b]	97.6 (50)		5.05	22.1	−8.7
p-H	486 (100)	45.7 (75)	0.123[e]	23.8	−10.2
p-CF_3[c]	516 (125)	57.3 (100)	8.59×10^{-3}[e]	25.3	−10.3
3,5-$(CF_3)_2$[d]	399 (150)	56.5 (125)	8.57×10^{-4}[e]	25.6	−14.2
9-CH_3	834 (125)	84.2 (100)	8.62×10^{-3}[e]	26.5	−6.6
9-H	94.9 (150)	11.4 (125)	6.79×10^{-5}[e]	27.8	−11.9

[a] All new compounds gave satisfactory spectral and microanalytical data. [b] Mp 145.5–146 °C. [c] Mp 146.5–147 °C. [d] Mp 164–164.5 °C. [e] Calculated from data at higher temperatures.

The tool of increasing electron demand has unambiguously proven the presence or absence of π-, $\pi\sigma$-, and σ-participation in representative systems where such participation could be significant in solvolytic behavior.[1] The solvolysis of the parent 9-pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonyl *p*-nitrobenzoate (**1**, R = H) proceeds 10^{10}–10^{12} times faster than the related 7-norbornyl derivative (**2**).[2,3] This major rate enhancement was attributed to participation by the remote cyclopropane bond leading to the formation of a trishomocyclopropenyl cation (**3**).[2] Moreover, the solvolysis regenerates the parent alcohol in which the degenerate rearrangement has been demonstrated.[2,4] It was of major interest to test whether the tool of increasing electron demand could establish the presence of $\pi\sigma$-participation in such a system.



1



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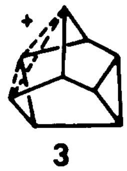


3

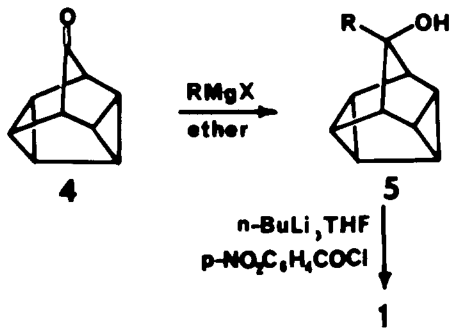
Accordingly, 9-aryl-9-pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonyl *p*-nitrobenzoates containing representative substituents in the aryl ring (**1**, R = X-C_6H_4-: X = *p*-CH_3O, *p*-H, *p*-CF_3, 3,5-$(CF_3)_2$) were synthesized by the addition of the appropriate Grignard reagents to the ketone (**4**).[5] The tertiary alcohols (**5**) were converted to the *p*-nitrobenzoates by treating their lithium salts with *p*-nitrobenzoyl chloride. The rates of solvolysis of the esters were determined in 80% aqueous acetone by the standard titrimetric procedure.[6] For comparative purposes, the rates of solvolysis of the secondary ester (**1**, R = H) and the tertiary methyl ester (**1**, R = CH_3) were also measured in this solvent. The pertinent rate data are summarized in Table I.

The aryl derivatives (**6**) reveal an excellent $\rho^+\sigma^+$ relationship.[7] The system yields a ρ^+ of −2.05 (correlation coefficient 0.999). This is comparable with the ρ^+ observed in the sol-

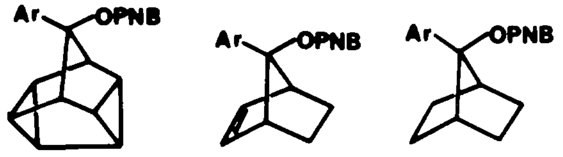
Table II. Comparison of the Rates of Solvolysis of 9-Pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonyl *p*-Nitrobenzoates with the Corresponding 7-Norbornyl Derivatives

	Relative Rate	
Substituent	**2**[a] (taken as unity)	**1**
p-CH_3O	1.00[b]	159
p-H	1.00[b]	5.85×10^3
p-CF_3	1.00[b]	4.90×10^6
3,5-$(CF_3)_2$	1.00[b]	3.47×10^8
CH_3	1.00[b]	9.3×10^7
H	1.00[c]	9.8×10^{13}

[a] Reference 8, 9. [b] Corrected from 70% dioxane to 80% acetone.[9] [c] Corrected from tosylate in acetic acid to *p*-nitrobenzoate in 80% acetone.[9]



volysis of 7-norbornenyl derivatives (**7**) where π-participation is significant,[8] and much larger than ρ^+ for 7-norbornyl (**8**). Hence the πσ-participation from the cyclopropane ring is a linear function of the electron demand of the incipient carbonium ion center.



6 **7** **8**

ρ^+ −2.05 −2.30 −5.27

The rates of solvolysis of **1** are compared with the 7-norbornyl *p*-nitrobenzoates (**2**)[8,9] and are listed in Table II. The relative rate data reveal that with increasing electron demand at the cationic center the rates of solvolysis of the pentacyclic derivatives (**1**) increase markedly relative to the rates of the corresponding 7-norbornyl derivatives (**2**).

It is interesting to note that very low 9-methyl/9-hydrogen (127) and 9-phenyl/9-methyl (14) ratios are evident in this system (Table I). These values should be compared with the very large methyl/hydrogen (1.23×10^8)[10] and phenyl/methyl ratios (2.3×10^5)[11] observed in the solvolysis of the parent 7-norbornyl derivatives. The low methyl/hydrogen and phenyl/methyl ratios can be attributed to the fact that the cation is so stabilized by πσ-participation that it makes relatively little demand upon substituents for further stabilization. Similar diminished methyl/hydrogen (420)[12] and phenyl/methyl ratios (9.5)[11] are also observed in the solvolysis of 7-norbornenyl derivatives (**7**) where the solvolysis proceeds through π-participation.

The major product of solvolysis of 9-phenyl-9-pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonyl *p*-nitrobenzoate (**1**, R = Ph) in 80% aqueous acetone at 75 °C after ten half-lives is the unrearranged tertiary alcohol (95%). The solvolysis also furnished a minor amount, 5%, of the secondary alcohol.

In conclusion, both the application of the tool of increasing electron demand and the low methyl/hydrogen and phenyl/methyl ratios observed in the solvolysis of **1** unambiguously support the earlier conclusion that the solvolysis of this system proceeds with carbon (πσ)-participation. However, it should be pointed out that the application of the same criteria to 2-norbornyl fails to reveal such participation under solvolytic conditions.[13,14]

References and Notes

(1) For leading references, see H. C. Brown et al., *J. Am. Chem. Soc.*, **97**, 7442, 7449, 7454 (1975); H. C. Brown, "The Nonclassical Ion Problem", Plenum, New York, N.Y., 1977.
(2) R. M. Coates and J. L. Kirkpatrick, *J. Am. Chem. Soc.*, **92**, 4883 (1970).
(3) R. M. Coates and E. R. Fretz, *J. Am. Chem. Soc.*, **97**, 2538 (1975).
(4) R. E. Leone, J. C. Barborak, and P. v. R. Schleyer, "Carbonium Ions", Vol. IV, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1973.
(5) We are grateful to Professor R. M. Coates for a sample of the pentacyclic ketone and the phenyl and the secondary *p*-nitrobenzoates.
(6) H. C. Brown and E. N. Peters, *J. Am. Chem. Soc.*, **97**, 1927 (1975).
(7) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).
(8) P. G. Gassman and A. F. Fentiman, Jr., *J. Am. Chem. Soc.*, **92**, 2549 (1970).
(9) The rates of solvolysis of the 7-norbornyl *p*-nitrobenzoates in 70% dioxane[8] were converted to rates of *p*-nitrobenzoates in 80% acetone by the factor of 0.206 and the rates of tosylates in acetic acid to *p*-nitrobenzoates in 80% acetone by multiplying the rates of tosylates by a factor of 3.27×10^{-11}. See E. N. Peters, *J. Am. Chem. Soc.*, **98**, 5627 (1976).
(10) P. G. Gassman and J. M. Pascone, *J. Am. Chem. Soc.*, **95**, 7801 (1973).
(11) The rate of solvolysis of 7-phenylnorbornyl *p*-nitrobenzoate in 70% dioxane was converted to the rate of tosylate in acetic acid by multiplying by a factor of 6.3×10^9.[8] For methyl/hydrogen and phenyl/hydrogen ratios, see also R. M. Coates and E. R. Fretz, *J. Am. Chem. Soc.*, preceding paper in this issue.
(12) R. K. Lustgarten, J. Lhomme, and S. Winstein, *J. Org. Chem.*, **37**, 1075 (1972).
(13) H. C. Brown, M. Ravindranathan, K. Takeuchi, and E. N. Peters, *J. Am. Chem. Soc.*, **97**, 2899 (1975).
(14) H. C. Brown and M.-H. Rei, *J. Am. Chem. Soc.*, **86**, 5008 (1964).
(15) Postdoctoral research associate on a grant supplied by Exxon Research and Engineering Company.

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Reduction of Excited Singlet State Acetone by 2-Propanol

Sir:

While the intermediacy of the nπ* triplet states (T_1) of alkanones in their photoreductions by hydrogen donors is well established, less is known about the reactivities of the corresponding nπ* singlet states (S_1). Theory[1,2] predicts similar reactivities for S_1 and T_1, in keeping with the quenching of adamantanone fluorescence by hydrogen donors.[3] The S_1 reaction may be less efficient, however, since ground state educts and radical pair product lie on a common energy hypersurface, and return to the ground state can compete with radical pair formation.[1,2] Wagner's finding of no[4] or only little[5] 2-propanol formation during reaction of excited acetone with tributylstannane under conditions where only S_1 should react may point to a low efficiency of the S_1 reaction. However, this explanation conflicts with the unit quantum yield of 2-propanol formation under conditions where both S_1 and T_1 states of acetone react with the stannane.[4,5]

Extending our studies[6] on the acetone/2-propanol photosystem we have now observed the formation of the photoreduction product pinacol from a singlet reaction of excited acetone, and confirm that S_1 and T_1 states are about equally reactive towards 2-propanol.

Samples (560 μl) of three different reaction mixtures consisting of (a) 5 M 2-propanol plus 5 M 2-propanol-d_6 in di-*tert*-butyl peroxide, (b) 1 M acetone plus 10 M 2-propanol-d_6