(26) For a detailed discussion of B strain effects, see H. C. Brown, "Boranes in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1972, Chapter VIII.

(27) P. D. Bartlett and M. Stiles, *J. Am. Chem. Soc.*, **77**, 2806 (1955); P. D. Bartlett and T. T. Tidwell, *ibid.*, **90**, 4421 (1968); P. D. Bartlett and M. S. Swain, *ibid.*, **77**, 2801 (1955).

(28) (a) H. Tanida and H. Matsummura, *J. Am. Chem. Soc.*, **95**, 1586 (1973); (b) K. Yates and J. J. Perie, *J. Org. Chem.*, **39**, 1902 (1974); (c) L. R. C. Barclay et al., *Can. J. Chem.*, **50**, 2318, 3965 (1972); (d) J. C. Carlton and E. D. Hughes, *J. Chem. Soc.*, 850 (1956); (e) G. Baddeley, J. Chadwick and H. T. Taylor, *ibid.*, 2405 (1954); (f) G. Baddeley and J. Chadwick, *ibid.*, 368 (1951).

A Method for the Evaluation of Steric Contributions to ρ^+ Based on Aryl/Methyl Rate Ratios. Application to the Gassman–Brown Tool of Increasing Electron Demand

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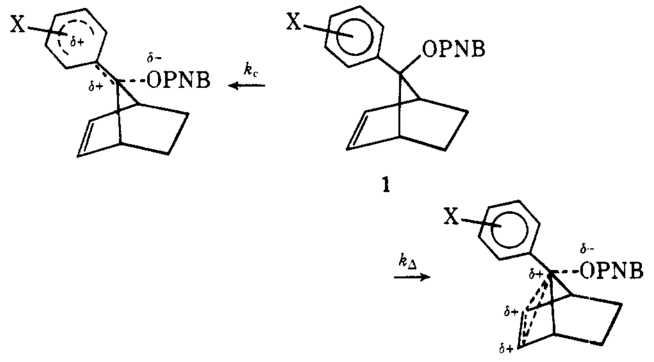
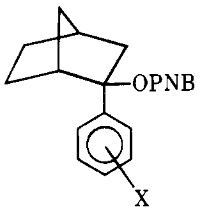
It has been shown that either of two factors may cause a large decrease in the magnitude of ρ^+ values determined for the solvolysis of a series of aryl-substituted tertiary derivatives. The factors are steric effects and neighboring group participation. In this article we define a method which can be empirically used to assess whether or not steric factors are affecting the magnitude of ρ^+. Toward this end a substituent constant, γ^+, for the methyl group directly attached to an incipient cationic center has been obtained by comparing *tert*-cumyl derivatives with *tert*-butyl derivatives. The constant is apparently solvent dependent with a value of 0.63 in 70–90% aqueous acetone and 0.79 in pure alcohols (methanol, ethanol, and 2-propanol). Using the derived γ^+ values, rate constants for methyl-substituted derivatives **6** were calculated. A comparison of calculated and observed rates for a variety of substrates reveals that the rates of **6** calculated from the rates of **7**, X = H, and ρ^+ are within 0.7 log units except when unusual steric effects cause a deviation. Both steric acceleration and steric deceleration of some aryl-substituted tertiary derivatives **7** were detected by the application of this treatment. The method described is applicable to both k_c and k_Δ substrates.

Gassman and Fentiman[1] have observed that decreasing the electron demand at the reaction site in a substrate undergoing anchimerically assisted solvolysis can cause abrupt cessation in assistance by a neighboring group. Thus the *anti*-7-norbornenyl system (**1**) undergoes a change in mechanism from k_Δ to k_c as the aryl group becomes sufficiently electron releasing to overcome the stabilization afforded by electron donation from the C_2–C_3 π bond. This change in mechanism is reflected by the magnitude of ρ^+, which is −5.2 for hydrolysis of **1** in 70% aqueous dioxane when X = p-NMe$_2$ and p-OMe and −2.30 when X = H, p-CF$_3$, and m,m'-di-CF$_3$.

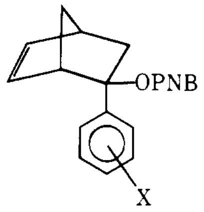


1

Brown and his co-workers[2–17] have made extensive use of the tool of increasing electron demand in characterizing a variety of systems. The method has been successfully used in detecting contributions from π and σ participation[1–15,17,18] and from other conjugating groups.[16] Yet examples where participation was not detected (e.g., the *exo*-2-norbornyl system, **2**)[2,11,18] or was too weak to positively identify (e.g., the *exo*-norbornen-2-yl system, **3**)[13,19] have also been treated.



2



3

Sargent[20] has claimed that the tertiary 2-norbornyl system (**2**) may undergo accelerated ionization because of relief of the nonbonded repulsion between the endo 6-H and the endo 2 substituent. Brown, however, has maintained[21] that his own data[22] and that of Goering and Schewene[23] show only a small difference (~0.4 kcal) between the ground-state free energies of the isomeric tertiary 2-norbornyl derivatives. Hence the tool of increasing electron demand is claimed to be valid for these systems since steric factors are similar in the exo and endo derivatives.[24] However, the fact that Brown and others have established that exo and endo tertiary 2-norbornyl derivatives have similar *ground state* energies does not rule out significant energy differences in the solvolytic *transition state*. Since the *preferred* ground state conformation and the *required* transition state conformations of aryl-substituted tertiaries may differ,[25] steric factors affecting the energy of the transition state are obviously the quantities which need assessing.

It is established that either steric factors[26] or neighboring group participation[1,7,10,17] can produce a remakable change in the magnitude of ρ^+. However, it has not been established whether or not these factors act independently or in concert in producing an effect on ρ^+, because previously there has been no method available to separate the effects of these factors. Accordingly, we have sought a method to evaluate the im-

Table I. Determination of γ^+ for the Methyl Group by a Hammett–Brown Treatment of *tert*-Cumyl and *tert*-Butyl Derivatives

Entry no.	Solvent	Leaving group, L	ρ^+, 25 °C, *t*-cumyl series (4)	Log *k*, 25 °C, **4**, X = H	Log *k*, 25 °C, *tert*-butyl-L (5)	Calcd γ^+
1	70% aq acetone	OPNB[b]	−3.74[c]	−2.83[c]	−5.17[d]	0.63
2	80% aq acetone	OPNB[b]	−4.72[e]	−7.14[f]	−10.13[g]	0.63
3	90% aq acetone	Cl	−4.54[h]	−3.88[h]	−6.80[i]	0.64
4	Methanol	Cl	−4.82[h]	−2.29[h]	−6.12[j]	0.79
5	Ethanol	Cl	−4.67[h]	−3.40[h]	−7.07[j]	0.79
6	2-Propanol	Cl	−4.43[h]	−4.29[h]	−7.76[k]	0.78

[a] Using eq 1. [b] *p*-Nitrobenzoate. [c] At 100 °C, ref 26. [d] At 100 °C, cf. C. F. Wilcox, Jr., and M. E. Mesirov, *J. Am. Chem. Soc.*, **84,** 2757 (1962). [e] H. C. Brown, E. N. Peters, and M. Ravindranathan, unpublished results, cf. ref 16. [f] Reference 9. [g] H. C. Brown and W. C. Dickason, *J. Am. Chem. Soc.*, **91,** 1226 (1969). [h] Y. Okamoto, T. Inukai, and H. C. Brown, *ibid.*, **80,** 4972 (1958). [i] Extrapolated from *t*-BuBr in 90% aqueous acetone, log *k* = −4.90; cf. L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, *J. Chem. Soc.*, 979 (1940), using average Br/Cl-ratio from 80% acetone, Br/Cl = 56.7, cf. E. D. Hughes, *ibid.*, 255 (1935), and L. C. Bateman, K. A. Cooper, E. D. Hughes, and C. K. Ingold, *ibid.*, 925 (1940), and from absolute ethanol which has a similar *Y* value to 90% aqueous acetone, Br/Cl = 66.2, cf. E. D. Hughes, C. K. Ingold, S. Masterman, and B. J. McNulty, *ibid.*, 899 (1940). [j] A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78,** 2770 (1956). [k] Extrapolated from rate of *t*-BuBr using *Y* = −2.73, cf. footnote *j*.

portance of steric factors on the rates of ionization of aryl-substituted tertiary derivatives.

For maximum stabilization of a cationic transition state in a *tert*-cumyl solvolysis, the benzene ring must adopt a conformation in which its plane is perpendicular to the axis of the bond between carbon and the leaving group.[25] Tanida and Matsumura convincingly demonstrated that bulky groups attached to the reaction site of aryl-substituted tertiaries show low ρ^+ values. This was attributed to the preferred transition state geometry of the aryl group being difficult to attain in these cases, thus leading to an effect on the magnitude of ρ^+. On the other hand, no special methyl group orientation for carbocation stabilization in the transition state is expected; the methyl group is assumed to be spherically symmetrical in the transition state since ab initio calculations on the ethyl cation have revealed no significant barrier to C–C bond rotation.[27] This essential difference between the transition state requirements of an aryl and methyl group provides the basis for our method of evaluating steric factors on the rates of ionization of aryl-substituted tertiary derivatives. Thus we report the determination of a substituent constant which is a special kind of σ^+ constant, called the γ^+ constant,[28] for a methyl group directly substituted on a tertiary carbon undergoing ionization. We use this constant and ρ^+ for the tertiary aryl-substituted compounds to calculate the rates of ionization of methyl-substituted tertiary derivatives. If this calculated rate of the methyl-substituted derivative agrees with the observed rate, then we assume that there are no unusual steric factors operating in solvolysis of the aryl derivatives. However, if the calculated and observed rates for the methyl-substituted derivatives differ, then we assume that the ρ^+ value from solvolysis of the aryl derivatives is affected by special steric requirements (recall that methyl has no orientational requirements). These conclusions also apply to the use of Ph/Me ratios, which of course are directly related to the present consideration.

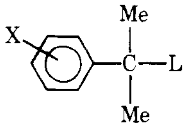
Incidental to this work we have observed that the derived γ^+ constant for the methyl group is solvent dependent. The significance of this observation is briefly discussed.

Results and Discussion

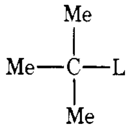
Calculation of γ^+ Values for the Methyl Group. Solvent Effects. We have calculated γ^+ values for the methyl group, Table I, by applying the modified Hammett–Brown equation,[30] eq 1, to a large body of available data on the solvolysis of *tert*-cumyl (**4**) and *tert*-butyl (**5**) derivatives.

$$\gamma^+ = \frac{\log k - \log k_0}{\rho^+} \tag{1}$$

Equation 1 may be used to calculate a γ^+ value for the methyl group when log *k* (the rate constant for **5**), log k_0 (the rate constant for **4**, X = H), and ρ^+ (for the aryl series **4**) are known.



4



$$\mathrm{Me{-}\overset{\displaystyle Me}{\underset{\displaystyle Me}{C}}{-}L}$$

5

The data in Table I show that the same γ^+ value can be calculated from three different studies in aqueous acetone (entries 1–3). Surprisingly, however, *there appears to be a significant solvent effect on the γ^+ value* calculated in aqueous acetone as compared to that calculated in alcoholic solvents.

A number of reasons for the observed solvent effect can be postulated: (1) there may be a change in mechanism for solvolysis in aqueous acetone as compared to alcoholic solvents; (2) the observed effect may be a leaving group effect; (3) the σ^+ values of the aryl substituents (X in **4**) may vary with solvent causing ρ^+ to be solvent dependent, so that γ^+ may or may not be solvent dependent; and (4) γ^+ may be solvent dependent. These points are considered below.

A change in mechanism from rate-limiting ionization to rate-limiting elimination has been proposed[31] to account for the deviant behavior of *tert*-butyl chloride in aqueous trifluoroethanol (TFE). Thus it is possible that rate-limiting elimination may be occurring for the *tert*-butyl derivatives in the relatively basic alcohol solvents, although such behavior might be just as probable in the *tert*-cumyl derivatives. Nevertheless, this possibility can be experimentally tested. Schleyer et al.[32] have found that, with the exception of aqueous TFE results, a linear relationship results when log *k* for 1-adamantyl bromide in a particular solvent is plotted vs. the *Y* value of that solvent. Since *Y* values were determined from the solvolysis of *tert*-butyl chloride, any point that falls on the log *k*, 2-adamantyl bromide, vs. *Y* plot is considered

Table II. Correlation of Cyclic Methyl-Substituted Chlorides and *p*-Nitrobenzoates with Aryl-Substituted Analogues

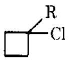
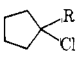
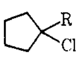
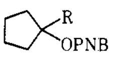
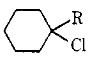
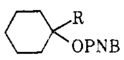
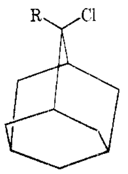
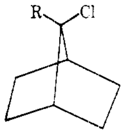
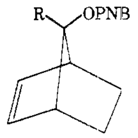
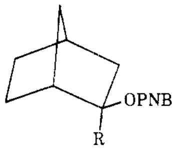
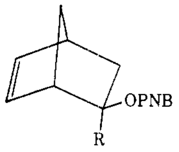
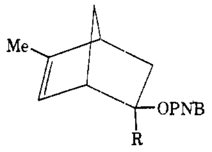
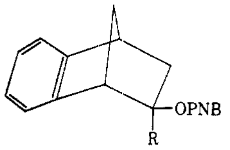
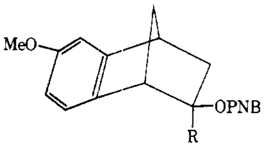
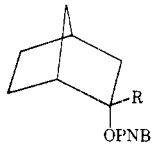
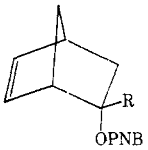
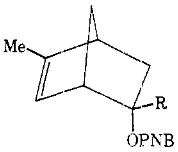
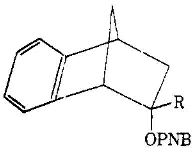
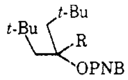
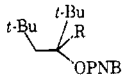
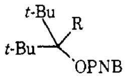
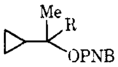
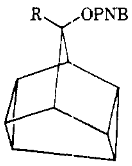
Structure no.	Substrate	ρ^+, R = Ar (Solvent, temp)	k, s^{-1}, R = Ph (log k_0)	k_{calcd}, s^{-1}, R = Me (log k_{calcd})	k_{obsd}, s^{-1}, R = Me (log k_{obsd})	log k_{calcd} − log k_{obsd}
8		-4.48[a] (90% aq acetone, 25°C)	2.74×10^{-5}[a] (-4.56)	4.16×10^{-8} (-7.38)	8.76×10^{-9} (-8.06)	0.68
9		-4.10[a] (90% aq acetone, 25°C)	7.23×10^{-3}[a] (-2.14)	1.91×10^{-5} (-4.72)	5.12×10^{-6}[b] (-5.29)	0.57
10		-4.5[c] (abs ethanol, 25°C)	1.88×10^{-2}[c] (-1.73)	5.25×10^{-5} (-5.28)	3.39×10^{-6}[d] (-5.47)	0.19
11		-3.82[e] (80% aq acetone, 25°C)	2.6×10^{-6}[e] (-5.59)	1.00×10^{-8} (-8.00)	2.11×10^{-9}[f] (-8.68)	0.68
12		-4.65[a] (90% aq acetone, 25°C)	1.96×10^{-5}[a] (-4.71)	2.29×10^{-8} (-7.64)	4.07×10^{-8}[b] (-7.39)	-0.25
13		-4.60[g] (80% aq acetone, 25°C)	1.46×10^{-8}[h] (-7.84)	1.82×10^{-11} (-10.74)	5.48×10^{-11}[i] (-10.26)	-0.48
14		-4.83[a] (90% aq acetone, 25°C)	4.59×10^{-4}[a] (-3.34)	4.17×10^{-7} (-6.38)	9.12×10^{-7}[j] (-6.04)	-0.34
15		-5.64[a] (90% aq acetone, 25°C)	3.98×10^{-8}[a] (-7.40)	1.22×10^{-11} (-10.95)	6.03×10^{-12}[k] (-11.22)	0.27
16		-2.30[l,m] (70% aq dioxane, 25°C)	4.23×10^{-9}[m] (-8.37)	1.51×10^{-10} (-9.82)	4.44×10^{-10}[n] (-9.35)	-0.47
17		-3.83[e] (80% aq acetone, 25°C)	7.56×10^{-6}[o] (-5.12)	2.95×10^{-8} (-7.53)	1.00×10^{-8}[q] (-8.00)	0.47
18		-4.21[r] (80% aq acetone, 25°C)	1.22×10^{-6}[r,s] (-5.91)	2.75×10^{-9} (-8.56)	4.70×10^{-10}[t] (-9.33)	0.77
19		-3.28[u] (80% aq acetone, 25°C)	9.18×10^{-6}[u] (-5.04)	7.76×10^{-8} (-7.11)	5.75×10^{-8}[t] (-7.24)	0.13
20		-4.50[v] (80% aq acetone, 25°C)	2.78×10^{-7}[v] (-6.56)	3.98×10^{-10} (-9.40)	6.31×10^{-11}[w] (-10.20)	0.80
21		-3.72[x] (80% aq acetone, 25°C)	1.36×10^{-6}[x] (-5.87)	6.16×10^{-9} (-8.21)	1.51×10^{-9}[w] (-8.82)	0.61
22		-3.75[e] (80% aq acetone, 25°C)	5.30×10^{-8}[o] (-7.28)	2.29×10^{-10} (-9.64)	1.13×10^{-11}[q] (-10.95)	1.31

Table II (*Continued*)

Structure no.	Substrate	ρ^+, R = Ar (Solvent, temp)	k, s^{-1}, R = Ph (log k_0)	k_{calcd}, s^{-1}, R = Me (log k_{calcd})	k_{obsd}, s^{-1}, R = Me (log k_{obsd})	log k_{calcd} − log k_{obsd}
23		−4.17^r (80% aq acetone, 25°C)	6.03×10^{-9r} (−8.22)	1.41×10^{-11} (−10.85)	5.25×10^{-13t} (−12.28)	1.43
24		−4.19^u (80% aq acetone, 25°C)	7.28×10^{-9u} (−8.14)	1.66×10^{-11} (−10.78)	5.13×10^{-13t} (−12.29)	1.51
25		−4.52^v (80% aq acetone, 25°C)	9.71×10^{-11v} (−10.01)	1.38×10^{-13} (−12.86)	5.5×10^{-14w} (−13.26)	0.40
26		−2.91^y (70% aq acetone, 100°C)	2.79×10^{-4y} (−3.55)	4.17×10^{-6} (−5.38)	1.17×10^{-3y} (−2.93)	−2.45
27		−2.64^y (70% aq acetone, 100°C)	1.20×10^{-3y} (−2.92)	2.63×10^{-5} (−4.58)	2.23×10^{-3y} (−2.65)	−1.93
28		−1.30^y (70% aq acetone, 100°C)	1.38×10^{-4y} (−3.86)	2.09×10^{-5} (−4.68)	7.13×10^{-4y} (−3.15)	−1.53
29		−2.78^z (80% aq acetone, 25°C)	2.41×10^{-4z} (−3.62)	4.27×10^{-6} (−5.37)	3.75×10^{-5aa} (−4.43)	−0.94
30		−2.05^{bb} (80% aq acetone, 25°C)	1.23×10^{-7bb} (−6.91)	6.31×10^{-9} (−8.20)	8.62×10^{-9bb} (−8.06)	−0.14

[a] H. Tanida and T. Tsushima, *J. Am. Chem. Soc.*, **92**, 3397 (1970). [b] Calculated from the rate constant in 80% aqueous EtOH; cf. H. C. Brown and M. Borkowski, *ibid.*, **74**, 1894 (1952), assuming $m = 1$ and $Y = -1.856$, cf. E. M. Kosower, "An Introduction to Physical Organic Chemistry", Wiley, New York, N.Y., 1968, p 306. [c] H. C. Brown and K. Takeuchi, *J. Am. Chem. Soc.*, **88**, 5336 (1966). [d] Calculated from the rate constant in 80% aqueous EtOH, cf. H. C. Brown and M. Borkowski, *ibid.*, **74**, 1894 (1952), assuming $m = 1$ and $Y = -2.033$, cf. E. M. Kosower in footnote *b*. [e] Reference 11. [f] H. C. Brown and W. J. Hammer, *J. Am. Chem. Soc.*, **89**, 6378 (1967). [g] Reference 16. [h] E. N. Peters, unpublished result; see footnote *g*. [i] E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **96**, 263 (1974). [j] Calculated from the value in 80% aqueous ethanol; J. M. Harris, unpublished result quoted by J. M. Harris and S. P. McManus, *ibid.*, **96**, 4693 (1974). [k] Calculated from the rate in 80% aqueous acetone; cf. R. K. Lustgarten, J. Lhomme, and S. Winstein, *J. Org. Chem.*, **37**, 1075 (1972), assuming $m = 1$ and $Y = -1.856$ for 90% aqueous acetone and −0.673 for 80% aqueous acetone, cf. E. M. Kosower in footnote *b*. [l] For the k_Δ portion of the aryl series only. [m] Reference 1. [n] P. G. Gassman and J. M. Pascone, *J. Am. Chem. Soc.*, **95**, 7801 (1973). [o] D. L. Vander Jagt, Ph. D. Thesis, Purdue University, 1967; cf. ref 4. [p] Reference 4. [q] S. Ikegami, D. L. Vander Jagt, and H. C. Brown, *J. Am. Chem. Soc.*, **90**, 7124 (1968). [r] Reference 8. [s] E. N. Peters, and H. C. Brown, *J. Am. Chem. Soc.*, **94**, 7920 (1972). [t] Reference 12. [u] Reference 10. [v] Reference 6. [w] Calculated from values in 50% aqueous acetone using $m = 0.58$ or $k_{50A}/k_{80A} = 24.2$; J. P. Dirlan and S. Winstein, *J. Am. Chem. Soc.*, **91**, 5905 (1969); H. C. Brown and G. L. Trittle, *ibid.*, **88**, 1320 (1966). [x] Reference 5. [y] Reference 26. [z] Reference 7. [aa] Reference 9. [bb] Reference 17.

evidence that *tert*-butyl chloride is solvolyzing with rate-limiting ionization.

We have solvolyzed 1-adamantyl bromide in absolute ethanol and find that the logarithm of its rate constant falls on the plot of log k for 1-adamantyl bromide against Y. The aqueous acetone solvolyses have previously been correlated.[32] Hence the solvent effect on the γ^+ constant calculated for the methyl group is not indicated to be a result of a change in mechanism.

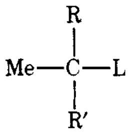
When entries 1 and 2 of Table I are compared with entry 3, one notes that essentially the same value for γ^+ is calculated for solvolysis of the *p*-nitrobenzoates in aqueous acetone as for chlorides in aqueous acetone. Therefore, there seems to be no leaving group effect on the γ^+ constant.[33]

The possibility that σ^+ values for aryl substituents are solvent dependent has been considered before, but there is little evidence indicating that this is a general problem.[34,35] Thus we dismiss this as the cause of the calculated solvent effect on the γ^+ constant.

We therefore conclude that γ^+ for the methyl group is solvent dependent. If this conclusion withstands further scrutiny, it implies that alkyl groups in general have a solvent dependent electronic effect when compared to aryl groups. Also, in the application of the Taft equation, σ^* values obtained in one solvent may not be applicable in another solvent.[36]

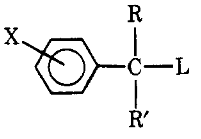
Use of γ^+ Values in Evaluating Structural Effects. Recognizing the limitations imposed by the above conclusion, we have used our γ^+ values to compare calculated rate constants for solvolysis of methyl-substituted tertiary substrates (**6**) with the corresponding aryl-substituted tertiary substrates

(7), Table II. The γ^+ value of 0.63 was used for calculations in aqueous acetone and aqueous dioxane and the γ^+ value of 0.79 was used for calculations in absolute ethanol.



$$\mathrm{Me{-}\overset{\displaystyle R}{\underset{\displaystyle R'}{C}}{-}L}$$

6

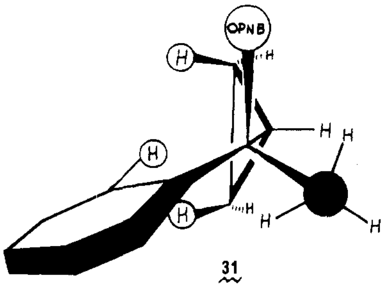


7

Examination of Table II shows that the rate of the methyl-substituted compound is calculated within 0.7 log units for most systems. While it might be tempting to evaluate any difference between the calculated and observed rates, we have assumed that a difference between log k_{calcd} and log k_{obsd} for **6** of less than 0.7 represents the limits of our method, and is thus consistent with there being no significant steric effect on the magnitude of ρ^+. Differences greater than ~0.7 are assumed to reflect an unusual effect.

There are two mechanistic types among the substrates studied which fall within the "normal" category. Compounds **8–15, 17,** and **25** describe substrates which solvolyze by a k_c mechanism, and entries **16, 19, 21,** and **30** are examples of substrates which solvolyze by k_Δ mechanisms.[37] Thus it appears that our method is applicable to both k_c and k_Δ mechanisms as long as the ρ^+ used for calculating log k for the methyl-substituted tertiary derivative is from a linear plot for the range of aryls which includes phenyl and *p*-trifluoromethylphenyl.[38]

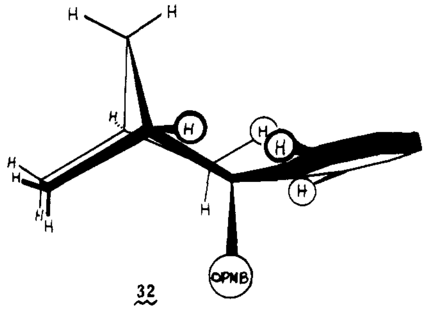
It is interesting to note the entries which correlate poorly, that is, those for which log k_{calcd} − log $k_{\mathrm{obsd}} > \pm 0.7$. We believe that these systems are examples in which unusual steric factors are operating. Entry **29** provides an example. It is well established that the cyclopropyl group requires a bisected conformation for maximum conjugation with the developing positive center.[39] Steric factors which prohibit this conformation reduce stabilization by the cyclopropyl group. Examination of molecular models shows that if the aryl group is put in a configuration where it can best stabilize the incipient cationic center in **29**, the cyclopropyl group in *either* bisected configuration interferes; e.g. structure **31**.[40] Thus, it is likely that the aryl groups do not offer their normal stabilizing effect because of steric inhibition to resonance. The sign of the variance (methyl faster than predicted by calculation from aryl rates) is consistent with this explanation.



31

Compounds **26, 27,** and **28** are well known[26] examples of substrates where, like compound **29**, steric effects prevent the aryl groups from providing their full stabilizing effect. With these compounds the methyl group is far better at stabilizing the transition state than aryl groups with σ^+ values similar to the γ^+ value of the methyl group.

The final group of compounds that correlate poorly, **22–24**, are of interest because a great deal of attention has been given to them. Brown has claimed that these *endo*-2-norbornyl derivatives all ionize slowly because of steric hindrance to ionization.[21] Since both the aryl- and methyl-substituted compounds should be subject to the same steric hindrance to ionization, the failure of our γ^+ method to accurately predict the rates of the methyl-substituted compounds for **22, 23,** and **24** must have some origin other than that suggested by Brown. A possible explanation can be based on the nonbonded interaction of the exo aryl groups with the C-1 and exo C-3 hydrogens as shown in **32**. The aryl group must adopt the conformation shown if it is to provide effective stabilization of the developing positive center. As ionization proceeds and the aryl group swings down, the nonbonded interactions shown in **32** are relieved. There is no counterpart for this strain relief in the methyl group. Consequently, the aryl series is fast relative to the methyl-substituted derivative, and a positive value of log k_{calcd} − log k_{obsd} is observed for the methyl-substituted derivative.



32

A cursory comparison of ρ^+ values for the *exo*- and *endo*-2-norbornyl derivatives (e.g., compare compounds **17** and **22**, and **18** and **23**) indicates nothing unusual about either series.[41] The exo and endo derivatives having similar ρ^+ values has been assumed to mean that the isomeric pairs have similar mechanisms with similar electron demand.[8,11,13] We have just concluded that steric factors affect the magnitude of ρ^+ values for the endo derivatives **22–24**. Examination of the log k_{calcd} − log k_{obsd} values for the corresponding exo derivatives (**17–19**) shows that steric effects are relatively unimportant. Thus the similarity of ρ^+ values for these exo and endo isomers must result from a blending of electronic and steric factors, and the prior assumption that the isomers react with similar electron demand at the developing cationic center must be incorrect.[42]

In summary, low Ph/Me rate ratios and low ρ^+ values have been taken as evidence for neighboring group participation.[43] However, our treatment reveals that these parameters can be dramatically influenced by steric factors. Those instances in which steric complications are involved can be readily identified by use of the method described in this article. Hence we strongly encourage the use of this method of assessing the steric characteristics of a reaction when Ph/Me rate ratios and ρ^+ values are to be utilized as mechanistic probes.

Finally, ρ^+ values may be unusually low for steric reasons, because of neighboring group effects, or because of a combination of these factors. For example, the solvolysis of **27** results in low values of the Ph/Me rate ratio and of ρ^+,[26] yet the high negative value of log k_{calcd} − log k_{obsd} (Table II) shows that the "low" values actually result from steric inhibition to resonance when R = aryl. In **30**, however, no unusual steric factors are indicated, and the low Ph/Me rate ratio and low ρ^+ values are assignable solely to the presence of σ participation[17] which lowers the requirement for stabilization by the group R whether it be methyl or aryl. For **29**, a low ρ^+ value combined with a negative value of log k_{calcd} − log k_{obsd} of 0.94 signals that a combination of steric and electronic factors are causing the observed change in ρ^+ as compared to model compounds.[44]

Experimental Section

Ethanolysis of 1-Adamantyl Bromide. The solvolysis rate of

1-adamantyl bromide in absolute ethanol was measured in routine fashion:[32]

Temp, °C	k, s^{-1}
119.9 ± 0.1	$1.22 \pm 0.02 \times 10^{-3}$
100.3	$1.58 \pm 0.18 \times 10^{-4}$
75.6	5.06×10^{-6}
75.1	3.53×10^{-6}
25.0 (extrapolated)	8.64×10^{-10}

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research (S.P.M.). Discussions with Professors H. C. Brown, D. J. Raber, P. E. Peterson, P. v. R. Schleyer, and T. T. Tidwell are also acknowledged.

Registry No.—**8** (R = Me), 10523-97-4; **9** (R = Me), 61491-20-1; **10** (R = Me), 6196-85-6; **11** (R = Me), 19013-42-4; **12** (R = Me), 931-78-2; **13** (R = Me), 31058-46-5; **14** (R = Me), 37723-65-2; **15** (R = Me), 33686-58-7; **16** (R = Me), 33686-61-2; **17** (R = Me), 22467-58-9; **18** (R = Me), 55829-78-2; **19** (R = Me), 57955-29-0; **20** (R = Me), 7525-46-4; **21** (R = Me), 26184-43-0; **22** (R = Me), 13351-30-9; **23** (R = Me), 55829-76-0; **24** (R = Me), 55829-77-1; **25** (R = Me), 7572-53-4; **26** (R = Me), 40544-08-9; **27** (R = Me), 40544-09-0; **28** (R = Me), 40544-10-3; **29** (R = Me), 23437-99-2; **30** (R = Me), 61491-21-2; methyl, 2229-07-4.

References and Notes

(1) P. G. Gassman and A. F. Fentiman, Jr., *J. Am. Chem. Soc.*, **92**, 2549 (1970).

(2) H. C. Brown and M.-H. Rei, *J. Am. Chem. Soc.*, **86**, 5008 (1964).

(3) H. C. Brown and K. Takeuchi, *J. Am. Chem. Soc.*, **90**, 2691, 2693 (1968).

(4) K. Takeuchi and H. C. Brown, *J. Am. Chem. Soc.*, **90**, 2693 (1968).

(5) H.C. Brown and K.-T. Liu, *J. Am. Chem. Soc.*, **91**, 5909 (1969).

(6) H. C. Brown, S. Ikegami, and K.-T. Liu, *J. Am. Chem. Soc.*, **91**, 5911 (1969).

(7) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **95**, 2397 (1973).

(8) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **95**, 2398 (1973).

(9) H. C. Brown and E. N. Peters, *J. Am. Chem. Soc.*, **95**, 2400 (1973).

(10) H. C. Brown, M. Ravindranathan, and E. N. Peters, *J. Am. Chem. Soc.*, **96**, 7351 (1974).

(11) H. C. Brown, M. Ravindranathan, K. Takeuchi, and E. N. Peters, *J. Am. Chem. Soc.*, **97**, 2899 (1975).

(12) H. C. Brown, E. N. Peters, and M. Ravindranathan, *J. Am. Chem. Soc.*, **97**, 2900 (1975).

(13) H. C. Brown and E. N. Peters, *J. Am. Chem. Soc.*, **97**, 7442 (1975).

(14) H. C. Brown, E. N. Peters, and M. Ravindranathan, *J. Am. Chem. Soc.*, **97**, 7449 (1975).

(15) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **97**, 7454 (1975).

(16) H. C. Brown, M. Ravindranathan, and M. M. Rho, *J. Am. Chem. Soc.*, **98**, 4216 (1976).

(17) H. C. Brown and M. Ravindranathan, *J. Am. Chem. Soc.*, **99**, 299 (1977).

(18) For a brief review on the use of this method see B. Capon and S. P. McManus, "Neighboring Group Participation", Vol. 1, Plenum Press, New York, N.Y., 1976, pp 89–94.

(19) Pi participation has been ruled out in some cases; cf. ref 15.

(20) G. D. Sargent, *Q. Rev., Chem. Soc.*, **20**, 301 (1966); G. D. Sargent in "Carbonium Ions", Vol. 3, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1972, pp 1175–1177.

(21) H. C. Brown, *Acc. Chem. Res.*, **6**, 377 (1973); *Tetrahedron*, **32**, 179 (1976).

(22) M.-H. Rei and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 5335 (1966).

(23) H. L. Goering and C. B. Schewene, *J. Am. Chem. Soc.*, **87**, 3516 (1965).

(24) H. C. Brown, private communication.

(25) Cf. E. L. Eliel in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1956, pp 88–92.

(26) H. Tanida and H. Matsumura, *J. Am. Chem. Soc.*, **95**, 1586 (1973).

(27) For example, the barrier to rotation in the ethyl cation is close to zero; cf. L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94**, 5935 (1972), and references cited therein.

(28) The designation given is to avoid confusion between the σ^+ for the methyl group as an aryl substituent and a constant useful in correlating reaction rates where methyl is directly attached to a reaction center; cf. ref 29. E. N. Peters [*J. Am. Chem. Soc.*, **98**, 5627 (1976)] sets the precedent for the use of γ^+.

(29) K. Oyama and T. T. Tidwell, *J. Am. Chem. Soc.*, **98**, 947 (1976).

(30) Review: P. R. Wells, "Linear Free Energy Relationships", Academic Press, New York, N.Y., 1968. Peters, cf. ref 28, discusses the modification.

(31) J. M. Harris, D. J. Raber, W. C. Neal, Jr., and M. D. Dukes, *Tetrahedron Lett.*, 2331 (1974).

(32) D. J. Raber, R. C. Bingham, J. M. Harris, J. L. Fry, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 5977 (1970).

(33) No temperature effect on the value of ρ^+ is evident; cf. entries 2 and 3 vs. entry 1, Table I.

(34) Y. Okamota, T. Inukai, and H. C. Brown, *J. Am. Chem. Soc.*, **80**, 4972 (1958).

(35) There are exceptions; cf. D. N. Kevill, K. C. Kolwyck, D. M. Shold, and C.-B. Kim, *J. Am. Chem. Soc.*, **95**, 6022 (1973).

(36) The discussion here could include solvent effects on ρ^+ and ρ^* but the reasoning tends to become cyclical and largely conjectural.

(37) Refer to Table II for references for a particular system.

(38) The σ^+ value for p-CF_3 is 0.61. Thus, this group should generally have a polar response similar to the methyl group.

(39) H. G. Richey, Jr., in "Carbonium Ions", Vol. 3, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1972, Chapter 25; K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe, III, *ibid.*, Chapter 26.

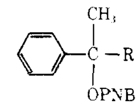
(40) The alternate configuration with a bisected cyclopropyl group has nonbonding interactions between the cyclopropyl C-1 hydrogen and the aryl group. It is difficult to determine from models which conformation is the poorer.

(41) M. A. Battiste and R. A. Fiato, *Tetrahedron Lett.*, 1255 (1975), have treated the constancy of the exo/endo rate ratio of 2-norbornyl derivatives.

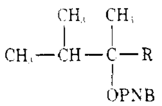
(42) It is bothersome to see that entry **25**, an *endo*-norbornyl derivative, behaves "normally". Apparently some other factor has become important to change the steric requirements for ionization. There, of course, may be alternate explanations for these endo derivatives since it is observed that *exo*-2-norbornyl derivatives with a 5,6 double bond or with a 5,6 fused aryl group, i.e., **18, 20,** and **21,** correlate somewhat poorly

(43) For example, ref 17.

(44) After submission of this manuscript, experimental data on two interesting systems were found in preprints kindly furnished by Professor H. C. Brown.



i, R = CH_3 or Ar



ii, R = CH_3 or Ar

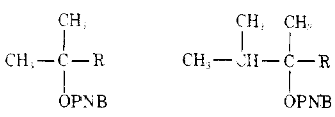
The systems are the 1-substituted 1-phenyl-1-ethyl-*p*-nitrobenzoate (i) and the 2-substituted 3-methyl-2-butyl-*p*-nitrobenzoate (ii). Using the format of Table II, the pertinent data for the aryl/methyl treatment (all rates are for solvolysis in *80%* aqueous acetone extrapolated to 25 °C) are

Substrate	ρ^+, R = Ar	Log k_0, R = Ph	Log k_{calcd}, R = Me	Log k_{obsd}, R = Me	Log k_{calcd} − log k_{obsd}
i	-3.23^a	-6.11^a	−8.15	-7.14^b	−1.01
ii	-4.76^c	-8.02^c	−11.02	-9.67^d	−1.35

[a] H. C. Brown, M. Ravindranathan, and E. N. Peters, unpublished results. [b] Reference 9. [c] H. C. Brown, E. N. Peters, and M. Ravindranathan, *J. Am. Chem. Soc.*, **99**, 505 (1977). [d] E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **96**, 263 (1974).

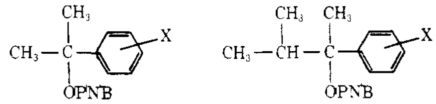
The γ^+ treatment clearly indicates that the aryl-substituted tertiary systems i and ii *suffer from a degree of steric hindrance to ionization*. Thus, when i bears two aryl groups, both cannot stabilize the transition state to an equal extent because of steric factors; hence the ρ^+ value is lowered for the series i, R = Ar. 1-Aryl-1-phenylethyl cations have been well studied (cf. ref 45) and are known to have the aryl groups in a propeller-like conformation owing to nonbonding interactions between the ortho protons. Our results then imply that the steric factors also operate in the transition *state to form these cations.*

The result with ii was surprising since we did not expect the isopropyl group to interfere with aryl conjugation in ii, R = Ar; yet, as indicated by a log k_{calcd} − log k_{obsd} of −1.35, an effect is apparent. The following rate comparison taken from data in our tables verifies that the steric effect is real.



k_{rel}, R = Me	1.0	2.9
k_{rel}, R = Ph	1.0	0.131

Furthermore, Hart and Law (ref 46) concluded that the isopropyl group is more sterically demanding than the cyclopropyl group. Thus, our intuition must yield to the data forcing the conclusion that ii, R = Ar, is experiencing steric inhibition to resonance stabilization of the solvolytic transition state. This conclusion, however, is difficult to accept since the ρ^+ value *is not lowered* by replacing methyl with isopropyl. Further study may be necessary *before this dilemma is resolved.*



ρ^+	−4.72	−4.76

(45) B. Ancian, J.-P. Doucet, and J.-E. Dubois, *J. Am. Chem. Soc.*, **98, 4764** (1976).

(46) H. Hart and P. A. Law, *J. Am. Chem. Soc.*, **86,** 1957 (1964).