Table II. Comparison of Swain–Scott Type Compound Parameters from Various Sources

R	$m_{\mathrm{PW}}/1.451$ ROTs	m_{SMB} RBr	m_{AF} ROTs	m_{EW} ROTs	s_{PW} ROTs	s_{SMB} RBr	s_{SMB} ROTs
Methyl	0.30[a]	0.33	0.30[a,b]	0.23[a,c]	0.9[a]	1.00	
Ethyl	0.41[a]	0.41	0.37[a,b]	0.25[d,c]	0.75[a]	0.83	0.77
Propyl	0.39[a,e]				0.71[a]	0.81[f]	
Isobutyl	0.36[a,e]				0.65[a]		
Isopropyl	0.70[g]	0.62	0.72[g,h]	0.42[g,c]	0.58[g]	0.60	0.28[i]
2-Butyl	0.68[g]		0.70[g,j]		0.39[g]		
3-Heptyl	0.70[g]		0.71[g,j]		0.28[g]		
2-Adamantyl	0.88[g]		0.89[g,c]	0.91[g,c]	0.0[g]		

[a] 75°. [b] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 64. [c] Reference 6b. [d] 50°. [e] The *m* value was calculated using the estimated value for k_s, which reflects solvolysis without neighboring group participation; *cf.* I. L. Reich, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 5635 (1969). [f] *n*-Butyl. [g] 25°. [h] Reference 6d. [i] Brosylate. [j] P. E. Peterson, R. E. Kelley, Jr., R. Belloli, and K. A. Sipp, *J. Amer. Chem. Soc.*, **87**, 5169 (1965).

Table III. Comparison of Solvent Nucleophilicity Scales

Nucleophile	N_{PW}[a]	N_{SMB}	N_{SFLL}[b]	N_{SS}[c]
I^-				5.04
HO^-				4.20
$CH_3CO_2^-$				2.72
EtOH, 100%	0.76[d]	−0.19	0.9	
80%	0.00[d]	0.00	0.00	
50%			−0.80	
H_2O		−0.44		0.00
MeOH		+0.02		
Acetone, 90%		−0.16		
50%		−0.06		
Formic acid	−1.52	−2.46	−1.60	
Acetic acid	−1.66	−2.46	−1.00	
Chloroacetic acid	−2.65			
Dichloroacetic acid	−3.91			
Trifluoroacetic acid	−5.33		−4.35	

[a] Values from Table I referenced to 80% EtOH by subtracting 0.27. [b] Reference 6d; values scaled to 80% EtOH. [c] Reference 3b. [d] Based on methyl tosylate solvolysis data *s* and *m* values (PW) from Table II.

insensitive to nucleophilicity, since the solvolyses proceed by phenyl participation pathways.[5]

Rearranging eq 2 yields eq 8, which indicates that for

$$\log (k_{\mathrm{A}}/k_{\mathrm{B}}) = m[(s/m)N_{\mathrm{A}}{}^{\mathrm{B}} + Y_{\mathrm{A}}{}^{\mathrm{B}}] \qquad (8)$$

a series of compounds having increasing *s* values plots of log *k vs.* *Y* may be increasingly nonlinear. The hindered secondary, primary, and methyl tosylates fulfill this expectation (*cf.* Figure 1), confirming the influence of nucleophilicity upon solvolytic rates[6] in carboxylic acid solvents.

By adding the term, $(s/m)N$, to the ordinates, the nonlinear plots of Figure 1 may be corrected to straight lines for log *k* data in acetic, formic, and trifluoroacetic acid (designated $\log k^{\mathrm{A}}$, $\log k^{\mathrm{F}}$, and $\log k^{\mathrm{T}}$). It may be shown that s/m is given by eq 9. Using this value of s/m, we obtain *m* and *s* by application of eq 8. The resulting values, designated m_{PW} and s_{PW} are given in Table II, along with the Swain–Mosely–Bown values and values obtained from data for *tert*-butyl chloride reacting in acetic–formic acids (AF) and ethanol–water (EW).

$$\frac{s}{m} = \frac{[(Y^{\mathrm{F}} - Y^{\mathrm{A}})/(\log k^{\mathrm{F}} - \log k^{\mathrm{A}}) - (Y^{\mathrm{A}} - Y^{\mathrm{T}})/(\log k^{\mathrm{A}} - \log k^{\mathrm{T}})]}{[(N^{\mathrm{A}} - N^{\mathrm{T}})/(\log k^{\mathrm{A}} - \log k^{\mathrm{T}}) - (N^{\mathrm{F}} - N^{\mathrm{A}})/(\log k^{\mathrm{F}} - \log k^{\mathrm{A}})]} \qquad (9)$$

In Table III both sets (PW and SMB) of the previously unavailable nucleophilicity parameters, *N*, are tabulated, along with a scale recently suggested by Schleyer, Fry, Lam, and Lancelot[6d] and some ion nucleophilicity values of Swain and Scott.[3b]

The approximate agreement among various parameters shown in Tables II and III should encourage further exploration of the approaches outlined here and elsewhere.[7]

Acknowledgment. We thank Professor Paul Schleyer for informing us of his alternative treatment (accompanying communication[7]). D. Warren Vidrine contributed to the derivation of eq 4–7. Support by the National Science Foundation (Grant No. GP 10919) is gratefully acknowledged.

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(5) (a) A. Diaz, I. Lazdins, and S. Winstein, *J. Amer. Chem. Soc.*, 90, 6546 (1968); (b) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2763 (1956).

(6) (a) P. E. Peterson, R. J. Bopp, D. M. Chevli, E. L. Curran, D. E. Dillard, and R. J. Kamat, *ibid.*, **89**, 5902 (1967); (b) J. L. Fry, C. J. Lancelot, L. K. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **92**, 2538 (1970); (c) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **92**, 2540 (1970); (d) P. v. R. Schleyer, J. L. Fry, L. K. Lam, and C. J. Lancelot, *ibid.*, **92**, 2542 (1970).

(7) T. W. Bentley, F. L. Schadt, and P. v. R. Schleyer, *ibid.*, **94**, 992 (1972).

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Correlation of Solvolysis Rates with Three- and Four-Parameter Relationships. A Scale of Solvent Nucleophilicities

Sir:

It was recognized 20 years ago[1] that the effect of variation of solvents on solvolysis rates might be correlated by an equation of the type[1–3]

$$\log (k/k_0) = lN + mY \qquad (1)$$

Here *l* and *m* are substrate sensitivity factors; *Y* is a measure of the "ionizing power" of the solvent and *N* of its "nucleophilicity." However, this equation

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(1) S. Winstein, E. Grunwald, and H. W. Jones, *J. Amer. Chem. Soc.*, 73, 2700 (1951).

(2) S. Winstein, A. H. Fainberg, and E. Grunwald, *ibid.*, **79**, 4146 (1957).

(3) For a critical review of the background to this paper, see A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, pp 43–49, 63–66.

was never explicitly evaluated. Instead, the lN term was considered either to make a negligible contribution or to be relatively constant, and eq 2 generally has been employed.[1–3]

$$\log (k/k_0) = mY \qquad (2)$$

Although eq 2 strictly should be applicable only to limiting SN1-type solvolyses, even SN2 substrates, such as methyl tosylate, correlate well within a restricted series of solvents, such as ethanol–water mixtures. The deficiencies of eq 2 are revealed by the dispersion of points found with most primary and secondary substrates when a wider range of solvents is employed.[1,3]

Swain and Scott[4] proposed eq 3 consisting of nucleophilicity (sn) and electrophilicity ($s'e$) terms. Only the sn term was evaluated but not for solvents, only for various nucleophiles. A similar equation with different symbols was employed empirically by Swain, Mosely, and Bown,[5] but the arbitrary choice of conditions imposed has been severely criticized.[2,3] Another approach, represented by eq 4, showed promise,[6] but has received little further attention.

$$\log (k/k_0) = sn + s'e \qquad (3)$$

$$\log (k/k_0) - \log (k/k_0)_{\mathrm{CH_3Br}} = ab \qquad (4)$$

Peterson and Waller have recently proposed several ways to evaluate equations of type 1 and 3.[7] The most direct of these involves the explicit determination of the nucleophilicities of solvents by low-temperature measurements of rates of displacement on tetramethylenehalonium ions in liquid SO_2. Unfortunately, this method is neither easy to carry out nor yet applicable to noncarboxylic acid solvents.

We propose here two practical approaches to this problem. The first utilizes a three-parameter equation (eq 5) which permits good correlation for compounds subject to varying amounts of solvent (but not anchimeric) assistance. The second proposal presents a simple way (eq 6) to evaluate the N (nucleophilicity) parameter in eq 1.

The three-parameter approach (eq 5) involves the use of *two* reference substrates, where (k/k_0) = the rate

$$\log (k/k_0) = (1 - Q) \log (k^{\mathrm{A}}/k_0^{\mathrm{A}}) + Q \log (k^{\mathrm{B}}/k_0^{\mathrm{B}}) \qquad (5)$$

of solvolysis of the substrate in a given solvent relative to 80% ethanol, $(k^{\mathrm{A}}/k_0^{\mathrm{A}})$ = the rate of solvolysis of the reference substrate A (with high sensitivity to nucleophilicity) in a given solvent relative to 80% ethanol, $(k^{\mathrm{B}}/k_0^{\mathrm{B}})$ = the rate of solvolysis of the reference substrate B (with low sensitivity to nucleophilicity) in a given solvent relative to 80% ethanol, and Q = an adjustable blending parameter ideally depending only on the substrate and reflecting its sensitivity to solvent nucleophilicity relative to the standards chosen.

The possible use of different standard substrates, A and B, provides added flexibility since it is now apparent that there are substantial leaving group and symbiotic effects, the latter expected to be more important in SN2 than SN1 processes.[2,6,8,9] These leaving group effects contribute to the dispersions often found when eq 2 is employed. In this paper we describe tosylate correlations using methyl tosylate as reference substrate A, and 2-adamantyl tosylate as reference substrate B.[10] Solvolysis of methyl tosylate depends on both ionizing power and nucleophilicity (see below), but it is a convenient model for incorporating a term for nucleophilicity or SN2-type behavior into eq 2. Detailed studies of the mechanism of solvolysis of 2-adamantyl tosylate[11] have provided a wide body of data and established that the solvents played little or no role as nucleophiles; therefore, 2-adamantyl is a satisfactory reference for SN1-type behavior.

Values of Q are shown in Table I.[12] The average of the standard deviations in $\log (k/k_0)$ is 0.18. This agreement is certainly very good considering the wide range of reactivities (nearly 10^9), solvents, and sources of data, and the fact that errors due to extrapolation to common temperatures are also included. Even omitting the primary compounds of Table I, the average of the standard deviations by eq 2 is 0.37 in $\log (k/k_0)$ for the same set of solvents; for all nonreference compounds this average is much worse, 0.51. The average value of the probable error (r) for the treatment of the data in Table I by eq 5 is 0.17.[2]

The high precision of the correlations using eq 5 appears to justify the assumption inherent in this treatment: there is a continuum of solvolytic behavior from methyl to 2-adamantyl. Although detailed mechanistic information is not provided,[18] the Q values fit nicely into an expected pattern: the lower the Q value the more sterically accessible the substrate is to nucleophilic attack. Equation 5 is applicable to k_s- but not to k_Δ-type substrates. For the latter it would be necessary to introduce a proportionality factor into eq 5. We prefer to consider such substrates by the more general treatment, eq 1.

Peterson and Waller[7] have recently shown that acetic and formic acids are almost equally reactive toward halonium ions in SO_2 as solvent. As this reaction

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[4] C. G. Swain and C. B. Scott, *J. Amer. Chem. Soc.*, **75**, 141 (1953).

[5] C. G. Swain, R. B. Mosely, and D. E. Bown, *ibid.*, **77**, 3731 (1955).

[6] C. G. Swain, D. C. Dittmer, and L. E. Kaiser, *ibid.*, **77**, 3737 (1955), and references therein.

[7] P. E. Peterson and F. J. Waller, *ibid.*, **94**, 991 (1972).

[8] R. G. Pearson and J. Songstad, *J. Org. Chem.*, **32**, 2899 (1967).

[9] H. M. R. Hoffmann, *J. Chem. Soc.*, 6753 (1965).

[10] In evaluating eq 4, similar in spirit to eq 5, Swain and Ditimer[6] chose methyl bromide and *tert*-butyl chloride as standards. *tert*-Butyl chloride may be used in place of 2-adamantyl tosylate in eq 5, but the resulting fit is not as good. Tosylates correlate best with tosylate data.[6]

[11] (a) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2538 (1970); (b) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **92**, 2540 (1970); (c) P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *ibid.*, **92**, 2542 (1970); (d) J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **93**, 2551 (1971); (e) D. J. Raber, J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **93**, 4821 (1971); (f) V. J. Shiner, Jr., and R. D. Fisher, *ibid.*, **93**, 2553 (1971).

[12] The necessary kinetic data (sec^{-1}) for methyl tosylate are provided in Table II, and for 2-adamantyl tosylate at 25° are: acetic acid, $k = 5.9 \times 10^{-9}$;[11c,13] formic acid, $k = 2.6 \times 10^{-5}$;[14,15] trifluoroacetic acid, $k = 9.0 \times 10^{-4}$;[15,16] 50% (v/v) aqueous ethanol, $k = 4.7 \times 10^{-7}$;[13–15] 80% v/v aqueous ethanol, $k = 2.4 \times 10^{-8}$;[11c,13] ethanol, $k = 6,3 \times 10^{-10}$;[17] methanol, $k = 3.5 \times 10^{-9}$.[17]

[13] Calculated from values at other temperatures.

[14] Unpublished work.

[15] Redetermination of data previously reported in ref 11c.

[16] R. E. Hall, A.B. Thesis, Princeton University, 1970.

[17] Calculated from eq 1 using 50, 60, 80, and 90% v/v ethanol–water.

[18] Several workers[19] now favor ion-pair mechanisms for solvolyses of primary substrates.

[19] (a) R. A. Sneen and J. W. Larsen, *J. Amer. Chem. Soc.*, **91**, 6031 (1969); (b) J. M. W. Scott, *Can. J. Chem.*, **48**, 3807 (1970); (c) see also V. J. Shiner, Jr., and W. Dowd, *J. Amer. Chem. Soc.*, **91**, 6528 (1969).

Table I. Comparison of Q (Eq 5) and m (Eq 2) Treatments[a]

Tosylate	Q[b]	Std dev log (k/k_0)	m[c]	Std dev log (k/k_0)	Solvents[d]	Ref to data
Methyl	0.00[e]		−0.34	1.54	1–7	*g*
Ethyl	0.16	0.12	−0.14	1.24	1–7	*h–l*
Benzyl	0.22[f]	0.09[f]	0.67	0.87	1–3, 5	*h*
2-Propyl	0.56	0.19	0.36	0.49	1–7	*i, m–s, z*
2-Butyl	0.64	0.21	0.47	0.40	1, 3–7	*m, o, p, t*
Cyclopentyl	0.67	0.18	0.50	0.32	1–3, 5–7	*s, u–x*
2-Pentyl	0.69	0.19	0.52	0.40	3–7	*m, o, p*
3-Pentyl	0.69	0.27	0.54	0.33	2–7	*m, o, p, t*
4-Heptyl	0.76	0.23	0.61	0.28	3–7	*m, o, p*
Cyclohexyl	0.75	0.14	0.62	0.24	1–7	*m, u–y*
2-Adamantyl	1.00[e]		0.93	0.54	1–7	*g*

[a] Data are at 25° except methyl and ethyl which are at 50°. [b] Values of $1-Q$ are approximately equivalent to the l values of eq 1 (see text). [c] From eq 2. [d] Solvent designations: 1 = methanol; 2 = ethanol; 3 = 80% (v/v) aqueous ethanol; 4 = 50% (v/v) aqueous ethanol; 5 = acetic acid; 6 = formic acid; 7 = trifluoroacetic acid. [e] By definition. [f] Inclusion of formolysis data (H. C. Brown, R. Bernheimer, C. J. Kim, and S. C. Scheppele, *J. Amer. Chem. Soc.*, **89**, 370 (1967)) produces substantial dispersion; Q is raised to 0.49 and the standard deviation in log (k/k_0) is increased to 0.41. [g] Reference 12. [h] Reference 1. [i] R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953). [j] S. Winstein and H. Marshall, *J. Amer. Chem. Soc.*, **74**, 1120 (1952). [k] I. Lazdins Reich, A. Diaz, and S. Winstein, *ibid.*, **91**, 5635 (1969). [l] E. Tommila and J. Juttla, *Acta Chem. Scand.*, **6**, 844 (1952). [m] Reference 14. [n] P. M. Laughton and R. E. Robertson, *Can. J. Chem.*, **33**, 1207 (1955). [o] C. J. Lancelot, J. J. Harper, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 4294 (1969). [p] P. E. Peterson, R. E. Kelley, Jr., R. Belloli, and K. A. Sipp, *ibid.*, **87**, 5169 (1965). [q] J. E. Nordlander and W. J. Kelly, *ibid.*, **91**, 996 (1969). [r] A. Streitwieser, Jr., and G. A. Dafforn, *Tetrahedron Lett.*, 1263 (1969). [s] W. Hückel and K. Tomopulos, *Justus Liebigs Ann. Chem.*, **610**, 78 (1957). [t] W. Hückel and Y. Riad, *ibid.*, **678**, 19 (1964). [u] S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *J. Amer. Chem. Soc.*, **74**, 1127 (1952). [v] D. D. Roberts, *J. Org. Chem.*, **33**, 118 (1968). [w] D. D. Roberts and W. Hendrickson, *ibid.*, **34**, 2415 (1969). [x] W. Hückel and H. D. Sauerland, *Justus Liebigs Ann. Chem.*, **592**, 190 (1955). [y] S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.*, **77**, 5562 (1955). [z] Reference 11c.

Table II. Estimates of the Nucleophilicities of Solvents

Solvent	CH_3OTs $k_{50°}$, sec^{-1}	N_{BS}[a]	N_{PW}[b]	Ref to data
2-Propanol	4.14×10^{-6} [e]	+0.09		*g*
Ethanol	6.55×10^{-6} [e]	+0.09	+0.76	*h*
Methanol	1.06×10^{-5}	+0.01		*h*
80% v/v aqueous ethanol	2.22×10^{-5}	0.00	0.0	*h*
56% w/w aqueous acetone	1.22×10^{-5} [d]	−0.47[c]		*i*
50% v/v aqueous ethanol	4.41×10^{-5}	−0.20		*h*
Water	1.38×10^{-4}	−0.26		*j*
50% w/w aqueous dioxane	2.29×10^{-5}	−0.41[c]		*h*
Acetic acid	6.32×10^{-8} [e]	−2.05	−1.52	*k*
Formic acid	8.3×10^{-7} [e]	−2.05	−1.66	*k*
Trifluoroacetic acid	1.43×10^{-9} [e]	−5.55	−5.33	*l*
Fluorosulfonic acid	8.17×10^{-4}	~−5.5[f]		*m*

[a] Defined by eq 7. [b] Reference 7. [c] Values for other mixtures can be calculated from available data for ethyl benzenesulfonate (see Table I, footnotes *i* and *l*). [d] Estimate based on methyl benzenesulfonate. [e] Extrapolated values. [f] Assuming $Y = 20$ (based on neophyl tosylate; see Table I, footnote *k*). [g] J. B. Hyne and R. E. Robertson, *Can. J. Chem.*, **34**, 863 (1956). [h] See Table I, footnote *i*. [i] See Table I, footnote *l*. [j] R. E. Robertson, *Can. J. Chem.*, **33**, 1536 (1955). [k] See Table I, footnote *j*. [l] See Table I, footnote *k*. [m] A. Diaz, I. Lazdins Reich, and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 5637 (1969).

should be almost independent of the ionizing power of the acids, it follows that acetic and formic acids are almost equally nucleophilic, thus confirming earlier conclusions.[1,3] This means that the "apparent m" values (designated by Peterson and Waller and hereafter as m_{AF}) of Winstein,[1,3,20] determined from eq 2 by using acetic and formic acids, should be reasonably good approximations for the "true" susceptibility of substrates to solvent ionizing power, and suggests a simple method (eq 6) for evaluating the nucleophilicity lN term of eq 1 for any solvent.

$$lN = \log (k/k_0) - m_{AF}Y \qquad (6)$$

We propose that $l = 1.00$ be assigned to methyl tosylate, which has the lowest m_{AF} value (0.30) yet measured.[1,20] By means of eq 7, a series of nucleophilicity constants of solvents, designated N_{BS}, may be

$$N_{BS} = \log (k^{CH_3OTs}/k_0^{CH_3OTs}) - 0.30Y \qquad (7)$$

obtained (k^{CH_3OTs} is the rate constant for solvolysis of CH_3OTs in a solvent of ionizing power Y, and $k_0^{CH_3OTs}$ is the rate constant for solvolysis in 80% ethanol).

Available literature data permit the calculation of N_{BS} values for many solvents (Table II) by the use of eq 7. The agreement of N_{BS} with Peterson and Waller's N_{PW} is reasonably good (Table II), especially when one considers the different assumptions involved, and the fact that possible mechanistic differences are ignored.[18] It can also be seen that the alcoholic and aqueous solvents have N_{BS} values very close to 80% ethanol, which explains why satisfactory correlations in such solvents are generally obtained using eq 2, even for primary substrates.

Our values of N_{BS} can be used in eq 1, which should provide a more general treatment of nucleophilic displacement reactions than eq 5. Furthermore, eq 7 enables us to relate eq 1 and 5 if we approximate log $(k/k_0)_{2\text{-Ad}}$ with Y;[21] it can then be shown that

$$l \cong 1 - Q$$

$$m \cong (0.3 + 0.7Q)$$

This simple solution is true only for substrates which fit eq 5, based on methyl and 2-adamantyl tosylates. We emphasize that this is a limited class. The inter-

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(20) See Table I, footnote *j*.

(21) Probably mainly because of differences in leaving groups, log $(k/k_0)_{2\text{-Ad}}$ and $Y_{t\text{-BuCl}}$ do not relate perfectly.[10] For this reason, the interrelationships between l, Q, and m are less than satisfactory when $Y_{t\text{-BuCl}}$ is employed.

dependence of l and m, *i.e.*, $l \cong (1 - m)/0.7$, and the equivalence of l and $(1 - Q)$ values (see Table I) for such substrates should be noted.

The full paper describing this work will present comprehensive analyses of literature data using eq 1 and 5, as well as more extensive listings of N_{BS} and l constants, and will provide comparisons of various treatments.

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Electron Spin Resonance Spectra and Structure of Bridgehead Adamantyl and Bicyclo[2.2.2]octyl Free Radicals

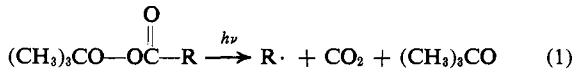
Sir:

The behavior of organic intermediates can be probed effectively at bridgehead positions of bridged ring systems.[1] Large variations in carbonium ion reactivities are observed.[1a,c] Reactivity differences in radical reactions are smaller, but are still appreciable.[1a,1c,2]

There have been several recent studies of the radicals derived from γ- and X-irradiated adamantane.[3] Although production of the 1-adamantyl radical was claimed,[3a] this interpretation has been shown to be in error.[3b,c]

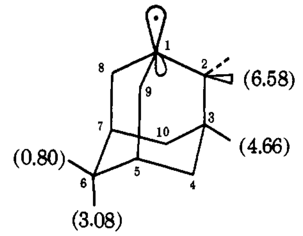
The esr spectra of the authentic 1-adamantyl (I) and 1-bicyclo[2.2.2]octyl (II) radicals are reported here for the first time.[4] These spectra show noteworthy features: anomalously low β hyperfine coupling constants but large δ long-range couplings. In addition, I shows a large γ coupling constant.

The esr spectrum of the 1-adamantyl radical (Figure 1) can be obtained by *in situ* uv photolysis of a dilute solution of *tert*-butyl 1-peroxyadamantanecarboxylate in cyclopropane[5] (eq 1, R = 1-adamantyl). The com-



$$(CH_3)_3CO{-}O\overset{\overset{\displaystyle O}{\|}}{C}{-}R \xrightarrow{h\nu} R\cdot + CO_2 + (CH_3)_3CO \qquad (1)$$

plex hyperfine structure can be reconstructed (Figure 1) on the basis of a septet of 6.58 G and three quartets of 4.66, 3.08, and 0.80 G, respectively ($T = -120°$). Comparison with the results of INDO calculations (*vide infra*) suggests the assignment of the quartet hyperfine coupling constants given below (I).[6]



I

Similarly, photolysis of *tert*-butyl peroxybicyclo[2.2.2]octanecarboxylate yields the spectrum of the 1-bicyclo[2.2.2]octyl radical[4] which is readily analyzed in terms of two septets of 6.64 and 0.89 G and a doublet of 2.69 G ($T = -74°$). These coupling constants are nearly independent of temperature: at −102° the values are 6.59, 0.89, and 2.69 G (peak-to-peak line width, −0.12 G). The 2.69-G doublet is obviously caused by the interaction of the unpaired electron with

Table I. INDO Hyperfine Coupling Constants (G) for Bridgehead Radicals[a]

ΔZ, Å[b]	a_β^H	a_γ^H	a_δ^H		$a_{^{13}C_1}$	Rel energy[c]
			1-Adamantyl (I)			
0.0	5.37	3.47	1.04[d]	4.21[e]	114.5	0.0
0.1	6.45	4.76	1.18[d]	4.20[e]	81.8	−17.07
0.2	7.59	6.57	1.31[d]	3.91[e]	52.9	−24.95
(Exptl	6.58	4.66	0.80[d]	3.08)[e]		
			1-Bicyclo[2.2.2]octyl (II)			
0.0	5.12	0.72	3.28		114.9	0.0
0.1	6.07	1.05	2.17		81.6	−16.57
0.2	7.01	1.54	0.84		52.3	−24.16
(Exptl	6.64	0.89	2.69)			

[a] For the radicals retaining the structure of the parent hydrocarbons ($\Delta Z = 0$), the calculations assume tetrahedral angles throughout, C–C bond lengths of 1.54 Å, and C–H bond lengths of 1.09 Å. All calculated constants are positive. [b] Inward displacement of the spin-bearing bridgehead carbon along the symmetry axis. [c] Difference between the energy of the tetrahedral radical and the energies of the flattened radicals in kilocalories per mole. [d] Equatorial δ protons. [e] Axial δ protons.

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(1) Reviews: (a) R. C. Fort, Jr., and P. v. R. Schleyer, *Advan. Alicyclic Chem.*, **1**, 283 (1966); (b) R. C. Fort, Jr., and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964); (c) R. C. Bingham and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 3189 (1971).

(2) For a review with pertinent references, see C. Rüchardt, *Angew. Chem.*, **82**, 845 (1970); *Angew. Chem., Int. Ed. Engl.*, **9**, 830 (1970).

(3) (a) D. R. Gee, L. Fabes, and J. K. S. Wan, *Chem. Phys. Lett.*, **7**, 311 (1970); (b) L. Bonazzola and R. Marx, *ibid.*, **8**, 413 (1971); (c) J. R. Ferrell, G. R. Holdren, Jr., R. V. Lloyd, and D. E. Wood, *ibid.*, **9**, 343 (1971).

(4) γ-Irradiation of bicyclo[2.2.2]octane gives the 2 and not the 1 radical (L. Bonazzola and R. Marx, *Mol. Phys.*, **19**, 405 (1970)).

(5) For experimental details see: (a) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **90**, 7155 (1968); (b) *ibid.*, **93**, 846 (1971); (c) J. K. Kochi and P. J. Krusic, *ibid.*, **91**, 3940 (1969).

(6) The γ bridgehead protons, assigned the largest of the quartet splittings, are in the perfect W arrangements with the half-occupied orbital expected to lead to strong interaction with the unpaired electron (G. A. Russell, "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience, New York, N. Y., 1968, p 87 ff; G. A. Russell, P. R. Whittle, and R. G. Keske, *J. Amer. Chem. Soc.*, **93**, 1467 (1971)).