the ether extract analyzed by thin-layer chromatography in solvent systems II and III. As chromatographic controls, various amino alcohols were trinitrophenylated under the same conditions. With the exception of TNP-leucinol and -isoleucinol all of these TNP-amino alcohols were well separable in both solvent systems. TNP-tryptophanol showed up as the major Ehrlich-positive neutral product besides TNP-aminoethanol, picramide, and one or two minor components.

COMMUNICATIONS TO THE EDITOR

Correlation of Solvolysis Rates and Estimation of Rate Enhancements

Sir:

The acetolysis rates of many arenesulfonates (RR'CHOSO$_2$Ar) are quantitatively correlated with the infrared carbonyl stretching frequencies of the corresponding ketones (RCOR'). Table I lists rates and frequencies of twenty compounds for which reliable data are available.[1]

TABLE I

Arenesulfonate	No.	log k_{rel}	$\nu_{C=O}$ for ketone, cm.$^{-1}$
Cyclohexyl	1	(0.00)[a]	1716
Cycloheptyl	2	1.78[b]	1705[c]
Cyclooctyl	3	2.76[b]	1703
Cyclononyl	4	2.70[b]	1703[d]
Cyclodecyl	5	2.98[b]	1704
Cycloundecyl	6	2.05[b]	1709[e]
Cyclododecyl	7	0.50[b]	1713[d]
Cyclotridecyl	8	0.66[b]	1713[d]
Cyclotetradecyl	9	0.08[b]	1714[d]
Cyclopentadecyl	10	0.42[b]	1715[d]
Isopropyl	11	0.15[f]	1718
2-Butyl	12	0.53[f]	1721
Methylisopropylcarbinyl	13	0.93[f]	1718
Methyl-*t*-butylcarbinyl	14	0.62[f]	1710
7-Norbornyl	15	−7.00[g,h]	1773
endo-8-Bicyclo[3.2.1]octyl	16	−4.11[i]	1752
2-Adamantyl	17	−1.18[c]	1727[c]
α-Nopinyl	18	−0.73[j]	1717
β-Nopinyl	19	0.04[j]	1717
1,4-α-5,8-β-Dimethanoperhydro-9-anthracyl	20	2.67[k]	1696

[a] S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *J. Am. Chem. Soc.*, **74,** 1127 (1952). [b] H. C. Brown and G. Ham, *ibid.*, **78,** 2735 (1956). [c] See ref. 2. [d] T. Bürer and H. H. Günthard, *Helv. Chim. Acta*, **39,** 356 (1956). [e] N. J. Leonard and F. H. Owens, *J. Am. Chem. Soc.*, **80,** 6039 (1958). [f] S. Winstein and H. Marshall, *ibid.*, **74,** 1120 (1952). [g] S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, **77,** 4183 (1955). [h] C. J. Norton, Ph.D. Thesis, Harvard, 1955. [i] See ref. 3. [j] S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, **77,** 3054 (1955). [k] S. Winstein and L. deVries, unpublished work, quoted in R. Piccolini, Ph.D. Thesis, U.C.L.A., 1960.

Representation in the table has been limited to saturated, secondary arenesulfonates without heterosubstituents; in addition, the following types were specifically excluded: (1) compounds in which ground-state eclipsing interactions are relieved in the solvolytic transition state (for example, cyclopentyl and *endo*-2-norbornyl derivatives), and (2) compounds which have been shown to undergo anchimerically accelerated solvolysis (for example, *exo*-2-norbornyl and cyclobutyl derivatives).

Figure 1 is a plot of the data from Table I. The least-squares straight line through the points obeys the equation log k (relative to cyclohexyl, 25°) = $-0.132 \cdot (\nu_{C=O} - 1720)$; the correlation coefficient is -0.97.

A qualitative relationship between ketone frequency and solvolysis rate was observed by Schleyer and Nicholas[2] and would, indeed, be expected, since both carbonyl frequency and solvolysis rate are sensitive to bond angle and hybridization.[2-4] It is surprising, however, that the correlation should be so excellent for so many dissimilar compounds; the acetolysis rates cover a range of ten powers of ten, yet no rate varies from the line by much more than about one power of ten.

The correlation provides an extremely useful semiempirical relationship for the prediction of solvolysis rates. It also allows the magnitude of the combined effects of anchimeric acceleration and other interactions to be estimated by providing a "model" rate from which the effects of angle strain have been factored out.

As an example of the predictive usefulness of the correlation, Table II lists experimental and calculated data for several compounds which were not included in the calculation of the least-squares line, either because they were of slightly different type from those in Table I, or because the infrared data were considered somewhat less reliable. The calculated acetolysis rates agree extremely well with the experimental, even though several of the compounds are primary or unsaturated. It should be noted that although both polar substituents and conjugation affect rate and carbonyl frequency in the same way as angle strain (increased rates corresponding to decreased carbonyl frequencies), it is not clear that the relative effect would necessarily be of the same magnitude as for angle strain. Further testing of this point would be desirable.

Table III lists data for a number of compounds which were excluded from Table I because their acetolysis

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(1) Infrared spectra for which no literature reference is cited were measured in dilute solution (CCl$_4$) on a calibrated Perkin-Elmer 421 grating spectrograph by Mr. Donald Steele. Expanded scale, reduced slit width, and nitrogen sweep were used; frequencies are believed accurate to ±1 cm.$^{-1}$. Other infrared data were chosen from sources which reported similar measurement conditions. Many absorptions were doublets or multiplets; in these cases, weighted average peak positions are given. All acetolysis rates of toluenesulfonates or bromobenzenesulfonates are relative to cyclohexyl toluenesulfonate or bromobenzenesulfonate, respectively, at 25°.

(2) P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83,** 182 (1961).

(3) C. S. Foote and R. B. Woodward, *Tetrahedron*, in press.

(4) (a) J. O. Halford, *J. Chem. Phys.*, **24,** 830 (1956); (b) R. Zbinden and H. K. Hall, Jr., *J. Am. Chem. Soc.*, **82,** 1215 (1960); (c) H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

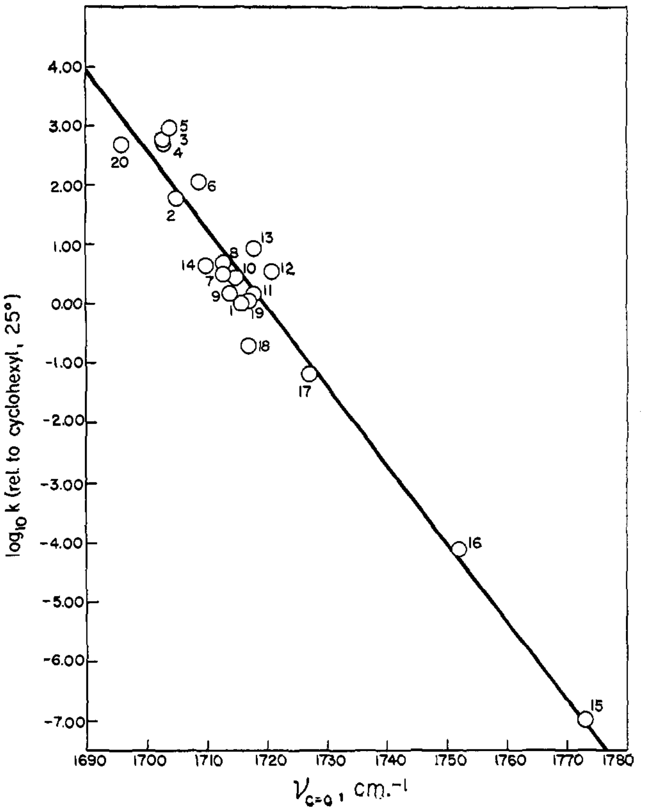

Fig. 1.—Acetolysis rates of arenesulfonates and carbonyl frequencies of corresponding ketones.

rates were considered to be accelerated either by ground-state eclipsing interactions or by anchimeric acceleration. All these compounds have rates which are *faster* than the rates calculated by the correlation; the difference is the sum of rate enhancements from anchimeric acceleration and steric effects (other than those of internal angle strain).

TABLE II

Arenesulfonate	$\nu_{C=O}$ for ketone (or aldehyde), cm.$^{-1}$	log k_{rel}	
		Obsd.	Calcd.
Methyl	1728[a,b]	−1.14[c]	−1.1
Ethyl	1730[b]	−1.45[c]	−1.3
Benzyl	1709[b]	1.73[d]	1.5
trans-2-*t*-Butylcyclohexyl	1700[e,f]	2.20[f]	2.6
cis-2-*t*-Butylcyclohexyl	1700[e,f]	2.61[f]	2.6

[a] Corrected from gas phase by subtracting 16 cm.$^{-1}$, which gives good agreement with solution values for acetaldehyde and propionaldehyde. [b] J. Depireux, *Bull. Soc. Chim. Belges*, **66**, 218 (1957). [c] See Table I, ref. *f*. [d] S. Winstein, E. Grunwald, and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951). [e] Solvent not specified. [f] H. Goering, R. L. Reeves, and H. H. Espy, *J. Am. Chem. Soc.*, **78**, 4926, 4931 (1956).

This novel correlation is a further demonstration of the importance of angle strain and hybridization effects in organic reactions.[2,3,4c,5] It should be possible to extend the correlation to other types of reactions involving tetrahedral ground states and trigonal transition states (or *vice versa*).[6]

Acknowledgments.—The least-squares program and advice on its use were kindly supplied by Dr. Paul Haake. Computation was carried out on an IBM 7090 at the Computing Facility of the Department of Engineering, U.C.L.A. The author is particularly indebted to Prof. R. B. Woodward for encouragement and stimulation, and to Prof. P. D. Bartlett for interest in this work, which was originally presented in part in C. S. Foote, Ph.D. Thesis, Harvard, 1961. Part of this work was supported by Petroleum Research Fund Grant No. 1428 A 1, 4.

TABLE III

Arenesulfonate	$\nu_{C=O}$ for ketone, cm.$^{-1}$	log k_{rel}		log (accel.)
		Obsd.	Calcd.	
Cyclopropyl	1815[a,b]	−5.32[c]	−12.5	7.2
Cyclobutyl	1791[d]	0.99[c]	−9.4	10.4
Cyclopentyl	1748	1.51[e]	−3.7	5.2
exo-2-Norbornyl	1751[d]	2.71[e]	−4.1	6.8
endo-2-Norbornyl	1751[d]	0.18[e]	−4.1	4.3
2-Bicyclo[2.2.2]octyl	1731[d]	1.85[f]	−1.5	3.4
2-Bicyclo[3.2.1]octyl (axial)	1717[d]	1.62[f]	0.4	1.2
2-Bicyclo[3.2.1]octyl (equatorial)	1717[d]	0.47[f]	0.4	0.1
endo-2-Bicyclo[2.2.2]oct-5-enyl	1735[g]	2.49[f]	−2.0	4.5
exo-2-Bicyclo[2.2.2]oct-5-enyl	1735[g]	4.10[h]	−2.0	6.1
exo-2-Norbornenyl	1745[g]	2.42[i]	−3.3	5.7
endo-2-Norbornenyl	1745[g]	−1.48[i]	−3.3	1.8
Nortricyclyl	1762[d]	1.82[i]	−5.6	7.4
anti-7-Norbornenyl	1780[j]	4.11[j,k]	−7.9	12.0
anti-8-Dicyclopentadienyl	1780[l]	4.33[m]	−7.9	12.2
syn-7-Norbornenyl	1780[j]	−3.28[n]	−7.9	4.6
anti-7-Benznorbornenyl	1792[o]	−1.22[o]	−9.5	8.3
exo-2-Benznorbornenyl	1756[o]	1.63[o]	−4.8	6.4
endo-2-Benznorbornenyl	1756[o]	−2.22[o]	−4.8	2.6
7-Dibenznorbornadienyl	1792[p,q]	−0.79[q,t]	−9.5	8.7
exo-8-Bicyclo[3.2.1]octyl	1752	−0.21[r]	−4.2	4.0
9-Bicyclo[3.3.1]nonyl	1726	0.48[r]	−0.8	1.3
5,5-Dimethyl-2-bicyclo-[2.1.1]hexyl	1764[s]	1.18[s,t]	−5.8	7.0

[a] In vapor. [b] W. B. De More, H. D. Pritchard, and N. Davidson, *J. Am. Chem. Soc.*, **81**, 5878 (1959). [c] J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5034 (1951). [d] See ref. 4b. [e] See Table I, ref. *a*. [f] H. L. Goering and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1992 (1961). [g] Private communication from Dr. A. Gagnieux. [h] N. A. LeBel and J. E. Huber, *J. Am. Chem. Soc.*, **85**, 3193 (1963). [i] S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956); S. Winstein, H. M. Walborsky, and K. Schreiber, *ibid.*, **72**, 5795 (1950). [j] See Table I, ref. *h*. [k] See Table I, ref. *g*. [l] R. C. Cookson, J. Hudec, and R. O. Williams, *Tetrahedron Letters*, **No. 22**, 29 (1960). [m] R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959). [n] S. Winstein and E. T. Stafford, *J. Am. Chem. Soc.*, **79**, 505 (1957). [o] P. D. Bartlett and W. P. Giddings, *ibid.*, **82**, 1240 (1960); W. P. Giddings, Ph.D. Thesis, Harvard, 1959. [p] Solvent not specified. [q] J. Meinwald and E. G. Miller, *Tetrahedron Letters*, **No. 7**, 253 (1961). [r] See ref. 3. [s] J. Meinwald and P. G. Gassman, *J. Am. Chem. Soc.*, **85**, 57 (1963). [t] At 75°.

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(5) C. S. Foote, *Tetrahedron Letters*, **No. 9**, 579 (1963).

(6) Schleyer has recently extended this correlation by adding terms for torsional strain, nonbonded interactions, and inductive effects: P. von R. Schleyer, Abstracts, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan., 1964, p. 7C; P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1854 (1964).

(7) Contribution No. 1613.

Estimation of Nonassisted Solvolysis Rates[1]

Sir:

Despite anticipated difficulties, many solvolysis rates can be calculated with high accuracy very easily, using

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(1) Presented at the Gordon Research Conference on Hydrocarbon Chemistry, Colby Jr. College, New London, N. H., June, 1963, and at the