concentrated to produce the amine **9**, which required no further purification.

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Supplementary Material Available: Experimental details for the preparation of **1**, **5**, and **8**–**12** and physical data for all compounds (8 pages). Ordering information is given on any current masthead page.

Variable Transition-State Structure in the Solvolyses of Substituted-Benzyl *p*-Toluenesulfonates[†]

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Summary: Specific rates of solvolysis of seven benzyl *p*-toluenesulfonates (tosylates) in 11 solvents have been analyzed for each substrate in terms of the extended Grunwald–Winstein equation and for each solvent in terms of the Hammett equation; of especial interest is that the Hammett ρ values give a good correlation with a linear combination of solvent nucleophilicity and solvent ionizing power values.

Sir: The extent to which changes in reactant and substrate bring about changes in transition-state structure for bimolecular substitution reactions at carbon has been described as highly controversial.[3] In reactions of *p*-nitrobenzyl sulfonates, only small changes in selectivities were observed over large ranges of reactivities.[3] In contrast, in an approximate analysis[4,5] of the solvolyses of a series of substituted benzyl tosylates using the extended Grunwald–Winstein equation (1),[1,2]

$$\log (k/k_0) = lN + mY \tag{1}$$

where k and k_0 are the specific solvolysis rates in a given solvent and in the standard solvent (80% ethanol), extremely large variations in the sensitivities (l) toward solvent nucleophilicity (N) were observed. The sensitivities (m) toward solvent ionizing power (Y) showed only modest variations ($l = 0$, $m = 0.47$ for the *p*-methyl derivative, varying to $l = 1.5$, $m = 0.38$ for the *p*-nitro derivative).

The estimated values[4] are unusual in that a large variation in l is accompanied by only a small variation in m, contrary to what one would expect from the concept of the variation being related to the "tightness" of the transition state. Further, the l value of zero for the *p*-methyl derivative is accompanied by a m value much lower than the value of close to unity that one would expect for a reaction without nucleophilic assistance.

Our detailed analysis avoids any approximations, other than those inherent in linear free energy relationships, and it has been carried out using Y_{OTs} values,[2,6] with either $N_{Et_3O^+}$ values[7-9] or N_{OTs} values.[2] The results (Table I) show the same general trends[4] but a much more reasonable variation pattern; using N_{OTs}, values range from 0.31 to 0.89 for l and from 0.91 to 0.33 for m.

Linear Hammett plots are obtained for the parent together with derivatives having positive σ values.[10] The slopes (ρ values) range from −1.3 to −5.1. If the magnitude is considered to reflect charge developed on the α carbon, a trend of increased charge (looser transition state) with either an increase in Y or decrease in N can be seen. Indeed, a good correlation of ρ with N and Y (modified eq 1) is observed; with N_{OTs} and Y_{OTs}, $l = 0.60$, $m = -0.44$ ($r = 0.971$), and with $N_{Et_3O^+}$ and Y_{OTs}, $l = 0.70$, $m = -0.36$ ($r = 0.954$).[11] In acetic acid and 95% acetone specific rates were obtained at 50.0 °C for the *p*-methyl derivative. These points lie appreciably above the Hammett plots based on the other substituents,[12] by 1.26 and 0.87 log k units, respectively.

Table I. Correlation of the Specific Rate of Solvolysis of Substituted Benzyl *p*-Toluenesulfonates at 50.0 °C,[a] Using Y_{OTs} Values and either $N_{Et_3O^+}$ or N_{OTs} Values within the Extended Grunwald–Winstein Equation[b]

subst	l[c]	m[c]	r[d]
	(a) Using $N_{Et_3O^+}$ Values[e]		
p-Me[f,g]	0.467 ± 0.165	1.027 ± 0.092	0.979
H	0.770 ± 0.094	0.827 ± 0.049	0.988
p-Cl	0.755 ± 0.105	0.785 ± 0.054	0.983
p-Br	0.820 ± 0.120	0.797 ± 0.062	0.978
m-F	1.003 ± 0.086	0.666 ± 0.044	0.983
p-CF_3	1.167 ± 0.094	0.654 ± 0.049	0.981
p-NO_2	1.229 ± 0.108	0.562 ± 0.056	0.972
	(b) Using N_{OTs} Values[h]		
p-Me[f,g]	0.314 ± 0.150	0.908 ± 0.117	0.956
H	0.496 ± 0.104	0.646 ± 0.075	0.956
p-Cl	0.488 ± 0.110	0.609 ± 0.079	0.946
p-Br	0.571 ± 0.125	0.654 ± 0.090	0.940
m-F	0.702 ± 0.090	0.474 ± 0.065	0.955
p-CF_3	0.842 ± 0.072	0.443 ± 0.051	0.977
p-NO_2	0.893 ± 0.050	0.334 ± 0.036	0.989

[a] Using log k values from studies in the 11 solvents listed in Table II. [b] Log $(k/k_0) = lN + mY$ (see text for definitions). [c] With associated standard errors. [d] Correlation coefficient. [e] Using a Y_{OTs} value of −2.95 for 95% acetone. [f] At 0.0 °C. [g] Excluding HCOOH (specific rate not available). [h] Unless otherwise indicated, using data in ten solvents; the value for 95% acetone is excluded (N_{OTs} value not available).

[†] Dedicated to Professor Christoph Rüchardt on the occasion of his 60th birthday.

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Table II. Variation of the Hammett Equation[a] ρ Value with Solvent, at 50.0 °C[b]

solvent[c]	ρ[d]	r[e]
EtOH	-1.73 ± 0.21	-0.971
80% EtOH	-1.92 ± 0.33	-0.947
60% EtOH	-2.32 ± 0.29	-0.971
MeOH	-1.97 ± 0.23	-0.974
97% TFE[f]	-4.95 ± 0.75	-0.957
80% TFE	-3.71 ± 0.58	-0.955
50% TFE	-3.65 ± 0.52	-0.962
CH_3CO_2H	-2.83 ± 0.49	-0.945
HCO_2H	-5.12 ± 0.77	-0.958
95% Me_2CO	-1.32 ± 0.19	-0.961
60T-40E[g]	-2.74 ± 0.33	-0.972

[a] $\log (k/k_0) = \rho\sigma$. [b] Using log k values for the unsubstituted compound and the five derivatives (see Table I) with electron-withdrawing groups; the σ values used are from ref 10. [c] On volume–volume basis (at 25.0 °C) with other component water, except for TFE–H_2O mixtures, which are on a weight–weight basis. [d] With associated standard errors. [e] Correlation coefficient. [f] 2,2,2-Trifluoroethanol. [g] TFE–ethanol.

The magnitude of the l and m values and the nature of their variation with substrate plus the nature of the variation of the ρ value with solvent suggest a S_N2 mechanism,[13-16] with variable transition-state structure, for the solvolyses of all but one of the esters. For the p-methyl derivative, the sharply lower l value (similar to values previously observed in solvolyses of the *tert*-butyldimethylsulfonium ion[17] and *tert*-butyl chloride[18] and ascribed[19] to nucleophilic solvation of a developing carbocation) and the large increase in the m value (to a value of close to unity) suggest a large superimposed component from an ionization (S_N1) process. The positive deviation from the Hammett plots supports this concept.

Supplementary Material Available: Table S1, containing the logarithmic values of the specific rates of sovolysis of the seven benzyl tosylates listed in Table I in the 11 solvents listed in Table II (1 page). Ordering information is given on any current masthead page.

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Oxygenation of Alkenylsilanes in the Presence of Thiophenol. Direct and Regiospecific Conversion to α-Phenylthio Carbonyl Compounds

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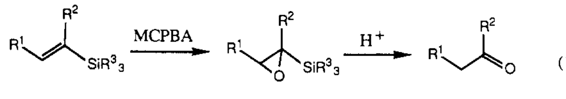
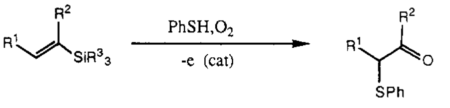
Summary: Electroinitiated oxygenation of alkenylsilanes was found to proceed smoothly in the presence of thiophenol to give the corresponding α-phenylthio carbonyl compounds regiospecifically.

Sir: Alkenylsilanes have been utilized as remarkably versatile intermediates in a variety of organic syntheses.[1] For example, alkenylsilanes are efficient precursors of carbonyl compounds which can be unmasked by epoxidation followed by acid catalyzed rearrangement (eq 1).[2]



(1)

Herein we report the direct transformation of alkenylsilanes into the carbonyl compounds having an activating group at the α-position. The electroinitiated oxygenation[3] of alkenylsilanes in the presence of thiophenol[4] took place smoothly to give the corresponding α-phenylthio carbonyl compounds as shown in eq 2. It is worth noting that the present reaction involves the cleavage of the carbon–silicon bond with triplet molecular oxygen.[5]



(2)

A typical procedure is as follows: 2-(Trimethylsilyl)-1-decene (0.50 mmol) and thiophenol (2.0 mmol) were dissolved in 0.2 M $Et_4NOTs/AcOH$ (5.0 mL), and oxygen gas was bubbled through the solution at room temperature. Constant electric current (20 mA) was passed using a carbon rod anode and a platinum plate cathode for 1 min. The electrolysis was repeated several times with an interval of 0.5 h until the most of the alkenylsilane was consumed (0.30 F/mol based upon the alkenylsilane) (method B). Workup with aqueous $NaHCO_3$ followed by flash chromatography afforded 1-(phenylthio)-2-decanone in 73% yield. The reaction also took place without electrochemical initiation (method A), but much longer reaction time was required for the completion, and the yields of the products were somewhat lower. Table I summarizes the results

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