irradiation, the samples were placed in the dark because biacetyl absorbs visible light and may undergo photochemical reaction. The concentrations of the styrylamines were 3.5 mmol/dm³ (1a) and 1.5 mmol/dm³ (1b) and those of biacetyl were 5-20 mmol/dm³. The consumption of biacetyl during irradiation was negligible.

Stern–Volmer Plot for the Fluorescence of 1a or 1b. The samples were purged with argon. The extinction coefficients of the styrylamines and biacetyl at the excitation wavelength (254 nm) are as follows: 1a, ϵ_{254} = 5600; 1b, ϵ_{254} = 12600; biacetyl, ϵ_{254} = 14.

Quantum Yield Determination. Hexanone actinometry was used. Irradiation was performed with the Rayonet photochemical

reactor. The samples in quartz tubes were purged with argon. After irradiation the degree of reaction was determined by the NMR spectroscopy.

Correlation of Solvolytic Reactivities of 1,1,1-Trifluoro-2-phenyl-2-propyl, 1-tert-Butyl-1-phenylmethyl, and Some Related Tosylates[†]

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Solvolysis of 1,1,1-trifluoro-2-phenyl-2-propyl tosylate (3), 2,2,2-trifluoro-1-(4'-methylphenyl)ethyl tosylate (4), 1-tert-butyl-1-phenylmethyl tosylate (5), 1-tert-butyl-1-(3'-chlorophenyl)methyl tosylate (6), and 1-(3',5'-dichlorophenyl)-2,2,2-trifluoro-1-phenylethyl tosylate (7) in a variety of solvents were found to give log k − Y_{OTs} plots with significant deviations from linearity (R = 0.95–0.98). The data points for those measured in aqueous acetone always showed depression from the line, whereas those measured in nonnucleophilic solvents were on the line. On the other hand, 3, 4, 6, and 7 all showed excellent linear relationships (R > 0.99) for log k against log $k(5)$. Additional evidence for the limiting S_N1 mechanism in the solvolysis of 5 was given. Similar to the previous work (refs 11–13) a new Y_{BnOTs} scale based on the solvolysis rates of 5 for correlating the solvolytic reactivity of benzylic tosylates involving charge delocalizations to the aryl moiety in the cationic transition states was then proposed. The advantages of using this new Y scale of solvent ionizing powers were discussed. The importance of solvent nucleophilicities in the solvolysis of primary benzylic tosylate 8 and unhindered deactivating secondary benzylic tosylates 9 and 10 was confirmed.

In 1948 the Grunwald–Winstein equation (1) was stated to define the first scale of empirical solvent ionizing power (Y) based on the solvolytic rate constants of *tert*-butyl chloride.[1] Multiparameter equations, such as (2),[2] were

$$\log (k/k_o) = mY \qquad (1)$$

$$\log (k/k_o) = mY + lN \qquad (2)$$

then introduced to accommodate the effect of the solvent nucleophilicity. Later studies indicated the use of 1- or 2-adamantyl tosylate as a better reference for defining the solvent ionizing power.[3,4] Moreover, the necessity of using different Y_X scales to correlate the solvolytic reactivity of substrates containing different leaving groups (X) was first shown by Bentley and co-workers.[5] A variety of Y_X scales based on 1- or 2-substituted adamantanes have thus been developed[6] and have been generally considered as an important set of solvent parameters for the understanding of the correlation of solvolytic reactivities.[7] The observation of dispersed log k − Y_X plots due to the rate constants measured in nonnucleophilic solvents, such as those that have been noted in the cases of *tert*-butyl halides[5,8] and 2-(trifluoromethyl)-2-propyl triflate,[9] has been considered as an useful probe for detecting nucleophilic solvent assistance.[10]

On the other hand, we recently demonstrated the advantage of using a new Y_{BnCl} scale based on 2-aryl-2-chloroadamantane 1a[11] over the Y_{Cl} based on 1-chloro-adamantane (2)[5] to describe the solvent ionizing power of a large number of solvents for correlating the solvolytic reactivity of tertiary benzylic chlorides by eq 1. A similar approach has also been found to be successful for benzylic bromides[12] and *p*-nitrobenzoates[13] by employing the corresponding 2-aryl-2-adamantyl derivatives 1b and 1c, re-
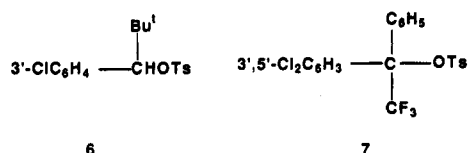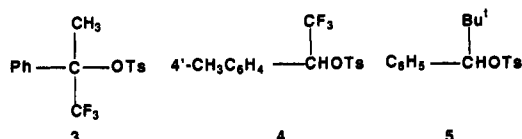
(1) Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846.

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spectively, as the reference substrates.
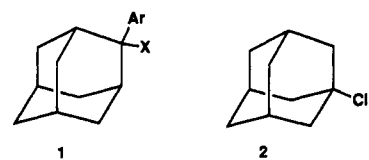
1a Ar = 3'-ClC$_6$H$_4$, X = Cl
1b Ar = 4'-CF$_3$C$_6$H$_4$, X = Br
1c Ar = C$_6$H$_5$, X = OPNB
1d Ar = 4'-CF$_3$C$_6$H$_4$, X = OTs

$$Ph-\overset{CH_3}{\underset{CF_3}{C}}-OTs \qquad 4'-CH_3C_6H_4-\overset{CF_3}{CH}OTs \qquad C_6H_5-\overset{Bu^t}{CH}OTs$$

3   4   5

$$3'-ClC_6H_4-\overset{Bu^t}{CH}OTs \qquad 3',5'-Cl_2C_6H_3-\overset{C_6H_5}{\underset{CF_3}{C}}-OTs$$

6   7

Tosylates are among the most commonly employed substrates in solvolytic studies. The solvolysis of 1,1,1-trifluoro-2-phenyl-2-propyl tosylate (3) was considered to be a limiting S_N1 process from the linear log k - Y_{OTs} relationship realized in alcoholic and acidic solvents and from other kinetic evidence.[14,15] The same conclusion was also reached in the case of 2,2,2-trifluoro-1-(4'-methylphenyl)ethyl tosylate (4).[16] Extended study on the solvolytic behavior of tosylates 3 and 4 in additional solvents is thus desirable to examine the applicability of Y_{OTs} or the necessity of developing a new Y_{BnX} scale in correlating log ks for benzylic tosylates.

Preliminary study on the solvolysis of 3 in aqueous acetone revealed deviations from the original linear log k - Y_{OTs} plot.[17] The tertiary 2-aryl-2-adamantyl tosylate 1d would be expected to be unstable and too reactive to define a "Y_{BnOTs}" scale for benzylic tosylates from accurate kinetic measurements. Other tosylates will thus used. The solvolysis of 1-aryl-1-*tert*-butylmethyl tosylates has been shown to proceed with k_c mechanism without nucleophilic solvent assistance or methyl participation.[18,19] We now wish to report the results of our independent studies on the solvolysis of 1-*tert*-butyl-1-phenylmethyl tosylate (5) and some other representative tosylates. The Y_{OTs} scale was found to be not an appropriate one for the correlation of reactivities. A new Y_{BnOTs} scale[17b] is proposed, and its advantages over Y_{OTs} will also be discussed.

Results

1,1,1-Trifluoro-2-phenyl-2-propyl tosylate (3), 2,2,2-trifluoro-1-(4'-methylphenyl)ethyl tosylate (4), 1-*tert*-bu-

Figure 1. Correlation of logarithms of rate constants for 3 (O) and 4 (●) against Y_{OTs}.

Figure 2. Correlation of logarithms of rate constants for 5 (O), 6 (●), and 7 (□) against Y_{OTs}.

tyl-1-phenylmethyl tosylate (5), 1-*tert*-butyl-1-(3'-chlorophenyl)methyl tosylate (6), and 1-(3',5'-dichlorophenyl)-2,2,2-trifluoro-1-phenylethyl tosylate (7) were prepared from the corresponding alcohols using known procedures.[15] Spectral data and elemental analyses all agreed with the assigned structures. Solvolytic rate constants for these tosylates in various solvents were measured by the conductimetric method, with the exception of the rates of acetolysis which were monitored titrimetrically. The results are shown in Table I. The solvolysis products were all unarranged.[20]

In most cases, the rate constants for substrates 3-5 in most solvents are in good agreement, generally within 10%, with the literature data.[14-16,19] However, larger deviation was observed in some occasions for which the ks at 25 °C were calculated from the data measured at quite high temperature, such as 90 °C and higher. For example, the extrapolation of the rates of ethanolysis for 4 at 90-130 °C gave a k, 8.89 × 10^{-10}/s, and deviated significantly from the reported data, 1.93 × 10^{-10}/s.[16] For k(4) in 60% ethanol, which was calculated from the data at 55 and 75 °C, the literature value (1.20 × 10^{-7}/s)[16] was very close to 1.16 × 10^{-7}/s as was found in the present work.

The plots of the logarithm of rate constants, k(3) and k(4), respectively, with Y_{OTs}[6,21] showed that additional rate constants measured in aqueous acetone and in aqueous

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(17) (a) Lin, Y.-S. M.S. Thesis, National Taiwan University, June 1988. (b) A preliminary account of the work on the development of Y_{BnOTs} was presented at the 198th National Meeting of the American Chemical Society, Miami Beach, FL, Sept 10-15, 1989; *Abstracts of Papers*, ORGN 281.

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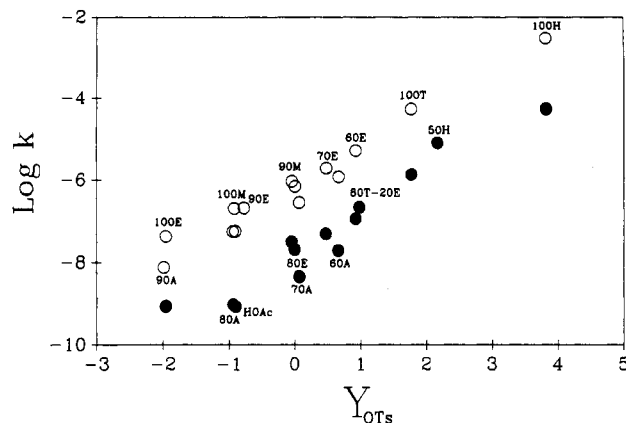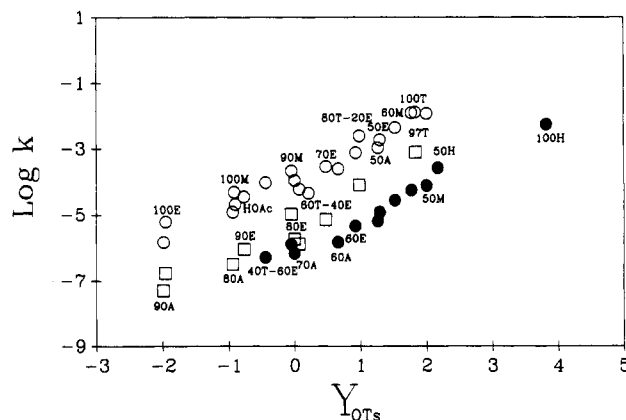
(20) The details on the product study will be reported elsewhere.

(21) Although some "corrected" Y_{OTs} values are available (Allard, B.; Casadevall, E. *Nouv. J. Chim.* 1983, *7*, 569), they are limited to ethanol-water and fluorinated alcohol-water mixtures only. In addition, they were derived from the rate data of 2-*endo*-norbornyl methanesulfonates and might not be appropriate for tosylates. In this study, the revised Y_{OTs} values reported in the recent review (ref 6) were employed.

Table I. Pertinent Solvolytic Rate Constants for Tosylates

solvent[a]	k, s⁻¹ (25 °C)[b]				
	3	4	5	6	7
100E	4.32×10^{-6}[d]	8.89×10^{-10}[o]	6.14×10^{-6}[z]		1.72×10^{-7}[hh]
90E	2.14×10^{-7}[e]		3.52×10^{-5}		9.06×10^{-7}[ii]
80E	7.02×10^{-7}[f]	2.10×10^{-8}[p]	1.07×10^{-4}	6.74×10^{-7}[cc]	1.84×10^{-6}[jj]
70E	1.95×10^{-6}[g]	5.00×10^{-8}[q]	2.88×10^{-4}		7.21×10^{-6}
60E	5.24×10^{-6}[g]	1.16×10^{-7}[r]	7.60×10^{-4}	4.55×10^{-6}[dd]	
50E			1.87×10^{-3}	1.18×10^{-5}	
90A	7.69×10^{-9}[h]		1.50×10^{-6}[aa]		5.04×10^{-8}[kk]
80A	5.61×10^{-8}[i]	9.62×10^{-10}[s]	1.21×10^{-5}		3.18×10^{-7}[ll]
70A	2.87×10^{-7}[j]	4.65×10^{-9}[t]	5.90×10^{-5}		1.32×10^{-6}[mm]
60A	1.21×10^{-6}[k]	1.99×10^{-8}[u]	2.48×10^{-4}	1.48×10^{-6}[ee]	
50A			1.08×10^{-3}	6.42×10^{-6}	
100M	2.07×10^{-7}[l]		4.87×10^{-5}		
90M	9.46×10^{-7}[m]	3.22×10^{-8}[v]	2.12×10^{-4}	1.28×10^{-6}[ff]	1.04×10^{-5}
60M			4.41×10^{-3}	2.72×10^{-5}	
50M			1.17×10^{-2}	7.62×10^{-5}	
100T	5.38×10^{-5}	1.36×10^{-6}[w]	1.25×10^{-2}	5.57×10^{-5}	
97Tw[c]			1.30×10^{-2}		7.81×10^{-4}
80Tw[c]			1.44×10^{-2}		
70Tw[c]			1.48×10^{-2}		
50T			1.55×10^{-2}	7.76×10^{-5}	
80T-20E		2.21×10^{-7}[x]	2.48×10^{-3}		7.93×10^{-5}
60T-40E			4.52×10^{-4}		
40T-60E			9.52×10^{-5}	5.23×10^{-7}[gg]	
HOAc	5.76×10^{-8}[n]	8.61×10^{-10}[y]	2.07×10^{-5}		
100H	2.98×10^{-3}	5.66×10^{-5}	1.09[bb]	5.54×10^{-3}	
50H		8.17×10^{-6}	4.84×10^{-2}[bb]	2.62×10^{-4}	
50H-50T		2.35×10^{-5}	0.147[bb]	7.78×10^{-4}	

[a] For abbreviation of solvents: A, acetone; E, ethanol; M, methanol; H, hexafluoro-2-propanol; T, 2,2,2-trifluoroethanol. The numbers denote the volume percent of the specific solvent in the solvent mixture, unless otherwise mentioned. The amount of water is not recorded. [b] Obtained in this work unless otherwise mentioned. [c] Weight percent. [d] Reference 6. [e-f] Calculated from data at other temperature, k, s⁻¹ (°C): (e) 9.73×10^{-5} (75.0), 1.88×10^{-5} (60.0); (f) 3.47×10^{-4} (75.0), 5.82×10^{-5} (60.0); 2.05×10^{-5} (50.0). [g] Reference 15. [h-o] Calculated from data at other temperature, k, s⁻¹ (°C): (h) 7.79×10^{-4} (125.0), 7.79×10^{-5} (100.0); (i) 1.54×10^{-4} (90.0), 4.24×10^{-5} (75.0), 9.86×10^{-6} (65.0); (j) 1.58×10^{-4} (75.0), 2.90×10^{-5}; (k) 3.64×10^{-4} (70.0), 1.01×10^{-4} (60.0), 3.58×10^{-5} (50.0); (l) 1.29×10^{-4} (75.0), 2.29×10^{-5} (60.0); (m) 4.19×10^{-4} (75.0), 8.16×10^{-5} (60.0); (n) 5.18×10^{-4} (100.0), 1.63×10^{-4} (90.0), 3.83×10^{-5} (75.0); (o) 8.78×10^{-5} (130), 2.28×10^{-5} (113.6), 1.05×10^{-5} (105.0), 2.40×10^{-6} (90.0). [p] Reference 16. [q-aa] Calculated from data at other temperature, k, s⁻¹ (°C): (q) 1.08×10^{-4} (105.0), 2.20×10^{-5} (90.0), 4.30×10^{-6} (75.0); (r) 5.93×10^{-5} (75.0), 6.15×10^{-6} (55.0); (s) 6.44×10^{-5} (115.0), 2.52×10^{-5} (105.0), 5.12×10^{-6} (90.0); (t) 1.08×10^{-4} (105.0), 2.20×10^{-5} (90.0), 4.30×10^{-6} (75.0); (u) 5.37×10^{-4} (110.0), 1.91×10^{-4} (100.0), 4.40×10^{-5} (85.0); (v) 1.49×10^{-4} (100.0), 3.41×10^{-5} (85.0), 1.37×10^{-5} (75.0); (w) 1.64×10^{-4} (75.0), 4.52×10^{-5} (60.0); (x) 1.09×10^{-4} (85.0), 4.48×10^{-5} (75.0), 1.75×10^{-5} (65.0); (y) 1.99×10^{-4} (130.0), 1.94×10^{-5} (105.0); (z) 9.43×10^{-4} (65.0), 4.71×10^{-5} (40.0); (aa) 6.00×10^{-4} (75.0), 3.78×10^{-6} (50.0). [bb] Extrapolated from linear plots with log k (6). [cc-mm] Calculated from data at other temperature, k, s⁻¹ (°C): (cc) 3.35×10^{-4} (75.0), 1.91×10^{-5} (50.0); (dd) 6.67×10^{-4} (65.0), 6.37×10^{-5} (40.0); (ee) 5.58×10^{-4} (75.0), 3.61×10^{-5} (50.0); (ff) 5.78×10^{-4} (75.0), 1.93×10^{-4} (65.0), 6.27×10^{-5} (55.0); (gg) 1.94×10^{-4} (75.0), 2.26×10^{-5} (50.0); (hh) 8.20×10^{-5} (75.0), 4.77×10^{-6} (50.0); (ii) 3.92×10^{-4} (75.0), 7.49×10^{-5} (60.0), 2.40×10^{-5} (50.0); (jj) 2.48×10^{-4} (60.0), 6.80×10^{-5} (50.0); (kk) 2.48×10^{-4} (100.0), 6.80×10^{-5} (75.0); (ll) 1.72×10^{-4} (75.0), 3.18×10^{-5} (60.0); (mm) 6.46×10^{-4} (60.0), 5.92×10^{-5} (40.0).

Table II. Correlation Analyses of Rate Data against Y_{OTs}

substrate	n[a]	m	R	SD
3	14	0.911	0.979	0.054
4	13	0.976	0.964	0.081
5	21	0.964	0.976	0.049
6	12	1.000	0.981	0.062
7	10	0.992	0.953	0.112

[a] Number of solvents.

Table III. Correlation Analyses of Rate Data against Y_{OTs} and $N(OTs)$

substrate	n[a]	m	l	R
3	10	0.863	−0.247	0.983
4	8	0.672	−0.217	0.990
5	12	0.837	−0.130	0.989
6	6	0.963	−0.081	0.996
7	5	0.616	−0.482	0.997

[a] Number of solvents whose $N(OTs)$ values are available.

Figure 3. Correlation of logarithms of rate constants for 5 (●) against that for 6.

methanol deviated from the original linear relationships[14-16] (Figure 1). Similar deviations were also observed in the solvolysis of secondary tosylates 5 and 6 and the tertiary tosylate 7 as well (Figure 2). The results of correlation analyses using eqs 1 and 2 are summarized in Tables II and III, respectively.
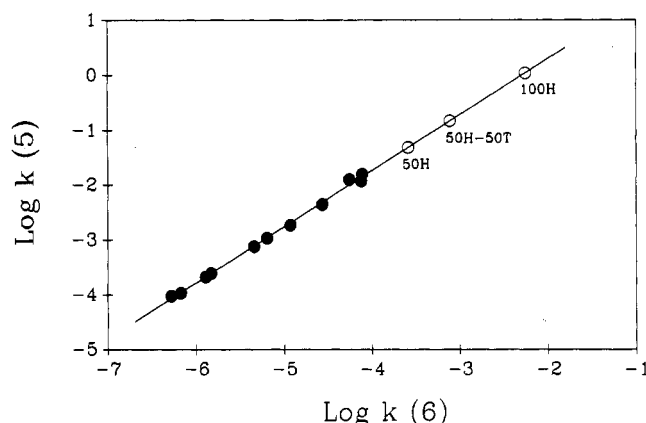
However, an excellent linear relationship between log $k(5)$ and log $k(6)$, $m = 1.019$ and $R = 0.998$, was observed. Therefore, some very fast rate constants for 5 could be calculated by extrapolation (Figure 3, open circle). Moreover, excellent linear correlations were also found if log ks for 5 were plotted against log ks for 3, 4, and 7, respectively. A new Y_{BnOTs} scale of solvent ionizing powers based on the logarithms of the ks for 5 can thus be de-
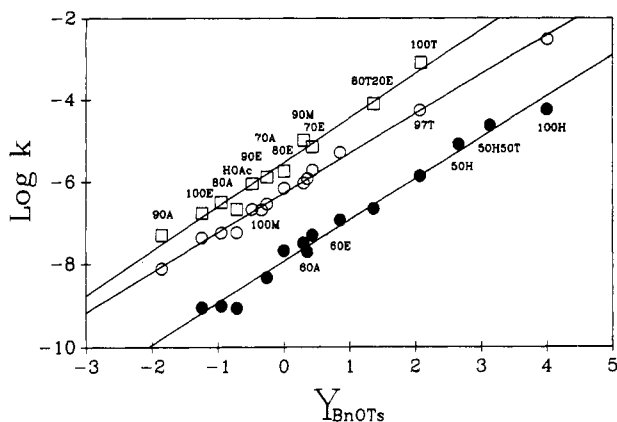
Figure 4. Correlation of logarithms of rate constants for 3 (O), 4 (●), and 7 (□) against Y_{BnOTs}.

Table IV. Comparison of Y Scales

solvent	Y_{BnOTs}	Y_{OTs}[a]
100E	-1.24	-1.96
90E	-0.483	-0.77
80E	0.000	0.00
70E	0.430	0.47
60E	0.851	0.92
50E	1.24	1.29
90A	-1.85	-1.99
80A	-0.947	-0.94
70A	-0.259	0.07
60A	0.354	0.66
50A	1.00	1.26
100M	-0.342	-0.92
90M	0.297	-0.05
60M	1.62	1.52
50M	2.04	2.00
HOAc	-0.713	-0.90
100T	2.07	1.77
97Tw	2.09	1.83
80Tw	2.13	
70Tw	2.14	2.00
50T	2.16	
80T-20E	1.37	0.98
60T-40E	0.626	0.21
40T-60E	-0.051	-0.44
100H	4.01	3.82
50H	2.66	2.17[b]
50H-50T	3.14	

[a] Reference 2b. [b] Allard, B.; Casadevall, E. *Nouv. J. Chem.* **1983**, 7, 569.

Table V. Correlation Analyses of Rate Data against Y_{BnOTs}

substrate	n[a]	m	R	SD
3	14	0.964	0.996	0.024
4	14	0.999	0.992	0.038
6	14	0.979	0.999	0.010
7	10	1.06	0.994	0.043

[a] Number of solvents.

veloped. The values are shown in Table IV, and the results of correlation analyses by using these new Ys are listed in Table V.

Discussion

It has been shown that solvent nucleophilicity plays an important role in the solvolysis of primary benzyl tosylates[22] and secondary deactivated 1-arylethyl tosylates.[23] For tosylates 3–7, although a small deceleration of the rates

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(23) Allen, A. D.; Kanagasabathy, V. M.; Tidwell, T. T. *J. Am. Chem. Soc.* **1985**, *107*, 4513.

in acetic acid was realized, no significant deviation was observed for those in hexafluoro-2-propanol or trifluoroethanol (Figures 1 and 2). The nonlinear relationships could be improved from R = 0.95–0.98 by using eq 1 (Table II) to R = 0.98–0.99 (Table III) if the multiparameter eq 2 was employed. However, this improvement cannot be interpreted by an intervention of solvent nucleophilicity because in the cases of 3 and 7 the overcrowded tertiary reaction center in the solvolytic transition state excludes the possibility of solvent participation. Moreover, the limiting S_N1 mechanism has been demonstrated for the solvolysis of secondary substrates 4,[16,24,25] 5, and 6.[19] Therefore, it is likely that the Y_{OTs} scale might not be a proper one for benzylic tosylates.

The deviation from linear Grunwald–Winstein plots against Y_X (eq 1) observed in the present study is very similar to that has been shown in our previous work.[11-13] For instance, individual linear relationships could be found for the data in aqueous acetone, aqueous ethanol, aqueous methanol, and ethanol–trifluoroethanol, respectively. The data points for those measured in aqueous acetone always showed depression from the line defined by those measured in aqueous ethanol or methanol. Thus, the scattered plots did not result from random errors. Moreover, the order of reactivities such as $k(100M) > k(90E) > k(80A)$ could not be accomodated by Swain's parameter B,[26] which denotes the solvation ability of localized cations. Another possible explanation by the intervention of ion pair return would be unlikely, since no dependence of deviation on reactivities (Table I)[27] or on the amount of return[19c] could be observed. Consequently, it is likely that the Y_{OTs} scale is not appropriate to apply to systems with delocalized cationic transition states as that for bromides, chlorides, and p-nitrobenzoates, which have been found in the previous studies.[11-13]

Since the tertiary tosylate 1d would be very unstable and very reactive, other reference substrates should be chosen. Evidence for the absence of nucleophilic solvent assistance or methyl participation in the solvolysis of 1-aryl-1-*tert*-butylmethyl tosylates has already been shown.[19] The lack of solvent intervention in the solvolysis of the sterically hindered tosylate 5[18] can be further proved by additional evidence. The relative rate ratios of 141–256 for tosylate/bromide in aqueous ethanol[28] are in line with the value of 231 observed for the 2-adamantyl system.[29] In addition, the α-deuterium kinetic isotope effect, 1.19–1.21 in aqueous ethanol,[30] also agrees with that predicted for S_N1 process.[31] A new Y scale based on the rates of solvolysis of 5 is thus a reasonable choice. Accordingly, a Y_{BnOTs} scale could be developed on the basis of eq 1 for correlating the solvolytic reactivities of benzylic tosylates by using 5 as the reference standard and 6 for extrapolation.

The comparison of Y_{BnOTs} with Y_{OTs}[6] (Table IV) reveals that the latter is always more negative except in acetone–water and in ethanol–water. In those solvents the Y_{OTs} may be more negative than the new Y_{BnOTs} at lower

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Table VI. Comparison of Correlation Analyses of Some Tosylates Using eq 2

substrate	Y	$N(OTs)$				$N(T)$			
		n^a	l	m	R	n^a	l	m	R
8	Y_{OTs}[b]	7	0.488	0.568	0.959	6	0.510	0.712	0.925
			(0.104)[e]	(0.087)			(0.163)	(0.170)	
	Y_{BnOTs}[c]	7	0.520	0.668	0.992	6	0.585	0.913	0.989
			(0.046)	(0.043)			(0.066)	(0.079)	
9	Y_{OTs}[d]	8	0.198	0.759	0.991	7	0.180	0.798	0.986
			(0.063)	(0.059)			(0.091)	(0.102)	
	Y_{BnOTs}[c]	8	0.272	0.856	0.998	7	0.285	0.951	0.995
			(0.031)	(0.031)			(0.059)	(0.070)	
10	Y_{OTs}[d]	7	0.317	0.699	0.989	6	0.297	0.769	0.978
			(0.075)	(0.066)			(0.143)	(0.151)	
	Y_{BnOTs}[c]	7	0.347	0.757	0.997	6	0.357	0.873	0.989
			(0.045)	(0.041)			(0.104)	(0.116)	

[a] Number of solvents whose N values are available. [b] Recalculation of the literature data (ref 34) using Y_{OTs} (ref 6). [c] Recalculation of the literature data (ref 34) using Y_{BnOTs}. [d] Recalculation of the literature data (ref 23) using Y_{OTs} (ref 6). [e] Standard deviation.

water content (100E, 90E, 90A, and 80A), or more positive at higher water content (70E–50E and 70A–50A). It seems plausible that the delocalized benzylic cationic transition state will be relatively less favored than the localized 1-adamantyl cation in solvents of higher solvation energy, as has been realized in previous work.[11–13,32] Furthermore, both the electrophilicity and the nucleophilicity of the solvents[33] are likely to be important as in the cases of bromides[12] and chlorides.[11b]

The advantages of employing this new Y scale can be illustrated by the excellent correlation for 3, 4, 6, and 7 ion Table V ($R > 0.99$) as compared with the less satisfactory results in Table II ($R = 0.95$–0.98). The scattered log k – Y_{OTs} plots in the cases of 3 ($R = 0.979$) and 7 ($R = 0.953$) (Figure 1) are likely the outcome of using of an improper Y scale. Since both tosylates are highly hindered and are not susceptible to nucleophilic solvent participation, the observed good linear correlation for these substrates (Table III) with the multiparameter eq 2 (vide supra) could therefore be considered as artifacts. In the solvolytic study of benzyl tosylate (8), Kevill and co-workers[34] suggested the use of Y_{OTs} and $N(Et_3O^+)$[35] in eq 2. Other N scales, $N(T)$ and $N'(OTs)$, were also developed recently.[36] Recalculation using the new Y_{BnOTs} values, as compared Y_{OTs}, indicated the combination of Y_{BnOTs} and $N(OTs)$[37] ($R = 0.992$) or $N'(OTs)$ ($R = 0.997$) would be better than the use of other values ($R = 0.925$–0.989) in the correlation analyses. In other words, $N(OTs)$ or N'-(OTs) seems to be the choice for neutral substrates. In the cases of 1-(3′-bromophenyl)ethyl (9) and 1-[3′-(trifluoromethyl)phenyl]ethyl tosylates (10), Tidwell and co-workers[23] have found linear relationships by using Y_{OTs} and $N(OTs)$ in eq 2 for correlation analyses. Owing to the fact that only 4–6 $N'(OTs)$ or $N(Et_3O^+)$ values are available for substrates 9 and 10, the results of regression analyses using these values are not given in Table VI for comparison. Better linear relationships for 9 ($R = 0.998$) and 10 ($R = 0.997$) could be obtained if Y_{BnOTs} and $N(OTs)$ were used for calculation.[38] The standard deviations for l and m were

also smaller, so the superiority of using Y_{BnOTs} was obvious. The importance of solvent nucleophilicity in the solvolysis of 9 and 10[23] could thus be confirmed.

Consequently, the Y_{OTs} scale will not be as good as the new Y_{BnOTs} scale in correlating reactivities and in examining the nucleophilic solvent effect in the solvolysis of benzylic tosylates, in which delocalized cationic transition states were formed. The importance of the solvation on the cationic moiety in the transition state can also be demonstrated in the solvolysis of substituted naphthylmethyl tosylates.[27] More work on the solvolysis of other tosylates is in progress.

Experimental Section

General Remarks. Capillary melting points were uncorrected. NMR spectra were determined on a Varian EM390 instrument using tetramethylsilane as internal standard. IR spectra were measured on a Perkin-Elmer Model 983G spectrometer. Mass spectral analyses were obtained with a Finigan TSQ-16C instrument. Elemental analyses were done in the Microanalytical Laboratory of this department.

Materials. Solvents for the kinetic studies were spectral grade or reagent grade and purified according to standard procedures.[39] Dry solvents were freshly distilled before use.

The tosylates 3–7 were prepared according to literature procedures.[7] The spectral data are in harmony with the assigned structures, and the melting points for 3–6 agree with the reported values: 3, mp 103.5 °C;[7] 4, 82–83 °C (lit.[8] mp 81.5–82 °C; lit.[14] mp 85.5–85.8 °C); 5, 67–68 °C (lit.[9] mp 68.2–68.9 °C); 6, 83–84 °C.[9] The mp and pertinent spectral data for 7 are listed as follows: mp 117–118 °C; ^{1}H NMR, δ (CDCl$_3$) 2.28 (s, 3 H, CH$_3$), 7.03–7.33 (m, 12 H, aromatic protons); IR ν_{max} (KBr) 1370, 1180 (s, S=O) cm^{-1}; MS m/z (12 eV) 303 (100, M – OTs$^+$), 305 (65, M + 2$^{•+}$ – OTs), 474 (17, M$^{•+}$), 476 (11, M + 2$^{•+}$). Anal. Calcd for C$_{20}$H$_{15}$O$_3$F$_3$Cl$_2$: C, 53.06; H, 3.18. Found, C, 53.26; H, 3.18.

Kinetic Measurements. Conductimetric rate constants were measured, with the exception of acetolysis, using an automatically PC-AT or XT monitored multichannel system developed in this laboratory. The conductivity cells were placed in the thermostat with temperature variation of ±0.02 °C. Solutions of 10^{-4}–10^{-5} M were employed in this study. In some cases, the addition of a small amount of 2,6-lutidine to the solution was found to be necessary to prevent curvature of the rate constant plot. A titrametrical method was employed with a solution of 0.005–0.01 M for the study of acetolysis.[40]

All reactions were followed to 10 or more half-lives and showed excellent first-order behavior. Arrhenius plots of rate data obtained at other temperature were used to estimate rate constants

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at 25 °C which could not be measured directly. Each rate constant was determined at least in duplicate, and the deviation was smaller than ±3%. The mean values of these data are listed in Table I.

Synthesis of New Amphiphilic Perfluoroalkylated Bipyridines

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General and versatile synthetic methods have been developed for the preparation of a large variety of 2,2'-bipyridines bearing two various perfluoroalkylated side chains with an ester or a methylene junction in the 4,4'-positions, e.g., 4,4'-bis[[2''-(*F*-alkyl)ethenyl]alkyl]-2,2'-bipyridines, 4,4'-bis[[[(*F*-alkyl)alkyl]oxy]carbonyl]-2,2'-bipyridines, and 4,4'-bis[[[[2''-(*F*-alkyl)ethenyl]alkyl]oxy]carbonyl]-2,2'-bipyridines.

Introduction

An area of growing interest lies in the use of ligands and their transition-metal complexes exhibiting amphiphilic properties capable of being inserted into interfacial films, membranes, liposomes, and other organized supramolecular systems. A more important objective is to develop novel chemistry based on membrane-mediated processes in relatively simple systems. Such organized systems have been utilized in reactivity control, photochemical solar energy conversion and storage, transport, and drug encapsulation and providing unique environments for substrates and enzymes.[1]

Our goal is to develop metal complexes which may be transported by vesicles (or liposomes) or by injectable fluorocarbon emulsions to be used simultaneously as drug delivery systems and as artificial oxygen carriers. In order to achieve this goal, it was necessary to synthesize new highly amphiphilic ligands bearing, in particular, perfluoroalkylated side chains. Such derivatives may find several potential applications, namely in therapy for the transport and targeting of drugs based on transition-metal complexes and in the constitution of functionalized dispersed systems which may operate as catalytic microreactors.

We describe here the preparation of a new class of amphiphilic ligands in which the coordinating head consists of a bipyridine moiety and the hydrophobic part of two hydrocarbon chains of various lengths terminated by highly perfluoroalkylated tails.

The presence of the bipyridine head on these new compounds opens up a large field of applications. Very few organic ligands have received more attention than 2,2'-bipyridine and its analogues. Bipyridine ligands are widely used in coordination chemistry and catalysis.[2] The interest in such ligands stems, in particular, from their exceptional photoredox properties and from the peculiar photochemical and photophysical properties exhibited by several of their transition-metal complexes.[3] Elaborate

systems exploiting such properties have indeed emerged, especially in redox electrocatalysis[4] and light-induced electron-transfer reactions that convert solar energy into chemical energy.[5] Furthermore, several 2,2'-bipyridine-metal complexes were found to be endowed with antimicrobial,[6] antifungal,[7] and antineoplasmic[8] activity.

The perfluoroalkylated tails are intended to increase the hydrophobic and fluorophilic character of these amphiphilic ligands, hence of their transition-metal complexes, to facilitate, respectively, their incorporation into liposomes and into oxygen-delivering fluorocarbon emulsions. The encapsulation into liposomes of a drug usually improves its therapeutic index, hence its efficiency, by reducing its toxicity, prolonging its intravascular persistence, and modifying its biodistribution.[9] Furthermore, the incorporation of a drug in fluorocarbon emulsions is expected to combine the numerous advantages of drug encapsulation with the capacity of the fluorocarbon to deliver oxygen in radio-[10] and chemoresistant[11] tumors, thus enhancing the tumoricidal effects of radiations or of cytotoxic drugs. Such a synergistic effect has been shown in the treatment of tumors with alkylating agents, antimetabolites, and antibiotics used in conjunction with fluorocarbon emulsions.[12] In addition, the use of fluorocarbon emulsions in therapy as drug delivery systems is particularly attractive in view of their high intravascular persistence and

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