Solvolysis of 2-Aryl-2-chloroadamantanes. A New *Y* Scale for Benzylic Chlorides[1]

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A series of 2-aryl-2-chloroadamantanes **2**, Ar = 4′-methylphenyl, 4′-fluorophenyl, phenyl, 3′-chlorophenyl, 3′-(trifluoromethyl)phenyl, and 4′-(trifluoromethyl)phenyl, were prepared, and the solvolytic rate constants in 23 solvents were measured. Significant deviation from linear log $k - Y_{Cl}$ plots ($m = 1.002$, $R = 0.959$) was observed, and some orders of reactivities, e.g., k(100M) > k(90E) > k(80A), were in the reverse order of Swain's solvent parameter B. Different extent of solvation to the cationic transition state was then likely to play an important role. Excellent linear correlations between the logarithms of the ks for any pair in **2a**–**2f** were realized, and the best one was that with respect to **2d**. A new Y scale, Y_{BnCl}, for the correlation of solvolytic reactivities of benzylic chlorides based on k(**2d**) was established accordingly. The observation of decreasing m values with increasing electron-attracting ability of the substituent on the aryl ring of **2** also suggested the importance of charge delocalizations.

A number of 1- or 2-substituted adamantanes have been employed as the model compounds for establishing individual Y_X scales of the solvent-ionizing power in the Grunwald–Winstein-type correlation (eq 1)[2] of solvolytic

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

reactivities for substrates having different leaving groups.[3] For instance, 1-chloroadamantane is used to define the Y_{Cl} scale for the solvolysis of alkyl chlorides.[4] Significant dispersion of log $k - Y$ plots has been observed for substrates with relatively small steric hindrance, such as *tert*-butyl halide,[4] or of strong electron demand, such as 1,1,1-trifluoro-2-methyl-2-propyl triflate.[5] This phenomenom is generally attributed to nucleophilic solvent participation and has been employed as an useful probe in the study of reaction mechanisms.[6] Moreover, multiparameter equations, such as eqs 2[7] and 3,[8] have been introduced to accommodate the solvent nucleophilicities.

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

$$\log (k/k_0) = (1 - Q) \log (k/k_0)_{\mathrm{MeOTs}} + Q \log (k/k_0)_{\mathrm{2\text{-}AdOTs}} \qquad (3)$$

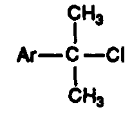
On the other hand, the solvolysis of 2-aryl-2-propyl substrates has long been considered to proceed via carbocationic transition states and to be the standard reaction to define the σ^+ constants[9] in the Hammett-type correlation analysis[10] (eq 4). However, we recently studied the

$$\log (k_X/k_H) = \sigma^+\rho \qquad (4)$$

solvolytic behavior of some 2-aryl-2-chloropropanes **1** and failed to observe a linear log $k - Y_{Cl}$ relationship in the case of **1d**. A new Y scale derived from 2-aryl-2-chloroadamantanes **2** has thus been proposed.[11] The details about the solvolysis of **2** and the development of Y_{BnCl} are now reported.

Results

A series of 2-aryl-2-adamantanols **3a**–**3f** were prepared from Grignard addition of the appropriate arylmagnesium bromides to adamantanone in isolated yields of 62–84%. The resulting alcohols were then treated with thionyl chloride to give 73–82% yield of the corresponding chlorides **2a**–**2f**, respectively. Spectral data and elemental analyses, if necessary, were in agreement with the assigned structures (see Experimental Section).



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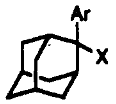

2, X = Cl
3, X = OH

a, Ar = 4′-methylphenyl
b, Ar = 4′-fluorophenyl
c, Ar = phenyl
d, Ar = 3′-chlorophenyl
e, Ar = 3′-(trifluoromethyl)phenyl
f, Ar = 4′-(trifluoromethyl)phenyl

The rates of solvolysis in 23 different solvents were monitored to at least two half-lives by using conductimetric and/or titrimetric techniques. Owing to the low solubility in binary aqueous systems and the high reactivity of these tertiary benzylic chlorides, the rate constants in solvents of high water content, such as 60% methanol and 40% acetone, and of high ionizing power, such as formic acid and hexafluoro-2-propanol, cannot be obtained with good accuracy or reproducibility. For k(**2c**) in 90% acetone, the measured value, 4.28×10^{-4} s^{-1}, agrees with the literature data, 4.59×10^{-4} s^{-1}.[12] The large deviation between the k(**2a**) measured in 90% acetone, 9.37×10^{-3} s^{-1}, and the one reported,[12] 1.59×10^{-2} s^{-1}, is probably due to the extrapolation of rate constants from quite low temperatures

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[1] A preliminary account of a part of this work was presented at the 198th National Meeting of the American Chemical Society, Miami Beach, FL, September 10–15, 1989. *Abstracts of Papers*, ORGN 280.

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Table I. Rate Constants for the Solvolysis of 2-Aryl-2-chloroadamantanes 2

	$k \times 10^3$ (s^{-1}, 25.0 °C)					
solvent[a]	**2a**	**2b**	**2c**	**2d**	**2e**	**2f**
100E	6.18	3.92	1.64	0.0259	0.005 27	0.002 84
95E			8.28	0.0926		
90E	369[b]	51.0	22.4[c]	0.238	0.0526	0.0265
80E			153[d]	1.05	0.232	0.128
70E			591[e]	3.91	0.693	0.359
60E			1.76×10^3[f]	12.4	2.23	1.22
90A	9.37	0.883	0.428	0.005 56	0.001 41	7.09×10^{-4}[g]
80A	166[h]	14.0	7.09	0.0864	0.0232	0.008 03
70A			49.0	0.579	0.127	0.0536
60A			517[i]	3.46	0.741	0.334[c]
50A			1.89×10^3[j]	17.9	3.38	1.66
100M		95.8	50.5[c]	0.586	0.171	0.0386
90M		1.18×10^3[k]	288[l]	4.04	0.754	0.319
80M			1.95×10^3[m]	13.9		1.36
i-PrOH	2.52	0.332	0.123	0.002 05		2.52×10^{-4}[n]
HOAc[o]			0.638	0.0113		
100T			2.79×10^5[p]	3.72×10^3[p]	240	110
85T				3.93×10^3[p]		118
70T			3.13×10^5[p]	4.19×10^3[p]	266	122
80T–20E				276[p]	27.1	12.1
60T–40E				15.9		
40T–60E		982[q]	148	1.59	0.282	0.171
formamide				24.9		

[a] Abbreviations of solvents: A, acetone; E, ethanol; M, methanol; T, 2,2,2-trifluoroethanol. The numbers denote the volume percent of the specific solvent in the mixed solvent, and the amount of water is omitted. [b] Calculated from $k = 5.45 \times 10^{-2}$ s^{-1} (0.1 °C), 3.53×10^{-2} s^{-1} (−5.0 °C). [c] Essentially unchanged in the presence of a slight excess of 2,6-lutidine. [d] Rate constants were calculated from data at other temperatures k s^{-1} (°C). 1.12×10^{-2} (5.0), 5.46×10^{-3} (0.1). [e] 7.78×10^{-2} (9.0), 2.27×10^{-2} (0.1). [f] 1.62×10^{-1} (5.0), 8.56×10^{-2} (0.1). [g] 1.20×10^{-4} (75.0), 1.13×10^{-5} (50.0). [h] 1.27×10^{-2} (0.1), 7.07×10^{-3} (−5.0). [i] 8.06×10^{-2} (9.0), 3.73×10^{-2} (4.5). [j] 1.02×10^{-1} (0.1), 3.51×10^{-2} (−8.0). [k] 4.34×10^{-2} (0.1), 1.76×10^{-2} (−6.0). [l] 5.72×10^{-2} (9.0), 2.14×10^{-2} (0.1). [m] Extrapolated from linear plots with log k(**2f**) (cf. Table II). [n] From $k = 5.36 \times 10^{-4}$ s^{-1} (75.0), 4.52×10^{-5} s^{-1} (50.0). [o] Measured titrimetrically. [p] Extrapolated from linear plots with log k(**2e**) and log k(**2f**) (cf. Table II), respectively. [q] From $k = 2.98 \times 10^{-2}$ s^{-1} (0.1 °C), 8.30×10^{-3} s^{-1} (−8.0 °C).

Table II. Hammett–Brown Treatment of Rate Data of 2

solvent	ρ	R	n[a]
i-PrOH	−4.40	0.999	5
90A	−4.56	0.999	6
	−4.63	0.999	8[b]
100E	−4.73	0.999	6
80A	−4.69	0.999	6
90E	−4.68	0.998	6
100M	−4.87	0.999	5
40T–60E	−5.53	0.996	5
90M	−5.10	0.998	5

[a] Number of points. [b] From the data in Table I and additional data for 4′-chloro and 4′-nitro derivatives.[12]

in the latter case. The rate constants for the solvolysis of **2a**–**2f** are listed in Table I.

The results of the Hammett–Brown treatment of the rate constants (eq 4) are shown in Table II. Scattered log k − Y_{Cl} plots have been observed in each case, and an example for **2c** ($m = 1.002$, $R = 0.959$) is given in Figure 1. However, excellent linear correlations between the logarithms of the ks for any pair of chlorides from **2a**–**2f** were observed. Table III reveals the best intercorrelation if the 2-(3′-chlorophenyl) derivative **2d** is used as the reference. The case for **2f** is illustrated in Figure 2, from which unknown rate constants can be calculated. In addition, Table I shows that **2d** is also the substrate for which most rate constants have been measured directly.

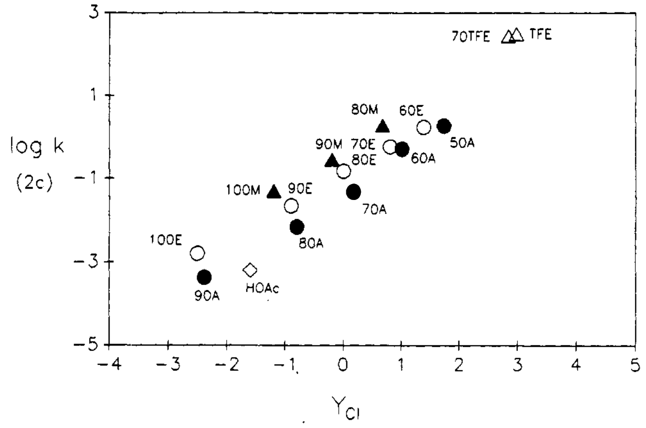

Figure 1. Correlation of logarithms of rate constants for **2c** against Y_{Cl}.

Consequently, a new Y scale, Y_{BnCl}, can be developed on the basis of the original concept[2] by using **2d** as the reference standard. The values are listed in Table IV.

Discussion

Nonlinear Grunwald–Winstein plots with the original Y scale have been observed in several cases in which the

Table III. Intercorrelations between log k's of 2[a]

	log k(**2c**)	log k(**2d**)	log k(**2e**)	log k(**2f**)
log k(**2a**)	0.973 (0.989)	1.052 (0.994)	0.975 (0.986)	1.013 (0.986)
log k(**2b**)	0.971 (0.999)	1.045 (0.999)	1.078 (0.995)	1.127 (1.000)
log k(**2c**)		1.015 (0.998)	1.124 (0.998)	1.116 (0.999)
log k(**2d**)	0.982 (0.998)		1.140 (0.996)	1.132 (0.996)
log k(**2e**)	0.886 (0.998)	0.871 (0.996)		0.992 (0.998)
log k(**2f**)	0.893 (0.999)	0.876 (0.996)	1.004 (0.998)	

[a] Slope (correlation coefficient).

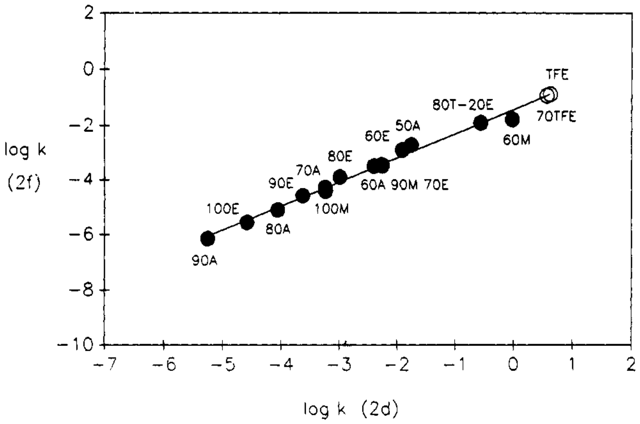

Figure 2. Correlation of logarithms of rate constants for **2f** against that for **2d**.

Table IV. Comparison of *Y* Values

solvent	Y_{BnCl}	Y_{Cl}[a]
100E	−1.61	−2.5
95E	−1.06	
90E	−0.645	−0.9
80E	0.00	0.00
70E	0.571	0.8
60E	1.07	1.38
90A	−2.28	−2.39[b]
80A	−1.09	−0.8
70A	−0.259	0.17
60A	0.518	1.00
50A	1.23	1.73
100M	−0.253	−1.2
90M	0.585	−0.2
80M	1.12	0.67
i-PrOH	−2.71	
HOAc	−1.97	−1.6
100T	3.55	2.83[c]
85T	3.57	
70T	3.60	2.96
80T–20E	2.42	
60T–40E	1.18	
40T–60E	0.18	
formamide	1.38	

[a] Reference 4. [b] Extrapolated value. [c] For 97% trifluoroethanol.

limiting S_N1 mechanism at saturated carbon is assumed.[13] A number of reasons had been suggested to account for such deviation,[14] but there was no unified conclusion. For scattered log k − Y_X plots with respect to the modified Y scale based on adamantyl derivatives, nucleophilic solvent participation is frequently the explanation.[4,5,15] Linear correlation with the multiparameter eq 2 has been found in certain cases.[15] Delocalization of the charge in benzylic carbocations was proposed to rationalize the dispersion effect in the Grunwald–Winstein plot of diphenylmethyl chloride.[16] However, no detailed study has yet been reported. More recently, the effect due to the solvation of aromatic ring in *p*-methoxybenzyl chloride was carefully examined.[14]

To avoid any possible intervention of solvent participation in the case of acyclic primary or secondary substrate, the tertiary 2-aryl-2-adamantyl system was examined in the present study. Similar to the ρ value of −4.83 measured from Hammett–Brown treatment of rate data in 90% acetone for **2a** and **2c**, the 4′-chloro and the 4′-nitro derivatives by Tanida and Tsushima,[12] the observation of the excellent correlations with ρ values of −4.10 to −5.53 for **2** in different solvents (Table II) suggests the cationic transition state of this reaction. Furthermore, the limiting S_N1 character of the solvolysis of 2-chloro-2-methyladamantane in several solvents has been demonstrated.[6] Consequently, back-side solvent attack will be unlikely with the even more crowded 2-aryl analogue **2**.

Table V. *m* Values for 2c–2f in Different Binary Solvents

	substrate			
solvent system	**2c**	**2d**	**2e**	**2f**
aqueous ethanol	0.787 (0.999)[a]	0.686 (0.998)	0.669 (0.999)	0.670 (0.998)
aqueous acetone	0.902 (0.996)	0.850 (0.998)	0.819 (0.999)	0.820 (0.996)

[a] Correlation coefficient.

Despite the limiting S_N1 character for the solvolysis of **2**, significant dispersal in the log k − Y_{Cl} plots was observed in each case. An example for the 2-phenyl derivative **2c** is shown in Figure 1. The deviation is by no means random. Individual linear relationships can be realized for the data in aqueous solutions of acetone, ethanol, and methanol, respectively. Pertinent m values for these plots are exhibited in Table V. The general trend is aqueous ethanol < aqueous acetone, which suggests some special effect due to different solvents. The relative order of reactivity in solvents of similar Y_{Cl} values, e.g., k(80M) > k(70E) $\doteq$ k(60A), is not in line with the order of solvent nucleophilicities.[17] Moreover, the orders k(100M) > k(90E) > k(80A) and k(90M) > k(80E) > k(70A) are the reverse of the order of Swain's solvent parameter B.[18] Therefore, the solvation to the cationic moiety and the charge delocalization are both likely to be important. In other words, different degrees of solvation of the localized charge on 1-adamantyl cation **4** and the delocalization tertiary benzylic cation **5** make the Y scale based on the adamantyl substrate inapplicable to the benzylic substrates **1** and **2**.

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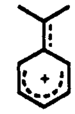

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Therefore, a new Y scale for the correlation of the solvolytic reactivities of benzylic substrates is necessary. Although recent studies suggested the presence of σ participation in the solvolysis of substituted 1-[19] and 2-adamantyl tosylates,[20] our preliminary work revealed only a small difference between the reactivities for the *cis*- and *trans*-4-fluoro derivatives of **2f**.[21] The charge delocalization in the adamantyl ring can thus be neglected, and it is plausible to establish the new Y scale for benzylic chlorides, Y_{BnCl}, on the basis of the 2-aryl-2-chloroadamantane derivative **2d**, (Table IV).

From Table IV, the comparison of Y_{Cl} with the new Y_{BnCl} indicates that in methanol–water and in trifluoroethanol–water the former is more negative, while in acetone–water the reverse is the case. In ethanol–water,

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(13) For example, see: Winstein, S.; Fainberg, A. H.; Grunwald, E. *Ibid.* **1957**, *79*, 4146.

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(21) Unpublished results.

however, the Y_{BnCl} may either be larger (100E and 90E) or smaller (70E and 60E) than Y_{Cl}. Hence, both the electrophilicity and the nucleophilicity of the solvents[22] seem to be important to the solvation in the transition state. Furthermore, with the exception of the deviation of data obtained in 40T–60E, the general trend of the more negative ρ value in solvents of more positive Y_{BnCl} values (Table II) also indicates a closed relationship between the significance of resonance interaction and the solvent ionizing power. The order of decreasing of m values with increasing electron-attracting ability of the substituent on the aryl ring shown in Table V strongly suggests the importance of charge delocalization. More work needs to be done to clarify these points.

The application of this new Y scale for the detection of nucleophilic solvent intervention has been demonstrated in the case of the solvolysis of 2-chloro-2-(3′-chlorophenyl)propane (**1d**).[11] Detailed study in this aspect will be reported elsewhere.

Experimental Section

General Remarks. Capillary melting points and boiling points are uncorrected. NMR spectra were determined on a Varian EM 390, a Bruker AC 200, or a Bruker AM 300 spectrometer with tetramethylsilane as internal standard. Infrared 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 after purification according to standard procedures.[23] Dry solvents were freshly distilled before use.

The preparations of 2-aryl-2-adamantanols (**3**) were carried out by using Grignard addition to 2-adamantanone in tetrahydrofuran. The chlorination of tertiary alcohols was proceeded with thionyl chloride, and the completion of reaction was indicated from the disappearance of the hydroxy peak in ^{1}H NMR. All the chlorides **2** were purified by recrystallization from *n*-hexane at ~0 °C. The chloride obtained was used immediately for the rate measurements. The yields, bps or mps, and spectral data are listed as follows.

2-(4′-Methylphenyl)-2-adamantanol (3a): yield 80%; bp 135 °C (1 mmHg); mp 83–84 °C (lit.[12] mp 75–77 °C[24]); ^{1}H NMR (CCl_4) δ 1.07 (s, 1 H, OH), 1.46–1.96 (m, 10 H, adamantyl protons), 2.33 (s, 3 H, CH_3), 2.47 (broad s, 4 H, adamantyl protons), 7.12 and 7.40 (A_2B_2, 4 H, J = 8.7 Hz, C_6H_4); IR (KBr) ν_{max} 3443 (broad, OH), 3054, 3006, 1607, 1509, 1462, 816 (C_6H_4), 2900, 2848, 1446, 1382 (CH_3, CH_2) cm^{-1}; MS m/z (12 eV) 242 (100, M$^{•+}$), 224 (M$^{•+}$ – H_2O).

2-(4′-Fluorophenyl)-2-adamantanol (3b): yield 81%; bp 160 °C (2 mmHg); mp 84–85 °C; ^{1}H NMR (CCl_4) δ 1.20 (s, 1, OH), 1.43–1.93 (m, 10 H, adamantyl protons), 2.40 (broad s, 4 H, adamantyl protons), 6.90 and 7.36 (A_2B_2C, 4 H, J = 8.4, 8.4, and 5 Hz, C_6H_4); IR (KBr) ν_{max} 3575, 3432 (broad, OH), 3061, 832 (C_6H_4), 2923, 2901, 2853 (CH_2) cm^{-1}; MS m/z (12 eV) 246 (M$^{•+}$), 228 (100, M$^{•+}$ – H_2O). Anal. Calcd for $C_{16}H_{19}FO$: C, 78.02; H, 7.77. Found: C, 77.92; H, 7.50.

2-Phenyl-2-adamantanol (3c): yield 84%; mp 78.5–79 °C (lit.[12] 78.5–79 °C); ^{1}H NMR (CCl_4) δ 1.15 (s, 1 H, OH), 1.45–1.97 (m, 10 H, adamantyl protons), 2.37 (s, 1 H, adamantyl proton), 2.47 (broad s, 3 H, adamantyl protons), 7.13–7.51 (m, 5 H, C_6H_5); IR (KBr) ν_{max} 3352 (broad, OH), 3085, 3055, 3017, 1594, 1576, 1488, 766, 695 (C_6H_5) cm^{-1}; MS m/z (12 eV) 228 (M$^{•+}$), 210 (100, M$^{•+}$ – H_2O).

2-(3′-Chlorophenyl)-2-adamantanol (3d): yield 75%; bp 175 °C (2 mmHg); mp 86.5–87 °C; ^{1}H NMR (CCl_4) δ 1.13 (s, 1 H, OH), 1.42–1.95 (m, 10 H, adamantyl protons), 2.25 (s, 1 H, adamantyl proton), 2.35 (broad s, 3 H), 7.06–7.47 (m, 4 H, C_6H_4); IR (KBr) ν_{max} 3338 (broad, OH), 1587, 1564, 1463, 783 (C_6H_4), 2905, 2850 (CH_2) cm^{-1}; MS m/z (12 eV) 264 (31.6 relative to M$^{•+}$), 262 (M$^{•+}$), 244 (100, M$^{•+}$ – H_2O). Anal. Calcd for $C_{16}H_{19}ClO$: C, 73.14; H, 7.29. Found: C, 73.26; H, 7.33.

2-[3′-(Trifluoromethyl)phenyl]-2-adamantanol (3e): yield 65%; bp 185 °C (3 mmHg); mp 83–83.5 °C; ^{1}H NMR (CCl_4) δ 1.42–2.07 (m, 11 H, OH and adamantyl protons), 2.27 (s, 1 H, adamantyl, proton), 2.38 (broad s, 3 H, adamantyl protons), 7.23–7.75 (m, 4 H, C_6H_4); IR (KBr) ν_{max} 3583, 3438 (broad, OH), 1486, 810 (C_6H_4), 1325, 1169, 1118 (CF_3) cm^{-1}; MS m/z (12 eV) 296 (M$^{•+}$), 278 (100, M$^{•+}$ – H_2O). Anal. Calcd for $C_{17}H_{19}F_3O$: C, 68.91; H, 6.46. Found: C, 68.97; H, 6.17.

2-[4′-(Trifluoromethyl)phenyl]-2-adamantanol (3f): yield 62%; bp 230 °C (3 mmHg); mp 85–86 °C; ^{1}H NMR (CCl_4) δ 1.52 (s, 1 H, OH), 1.57–2.00 (m, 10 H, adamantyl protons), 2.15 (s, 1 H, adamantyl proton), 2.45 (broad s, 3 H, adamantyl protons), 7.52 (s, 4 H, C_6H_4); IR (KBr) ν_{max} 3353 (broad, OH), 1612, 1447, 828 (C_6H_4), 1326, 1161, 1123 (CF_3) cm^{-1}; MS m/z (12 eV) 296 (M$^{•+}$), 278 (100, M$^{•+}$ – H_2O). Anal. Calcd for $C_{17}H_{19}F_3O$: C, 68.91; H, 6.46. Found: C, 68.82; H, 6.45.

2-Chloro-2-(4′-methylphenyl)adamantane (2a): yield 78%; mp 101–102 °C (lit.[10] mp 101–102 °C); ^{1}H NMR (CCl_4) δ 1.67 (broad s, 8 H, protons at C6, C7, C8, C10 (7 H), and C4 or C9 (1 H)), 1.77, 2.55, and 2.70 (3s, 3 H, protons at C4 and C9), 1.83 (s, 1 H, at C5), 2.27 (s, 3 H, CH_3), 2.77 (s, 2 H, at C1 and C3), 7.00 and 7.30 (A_2B_2, 4 H, J = 9.0 Hz, C_6H_4); IR (KB4) ν_{max} 2933, 2915, 1447, 1375 (CH_3, CH_2), 1606, 1508, 779 (C_6H_4) cm^{-1}; MS m/z (12 eV) 262 (M$^{•+}$ + 2, 28.6% relative to M$^{•+}$), 260 (M$^{•+}$), 225 (100, M$^{•+}$ – Cl).

2-Chloro-2-(4′-fluorophenyl)adamantane (2b): yield 82%; mp 66.5–67.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.76 (broad s, 8 H, protons at C6, C7, C8, C10 (7 H), and C4 or C9 (1 H)), 1.88, 2.61 and 2.66 (3s, 3 H, protons at C4 and C9), 1.97 (s, 1 H, at C5), 2.85 (s, 2 H, at C1 and C3), 7.03 and 7.5 (A_2B_2C, 4 H, J = 8.4, 8.4, 5.2 Hz, C_6H_4); ^{19}F NMR ($CDCl_3$) δ – 60.47 (tt, J = 8.4, 5.2 Hz); ^{13}C NMR ($CDCl_3$) δ 26.63 (C5), 27.15 (C7), 33.79 (C4, C9), 34.91 (C8, C10), 37.39 (C1, C3), 38.07 (C6), 96.12 (C2), 115.45 (d, C3′, C5′, J = 21.71 Hz), 126.98 (d, C2′, C6′, J = 7.16 Hz), 140.10 (C1′), 161.69 (d, C4′, J = 247.02 Hz); IR (KBr) ν_{max} 2925, 2856 (CH_2), 3062, 1595, 1505, 791 (C_6H_4) cm^{-1}; MS m/z (12 eV) 266 (M$^{•+}$ + 2, 27.8% relative to M$^{•+}$), 264 (100, M$^{•+}$), 229 (M$^{•+}$ – Cl). Anal. Calcd for $C_{16}H_{18}ClF$: C, 72.58; H, 6.85. Found: C, 72.58, H, 6.63.

2-Chloro-2-phenyladamantane (2c): yield 74%; mp 65–67 °C (lit.[10] 66–68 °C); ^{1}H NMR (CCl_4) δ 1.73 (broad s, 8 H, protons at C6, C7, C8, C10 (7 H) and C4 or C9 (1 H)), 1.83, 2.62 and 2.70 (3s, 3 H, protons at C4 and C9), 1.97 (s, 1 H, proton at C5), 2.80 (s, 2 H, protons at C1 and C3), 7.02–7.53 (m, 5 H, protons at Ph); IR (KBr) ν_{max} 3086, 3055, 3032, 1595, 1580, 1489, 740, 694 (C_6H_5), 2913, 2855 (CH_2) cm^{-1}; MS m/z (70 eV) 248 (M$^{•+}$ + 2, 32.0% relative to M$^{•+}$), 246 (M$^{•+}$), 211 (100, M$^{•+}$ – Cl).

2-Chloro-2-(3′-chlorophenyl)adamantane (2d): yield 78%; mp 86.5–87.3 °C; ^{1}H NMR ($CDCl_3$) δ 1.80 (broad s, 8 H, protons at C6, C7, C8, C10 (7 H) and C4 or C9 (1 H)), 1.86, 2.58, 2.65 (3s, 3 H, protons at C4 and C9), 1.97 (s, 1 H, proton at C5), 2.82 (s, 2 H, protons at C1 and C3), 7.18–7.51 (m, 4 H, C_6H_4); ^{13}C NMR ($CDCl_3$) δ 26.68 (C5), 27.09 (C7), 33.73 (C4, C9), 34.96 (C8, C10), 37.24 (C1, C3), 38.03 (C6), 96.16 (C2), 123.31 (C6′), 125.64 (C2′), 127.59 (C4′), 129.94 (C5′), 134.73 (C3′), 146.34 (C1′); IR (KBr) ν_{max} 2931, 2886, 2856 (CH_2), 1587, 1566, 1465, 768 (C_6H_4) cm^{-1}; MS m/z (12 eV) 282 (M$^{•+}$ + 2, 65.8% relative to M$^{•+}$), 280 (M$^{•+}$), 245 (100, M$^{•+}$ – Cl). Anal. Calcd for $C_{16}H_{18}Cl_2$: C, 68.34; H, 6.45. Found: C, 68.59; H, 6.50.

2-Chloro-2-[3′-(trifluoromethyl)phenyl]adamantane (2e): yield 74%; ^{1}H NMR ($CDCl_3$) δ 1.78 (broad s, 7 H, protons at C6, C7, C8, C10), 1.85, 1.91, 2.62, 2.69 (4s, 4 H, protons at C4 and C9), 2.00 (s, 1 H, at C5), 2.88 (s, 2 H, at C1 and C3), 7.41–7.85 (m, 4 H, C_6H_4); ^{19}F NMR ($CDCl_3$) δ –8.26 (s, CF_3); ^{13}C NMR[25] ($CDCl_3$) δ 26.67 (C5), 27.11 (C7), 33.68 (C4, C9), 34.89 (C8, C10), 37.20 (C1, C3), 37.99 (C6), 96.18 (C2), 122.11 (d, C2′, J = 4.29 Hz), 124.24 (d, C4′, J = 2.88 Hz), 128.60 (C6′), 129.22 (C5′), 131.17 (d, C3′, J = 32.11 Hz), 145.36 (C1′); IR (neat) ν_{max} 2913, 2857 (CH_2), 1591, 1488, 775 (C_6H_4), 1328, 1165, 1127 (CF_3) cm^{-1}; MS m/z (12 eV)

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[24] These data are probably an incorrect record of impure sample, since we have found a similar mp for crude **3a** during recrystallization.

[25] The signal of trifluoromethyl carbon would be a quartet and could not be detected due to the very low intensity.

316 ($M^{\bullet+}$ + 2, 32.30% relative to $M^{\bullet+}$), 314 ($M^{\bullet+}$), 279 (100, $M^{\bullet+}$ – Cl). Anal. Calcd for $C_{17}H_{18}ClF_3$: C, 64.87; H, 5.76. Found: C, 64.68; H, 5.68.

2-Chloro-2-[4-(trifluoromethyl)phenyl]adamantane (2f): yield 73%; mp 88–88.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.79 (broad s, 7 H, protons at C6, C7, C8, C10), 1.85, 1.90, 2.62, 2.69 (4s, 4 H, protons at C4 and C9), 2.00 (s, 1 H, proton at C5), 2.88 (s, 2 H, protons at C1 and C3), 7.66 (s, 4 H, C_6H_4); ^{19}F NMR ($CDCl_3$) δ −13.93 (s, CF_3); ^{13}C NMR[25] ($CDCl_3$) δ 26.65 (C5), 27.07 (C7), 33.68 (C4, C9), 34.93 (C8, C10), 37.18 (C1, C3), 37.95 (C6), 96.16 (C2), 125.56 (C2′, C6′), 125.72 (d, C3′, C5′, J = 2.77 Hz), 129.51 (d, C4′, J = 32.00 Hz), 148.11 (C1′); IR (KBr) ν_{max} 3066, 1612, 1448, 793 (C_6H_4), 2932, 2907, 2861, 2656 (CH_2), 1322, 1164, 1125 (CF_3) cm^{-1}; MS m/z (12 eV) 316 ($M^{\bullet+}$ + 2, 33.0% relative to $M^{\bullet+}$), 314 ($M^{\bullet+}$), 279 (100, $M^{\bullet+}$ – Cl). Anal. Calcd for $C_{17}H_{18}ClF_3$: C, 64.87; H, 5.76. Found: C, 65.14; H, 5.67.

Kinetic Measurements. Conductimetric rate constants were measured, with the exception of studies in acetic acid, using an automatically PC-AT- or XT-monitored multichannel conductivity rate measuring system developed in this laboratory.[26] The conductivity cells were placed in the thermostat with a 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.

For acetolysis, a solution of 0.01 M was prepared and aliquots of 2 mL were titrated using the modified Volhard method.[27]

All reactions were followed to two or more half-lives and gave excellent first-order behavior with correlation coefficients of greater than 0.99. Arrhenius plots of rate data obtained at other temperature were used to estimate rate constants at 25 °C that could not be measured directly. Each rate constant was determined at least in duplicate, and the deviation was in general smaller than 5%. The mean values of these data are listed in Table I.

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Micellar Effects upon Alkene Bromination. 2. The Role of Alkene Hydrophobicity[†]

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Surface polarity of cetyltrimethylammonium bromide (CTAB) aqueous micelles was checked by use of as a probe the bromination reaction of a series of 1-alkenes and a water-soluble alkene, *cis*-4-cyclohexene-1,2-dicarboxylic acid dimethyl ester (I). There was strong inhibition (10^5–10^6-fold) of the second-order reaction rate constants relative to those in water; moreover, both kinetics and the product distributions suggested that alkenes had different locations at the micellar surface. Kinetics in the presence of added NaBr and *n*-decane supported this location hypothesis.

Introduction

Alkene bromination with molecular bromine has been extensively investigated in homogeneous solution,[1] and the reaction rate is very sensitive to medium polarity.[2] Few studies have dealt with the reaction in micelles.[3] Here, we use medium sensitivity as a probe of micellar surface polarity.

The rate expression (1)

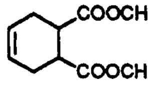
$$\text{rate} = (k_2[Br_2] + k_2'[Br_3^-] + k_3[Br_2]^2)[\text{alkene}] \quad (1)$$

for homogeneous alkene bromination has three terms;[1c,d] concentrations of bromine and tribromide are related by equilibrium (2), which is also affected by medium polarity.[4]

$$Br_2 + Br^- \xrightleftharpoons{K} Br_3^- \qquad (2)$$

It is usually difficult to carry out a kinetic micellar investigation on a reaction that obeys a complex kinetic law, but by choice of conditions, eq 1 is simplified to a one-term equation and observed rate constants can be used to calculate second-order rate constants at the micellar surface.

In this paper, we report data on bromination of a series of 1-alkenes and of the water-soluble cis-4-cyclohexene-1,2-dicarboxylic acid dimethyl ester (I) in the presence of



I

cetyltrimethylammonium bromide (CTAB). Since micelles affect rates of bimolecular nonsolvolytic reactions by acting as a pseudophase,[5] rate effects need to be analyzed

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[†] Dedicated to Prof. G. B. Marini Bettolo on the occasion of his 75th birthday.

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