of the appropriate peaks at 60 MHz to be useful for mixture analysis. Typical VPC retention times for **2**, **8**, and **5**, respectively, were 6, 10, and 13 min with the Apiezon column at 270 °C and 6, 13, and 16 min for the SE-30 column at 235 °C. Traces were integrated by planimeter and calibrated with traces from prepared mixtures of **8** and **5**.

Control Hydrogenations. Except in one instance control hydrogenations to establish absence of equilibration were run on the trans product (**5**), since evidence suggests that it is the less stable epimer.[8] These reactions employed substrate, catalyst, and solvent (diglyme) in the ratio indicated above, with material recoveries of 98–100%, and in no instance gave detectable evidence for epimerization: **5**, Pd/C, 1 atm; **8**, Pd/C, 1 atm; **5**, Pt/C, 1 atm; **5**, Pd/C, 3 atm; Na salt of **5**, Pd/C, 3 atm. Isomerizations through catalyst-associated states (e.g., double-bond migration) were tested for and found absent or negligible in the closely related system **1**;[5] for this reason such processes are believed also to be unimportant in the reactions of **2**.

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Registry No.—**2**, 53547-99-2; **3**, 59434-75-2; **4**, 59434-76-3; **5**, 59434-77-4; **6**, 59434-78-5; **7**, 59434-79-6; **8**, 59434-80-9.

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Steric Effects. 6. Hydrolysis of Amides and Related Compounds

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Data for eight sets of acidic and basic hydrolysis of amides, 18 sets of acidic and basic hydrolysis of *N*-acylimidazoles, and one set of acidic hydrolysis of hydroxamic acids were correlated with the modified Taft equation $\log k_X = \psi\upsilon_X + h$. Data for one set of basic hydrolysis of amides were correlated with the equation $\log k_X = \alpha\sigma_{IX} + \beta\sigma_{RX} + \psi\upsilon_X + h$. Best results were obtained upon the exclusion of the *tert*-butyl group from the correlations. The magnitude of the steric effect upon acid-catalyzed amide or *N*-acylimidazole hydrolysis is the same as the magnitude of the steric effect upon the base-catalyzed hydrolysis of amides or *N*-acylimidazoles. This is in contrast to the behavior of esters, for which a significant difference in the magnitude of the steric effect upon esterification of acid-catalyzed hydrolysis and upon base-catalyzed hydrolysis exists. The magnitude of the steric effect upon the acidic or basic hydrolysis of amides and related compounds is roughly comparable to the magnitude of the steric effect upon esterification, acidic or basic ester hydrolysis, and ester alcoholysis.

In previous papers of this series we have examined steric effects upon rates of esterification and acid-catalyzed hydrolysis of esters[1] and upon rates of base-catalyzed hydrolysis of esters.[2] It seemed of interest to extend these investigations to the question of steric effects upon the rates of hydrolysis of amides and related compounds. The objectives of this work are twofold: first, to determine whether the magnitude of the steric effect upon rates of acid-catalyzed hydrolysis of amides and related compounds is significantly different from the magnitude of the steric effect upon the rates of base-catalyzed hydrolysis; second, to compare the magnitude of the steric effect upon amide hydrolysis rates with the magnitude of the steric effect upon ester hydrolysis rates and upon esterification rates.

Twenty-seven sets of data taken from the literature for the rates of acid-catalyzed or base-catalyzed hydrolysis of amides, *N*-acylimidazoles, and hydroxamic acids were correlated with the modified Taft equation[1]

$$\log k_X = \psi\upsilon_X + h \quad (1)$$

by means of linear regression analysis. The data used in the correlations are set forth in Table I. The υ values required were generally taken from the first paper in this series;[1] some υ values are from our unpublished results. The results of the correlations are presented in Table II. The data for set 2 were correlated with the equation

$$\log k_X = \alpha\sigma_{IX} + \beta\sigma_{RX} + \psi\upsilon_X + h \quad (2)$$

as this set includes a number of nonalkyl substituents and involves base-catalyzed hydrolysis. Presumably the mechanism of amide hydrolysis is similar to that of ester hydrolysis. In that event, acid-catalyzed amide hydrolysis should be a

Table I. Data Used in Correlations

1. $10^4 k_2$, $XCONH_2 + H_3O^+$ in H_2O at 75.0 °C[a]
Me, 10.3; Et, 12.2; Pr, 6.89; Bu, 5.15; *i*-$PrCH_2$, 1.91; *t*-$BuCH_2$, 0.395; $ClCH_2$, 8.54; *i*-Pr, 6.64; *sec*-Bu, 2.08; *t*-Bu, 2.63
2. $10^4 k_2$, $XCONH_2 + OH^-$ in H_2O at 75.0 °C[a]
Me, 11.3; Et, 9.98; Pr, 4.32; Bu, 3.23; *i*-$PrCH_2$, 1.00; *t*-$BuCH_2$, 0.086; $ClCH_2$, 1430; *i*-Pr, 3.95; *sec*-Bu, 1.02; Cl_2CH, 18 400; *t*-Bu, 1.24; CCl_3, 135 000
3. $10^4 k_2$, $XCONH_2 + H_3O^+$ in H_2O at 65 °C[b]
Et, 5.64; Pr, 2.56; Bu, 2.70; *i*-Bu, 0.545; $ClCH_2$, 5.52; $BrCH_2$, 4.79; $MeOCH_2$, 3.79; Me, 4.30; *t*-Bu, 0.935
4. $10^4 k_2$, $XCONH_2 + H_3O^+$ in H_2O at 75 °C[b]
Et, 12.0; Pr, 5.99; Bu, 5.93; *i*-Bu, 1.29; $PhCH_2$, 5.19; c-$C_6H_{11}CH_2$, 1.24; $ClCH_2$, 12.1; *t*-$BuCH_2$, 0.193; $MeOCH_2$, 8.98; Me, 10.3; *i*-Pr, 6.06; Et_2CH, 0.176; *sec*-Bu, 1.51; c-C_6H_{11}, 3.96; c-C_5H_9, 9.04; *t*-Bu, 2.26
5. $10^4 k_2$, $XCONH_2 + H_3O^+$ in H_2O at 85 °C[b]
Et, 26.9; Pr, 13.0; *i*-Bu, 2.96; $PhCH_2$, 12.9; c-$C_6H_{11}CH_2$, 2.98; *t*-$BuCH_2$, 0.465; Me, 21.9; *i*-Pr, 13.7; Et_2CH, 0.477; *sec*-Bu, 3.86; c-C_6H_{11}, 8.90; c-C_5H_9, 11.5; *t*-Bu, 5.14
6. $10^4 k_2$, $XCONH_2 + H_3O^+$ in H_2O at 95 °C[b]
$PhCH_2$, 22.5; c-$C_6H_{11}CH_2$, 6.75; *t*-$BuCH_2$, 1.03; *i*-Pr, 29.6; Et_2CH, 1.04; *sec*-Bu, 8.50; c-C_6H_{11}, 20.5; c-C_5H_9, 29.6
7. $10^4 k_2$, $XCONH_2 + OH^-$ in H_2O at 75.0 °C[c]
Me, 13.6; Et, 13.1; Pr, 7.05; Bu, 5.52; *i*-Bu, 1.97; $PhCH_2$,[d] 17.7; c-$C_6H_{11}CH_2$, 1.77; c-C_6H_{11}, 4.24; c-C_5H_9, 7.80; *sec*-Bu, 1.65; *i*-Pr, 6.61; *t*-Bu, 2.57
8. $10^4 k_2$, $XCONH_2 + OH^-$ in H_2O at 85.0 °C[c]
Me, 24.6; Et, 25.5; Pr, 12.3; Bu, 10.4; *i*-Bu, 4.03; $PhCH_2$,[d] 29.4; c-$C_6H_{11}CH_2$, 3.94; c-C_6H_{11}, 6.22; c-C_5H_9, 13.6; *sec*-Bu, 3.38; *i*-Pr, 11.0; *t*-Bu, 5.08
9. $10^4 k_2$, $XCONH_2 + OH^-$ in H_2O at 95.0 °C[c]
Et, 44.0; Pr, 22.5; Bu, 18.9; *i*-Bu, 8.14; $PhCH_2$,[d] 47.3; c-$C_6H_{11}CH_2$, 6.80; c-C_6H_{11}, 12.2; c-C_5H_9, 27.3; *sec*-Bu, 5.79; *i*-Pr, 19.6; *t*-Bu, 10.3
10. k, *N*-acylimidazoles + H_2O in H_2O, μ = 1.0 M catalyzed by imidazole at 30 °C[e]
Me, 0.14; Et, 0.16; *i*-Pr, 0.26; *t*-Bu, 0.39; Pr, 0.12; *t*-$BuCH_2$, 0.023; Et_3C, 0.0002
11. k, *N*-acylimidazoles + H_2O in H_2O, μ = 1.0 M, catalyzed by imidazolinium ion at 30 °C[e]
Et, 0.034; *i*-Pr, 0.056; *t*-Bu, 0.11; Pr, 0.025; *t*-$BuCH_2$, 0.0045; Et_3C, 0.00007
12. k, *N*-acylimidazoles + H_3O^+ in 0.1 M aqueous HCl at 30 °C[f]
t-Bu, 31.6; *i*-Pr, 7.57; Et, 4.54; Pr, 2.74; *i*-Bu, 0.814; *t*-$BuCH_2$, 0.123; Et_3C, 0.0101; Me, 4.08
13. k, *N*-acylimidazoles + H_3O^+ in 1.20 M aqueous HCl at 30 °C[f]
t-Bu, 25.4; *i*-Pr, 5.77; Et, 3.11; Pr, 2.23; *t*-$BuCH_2$, 0.127; Et_3C, 0.00768
14. k, *N*-acylimidazoles + H_3O^+ in 2.38 M aqueous HCl at 30 °C[f]
t-Bu, 18.4; *i*-Pr, 4.28; Et, 2.53; Pr, 1.61; *i*-Bu, 0.496; *t*-$BuCH_2$, 0.129; Et_3C, 0.00663
15. k, *N*-acylimidazoles + H_3O^+ in 3.60 M aqueous HCl at 30 °C[f]
t-Bu, 12.4; *i*-Pr, 3.15; Et, 1.94; Pr, 1.24; *i*-Bu, 0.412; *t*-$BuCH_2$, 0.123; Et_3C, 0.00495
16. k, *N*-acylimidazoles + H_3O^+ in 4.77 M aqueous HCl at 30 °C[f]
t-Bu, 8.50; *i*-Pr, 2.28; Et, 1.36; Pr, 1.06; *i*-Bu, 0.362; *t*-$BuCH_2$, 0.125; Et_3C, 0.00282
17. k, *N*-acylimidazoles + H_3O^+ in 5.97 M aqueous HCl at 30 °C[f]
t-Bu, 5.86; *i*-Pr, 1.70; Et, 1.25; Pr, 0.884; *i*-Bu, 0.374; *t*-$BuCH_2$, 0.125; Et_3C, 0.00174
18. k, *N*-acylimidazoles + H_3O^+ in H_2O, 1.0 M in NaCl, 0.1 M in HCl at 30 °C[f]
t-Bu, 26.1; *i*-Pr, 5.47; Et, 3.08; Pr, 2.29; *t*-$BuCH_2$, 0.0843; Et_3C, 0.00960
19. k, *N*-acylimidazoles + H_3O^+ in H_2O, 2.0 M in NaCl, 0.1 M in HCl at 30 °C[f]
t-Bu, 15.9; *i*-Pr, 4.06; Et, 2.55; Pr, 1.43; *t*-$BuCH_2$, 0.0633; Et_3C, 0.00598
20. k, *N*-acylimidazoles + H_3O^+ in H_2O, 3.0 M in NaCl, 0.1 M in HCl at 30 °C[f]
t-Bu, 13.2; *i*-Pr, 2.76; Et, 1.49; Pr, 1.10; *t*-$BuCH_2$, 0.0406; Et_3C, 0.00446
21. k, *N*-acylimidazoles + H_3O^+ in H_2O, 4.0 M in NaCl, 0.1 M in HCl at 30 °C[f]
t-Bu, 9.42; *i*-Pr, 1.91; Et, 1.08; Pr, 0.700; *t*-$BuCH_2$, 0.0293; Et_3C, 0.00262
22. k, *N*-acylimidazoles + H_3O^+ in H_2O, 5.0 M in NaCl, 0.1 M in HCl at 30 °C[f]
t-Bu, 6.19; *i*-Pr, 1.18; Et, 0.683; Pr, 0.493; *t*-$BuCH_2$, 0.0200; Et_3C, 0.00208
23. k, *N*-acylimidazoles + H_3O^+ in 0.1 M aqueous HCl at 20.0–21.1 °C[g]
Me, 2.19; Et, 2.70; *i*-Pr, 4.71; *t*-Bu, 20.8; Pr, 1.57; *i*-Bu, 0.394; *t*-$BuCH_2$, 0.0627; Et_3C, 0.00535
24. k, *N*-acylimidazoles + H_3O^+ in 0.1 M aqueous HCl at 39.3–39.7 °C[g]
Me, 6.57; Et, 7.79; *i*-Pr, 12.0; Pr, 4.65; *i*-Bu, 1.42; *t*-$BuCH_2$, 0.197; Et_3C, 0.0211
25. k, *N*-acylimidazoles + H_3O^+ in 0.19 M HCl in 50% v/v dioxane–H_2O at 30 °C[g]
Et, 1.71; *i*-Pr, 3.02; *t*-Bu, 16.6; Pr, 1.07; *i*-Bu, 0.259; *t*-$BuCH_2$, 0.0470; Et_3C, 0.00415
26. k, *N*-acylimidazoles + H_3O^+ in 75% dioxane–H_2O, 0.19 M in HCl at 30 °C[g]
Et, 0.748; *i*-Pr, 1.27; *t*-Bu, 7.40; Pr, 0.454; *i*-Bu, 0.133; *t*-$BuCH_2$, 0.0255; Et_3C, 0.00291
27. k, *N*-acylimidazoles + OH^- in H_2O, μ = 1.0 M at 30 °C[e]
Me, 19 000; Et, 32 000; *i*-Pr, 50 000; *t*-Bu, 32 000; Pr, 28 000; *t*-$BuCH_2$, 13 000; Et_3C, 42
28. $10^5 k_2$, $XCONHOH + H_3O^+$, in H_2O, μ = 0.494 M, catalyzed by TsOH at 50.5 °C[h]
Me, 44.2; Et, 45.0; *i*-Pr, 15.7; *t*-Bu, 8.71; $PhCH_2$, 17.1

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function of steric effects only[1] and base-catalyzed hydrolysis should be a function of both electrical and steric effects. The other sets of base-catalyzed hydrolysis have not been correlated with eq 2, however, as only one nonalkyl substituent, the benzyl group, is available in these sets (sets 7, 8, 9). Correlation with these sets was therefore carried out with eq 1, excluding the value for the benzyl group, as we have previously shown that in the base-catalyzed hydrolysis of esters, data sets involving only alkyl groups show only steric effects upon hydrolysis rates.[2] The σ_I constants required for correlation with

Table II. Results of Correlations with Equation 1

Set	ψ	h	r[a]	F[b]	s_{est}[c]	s_{ψ}[c]	s_h[c]	n[d]
1	−1.44	1.81	0.920	43.85[e]	0.189	0.217[e]	0.192[e]	10
1A	−1.75	2.01	0.984	215.0[e]	0.0905	0.119[e]	0.0991[e]	9
3	−1.34	1.41	0.873	22.48[f]	0.186	0.282[g]	0.214[e]	9
3A	−2.26	1.99	0.955	62.21[e]	0.107	0.287[e]	0.194[e]	8
4	−1.87	2.11	0.942	109.3[e]	0.204	0.179[e]	0.162[e]	16
4A	−2.07	2.24	0.980	323.3[e]	0.123	0.115[e]	0.101[e]	15
5	−1.74	2.34	0.933	73.64[e]	0.214	0.203[e]	0.194[e]	13
5A	−1.93	2.46	0.979	233.3[e]	0.126	0.126[e]	0.118[e]	12
6A	−1.99	2.88	0.973	108.1[e]	0.151	0.191[e]	0.196[e]	8
7	−1.35	1.77	0.887	33.21[e]	0.163	0.235[e]	0.198[e]	11
7A	−1.87	2.14	0.974	145.9[e]	0.0824	0.155[e]	0.123[e]	10
8	−1.28	1.98	0.894	35.82[e]	0.148	0.213[e]	0.180[e]	11
8A	−1.78	2.34	0.988	336.9[e]	0.0516	0.0969[e]	0.0769[e]	10
9	−1.15	2.14	0.834	18.31[f]	0.167	0.270[g]	0.235[e]	10
9A	−1.79	2.61	0.976	139.7[e]	0.0695	0.151[e]	0.124[e]	9
10	−1.50	0.336	0.875	16.36[g]	0.603	0.372[g]	0.458[n]	7
10A	−1.59	0.239	0.976	78.75[e]	0.289	0.179[e]	0.221[n]	6
11	−1.50	−0.223	0.866	11.97[j]	0.655	0.434[j]	0.570[o]	6
11A	−1.55	0.394	0.983	86.12[f]	0.251	0.167[g]	0.221[m]	5
12	−1.40	1.62	0.773	8.891[i]	0.764	0.471[j]	0.566[j]	8
12A	−1.53	1.52	0.964	66.46[e]	0.303	0.188[e]	0.225[g]	7
13	−1.49	1.73	0.786	6.475[k]	0.884	0.586[k]	0.770[k]	6
13A	−1.56	1.50	0.971	50.12[g]	0.331	0.220[g]	0.292[h]	5
14	−1.42	1.48	0.777	7.601[j]	0.783	0.516[j]	0.656[k]	7
14A	−1.50	1.32	0.973	72.30[f]	0.268	0.177[g]	0.226[g]	6
15	−1.42	1.38	0.791	8.365[j]	0.747	0.492[j]	0.625[k]	7
15A	−1.50	1.22	0.979	90.07[e]	0.240	0.158[e]	0.202[g]	6
16	−1.48	1.33	0.813	9.349[j]	0.721	0.475[j]	0.604[k]	7
16A	−1.56	1.18	0.984	124.1[e]	0.212	0.140[e]	0.179[g]	6
17	−1.56	1.33	0.840	11.98[i]	0.684	0.450[h]	0.573[k]	7
17A	−1.63	1.19	0.989	171.9[e]	0.189	0.125[e]	0.159[g]	6
18	−1.45	1.67	0.767	5.711[k]	0.916	0.607[k]	0.797[m]	6
18A	−1.52	1.43	0.958	33.21[i]	0.396	0.263[h]	0.349[j]	5
19	−1.49	1.55	0.785	6.440[k]	0.886	0.587[k]	0.771[m]	6
19A	−1.55	1.33	0.961	36.67[g]	0.386	0.257[g]	0.341[j]	5
20	−1.46	1.37	0.767	5.667[k]	0.927	0.614[k]	0.806[m]	6
20A	−1.53	1.13	0.957	32.80[i]	0.402	0.267[h]	0.354[j]	5
21	−1.50	1.24	0.770	5.830[k]	0.935	0.619[k]	0.813[n]	6
21A	−1.56	0.997	0.962	37.10[g]	0.387	0.257[g]	0.341[k]	5
22	−1.45	1.01	0.764	5.599[k]	0.923	0.612[k]	0.803[n]	6
22A	−1.51	0.775	0.961	36.18[g]	0.379	0.252[g]	0.334[m]	5
23	−1.42	1.39	0.761	8.231[j]	0.804	0.495[j]	0.596[k]	8
23A	−1.56	1.29	0.959	56.59[e]	0.333	0.207[e]	0.248[g]	7
24A	−1.48	1.70	0.961	59.84[e]	0.309	0.192[e]	0.230[e]	7
25	−1.45	1.31	0.744	6.207[k]	0.885	0.583[k]	0.741[m]	7
25A	−1.54	1.13	0.957	44.00[f]	0.352	0.233[g]	0.297[h]	6
26	−1.33	0.868	0.727	5.597[k]	0.855	0.563[k]	0.716[n]	7
26A	−1.42	0.692	0.955	41.42[f]	0.334	0.221[g]	0.282[k]	6
27	−1.45	5.57	0.890	19.00[g]	0.538	0.332[g]	0.408[e]	7
27A	−1.50	5.51	0.937	28.59[g]	0.452	0.281[g]	0.345[e]	6
28	−0.970	2.07	0.902	13.13[j]	0.154	0.268[j]	0.214[g]	5
28A	−2.16	2.80	0.975	38.77[i]	0.0682	0.347[j]	0.223[g]	4

[a] Correlation coefficient. [b] F test for significance of correlations. Superscripts indicate confidence levels (CL). [c] Standard errors of the estimate, ψ, and h. Superscripts indicate confidence levels of the Student's t test. [d] Number of points in the set. [e] 99.9% CL (confidence level). [f] 99.5% CL. [g] 99.0% CL. [h] 98.0% CL. [i] 97.5% CL. [j] 95.0% CL. [k] 90.0% CL. [l] 90.0% CL. [m] 80.0% CL. [n] 50.0% CL. [o] 20.0% CL. [p] <20.0% CL.

eq 2 are taken from our compilation[3] with the exception of the value for $CHCl_2$ (0.30)[4] and the value for CCl_3 (0.38) which we have calculated from the value for CH_2CCl_3. Values of σ_R used were generally obtained from the equation

$$\sigma_R = \sigma_p - \sigma_I \quad (3)$$

using σ_p values reported by McDaniel and Brown.[5] Values of σ_R for the $CHCl_2$ (0.03) and CCl_3 (0.05) groups were obtained from $\sigma_R{}^{\circ}$ values reported by Sheppard[4] using $\sigma_R{}^{\circ} = 0.67\sigma_R$.

Results

Results of the correlations with eq 1 are given in Table II. Results of the correlations with eq 2 are reported in Table III. In all sets containing the t-Bu group, correlation is improved by excluding the value for this substituent. Such sets in Tables II and III are designated by the letter A. Sets involving acid-catalyzed hydrolysis of amides (sets 1, 3–6) gave excellent correlations both with and without the exclusion of the t-Bu group (as determined by the confidence level of the F test). Better results were obtained for the correlations excluding the t-Bu group.

With respect to base-catalyzed amide hydrolysis, set 2 was correlated with eq 2, with excellent results, set 2A giving best results. Sets 7, 8, and 9 were correlated with eq 1; excellent results were obtained, although better results were shown by

Table III. Results of Correlations with Equation 2

Set	α	β	ψ	h	R[a]	F[b]	r_{12}[c]	r_{13}[c]
2	8.94	8.64	−1.50	2.95	0.978	57.60[f]	0.961[f]	0.267[g]
2A	10.9	5.69	−2.09	3.05	0.988	99.29[f]	0.959[f]	0.389[g]

Set	r_{23}[c]	s_{est}[d]	s_α[d]	s_β[d]	s_ψ[d]	s_h[d]	n[e]
2	0.132[g]	0.465	3.87[h]	8.96[i]	0.537[h]	0.783[j]	12
2A	0.246[g]	0.351	3.02[j]	6.85[i]	0.461[j]	0.592[j]	11

[a] Multiple correlation coefficient. [b] F test for significance of correlation. Superscript indicates confidence level. [c] Partial correlation coefficients of σ_I on σ_R, σ_I on v, σ_R on v. Superscripts indicate confidence levels. [d] Standard errors of the estimate, α, β, ψ, and h. Superscripts indicate confidence levels of Student's t tests. [e] Number of points in the set. [f] 99.9% CL. [g] <90.0% CL. [h] 95.0% CL. [i] 50.0% CL. [j] 99.0% CL.

Table IV. Test of Taft Assumption

Acid set	$-\psi_{acid}$	$s_{\psi\,acid}$	n	Base set	$-\psi_{base}$	$s_{\psi\,base}$	n	$\Delta\psi$	t_{acid}	t_{base}
1A	1.75	0.119	9	2A	2.09	0.461	11	0.34	2.857[a]	0.738[b]
4A	2.07	0.115	15	7A	1.87	0.155	10	0.20	11.739[c]	1.290[b]
5A	1.93	0.126	12	8A	1.78	0.0969	10	0.15	1.90[b]	1.548[c]
6A	1.99	0.191	9	9A	1.79	0.151	9	0.20	1.047[b]	1.325[b]
12A	1.53	0.188	7	27A	1.50	0.281	6	0.03	0.160[d]	0.107[d]
11A	1.55	0.167	5	10A	1.59	0.179	6	0.04	0.240[d]	0.223[d]

[a] 95.0% CL. [b] 50% CL. [c] 80.0% CL. [d] 20.0% CL.

the A sets. Fifteen sets of acid-catalyzed N-acylimidazole hydrolysis rate constants were correlated with eq 1. Of 14 sets including the t-Bu group, two gave good, four gave fair, and eight gave poor results. Of 15 sets excluding the t-Bu group, nine gave excellent, four gave very good, and two gave good results. For imidazole-catalyzed hydrolysis of N-acylimidazoles (set 10) correlation with eq 1 gave very good results including and excellent results excluding the t-Bu group. For imidazolium-catalyzed hydrolysis of N-acylimidazoles (set 11) correlation with eq 1 gave fair results including and excellent results excluding the t-Bu group. In the case of the base-catalyzed hydrolysis of N-acylimidazoles (set 27) very good results were obtained with or without the t-Bu group, although the results without t-Bu are somewhat better. For the acid hydrolysis of hydroxamic acids (set 28) fair results including and good results excluding the t-Bu group were obtained.

Discussion

We have previously shown[2] that the Taft hypothesis that the magnitude of the steric effect upon rates of esterification or acid-catalyzed ester hydrolysis is the same as the magnitude of the steric effect upon base-catalyzed ester hydrolysis is incorrect. Thus, there is a significant difference between the magnitudes of these steric effects in ester hydrolysis. The question then arises, is there also a significant difference between the magnitudes of the steric effects on the acid-catalyzed and the base-catalyzed hydrolysis of amides and related compounds. As all of the available data have been determined in water, comparison is straightforward. In Table IV, the ψ values for acidic and basic hydrolysis of amides under comparable reaction conditions, and of N-acylimidazoles are presented. Also compared are ψ values of imidazole (base) catalyzed hydrolysis and the imidazolium (acid) catalyzed hydrolysis of N-acylimidazoles. Values of the Student's t test for the difference between ψ_{acid} and ψ_{base} have been calculated. t_{acid} values and t_{base} values were determined from the standard error of ψ_{acid} and ψ_{base}, respectively. The results of the comparisons show clearly that there is no significant difference between the magnitudes of the steric effect on acid-catalyzed and base-catalyzed hydrolysis of amides and related compounds. It must be pointed out, however, that while the Taft hypothesis has been shown to be valid for amide hydrolysis this is only true in the case of water. Unfortunately data are not available to test the hypothesis in other solvent systems. The solvent systems upon which the Taft separation of polar and steric effects rests are generally water–ethanol and water–acetone mixtures.

We now turn our attention to a comparison of steric effects upon rates of hydrolysis and related reactions of esters with steric effects upon rates of hydrolysis of amides and related compounds. (For values of ψ see paragraph at end of paper regarding supplementary material.)

The magnitude of ψ for the acidic hydrolysis of amides and related compounds is seen from Table IV to be comparable to the magnitude of ψ for esterification and the acidic hydrolysis of esters. Acidic alcoholysis of acyl-2-naphthoates gives somewhat higher ψ values. The magnitude of ψ for the basic hydrolysis of amides and N-acylimidazoles is somewhat less than that of ψ for most of the basic ester hydrolyses. It seems reasonable to conclude that steric effects upon the acidic or basic hydrolysis of amides and related compounds are roughly comparable in magnitude to steric effects upon esterification, acidic and basic hydrolysis, and ester alcoholysis.

We have noted above that the t-Bu group deviates significantly in all of the 26 sets in which it occurs. Two distinct types of behavior can be discerned. In all of the amide hydrolysis sets which contain the methyl, ethyl, isopropyl, and *tert*-butyl groups, and in the hydroxamic acid hydrolysis as well, the methyl, ethyl, and isopropyl group rate constants are greater than the *tert*-butyl group rate constant. In the case of the N-acylimidazoles the rate constants lie in the sequence t-Bu > i-Pr > Et in most of the sets studied. Obviously, then, the t-Bu group in the case of amide hydrolysis is behaving differently than in the case of N-acylamidazole hydrolysis. Bolton and Jackson[7,8] have reported in the case of both acidic and basic hydrolysis that best correlation with E_S values using the Taft–Pavelich equation

$$\log k = \rho^*\sigma^* + \delta_{E_S} + \log k_0 \quad (4)$$

gives best results with separate lines for amides bearing groups with one or two α hydrogen atoms. It might be argued then that groups with no α hydrogens should lie on still another correlation line. It must be noted, however, that these authors find best results on correlation with the equation

$$\log k = \rho^*\sigma^* + \delta_{E_S}{}^c + h(n - 3) + \log k_0 \quad (5)$$

and that while substituents with both one and two α hydrogens give an excellent fit to this equation, the *t*-Bu group deviates significantly. Bolton and Jackson have ascribed the effect of the *t*-Bu group to hyperconjugation. This is based on an analysis involving the $(n - 3)$ term in eq 5, which is considered to represent hyperconjugation by Hancock et al.[9] In our opinion this term represents an additional steric parameter, a point we shall take up in a future paper in this series.

It should be pointed out that our results for acid- and base-catalyzed ester hydrolysis,[1,2] our unpublished results for the reactions of aldehydes, acyl chlorides, and thioesters with hydroxide ion, water, and alcohols, and for the reaction of esters with ammonia show that the point for the *t*-Bu group lies on the correlation line. This leads us to the conclusion that the *t*-Bu group generally behaves normally in nucleophilic additions to the carbonyl group. Amide hydrolyses represent *an exception to this generalization.*

Supplementary Material Available. A table of ψ values for various reactions (1 page). Ordering information is given on any current masthead page.

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Sodium–Ethylenediamine Reductive Dimerization of Naphthalene to 5,6,7,12,13,14-Hexahydro-5,13:6,12-dimethanodibenzo[*a,f*]cyclodecene

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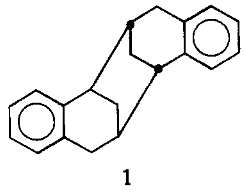
Crystallographic studies of the $C_{20}H_{20}$ reduced dimer, mp 179–180 °C, obtained from treatment of naphthalene with sodium and ethylenediamine showed the hydrocarbon to be the title compound. This analysis allowed ^1H NMR absorption assignments. Other properties of 1 and its oxidation products are reported.

The reaction of naphthalene or the dihydronaphthalenes with sodium and ethylenediamine[1a,b] affords a $C_{20}H_{20}$ reduced dimer, mp 179–180 °C, now shown by x-ray crystallographic analysis to have structure 1 rather than 2[1a,b] earlier proposed.



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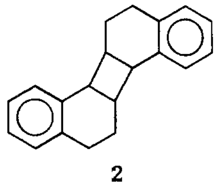

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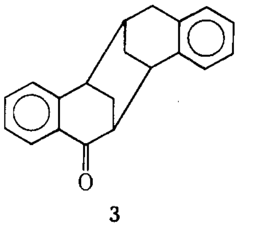

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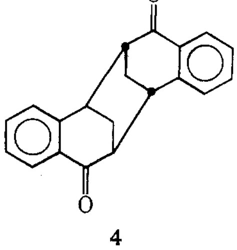

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Dimer 1 is also formed by reaction of dihydronaphthalene with potassium *tert*-butoxide and dimethyl sulfoxide (Me_2SO).[2a] Wideman reported isolation of a crystalline 1,2-bisdialin, mp 179–180 °C, using the preceding reagents.[2b]

The crystal structure of the dibromo derivative of Heller's dimer, a nitrogen analogue of the title compound, has been determined[3a] and hydroxy ketone derivatives of the title compound have also been prepared.[3b] Otherwise structure **1** appears to be new.

We also report additional properties of 1 and its oxidation to the mono- and diketone, **3** and **4.**

Results and Discussion

Figure 1 shows a stereoview[4a,b] of the dimer which consists of five six-membered carbon rings having a crystallographic center of symmetry.

Other data derived from the crystallographic study are summarized in Figures 2 and 3. Figure 2 shows the skeletal numbering[5] and carbon–carbon bond lengths[6] of **1.** The bond angles as well as the torsion angles for the three unique ring systems of 1 are given in Figure 3. These torsional angles may be compared with those calculated for six-membered cycloalkanes.[7] Experimentally determined torsion angles for the cyclohexene ring agree best with torsion angles for the C_s barrier conformation calculated by Hendrickson.[7] Planarity of the benzene ring is indicated by torsion angles of approximately 0°. The bond angle formed by C(13)–C(14)–C(14a) shows a large distortion from the normal bond angle of 109.5° for a tetrahedral carbon atom. No other significant deviations from the expected bond distances and angles are observed.