The Mechanism of Hydrolysis of Methyl Pseudo-8-aroyl-1-naphthoates in Aqueous Acid[1]

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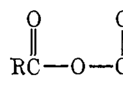
Abstract: The hydrolyses of the methyl esters of pseudo-8-benzoyl-, -8-*p*-toluyl-, and -8-*p*-bromobenzoyl-1-naphthoic acids have been studied in aqueous sulfuric and perchloric acid. The evidence unequivocally indicates that the hydrolyses proceed by a unimolecular mechanism involving an alkoxycarbonium ion. The criteria applied were: rate-acidity correlations (Zucker-Hammett, Bunnett w and ϕ), entropy of activation, deuterium oxide solvent isotope effect, and substituent effect. Exact values for methyl pseudo-8-benzoyl-1-naphthoate in H_2SO_4 are: slope of a plot of log k_ψ *vs.* $-H_0 = 1.07$, $w = -0.50$, $\phi = -0.083$, $\Delta S^* = 0.7$, and $k_{H_2O}/k_{D_2O} = 0.36$. The log k_ψ for the hydrolysis of the three compounds in sulfuric acid correlates with σ^+ and $\rho = -2.1$.

Several mechanisms can be written for the hydrolysis of partial acylals, **1**. Indeed, the indications are that the mechanism of hydrolysis of these compounds is a delicate function of substrate structure. Thus, methoxymethyl acetate[3] and γ-ethoxy-γ-butyrolactone[4] seem to be well-behaved examples of an A1 hydrolysis proceeding through an alkoxycarbonium ion. The behavior of methoxymethyl formate[3] and β-chloroethoxymethyl acetate[5] indicate that although most of the reaction is unimolecular there is a small bimolecular component. An A2 process predominates in the hydrolysis of β-chlorethoxymethyl formate.[5] We have reported[6] the application of various criteria used to investigate the mechanisms of hydrolysis reactions to the reaction of methyl pseudo-2-benzoylbenzoate (**2**) in sulfuric acid. The results of that study allowed us to conclude that the reaction clearly is not a well-behaved A1 process and is probably bimolecular. Additional study of this class of compounds seemed necessary.



$$\overset{O}{\overset{\|}{R C}}-O-\overset{OR^1}{\overset{|}{C}}HR''$$

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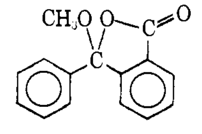

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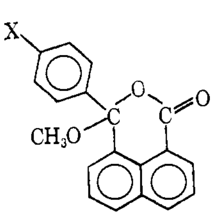

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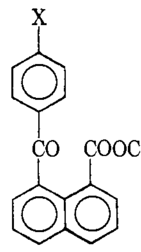

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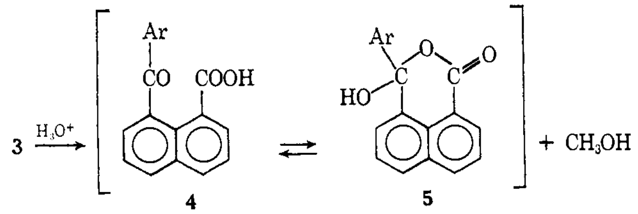
a, X = H
b, X = CH$_3$
c, X = Br

We now report the results of a study of the hydrolysis of several methyl pseudo-8-aroyl-1-naphthoates (**3**) in aqueous acid. These results, in contrast to those obtained with **2**, are entirely consistent with a unimolecular hydrolysis mechanism.

Results

Methyl pseudo-8-aroyl-1-naphthoates (**3**) react in aqueous acid to form 8-aroyl-1-naphthoic acids (**4** and **5**) and methanol. The reactions are conveniently followed in the ultraviolet and show straightforward pseudo-first-order behavior. Rate constants are listed in Tables I–III.



There is some question about whether the products exist in aqueous solution, as the keto acids, **4**, or the lactols, **5**, or as mixtures of the two forms. Infrared spectra of the 8-aroyl-1-naphthoic acids indicate that in the solid state these compounds exist as **5** (see Ex-

Table I. Methyl Pseudo-8-benzoyl-1-naphthoate (**3a**) Hydrolysis in Aqueous Acid

No.	[Catalyst acid], *M*	Temp, °C	10^4k_ψ,[a] sec^{-1}
	In Sulfuric Acid		
1	0.96	25.0	3.98
2	1.93	25.0	19.5
3	2.93	25.0	70.8
4	3.93	25.0	233.0
5	4.94	25.0	657.0
6	0.96	35.0	12.9
7	0.96	45.0	40.1
	In Perchloric Acid		
8	0.95	25.0	7.49
9	1.94	25.0	42.8
10	2.83	25.0	138.0
	In Sulfuric Acid-d_2		
11	0.96	25.0	11.1

[a] Average of at least two runs.

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[1] Presented, in part, at the 3rd Middle Atlantic Regional Meeting of the American Chemical Society, Philadelphia, Pa., Feb 1968, Abstract No. H-33.

[2] Taken from the Ph.D. dissertation submitted by G. W. Z. to Seton Hall University, 1968.

[3] P. Salomaa, *Acta Chem. Scand.*, **11**, 132, 141, 235 (1957).

[4] T. H. Fife, *J. Amer. Chem. Soc.*, **87**, 271 (1965).

[5] P. Salomaa and R. Linnantie, *Acta Chem. Scand.*, **14**, 586 (1960).

[6] D. P. Weeks, A. Grodski, and R. Fanucci, *J. Amer. Chem. Soc.*, **90**, 4958 (1968).

Table II. Methyl Pseudo-8-*p*-toluyl-1-naphthoate (**3b**) Hydrolysis in Aqueous Acid

No.	[Catalyst acid], *M*	Temp, °C	$10^4 k_\psi$,[a] sec^{-1}
	In Sulfuric Acid		
1	0.97	25.0	17.2
2	2.00	25.0	73.4
3	3.03	25.0	300.0
4	4.06	25.0	939.0
5	0.97	15.0	4.92
6	0.97	35.0	54.7
	In Sulfuric Acid-d_2		
7	0.97	25.0	46.3

[a] Average of at least two runs.

Table III. Methyl Pseudo-8-*p*-bromobenzoyl-1-naphthoate (**3c**) Hydrolysis in Aqueous Sulfuric Acid

No.	[H_2SO_4], *M*	Temp, °C	$10^4 k_\psi$,[a] sec^{-1}
1	0.97	35.0	5.70
2	0.97	45.0	18.8
3	0.97	55.0	50.7

[a] Average of at least two runs.

perimental Section). Earlier workers[7-10] concluded, on the basis of ultraviolet and nuclear magnetic resonance (nmr) spectra, that these and similar compounds assume a cyclic form in nonpolar solvents. An ultraviolet spectrum of an hydrolysis run in aqueous acid after ten half-lives (and, indeed, after several months) is identical with an equivalent solution of the appropriate 8-aroyl-1-naphthoic acid in the same acid solution. However, although the spectrum of the product of hydrolysis resembles the spectrum of **3** more closely than it does the spectrum of the normal ester, **6**, there are significant differences. Furthermore, the shape of the spectrum is sensitive to acid concentration, thus leading to our uncertainty about the exact form of the product of our hydrolysis studies. At any rate, this uncertainty has not interfered with our rate studies since whatever form is assumed by the product it is formed rapidly and is stable.

We have applied a number of the criteria which have been used to distinguish between unimolecular and bimolecular hydrolysis mechanisms to the hydrolysis of **3a**, **3b**, and **3c**. The results are summarized in Table IV.

Table IV. A Summary of Criteria of Mechanism Applied to the Hydrolysis of Methyl Pseudo-8-aroyl-1-naphthoates in Aqueous Acid[a]

Compd	*w*	Slope of log k_ψ *vs.* $-H_0$	ϕ	ΔS^*, eu	k_{H_2O}/k_{D_2O}
3a	−0.50	1.07	−0.083	0.7 ± 1.0	0.36
		1.30 ($HClO_4$)	−0.56 ($HClO_4$)		
3b	−0.75	1.08	−0.086	−2.5 ± 1.0	0.37
3c	...	...	...	−2.7 ± 1.0	...

[a] The values are for sulfuric acid unless otherwise noted.

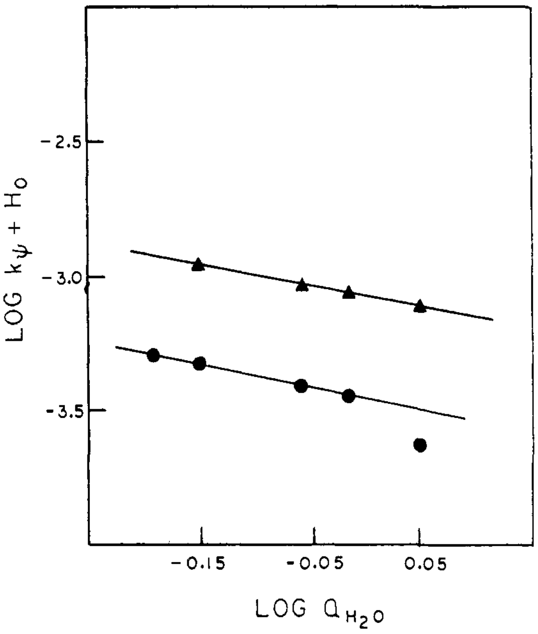

Figure 1. Hydrolysis of methyl pseudo-8-aroyl-1-naphthoates (**3a**, ●; **3b**, ▲) in sulfuric acid solutions; plot of log $k_\psi + H_0$ against log a_{H_2O}. Log a_{H_2O} values were taken from ref 11.

The data for the hydrolysis of **3a** and **3b** in sulfuric acid plotted according to the Bunnett *w* parameter[11] and according to the Zucker–Hammett hypothesis[12] are shown in Figures 1 and 2. In each case the linear correlation and the value of the slope are consistent with a unimolecular hydrolysis mechanism. Data for the hydrolysis of **3a** in perchloric acid are qualitatively the same. When log $k_\psi + H_0$ is plotted against H_0

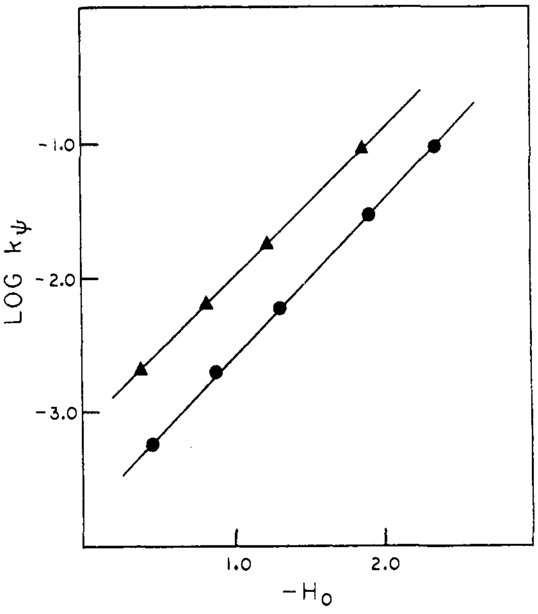

Figure 2. Hydrolysis of methyl pseudo-8-aroyl-1-naphthoates (**3a**, ●; **3b**, ▲) in sulfuric acid solutions; plot of log k_ψ against $-H_0$.

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(7) H. E. French and J. E. Kircher, *J. Amer. Chem. Soc.*, **66**, 298 (1944).

(8) D. V. Nightingale, W. S. Wagner, and R. H. Wise, *ibid.*, **75**, 4701 (1953).

(9) P. T. Lansbury and J. F. Bieron, *J. Org. Chem.*, **28**, 3564 (1963).

(10) V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966).

(11) J. F. Bunnett, *J. Amer. Chem. Soc.*, **83**, 4956, 4968, 4973, 4978 (1961).

(12) L. Zucker and L. P. Hammett, *ibid.*, **61**, 2791 (1939); L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp 273–277.

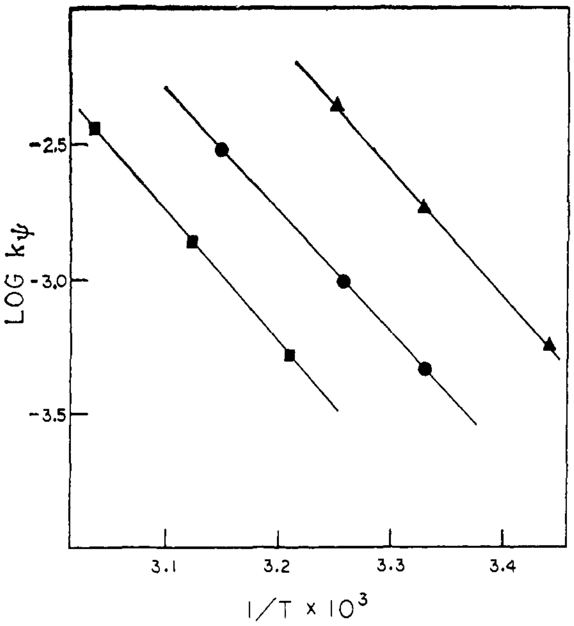


Figure 3. Hydrolysis of methyl pseudo-8-aroyl-1-naphthoates (**3a**, ●; **3b**, ▲; **3c**, ■) in 1 *M* sulfuric acid; plot of log k_ψ against $1/T$°K. Enthalpies of activation (kilocalories mole^{-1}) are 22.3 ± 0.5 for **3a**, 20.5 ± 0.5 for **3b**, and 21.1 ± 0.5 for **3c**.

+ log [HA] the slopes, ϕ, fall within a range established by a number of reactions known to proceed *via* A1 pathways.[13]

Plots of log k_ψ against the reciprocal of the absolute temperature for the three pseudo esters are linear as shown in Figure 3. The resulting entropies of activation (ΔS^*) are those expected for A1 processes, all being close to 0 eu.[14]

The rates of hydrolysis of **3a** and **3b** in *ca.* 1 *M* sulfuric acid are accelerated by a factor of about 3 when they are determined in deuterium oxide which contains the same concentration of sulfuric acid-d_2. This observation is typical for hydrolysis reactions of weakly basic substrates which proceed by preequilibrium protonation and rate-determining unimolecular cleavage.[15–19]

The logarithm of the pseudo-first-order rate constants for the hydrolysis of **3a**, **3b**, and **3c** at *ca.* 1 *M* sulfuric acid are plotted against the substituent constant, σ^+,[20] in Figure 4. The reaction constant, ρ^+, is −2.1.

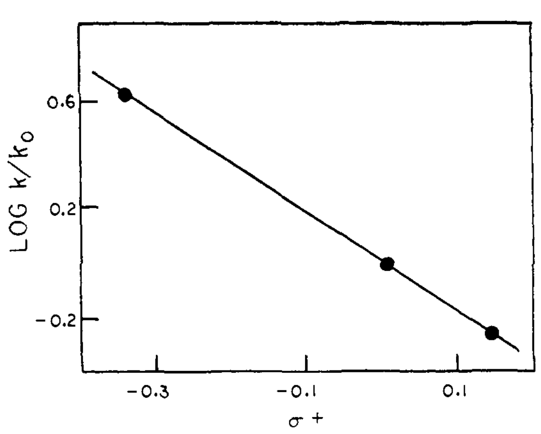


Figure 4. Hydrolysis of methyl pseudo-8-aroyl-1-naphthoates in *ca.* 1 *M* sulfuric acid; plot of log (k/k_0) against σ^+. The slope, ρ, is −2.1.

The hydrolysis of **3a** is specific hydronium ion catalyzed as shown by the results of the buffer experiments described in Table V. The rate constant depends only on the pH of the buffer solution and is independent of the concentration of the undissociated phosphoric acid.

Table V. Methyl Pseudo-8-benzoyl-1-naphthoate (**3a**) Hydrolysis in Buffer Solutions

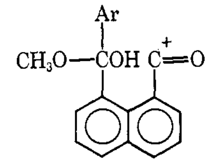
No.	[H_3PO_4] = [KH_2PO_4], *M*	[$LiClO_4$], *M*	10^4k_ψ,[a] sec^{-1}
1	0.20	0.00	6.99
2	0.15	0.05	6.99
3	0.10	0.10	6.98

[a] Average of two runs. The substrate concentration was 2.5 × 10^{-5} *M*. The temperature was 50.00 ± 0.05°. The pH of all solutions was 2.00 ± 0.01.

Discussion

The only surprise provided by the results in Table IV is their unanimity in pointing to an A1 mechanism for the hydrolysis of methyl pseudo-8-aroyl-1-naphthoates. It is unusual to find all of the rate–acidity correlations, the entropy of activation, and the solvent isotope effect in such good agreement. The observation of specific hydronium ion catalysis for this reaction is important in the sense that buffer catalysis clearly would have been irreconcilable with a unimolecular process.

One of the unimolecular hydrolysis mechanisms, the $A_{Ac}1$ pathway, can be ruled out straightway. Such a process would require the formation of an acylium ion, **7**, in the rate-determining step which cannot account for our observation of a healthy substituent effect (ρ^+ = −2.1) from the *para* position of the aryl ring. The sign and magnitude of ρ and the fact that the rate correlates with σ^+ implicate an hydrolysis mechanism involving a high degree of positive charge at the "benzylic" carbon atom. One would not expect an $A_{Ac}1$ mechanism in any case since the structural[21] and medium[22] requirements for observing this mechanism are not met in our study.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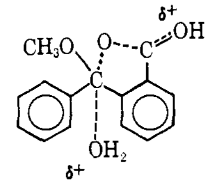
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Two mechanisms, either of which accounts for all of our observations, are shown in Scheme I. Each of these mechanisms involves unimolecular cleavage of a

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(13) J. F. Bunnett and F. P. Olsen, *Can. J. Chem.*, **44**, 1899, 1917 (1966).

(14) R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **74**, 5372 (1952); R. W. Taft, Jr., E. L. Purlee, P. Riesz, and C. A. DeFazio, *ibid.*, **77**, 1584 (1955).

(15) M.Kilpatrick, *ibid.*, **85**, 1036 (1963).

(16) M. L. Bender and M. S. Silver, *ibid.*, **85**, 3006 (1963).

(17) R. H. DeWolfe and J. L. Jensen, *ibid.*, **85**, 3264 (1963).

(18) T. H. Fife, *ibid.*, **87**, 271 (1965).

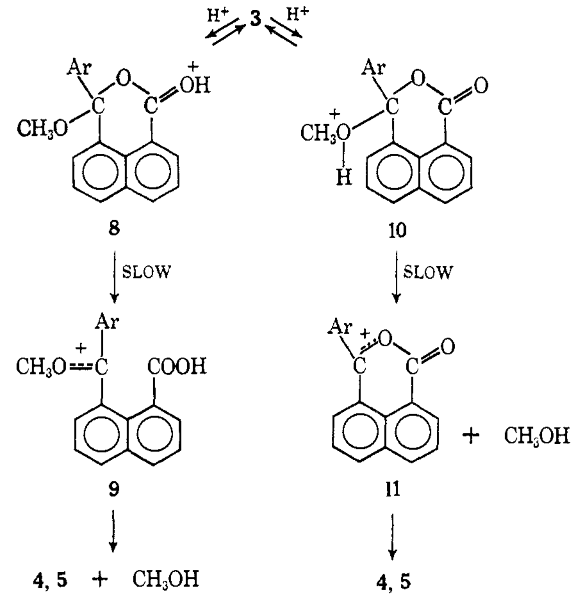
(19) J. G. Fullington and E. H. Cordes, *J. Org. Chem.*, **29**, 970 (1964).

(20) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **79**, 1913 (1957); Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

(21) M. L. Bender and M. C. Chen, *J. Amer. Chem. Soc.*, **85**, 37 (1963), and references cited therein.

(22) K. Yates and R. A. McClelland, *ibid.*, **89**, 2686 (1967).

Scheme I



protonated substrate to yield an alkoxycarbonium ion at the "benzylic" position. The differences between them are the position of protonation and whether the cationic intermediate is an open one, **9**, or a cyclic one, **11**. The question of the relative merits of these two pathways has given us an opportunity for considerable speculation. It is particularly stimulating to consider the fact that the rate of hydrolysis of **3a** is about twice as fast in perchloric acid as it is in sulfuric acid in view of Bunton's recently published work.[23] However, we have been unable to find an experimental observation which would lead us to favor one pathway over the other.[24]

It does seem useful to speculate briefly on the reason why the mechanism of hydrolysis of methyl pseudo-8-aroyl-1-naphthoates (**3**) is an uncomplicated A1 process whereas the mechanism for methyl pseudo-2-benzoylbenzoate (**2**) appears to require the active participation of water in the rate-determining step. In an earlier paper[6] we considered several mechanisms involving nucleophilic attack by water for the hydrolysis of **2**. Subsequent to the preparation of that paper we have observed a substituent effect ($\rho = -1.0$) in the hydrolysis of methyl pseudo-2-(*para*-substituted) benzoylbenzoates.[25] Therefore, we now favor the mechanism in which the site of nucleophilic attack is the "benzylic" carbon. The transition state for this process is shown as **12**. We believe that the explanation for this difference in behavior lies in the variation of the inductive influence of the carboxyl moiety in the two structures. That is, in **2** the electron-withdrawing carboxyl group is in a position to destabilize the developing carbonium ion and, therefore, nucleophilic participation by water is necessary. In **3** the carboxylic function is more remote and does not perturb the stability of the developing cation, **9** or **11**.

Experimental Section

Melting points are uncorrected. Microanalyses were performed by Bernhardt Mikroanalytisches Laboratorium, Mulheim, Germany, or by George Robertson, Florham Park, N. J. The infrared spectra were determined on a Beckman IR-10 recording spectrophotometer. The ultraviolet data were obtained using a Beckman DK-2 spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian A-60A high-resolution spectrometer at ambient temperatures.

Materials. Naphthalic anhydride was obtained from the Aldrich Company. For the kinetic runs, dioxane was purified by the method of Fieser.[26] Fresh solutions were prepared weekly. Sulfuric acid and perchloric acid solutions were individually standardized against sodium hydroxide. Deuteriosulfuric acid (99%) solutions were prepared by diluting with deuterium oxide (99.8%) and standardizing with sodium hydroxide solutions. Both deuterated compounds were obtained from the Stohler Isotope Company. Phosphate buffers were prepared by mixing the appropriate amounts of standardized phosphoric acid (Baker Reagent) solutions with stock solutions of potassium dihydrogen phosphate (Baker Reagent) and lithium perchlorate (G. F. Smith). Methanol was distilled from magnesium methoxide when needed. Doubly distilled water was used for all aqueous solutions.

8-Benzoyl-1-naphthoic Acid. The procedure used was an adaptation of the method of De Bennville[27] and Nightingale and coworkers.[28] Phenylmagnesium bromide was prepared from 15.7 g (0.1 mol) of bromobenzene and 3.0 g (0.13 g-atom) of magnesium turnings in 25 ml of anhydrous ether. The solution was cooled in ice, and 11.0 g (0.06 mol) of anhydrous cadmium chloride was added with rapid stirring. The mixture was heated and stirred for 90 min. The ether was removed by distillation and 100 ml of dry toluene was added. This solution of diphenylcadmium was cooled in ice, and 10.0 g (0.05 mol) of 1,8-naphthalic anhydride was added slowly during a period of 10 min. The mixture was heated for 3 hr at a temperature of 60–70° with constant stirring. After the solution cooled, the complex was hydrolyzed with a 1:1 solution of concentrated hydrochloric acid and water. The two liquid phases were separated from the solid materials by filtration through glass wool. The toluene layer was treated with 10% sodium carbonate solution to extract the naphthalic acid. A yellow solid was isolated and recrystallized five times from 70% acetic acid and twice from methanol, yielding 6.5 g (48%) of a white solid: mp 110–111° (lit.[29] mp 110°); uv max (dioxane) 326 (4.0), 308 (4.1), and 297 mμ (log ε 4.1); uv max (1 *M* H_2SO_4) 327 (4.1) and 305 mμ (log ε 4.2); ir (Nujol) 3100–3500 (O—H) and 1690 cm^{-1} (C═O); nmr (10% acetone-d_6) δ 8.05 (m, 11) and 4.13 ppm (s, 1).

Anal. Calcd for $C_{18}H_{12}O_3$: C, 78.25; H, 4.38. Found: C, 78.07; H, 4.40.

8-*p*-Toluyl-1-naphthoic Acid. The procedure was the same as described above. The Grignard reagent was prepared from 17.1 g (0.1 mol) of *p*-bromotoluene and 3.0 g (0.13 g-atom) of magnesium turnings in 25 ml of dry ether. The ditolylcadmium was prepared from 11.0 g (0.06 mol) of cadmium chloride. Ten grams of 1,8-naphthalic anhydride was added, and upon work-up a yellow solid was isolated. When recrystallized from 70% acetic acid and then from methanol, 7.0 g (49%) of the acid was isolated: mp 134–135° (lit.[28] mp 134–136°); uv max (dioxane) 326 (4.3), 308 (4.4), and 297 mμ (log ε 4.4); uv max (1 *M* H_2SO_4) 327 (4.0) and 305 mμ (log ε 4.2); ir (Nujol) 3100–3400 (O—H) and 1695 cm^{-1} (C═O); nmr (7% acetone-d_6) δ 7.80 (m, 10), 4.90 (s, 1), and 2.33 ppm (s, 3).

Anal. Calcd for $C_{19}H_{14}O_3$: C, 78.61; H, 4.86. Found: C, 78.83; H, 4.77.

8-*p*-Bromobenzoyl-1-naphthoic Acid. The procedure was the same as above. The acid was prepared from 23.4 g (0.1 mol) of *p*-dibromobenzene, 3.0 g (0.13 g-atom) of magnesium turnings, 11.0 g (0.06 mol) of cadmium chloride, and 10.0 g (0.05 mol) of 1,8-naphthalic anhydride. The yield was 8.9 g (50%): mp 165–167°; uv max (dioxane) 326 (4.5), 308 (4.6), and 297 mμ (log ε 4.6); uv max (1 *M* H_2SO_4) 327 (4.2) and 305 mμ (log ε 4.3); ir (Nujol) 3050–3400 (O—H) and 1695 cm^{-1} (C═O); nmr (5% acetone-d_6) δ 7.70 (m, 10) and 3.60 ppm (s, 1).

Anal. Calcd for $C_{18}H_{11}O_3Br$: C, 60.85; H, 3.10. Found: C, 61.08; H, 3.15.

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(23) C. A. Bunton, J. H. Crabtree, and L. Robinson, *J. Amer. Chem. Soc.*, **90**, 1258 (1968).

(24) A referee has pointed out that "an argument similar to that developed to explain the difference in behavior between 2 and 3 "(*vide infra*) leads to the conclusion that **9** is more stable than **11** and therefore that the left-hand side of Scheme I is probably the correct one." We agree and hope to provide evidence on this matter.

(25) D. P. Weeks and J. Cella, Abstracts, 3rd Middle Atlantic Regional Meeting of the American Chemical Society, Philadelphia, Pa., Feb 1968, No. H-58.

(26) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1957, p 284.

(27) P. De Benneville, *J. Org. Chem.*, **6**, 462 (1941).

(28) D. V. Nightingale, W. S. Wagner, and R. H. Wise, *J. Amer. Chem. Soc.*, **75**, 4701 (1953).

(29) F. Mason, *J. Chem. Soc.*, 2116 (1924).

3-Chloro-3-phenylnaphthalide. The acid chloride of 8-benzoyl-1-naphthoic acid was prepared by the method of Mason.[29] A mixture of 3.0 g (0.01 mol) of 8-benzoyl-1-naphthoic acid and 1.0 ml (0.013 mol) of thionyl chloride was heated on a water bath for 30 min after the initial vigorous reaction had subsided. The hot solution was filtered and, on standing, 2.90 g (90%) of a white solid separated: mp 126–127° (lit.[29] mp 125–127°); ir (Nujol) 1740 cm^{-1} (C=O).

3-Chloro-3-*p*-tolylnaphthalide. Mason's[29] procedure was used to prepare the acid chloride of 8-*p*-toluyl-1-naphthoic acid. From 3.0 g (0.01 mol) of the acid and 1.01 ml (0.013 mol) of thionyl chloride, 2.70 g (90%) of the acid chloride was prepared: mp 142–144° (lit.[29] mp 144–146°); ir (Nujol) 1735 cm^{-1} (C=O).

3-Chloro-3-*p*-bromophenylnaphthalide. Using Mason's[29] procedure 3.5 g (0.01 mol) of 8-*p*-bromobenzoyl-1-naphthoic acid and 1.0 ml (0.013 mol) of thionyl chloride were allowed to react yielding 3.0 g (80%) of acid chloride: ir (Nujol) 1730 cm^{-1} (C=O).

Methyl Pseudo-8-benzoyl-1-naphthoate (3a). The methyl ester of pseudo-8-benzoyl-1-naphthoic acid was prepared by a variation of the method of Newman and McCleary[30] and Newman and Lala.[31] About 25 ml of anhydrous methanol containing 0.5 g (0.008 mol) of urea was added to 1.55 g (0.005 mol) of 3-chloro-3-phenylnaphthalide. The resulting solution was allowed to stand for 2 days. On the third day, the solution was poured into 50 ml of water. The ester was extracted from the methanol–water solution by adding 25 ml of ether. The ether was removed by evaporation yielding 1.30 g (85%) of the ester: mp 132–133°; uv max (dioxane) 326 (4.2), 308 (4.3), and 297 mμ (log ε 4.2); uv max (1 *M* H_2SO_4) 327 (4.2) and 305 mμ (log ε 4.2); ir (Nujol) 1710 cm^{-1} (cyclic naphthoate C=O); nmr (10% $CDCl_3$) δ 7.77 (m, 11) and 3.42 ppm (s, 3).

Anal. Calcd for $C_{19}H_{14}O_3$: C, 78.61; H, 4.86. Found: C, 78.43; H, 5.03.

Methyl Pseudo-8-*p*-toluyl-1-naphthoate (3b). From 1.62 g (0.005 mol) of 3-chloro-3-tolylnaphthalide and 25 ml of anhydrous methanol, 1.37 g (90%) of the pseudo ester was obtained: mp 140–141°; uv max (dioxane) 326 (4.3), 308 (4.3), and 297 mμ (log ε 4.3); uv max (1 *M* H_2SO_4) 327 (4.1) and 305 mμ (log ε 4.2); ir (Nujol) 1710 cm^{-1} (C=O); nmr (10% $CDCl_3$) δ 7.67 (m, 10), 3.42 (s, 3, OCH_3), and 2.32 ppm (s, 3).

Anal. Calcd for $C_{20}H_{16}O_3$: C, 78.95; H, 5.26. Found: C, 78.77; H, 5.46.

Methyl Pseudo-8-*p*-bromobenzoyl-1-naphthoate (3c). From 1.87 g (0.005 mol) of 3-chloro-3-*p*-bromophenylnaphthalide and 25 ml of methanol, 1.67 g (90%) of the corresponding ester was formed: mp 150° dec; uv max (dioxane) 326 (4.2), 308 (4.3), and 297 mμ (log ε 4.3); ir (Nujol) 1710 cm^{-1} (C=O); nmr (10% $CDCl_3$) δ 7.82 (m, 10) and 3.40 ppm (s, 3).

Anal. Calcd for $C_{19}H_{13}O_3Br$: C, 61.79; H, 3.52; O, 13.01. Found: C, 61.72; H, 3.58; O, 13.14.

Methyl 8-Benzoyl-1-naphthoate (6a). After 1.0 g (0.003 mol) of the pseudo ester and 10 ml of methanol were refluxed for 1 hr, 0.90 g (90%) of a yellow compound was isolated which was identified as the normal ester: mp 144–145°; uv max (dioxane) 290 mμ (log ε 4.5); uv max (1 *M* H_2SO_4) 290 mμ (log ε 4.3); ir (Nujol) 1725 (ester C=O) and 1660 cm^{-1} (C=O); nmr (10% $CDCl_3$) δ 7.69 (m, 11) and 3.42 ppm (s, 3).

Methyl 8-*p*-Toluyl-1-naphthoate (6b). The normal ester was prepared from 0.9 g (0.003 mol) of the corresponding pseudo ester and 10 ml of methanol. A yield of 0.7 g (63%) of the normal ester was recovered: mp 149–150°; uv max (dioxane) 290 mμ (log ε 4.9); uv max (1 *M* H_2SO_4) 290 (4.4) and 267 mμ (log ε 4.5); ir (Nujol) 1725 (ester C=O) and 1660 cm^{-1} (C=O); nmr (10% $CDCl_3$) δ 7.67 (m, 10), 3.43 (s, 3, OCH_3), and 2.43 ppm (s, 3).

Rate Determinations. The hydrolyses of **3a**, **3b**, and **3c** were followed in the ultraviolet at 260, 245, and 250 mμ respectively, where there were substantial differences in the absorbances of starting materials and products. The molar absorptivities of interest are listed in Table VI. All compounds obeyed Beer's law.

Table VI. Molar Absorptivities of 8-Aroyl-1-naphthoic Acids, Methyl Pseudo-8-aroyl-1-naphthoates, and Methyl 8-Aroyl-1-naphthoates

Compound	Molar absorptivities, 10^4 (l. cm^{-1} mol^{-1})
Acid	
8-Benzoyl[a]	1.8
8-*p*-Toluyl[b]	10.0
8-*p*-Bromobenzoyl[c]	8.4
Pseudo Ester	
8-Benzoyl[a]	2.8
8-*p*-Toluyl[b]	12.0
8-*p*-Bromobenzoyl[c]	9.3
Normal Ester	
8-Benzoyl[a]	4.0
8-*p*-Toluyl[b]	16.0

[a] Determined at 260 mμ. [b] Determined at 245 mμ. [c] Determined at 250 mμ.

For the hydrolysis of methyl pseudo-8-benzoyl-1-naphthoate the rates of appearance of 8-benzoyl-1-naphthoic acid were measured spectrophotometrically with a Beckman DK-2 spectrophotometer in 1-cm silica cells. For the esters of pseudo-8-*p*-toluyl- and -8-*p*-bromobenzoyl-1-naphthoic acids, the rates of disappearance of ester were measured in 2-cm silica cells. The esters, dissolved in dioxane, were added to the acid solutions in thermostated silica cells by means of a syringe. The dioxane concentration was never more than 5% by volume in the acid solutions. The rates were usually followed to 75% of completion and infinity points were taken at greater than ten half-lives and were stable. Pseudo-first-order rate constants were obtained from plots of log $(A_t - A_\infty)$ *vs.* time. Mathematical operations were done by computer. For most reactions a correlation factor of 0.999 was obtained with no correlation ever being less than 0.991.

Product Determination. One gram (0.003 mol) of methyl pseudo-8-benzoyl-1-naphthoate was dissolved in a minimum of acetone. Approximately 1 *M* sulfuric acid (100 ml) was added. The solution was allowed to stand for 2 days. The organic acid was extracted with ether. The ether was allowed to evaporate slowly leaving 0.75 g (79%) of a solid material that was identified as the pseudo acid.

Similar large-scale reactions were performed for methyl pseudo-8-toluyl- and -8-*p*-bromobenzoyl-1-naphthoates and the products were identified as the corresponding pseudo acids. The over-all yields were over 65%.

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(31) M. S. Newman and L. K. Lala, *Tetrahedron Lett.*, 3267 (1967).