Associative and Dissociative Pathways in the Alkaline Hydrolysis of Aryl 2-Hydroxycinnamates

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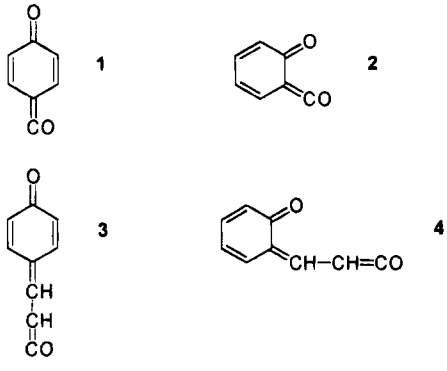
Aryl 2-hydroxycinnamate esters hydrolyze in alkaline solutions (20% dioxane–water v/v) obeying the rate law $k_{obs} = k_a + k_b[OH^-]/(1 + a_H/K_a)$, where K_a is the ionization constant of the hydroxy group of the ester and k_b is the second-order rate constant for the attack of hydroxide ion on the ionized ester. Kinetic data and activation parameters for the hydrolysis of the 2,4-dinitrophenyl ester show that the mechanism giving rise to the k_a term cannot be a simple $B_{Ac}2$ type process and suggest the occurrence of a E1cB mechanism involving an "extended" *o*-oxoketene intermediate. The Brönsted plot of the apparent second-order rate constants (k_aK_a/k_w) *versus* the pK of the leaving group indicates that the reaction mechanism changes from E1cB to $B_{Ac}2$ for esters with leaving groups having pK higher than about 6.

We have previously provided strong evidence[1] that aryl 4-hydroxybenzoates, possessing leaving groups with pK_a values lower than about 6.5, hydrolyze in aqueous alkaline solutions through a E1cB mechanism involving the participation of the unsaturated *p*-oxoketene intermediate **1**. We have not observed this intermediate directly, but similar species have precedent in the literature,[1a] and furthermore, compound **1** is related to the well-known quinones and quinone methides.



It is generally thought[2] that in acyl group transfer processes the dissociative route is an actual alternative to the more usual $B_{Ac}2$ mechanism if the substrate has a leaving group of high nucleofugality and if ionization of the acidic center of the substrate yields an anion able to support the expulsion of the leaving group with consequent formation of an unsaturated intermediate. Of course, also the stability of the intermediate, which will be reflected in the transition state, has the potential of controlling the mechanistic path taken.

In our previous investigations we have studied the leaving group[1a] effects as well as the internal nucleophilicity[1b] effects on the reactivity of elimination. In order to evaluate the significance of the intermediate stability the study was extended to aryl esters of 2-hydroxybenzoic acid with the aim to ascertain the possible intervention in the hydrolytic process of the intermediate **2**, which should possess somewhat different stability compared to isomer **1**, thus possibly allowing some speculation about the effect of the intermediate stability. Unfortunately, preliminary experiments indicated that 2,4-dinitrophenyl salicylate did not hydrolyze in alkaline solution through the *o*-oxoketene **2**: it was found[1a] that another degradative route, namely a Smiles-type[3] rearrangement, takes place affording a diaryl ether.

More recently, we have undertaken a study on the alkaline hydrolysis of some aryl 4-hydroxycinnamates, and we found[4] that esters of acidic phenols hydrolyze through a dissociative path with the participation of the "extended" *p*-oxoketene intermediate **3**. Reactivity comparison between the 2,4-dinitrophenyl esters of 4-hydroxycinnamic and 4-hydroxybenzoic acid suggested that the presence of the vinyl group could favor the dissociative hydrolysis mostly increasing the stability of the unsaturated intermediate **3** with respect to **1**, owing to a more extended delocalization of π electrons in the former.

In this paper we report the results of a study carried out on the alkaline hydrolysis of aryl 2-hydroxycinnamates; as these esters cannot undergo a "Smiles" rearrangement because of structural reasons, we hoped we could demonstrate the participation of the "extended" *o*-oxoketene intermediate **4** to reaction: this could offer the opportunity of a better understanding of the structural requirements controlling the E1cB mechanism in acyl group transfer.

Experimental Section

General. Starting reagents and solvents were purified and/or distilled before use. Buffer materials were of analytical reagent grade. Dioxane was purged of peroxides by passage of the analytical grade product through an activated alumina column; the absence of peroxides was checked by the KI test. Water was double distilled and preboiled to free it from dissolved carbon dioxide. The ^{1}H-NMR spectra were recorded with a Varian Gemini 200 spectrometer (200 MHz) with TMS as internal standard and acetone-d_6 as solvent.

Synthesis. The esters of *trans*-2-hydroxycinnamic acid were prepared following two alternative methods: the first

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(2) Williams, A.; Douglas, K. T. *Chem. Rev.* **1975**, *75*, 627.

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one, which was employed by us also in the synthesis of the aryl 4-hydroxycinnamates,[4b] is the well-known carbodiimide route (indicated as A). In the second procedure (route B) the silylation of *trans*-2-hydroxycinnamic acid, accomplished in very good yield with *tert*-butyldimethylchlorosilane,[5] afforded *tert*-butyldimethylsilyl 2-((*tert*-butyldimethylsilyl)oxy)cinnamate as a colorless liquid. The bissilylated compound was subsequently treated with oxalyl chloride–DMF[6] to give 2-((*tert*-butyldimethylsilyl)oxy)cinnamoyl chloride (in 92% yield). The reaction of this acid chloride with the appropriate phenol furnished the aryl 2-((*tert*-butyldimethylsilyl)oxy)cinnamate and finally, after removal of the silyl group carried out by aqueous hydrofluoric acid,[7] the desired aryl 2-hydroxycinnamate. All silyl derivatives as well as the desired esters gave satisfactory ^{1}H-NMR spectra. The vinylic coupling constants of the products clearly indicate formation of *trans*-esters. The characteristics of the new esters, recrystallized from toluene, were as follows: mp and synthetic route (A or B) are given together with analytical data. **2,4-Dinitrophenyl 2′-hydroxycinnamate**: mp 158–159 °C (A); δ 8.95 (d, 1, J = 2.0 Hz), 8.71 (m, 1), 8.25 (d, 1, J = 16.1 Hz), 7.88 (d, 1, J = 9.0 Hz), 7.74 (m, 1), 7.35 (m, 1), 6.99 (m, 2), 6.95 (d, 1, J = 16.1 Hz). Anal. Calcd for $C_{15}H_{10}N_2O_7$: C, 54.6; H, 3.1; N, 8.5. Found: C, 54.6; H, 3.3; N, 8.3. **2,6-Dinitrophenyl 2′-hydroxycinnamate**: mp 181–181.3 °C (A); δ 8.44 (d, 2, J = 4.0 Hz), 8.32 (m, 1), 8.25 (d, 1, J = 16.0 Hz), 7.73 (m, 1), 7.34 (m, 1), 7.00 (m, 2), 6.94 (d, 1, J = 16.0 Hz). Anal. Calcd for $C_{15}H_{10}N_2O_7$: C, 54.6; H, 3.1; N, 8.5. Found: C, 54.6; H, 3.2; N, 8.3. **2-Methyl-4,6-dinitrophenyl 2′-hydroxycinnamate**: mp 146–146.5 °C (B); δ 8.68 (m, 2), 8.27 (d, 1, J = 16.0 Hz), 7.75 (m, 1), 7.35 (m, 1), 7.00 (m, 2), 6.99 (d, 1, J = 16.0 Hz), 2.51 (s, 3). Anal. Calcd for $C_{16}H_{12}N_2O_7$: C, 55.8; H, 3.5; N, 8.1. Found: C, 56.0; H, 3.7; N, 8.0. **3,4-Dinitrophenyl 2′-hydroxycinnamate**: mp 149–150 °C (A); δ 8.34 (d, 1, J = 8.8 Hz), 8.24 (d, 1, J = 16.1 Hz), 8.14 (d, 1, J = 2.4 Hz), 7.90 (d, 1, J = 8.9 Hz), 7.72 (m, 1), 7.33 (m, 1), 7.01 (m, 2), 6.90 (d, 1, J = 16.0 Hz). Anal. Calcd for $C_{15}H_{10}N_2O_7$: C, 54.6; H, 3.1; N, 8.5. Found: C, 54.6; H, 3.4; N, 8.0. **2,5-Dinitrophenyl 2′-hydroxycinnamate**: mp 157.5–158.5 °C (A); δ 8.30 (m, 3), 8.17 (d, 1, J = 16.0 Hz), 7.64 (m, 1), 7.34 (m, 1), 6.95 (m, 2), 6.84 (d, 1, J = 16.0 Hz). Anal. Calcd for $C_{15}H_{10}N_2O_7$: C, 54.6; H, 3.1; N, 8.5. Found: C, 55.9; H, 3.4; N, 8.0. **2-Chloro-4-nitrophenyl 2′-hydroxycinnamate**: mp 153–154 °C (A); δ 8.44 (m, 2), 8.32 (m, 1), 8.25 (d, 1, J = 16.0 Hz), 7.73 (m, 1), 7.34 (m, 1), 6.99 (m, 2), 6.95 (d, 1, J = 16.0 Hz). Anal. Calcd for $C_{15}H_{10}NO_5Cl$: C, 56.4; H, 3.2; N, 4.4. Found: C, 56.2; H, 3.1; N, 4.1. **4-Chloro-2-nitrophenyl 4′-hydroxycinnamate**: mp 207–208 °C (B); δ 8.21 (m, 1), 7.90 (d, 1, J = 16.0 Hz), 7.73 (m, 1), 7.59 (m, 1), 7.34 (m, 1), 6.98 (m, 2), 6.90 (d, 1, J = 16.0 Hz). Anal. Calcd for $C_{15}H_{10}NO_5Cl$: C, 56.4; H, 3.2; N, 4.4. Found: C, 56.1; H, 3.3; N, 4.1. **4-Nitrophenyl 2′-hydroxycinnamate**: mp 158–158.5 °C (A); δ 8.36 (m, 2), 7.96 (d, 1, J = 16.0 Hz), 7.81 (m, 2), 6.99 (m, 2), 6.83 (d, 1, J = 16.1 Hz). Anal. Calcd for $C_{15}H_{11}NO_5$: C, 63.2; H, 3.9; N, 4.9. Found: C, 63.9; H, 4.0; N, 5.0. **4-Cyanophenyl 2′-hydroxycinnamate**: mp 135–136 °C (B); δ 8.19 (d, 1, J = 16.1 Hz), 7.89 (m, 2), 7.71 (m, 1), 7.48 (m, 2), 7.30 (m, 1), 6.99 (m, 2), 6.87 (d, 1, J = 16.1 Hz). Anal. Calcd for $C_{16}H_{11}NO_3$: C, 72.4; H, 4.2; N, 5.43. Found: C, 71.5; H, 4.0; N, 5.1. The synthesis of aryl cinnamates employed in this work has been previously reported.[4b]

Methods. Kinetic and other methods including the determination of pK_a of the substrates were described in a previous paper.[4b]

Results and Discussion

The observed pseudo-first-order rate constants for the alkaline hydrolysis, in 20% dioxane–water (v/v) solvent at 25 °C and ionic strength 0.1 M (KCl), of aryl 2-hydroxycinnamates were found to follow eq 1.

$$k_{obs} = k_a + k_b[OH^-]/(1 + a_H/K_a) \quad (1)$$

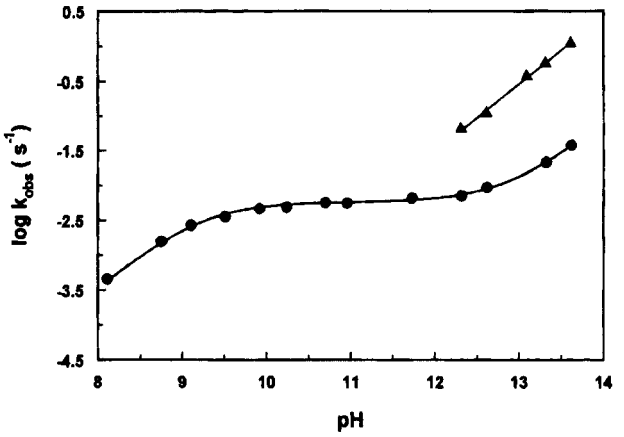

Figure 1. Dependence on pH of the hydrolysis of 2,4-dinitrophenyl 2′-hydroxycinnamate (●) and 2,4-dinitrophenyl cinnamate (▲) in 20% (v/v) dioxane/water at 25 °C and 0.1 M ionic strength made up with KCl. Lines are calculated from eq 1 and 2 from parameters in Tables 1 and 3.

The pH–rate profile for the hydrolysis of 2,4-dinitrophenyl 2′-hydroxycinnamate is illustrated in Figure 1 (●), and similar plots (not shown) were obtained for the other esters. In Table 1 are collected experimental conditions and the values of the kinetic parameters, obtained from primary kinetic data (reported in the supplementary material) by iterative nonlinear curve-fitting performed with the Fig.P program,[8] for the hydrolysis of the 2-hydroxycinnamates. If the reactivity of the ester under examination allows the construction of a sufficiently detailed pH–rate profile (in particular in and below the plateau region of pH) this program provides, together with the rate constants, the K_a values. Table 2 indicates that the kinetic pK_a values are in good agreement with those spectroscopically measured.

The dependence on pH of the pseudo-first-order rate constant (▲) for the hydrolysis of 2,4-dinitrophenyl cinnamate is also shown in Figure 1 and indicates, as expected, a simple second-order rate law in hydroxide ion and ester concentrations (eq 2).

$$k_{obs} = k_{OH}[OH^-] \quad (2)$$

The k_{OH} values for the $B_{Ac}2$ attack of hydroxide ion on aryl cinnamates, in 20% dioxane–water (v/v) solvent at 25 °C and ionic strength 0.1 M (KCl), are reported in Table 3.

The apparent second-order rate constant ($k_{app} = k_aK_a/K_w$ = *ca.* 1.5×10^3 M^{-1} s^{-1}, Table 1) for the hydrolysis of 2,4-dinitrophenyl 2′-hydroxycinnamate (the pK_w value of 14.62 has been reported[9] for the medium employed in this work) is about 150-fold *larger*, rather than *smaller* as expected, than the second-order rate constant related to the $B_{Ac}2$ attack of hydroxide ion on 2,4-dinitrophenyl cinnamate (11.12 M^{-1} s^{-1}, Table 3), thus suggesting that the reactions of these esters could occur through different pathways. A better assessment can be achieved by computing the rate constant (k_{calc}) for the bimolecular attack of hydroxide ion on the neutral 2,4-dinitrophenyl 2′-hydroxycinnamate from the Hammett relationship log

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(8) Fig.P from Biosoft, Cambridge, UK, 1991.
(9) Arned, H. S.; Fallon, L. *J. Am. Chem. Soc.*, **1939**, *61*, 2374.

Table 1. Hydrolysis of Aryl 2-Hydroxycinnamates in 20% Dioxane at 25 °C and μ = 0.1 (pK_w = 14.62)

leaving substituted phenoxide	pK_{LG}[a]	k_a, s^{-1}	k_b, $M^{-1}\ s^{-1}$	k_{app}, $M^{-1}\ s^{-1}$ [b]	N[c]	pH[d]
2,6-dinitro	3.71[e]	$(6.89 \pm 0.07) \times 10^{-3}$	0.041 ± 0.003	1399.92	12	8.11–13.62
2,4-dinitro	4.11	$(5.81 \pm 0.10) \times 10^{-3}$	0.329 ± 0.016	1493.17	13	8.15–13.61
2-methyl-4,6-dinitro	4.35[e]	$(1.05 \pm 0.02) \times 10^{-3}$	0.023 ± 0.001	253.70	12	8.16–13.99
2,5-dinitro	5.22[e]	$(1.69 \pm 0.06) \times 10^{-4}$	0.233 ± 0.011	39.08	11	8.11–13.62
3,4-dinitro	5.42[e]	$(1.44 \pm 0.08) \times 10^{-4}$	0.537 ± 0.038	57.23	12	8.11–13.62
2-chloro-4-nitro	5.45	$(4.03 \pm 0.13) \times 10^{-5}$	0.113 ± 0.004	9.88	10	9.26–13.62
4-chloro-2-nitro	6.46	$(1.16 \pm 0.10) \times 10^{-5}$	0.064 ± 0.004	2.29	9	9.53–13.61
4-nitro	7.14	$(1.38 \pm 0.08) \times 10^{-5}$	0.098 ± 0.004	4.21	7	9.96–13.61
4-cyano	7.95	$(8.36 \pm 0.56) \times 10^{-6}$	0.069 ± 0.003	1.88	7	9.96–13.61

[a] Jencks, W. P.; Regestein, J. *Handbook of Biochemistry and Molecular Biology*, 3rd ed.; Fasman, G., Ed.; Chemical Rubber Co.: Cleveland, 1976. [b] See text; K_a values are taken from Table 2. [c] Number of data points, not including duplicates. [d] pH range employed. [e] Kortum G.; Vogel, W.; Andrussov, K. *Dissociation Constants of Organic Acids in Aqueous Solution*; Butterworths: London, 1961.

Table 2. Ionization Constants of Aryl 2-Hydroxycinnamates in 20% Dioxane at 25 °C and μ = 0.1

leaving substituted phenoxide	λ,[a] nm	$10^{10} K_a$, M	pK_a[b]	pK_a[c]
2,6-dinitro	420	(4.85 ± 0.09)	9.32	9.28 ± 0.01
2,4-dinitro	406	(6.17 ± 0.22)	9.21	9.17 ± 0.02
2-methyl-4,6-dinitro	415	(5.80 ± 0.06)	9.24	9.19 ± 0.02
2,5-dinitro	411	(5.55 ± 0.07)	9.25	9.18 ± 0.05
3,4-dinitro	406	(9.53 ± 0.16)	9.02	8.98 ± 0.09
2-chloro-4-nitro	408	(5.88 ± 0.14)	9.23	9.02 ± 0.07
4-chloro-2-nitro	409	(4.74 ± 0.06)	9.33	
4-nitro	404	(7.32 ± 0.09)	9.13	
4-cyano	403	(5.39 ± 0.04)	9.27	

[a] Wavelength employed for the spectroscopic determination. [b] The error on these values is less than 0.01 pK unit. [c] Measured from the kinetics.

Table 3. Second-Order Rate Constants for the Hydrolysis of Aryl Cinnamates in 20% Dioxane at 25 °C and μ = 0.1

leaving substituted phenoxide	pK_{LG}[a]	λ,[b] nm	N[c]	k_{OH}, $M^{-1}\ s^{-1}$
2,4-dinitro	4.11	400	5	11.12 ± 0.28
4-chloro-2-nitro	6.46	400	4	1.97 ± 0.02
4-nitro	7.14	400	4	2.55 ± 0.01
3-nitro	8.40	408	4	1.58 ± 0.10

[a] See footnote *a* of Table 1. [b] Wavelength for kinetic runs. [c] Number of data points, not including duplicates.

$k/k_0 = 1.97\Sigma\sigma$ for the alkaline hydrolysis of substituted 2,4-dinitrophenyl benzoates.[1a] If the attenuation factor of 0.54 related to the vinylene group[10] is taken into account, the relationship becomes $\log k/k_0 = 1.06\Sigma\sigma$ and is now valid for the $B_{Ac}2$ hydrolysis of substituted 2,4-dinitrophenyl cinnamates. As stated by Charton,[11] ortho-substituted benzene reaction series in which reaction site and benzene ring are separated by some group Z (*e.g.*, −CH=CH−) can be correlated by the Hammett equation using the σ_p substituent constants. Therefore, since k_0 = 11.12 $M^{-1}\ s^{-1}$, employing the σ_p substituent constant (−0.37) for the hydroxy group we finally obtain k_{calc} = 4.47 $M^{-1}\ s^{-1}$. The apparent second-order rate constant (k_aK_a/K_w) for the 2,4-dinitrophenyl 2′-hydroxycinnamate is therefore in excess of this k_{calc} by about 330-fold, thus confirming the suggestion that the mechanism for the k_a term cannot be an associative one and the simplest hypothesis is that an E1cB process (depicted in Scheme 1) involving the participation of the "extended" *o*-oxoketene **4** intermediate occurs. At very high pH values the bimolecular attack of hydroxide ion on the anionic ester takes place (k_b term in eq 1) giving rise to an upward curvature in the pH−rate profile.

Scheme 1

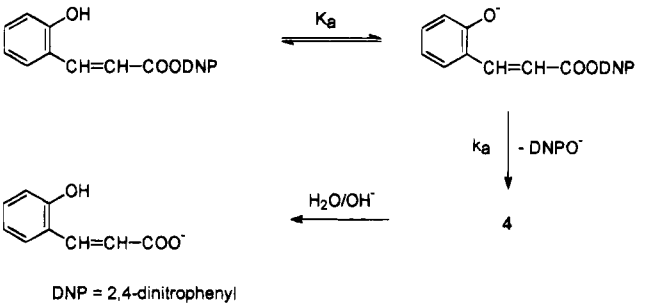

Table 4. Activation Parameters for the Hydrolysis of 2,4-Dinitrophenyl Esters in 20% Dioxane, μ = 0.1[a]

	pH	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$,[b] cal/mol K
2′-hydroxycinnamate	10.70	24.80 ± 0.10	14.30 ± 0.32
2′-hydroxycinnamate	7.70	27.23 ± 0.16	15.78 ± 0.55
cinnamate	10.78	11.23 ± 0.09	-25.22 ± 0.32

[a] Temperature range: 18.0–34.8 °C. [b] Calculated at 25 °C.

Further evidence that the hydrolysis of these two esters follows different pathways is provided by the activation entropy of the reactions (Table 4). For the hydrolysis of 2,4-dinitrophenyl 2′-hydroxycinnamate the values of $\Delta S^{\ddagger}$ for k_aK_a/K_w (measured at pH 7.70) and for the k_a term (measured at pH 10.70) are large and positive as expected for an unimolecular reaction, whereas the negative value of $\Delta S^{\ddagger}$ for the hydrolysis of 2,4-dinitrophenyl cinnamate (at pH 10.78) is consistent with an associative process.[12]

As is customary, the effect of the leaving group variation on reactivity was also investigated. The plot of the logarithms of the apparent second-order rate constants ($k_{app} = k_aK_a/K_w$) against the pK_a of the leaving substituted phenoxide (pK_{LG}) gave rise to a nonlinear Brønsted relationship (Figure 2, data taken from Table 1). Indeed, two different Brønsted equations correlate the data: esters having leaving groups with pK_a < *ca.* 6 (good nucleofuges) follow eq 3 whereas those possessing leaving groups with higher pK_a follow eq 4.

$$\log (k_aK_a/K_w) = (7.39 \pm 0.94) - (1.11 \pm 0.20)pK_{LG} \quad (3)$$

$$\log (k_aK_a/K_w) = (2.22 \pm 0.88) - (0.25 \pm 0.13)pK_{LG} \quad (4)$$

This break in linearity with upward curvature suggests the occurrence of a change in mechanism, from E1cB to $B_{Ac}2$, as the nucleofugality of the leaving group decreases.

(10) Williams, A. In *Chemistry of Enzyme Action*; Page, M. I., Ed.; Elsevier: Amsterdam, 1984; p 127.
(11) Charton, M. *Can. J. Chem.* **1960**, *38*, 2493.
(12) Schaleger, L. L.; Long, F. A. *Adv. Phys. Org. Chem.* **1963**, *1*, 1. Jencks, W. P. *Catalysis in Chemistry and Enzymology*; McGraw-Hill: New York, 1969. Douglas, K. T. *Progr. Bioorg. Chem.* **1976**, *4*, 194.

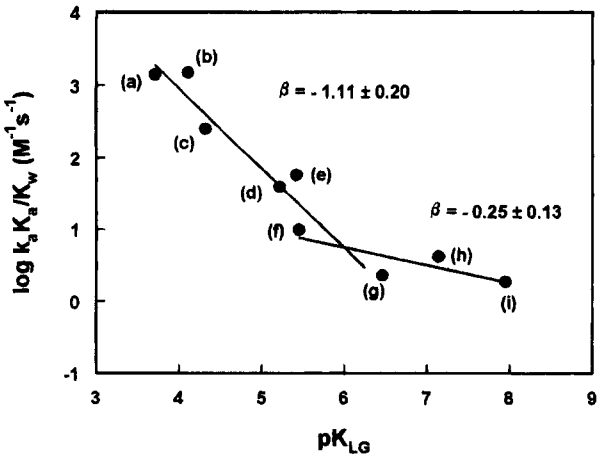

Figure 2. Brønsted plot for the hydrolysis of aryl 2-hydroxycinnamates. The lines are calculated from eqs 3 and 4. Identity, in increasing order of pK_a of the leaving substituted phenoxide: (a) 2,6-dinitrophenyl, (b) 2,4-dinitrophenyl, (c) 6-methyl-2,4-dinitrophenyl, (d) 2,5-dinitrophenyl, (e) 3,4-dinitrophenyl, (f) 2-chloro-4-nitrophenyl, (g) 4-chloro-2-nitrophenyl, (h) 4-nitrophenyl, (i) 4-cyanophenyl.

The high β_{LG} value (−1.11) related to esters possessing good leaving groups is consistent with a dissociative process[2] and is in good agreement with the values that we have previously found for the E1cB hydrolysis of aryl 4-hydroxybenzoates (−1.33)[1a] and 4-hydroxycinnamates (−1.32);[4b] on the contrary, the β_{LG} (−0.25) related to the esters having leaving groups with pK_{LG} higher than *ca.* 6 is within the range expected for a $B_{Ac}2$ mechanism.[13]

The parameter k_b, representing the bimolecular attack of hydroxide ion on the conjugate base of the hydroxycinnamate, fits (omitting the two esters in which the 2,6-positions of the phenolic moieties are occupied) a Brønsted equation having a slope ($\beta_{LG} = -0.21 \pm 0.08$, data from Table 1) consistent with an associative process. A very close value ($\beta_{LG} = -0.20 \pm 0.06$) is obtained from the data in Table 3 for the unambiguous $B_{Ac}2$ alkaline hydrolysis of aryl cinnamates.

It is interesting to note that similar values of k_{app} and k_{OH} were found for the 4-nitrophenyl and the 4-chloro-2-nitrophenyl esters of 2-hydroxycinnamic and cinnamic acids (Tables 1 and 3); this suggests the occurrence of a $B_{Ac}2$ process for these 2-hydroxycinnamates having not very good leaving groups, thus providing further evidence for the proposed changeover in mechanism on varying the leaving group ability.

From this work it appears therefore that the mechanistic behavior of the hydrolysis of aryl 2-hydroxycinnamates is analogous to that observed in the hydrolysis of aryl 4-hydroxybenzoates and 4-hydroxycinnamates.

We are now in a position to make a comparison between 2,4-dinitrophenyl 2′-hydroxycinnamate and 4′-hydroxycinnamate which, as we have shown, hydrolyze through E1cB mechanisms. Results from the present and previous work[4b] of ours indicate that the value of the apparent second-order rate constant for the hydrolysis of the 4-hydroxycinnamate is about 7-fold larger than that of the 2-hydroxycinnamate. Since these esters share the same leaving group and possess quite similar acidities (their pK_a values are 9.31 and 9.21, respectively), only a difference in the stability of the intermediates can be invoked to account for the observed difference in reactivity: in other words the intermediate **4** should be less stable than the intermediate **3**. This is what it should be expected on the basis of the well-known[14] higher stability of the *p*-quinones with respect to *o*-quinones. Moreover, also data available in the literature for quinone methides, which are species structurally related to our intermediates, support the same conclusion. It is known, indeed, that *o*-quinone methide is stable at the liquid nitrogen temperature,[15] but is unstable even at high dilution at room temperature;[16] on the contrary, the ultraviolet spectrum of *p*-quinone methide was easily recorded in dichloromethane.[17] Finally, further support to the proposed order of stability comes from the finding that attempts to trap the intermediate **4** failed, despite the fact that experiments were carried out under similar conditions and with the same nucleophiles previously employed in the successful trapping of the intermediate **3**.[4]

From our studies it emerges that the k_a values related to the dissociative hydrolysis of 2,4-dinitrophenyl esters decrease in the order 4-hydroxycinnamate, 2-hydroxycinnamate, and 4-hydroxybenzoate (even taking into account the correction for the contribution of the internal nucleophilicity effect for the latter)[4b] thus indicating that the intermediate stability could follow the order **3** > **4** > **1**.

Acknowledgment. The authors gratefully thank Mr. Roberto Pardini for his valuable assistance.

Supplementary Material Available: Primary kinetic data (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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