were conducted at 75 °C in 2-propanol containing 0.2, 0.6, and 2.5 M MeOH, respectively. The procedures and analysis were as described above. Relevant data are as follows (reaction time (h), % yield of **1**, % yield of **2**, % yield of 4-nitroanisole). For 0.2 M MeOH: 7.7, 21, 30, 40; 22.5, 1, 53, 27; 72, 0, 68, 2. For 0.6 M MeOH: 17, 0, 34, 60; 40.5, 0, 55, 34; 66, 0, 68, 19. For 2.5 M MeOH: 7.7, 1, 13, 82; 28, 0, 38, 53; 72, 0, 64, 14.

Reactions of 1 with Aryl Oxide Ions. Equimolar amounts of KOH and ArOH were dissolved in H_2O, and the solvent was removed under reduced pressure; the residue was warmed in a hot water bath and dried under vacuum. A solution of **1** (0.03 M) and of a GLC standard (0.01 M) in PhCl was added with Bu_4NBr, and the mixture was stirred with a mechanical stirrer and brough to reflux. In the absence of a catalyst the ArOK remained largely undissolved. Some precipitate was evident also in the presence of the ammonium salt. Aliquots were treated as described above.

Analytical Methods and Compounds. GLC analyses were performed on a Varian 3700 instrument with glass columns packed with 3% XE-60 on Chromosorb W AW DMCS and 10% UCW982 on Chromosorb W AW DMCS. NMR spectra were recorded on a Varian EM360A spectrometer. Mass spectra were recorded on a VG MM16F spectrometer.

Ether products, $ROC_6H_4NO_2$, used to calculate GLC molar responses, were prepared according to reaction 1 and characterized by their spectral properties (NMR, MS) and melting points. **1-(*sec*-Butoxy)-4-nitrobenzene:** oil [lit.[25] bp 106–108 °C (0.8 mmHg)]; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.0 (t, 3 H) 1.3 (d, 3 H), 1.7 (quintet, 2 H), 4.4 (sextet, 1 H), 6.8–8.2 (AA′BB′, 4 H); mass spectrum (70 eV), *m/e* (relative intensity) 195(M), 140 (100), 139, 123, 109, 93. **1-(Octyloxy)-4-nitrobenzene:** mp 24 °C (lit. 24,[26] 26 °C[27]); ^1H NMR ($CDCl_3$, Me_4Si) δ 0.8–1.9 (m, unresolved, 15 H), 4.0 (t, 2 H), 6.8–8.2 (AA′BB′, 4 H); mass spectrum (70 eV), *m/e* (relative intensity) 251(M), 139, 123, 112, 109, 71, 57, 43 (100). **4-Nitrophenyl phenyl ether:** mp 58–59 °C (lit. 59–59.3,[28] 56–58 °C[29]); ^1H NMR ($CDCl_3$, Me_4Si) matches literature data;[30] mass spectrum (70 eV), *m/e* (relative intensity) 215 (M, 100), 199, 185, 168, 141, 129, 115, 77. **Bis(4-nitrophenyl) ether:** mp 145–146 °C (lit. 145,[31] 147–148 °C[32]); ^1H NMR ($CDCl_3$, Me_4Si) 7.1–8.3 (AA′BB′, 2 H + 2 H); mass spectrum (70 eV), *m/e* (relative intensity) 260 (M, 100), 244, 230, 214, 184, 168, 139, 128.

A typical preparative reaction is described below. For reactions in 1-octanol the solvent was removed by distillation of the azeotrope with water.

1-Isopropoxy-4-nitrobenzene (2). KOH in pellets (1.76 g) was dissolved in warm 2-propanol (100 mL) in a two-necked 250-mL flask fitted with a reflux condenser. Bu_4NBr (15 g) and **1** (2.0 g) were then added, and the flask was immersed in a 75 °C bath. The progress of the reaction was followed by TLC analysis (eluent toluene). The mixture was filtered, and the solvent was removed from the filtrate at reduced pressure. The oily residue was taken up with ether, washed with H_2O, dilute HCl, and H_2O, dried with $CaCl_2$, and evaporated to dryness. The crude product (2.3 g, 79%) was purified by column chromatography at low pressure (petroleum ether/toluene) and recrystallization from pentane: yield 1.7 g (72%); mp 32–33 °C (lit. 33,[32] 32–33 °C[9]); ^1H NMR ($CDCl_3$, Me_4Si) 1.4 (d, 6 H), 4.6 (septet, 1 H), 6.75–8.2 (AA′BB′, 4 H); mass spectrum (70 eV), *m/e* (relative intensity) 181 (M), 139 (100), 123, 109, 93, 81, 65.

Registry No. 1, 100-00-5; **2**, 26455-31-2; Bu_4NHSO_4, 32503-27-8; Bu_4NBr, 32503-27-8; $CH_3OCH_2CH_2OCH_3$, 110-71-4; isopropoxide, 15520-32-8; 18-crown-6, 17455-13-9; Triton, 9002-93-1; Carbowax 20M, 56592-21-3; MPEG 5000, 54386-07-1; glyme-5, 143-24-8; 1-octanol, 111-87-5; 2-butanol, 78-92-2; *tert*-butyl alcohol, 75-65-0; chlorobenzene, 108-90-7; 1-*sec*-butoxy-4-nitrobenzene, 63929-88-4; 1-(octyloxy)-4-nitrobenzene, 78723-40-7; 4-nitrophenyl phenyl ether, 620-88-2; bis(*p*-nitrophenyl) ether, 101-63-3.

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Kinetic Study of the Acid-Catalyzed Rearrangement of 4-Acetyl-3,3-dimethyl-5-hydroxy-2-morpholino-2,3-dihydrobenzo[*b*]furan

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A kinetic study of the acid-catalyzed rearrangement of the title compound (**6**) to form 5,8-dihydroxy-4,4-dimethyl-1(4*H*)-naphthalenone (**4**) in dioxane–water, ethanol–water, and ethanol–dioxane is reported. In water mixtures the presence of 4-acetyl-2,5-dihydroxy-3,3-dimethyl-2,3-dihydrobenzo[*b*]furan (**7**) is detected, and it slowly leads to the rearrangement product **4**. The rate constant of the transformation **6** → **4** is more than 100-fold faster than **7** → **4**, and the kinetic data were evaluated as parallel first-order reactions **4** ← **6** → **7**. The hydrolysis and rearrangement rate constants behavior in different media is explained with a reaction scheme involving the participation of imonium and ethyl acetal intermediates more reactive than **7**.

In previous papers[1,2] we have described the acid-catalyzed rearrangement of some 4-acetyl-5-hydroxy-2,3-dihydrobenzo[*b*]furans containing a cyclic *O,N*-acetal group. This transformation involves the formation of a new carbocyclic ring, leading to 1(4*H*)-naphthalenone or 1,4-naphthoquinone systems, depending on the degree of substitution of the substrate at C-3 position. Scheme I shows the above reactions and the preparation of the corresponding heterocyclic substrates **2** and **3** from 2-acetyl-1,4-benzoquinones (**1**) and enamines.

The participation of hemiacetal intermediates has been established[2] when the rearrangement **3** → **5** is carried out in aqueous media. It is interesting to notice that the treatment of the cyclic *O,N*-acetal **2** in ethanol–hydrochloric acid solution leads to the rearrangement product 5,8-dihydroxy-4,4-dimethyl-1(4*H*)-naphthalenone (**4**) in

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(1) Valderrama, J. A.; Vega, J. C. *An. Quim.* **1977**, *73*, 1212.

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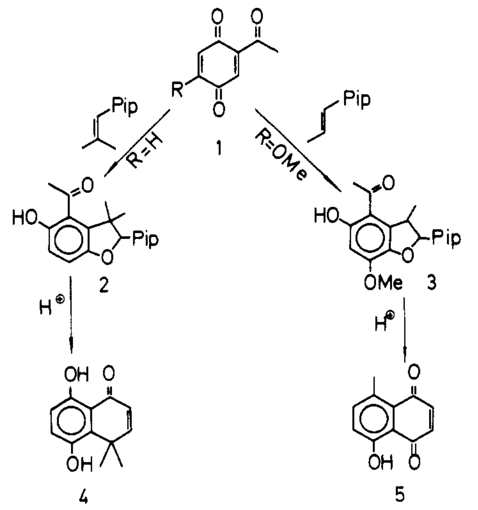
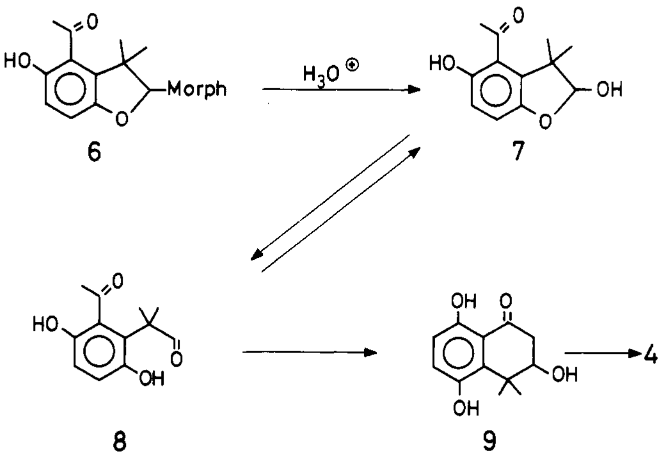
Scheme I



Scheme II



high yield, and neither the hemiacetal nor its ethyl acetal is detected (TLC) as an intermediate.[1]

Taking into account that experimentally 4-acetyl-3,3-dimethyl-5-hydroxy-2-morpholino-2,3-dihydrobenzo[*b*]furan (**6**) is more easily prepared than **2** and that **6** also yields only **4** (TLC) when treated with ethanol and hydrochloric acid (see Experimental Section), we decided to attempt the kinetic study of the acid-catalyzed rearrangement of **6** in dioxane–ethanol, dioxane–water, and ethanol–water mixtures.

Since the chemistry of these cyclic *O,N*-acetals such as **2** or **6** has been little studied, we decided to start the studies in this field with the present work. In this paper we report a set of reactions that describe the overall process and are consistent with the kinetic results of this work.

Experimental Section

Melting points were determined on a Kofler hot-stage microscope melting-point apparatus and are uncorrected. IR (KBr) spectra were obtained on a Perkin-Elmer Model 567 spectrophotometer. ^{1}H NMR spectra were taken with a Varian XL-100 spectrometer with tetramethylsilane as internal standard. UV–vis spectra were obtained on a Pye Unicam Model SP-1800 spectrophotometer. Elemental analyses were made at the Instituto de Química General (CSIC), Madrid, Spain.

Ethanol, dioxane, and hydrochloric acid were reagent grade, and hydrogen chloride in ethanol was prepared by bubbling HCl through ethanol and standardized by titration with aqueous NaOH.

Materials. 4-Acetyl-3,3-dimethyl-5-hydroxy-2-morpholino-2,3-dihydrobenzo[*b*]furan (6). *N*-Isobutenylmorpholine[3] (2.75 g, 19.5 mmol) in dry benzene (100 mL) was added at room temperature to a stirred solution of 2-acetyl-1,4-benzoquinone[4] (**1**, R = H; 2.91 g, 19.4 mmol) in the same solvent (100 mL). After 2 h, the reaction mixture was evaporated under reduced pressure and the oily residue was allowed to solidify in the presence of benzene–cyclohexane (1:1, 50 mL). This gave 4.97 g, (17 mmol, 88%) of crude **6**, which was purified by recrystallization from benzene: mp 173–174 °C; IR 3300 (OH) and 1655 (C=O) cm^{-1}; ^{1}H NMR (Me$_2$SO-d_6) δ 9.37 (s, 1 H, exchangeable with D$_2$O), 6.75 (s, 2 H), 4.84 (s, 1 H), 3.60 (t, 4 H), 1.37 (s, 3 H), 1.31 (s, 3 H), the signals of the other protons (CH_2NCH_2, COCH$_3$) are overlapped by the solvent signals (δ 2.7–2.2).

Anal. Calcd for $C_{16}H_{21}O_4N$: C, 65.96; H, 7.26; N, 4.81. Found: C, 66.27; H, 7.09; N, 5.27.

5,8-Dihydroxy-4,4-dimethyl-1(4*H*)-naphthalenone (4). A solution of **6** (381 mg, 1.3 mmol), ethanol (50 mL), and concentrated hydrochloric acid (2 mL) was heated under reflux for 4 h. Then the mixture was evaporated under reduced pressure and water was added. The resulting solid was crystallized from benzene containing a few drops of ethanol to give **4** (192 mg, 0.94 mmol, 72%) as yellow needles: mp 252–253 °C; IR 3300 (OH), 1650 (C=O), 1615 (C=C) cm^{-1}; ^{1}H NMR (Me$_2$SO-d_6) δ 12.54 (s, 1 H), 10.64 (s, 1 H), 7.10 (d, 1 H, $J \sim 9$ Hz), 7.10 (d, 1 H, $J \sim 10$ Hz), 6.73 (d, 1 H, $J \sim 9$ Hz), 6.24 (d, 1 H, $J \sim 10$ Hz), 1.61 (s, 6 H).

Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.64; H, 5.83.

Kinetic Measurements. The accurately weighed furan **6** was dissolved in each solvent mixture containing the appropriate hydrogen chloride concentration ([HCl] = 0.116 M for dioxane–water and ethanol–water mixtures and 0.100 M for ethanol–dioxane mixtures). Aliquots of the solution (the initial concentration of **6** was 7×10^{-4} M) were sealed in ampules, the samples were allowed to stand at 80 ± 0.1 °C, and after appropriate times, ampules were removed from the bath and cooled.

The kinetic runs were evaluated by following the absorption of **4** at λ 420 nm (neither **6** nor **7** absorbed at this wavelength under the reaction conditions). The observed rate constants (k_{obsd}) were determined by the Guggenheim method,[5] taking into account that the slow reaction **7** → **4** does not allow us the measurement of the A_∞ value.

The rearrangement (k_R) and hydrolysis (k_H) rate constants of the reactions **6** → **4** and **6** → **7**, respectively, were evaluated from the k_{obsd} value ($k_{obsd} = k_H + k_R$) and the concentration of **4** at different times, using the integrated equation as a model for parallel first-order reactions.[6] The experimental absorbance values agreed with those calculated by assuming parallel first-order reactions.

Results and Discussion

Preliminary examination, by thin-layer chromatography of the reaction mixtures obtained by acid treatment of **6** in water–ethanol and water–dioxane solutions, showed the presence of **4** along with the hemiacetal **7** as a minor product. This secondary product, which was isolated and characterized by its spectral properties and elemental analysis,[7] slowly reacts under acidic conditions and leads to the rearrangement product **4**.

The hemiacetal **7** presumably arises by acid-catalyzed hydrolysis of the O,N-acetalic group of **6**. The open form **8**, in equilibrium with **7**, may undergo cyclization in an

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(3) Stork, G.; Brizzolara, A.; Landesman, H.; Szmuszkovicz, J.; Terrel, R. *J. Am. Chem. Soc.* **1963**, *85*, 207.

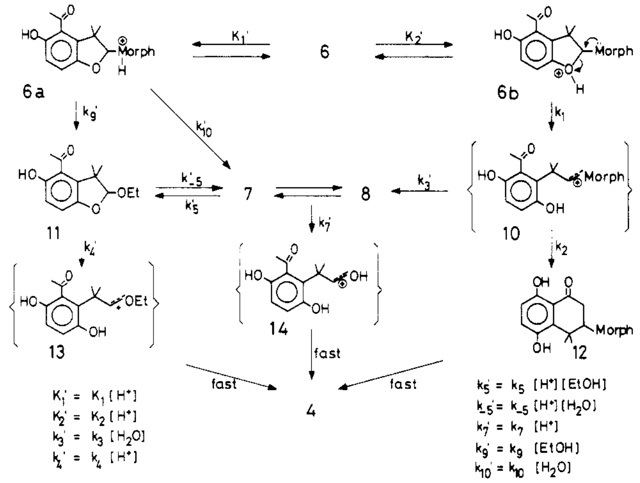
(4) Kurosawa, E. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 300.

(5) Guggenheim, E. A. *Philos. Mag.* **1926**, *2*, 538.

(6) Frost, A. A.; Pearson, R. G. "Kinetics and Mechanism", 2nd ed.; Wiley: New York, 1961; p 160.

(7) Compound **7** purified by recrystallization from benzene had the following: mp 172–174 °C; IR (KBr) 3150 (OH) and 1660 (C=O) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 6.68 (d, 1 H, $J \sim 8$ Hz), 6.60 (d, 1 H, $J \sim 8$ Hz), 5.88 (br, 1 H), 5.40 (s, 1 H), 2.97 (br, 1 H), 2.57 (s, 3 H), 1.32 (s, 3 H), 1.27 (s, 3 H). Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.91; H, 6.65.

Scheme III



aldol-type reaction[8] to give **9**, which then by a subsequent elimination of water leads to the 1(4*H*)-naphthalenone **4** (Scheme II).

The UV–vis spectra at different times of the above reaction mixtures showed a quite stable isobestic point at 340 nm. This suggests that the transformation **7** → **4** is very slow, and the kinetic data can be evaluated on the basis of two parallel first-order reactions:

$$4 \xleftarrow{k_R} 6 \xrightarrow{k_H} 7$$

The validity of this assumption was confirmed when the rearrangement rate constants of the transformations **6** → **4** and **7** → **4** were obtained in ethanol and in dioxane solutions containing water (5.35 M) and hydrochloric acid (0.116 M). In fact, the k_R values of the reaction **6** → **4** (5.3×10^{-4}, 1.7×10^{-4} s^{-1} in the dioxane and ethanol systems, respectively) indicated that this transformation is more than 100-fold faster than the reaction **7** → **4** (4.0×10^{-6}, and 1.2×10^{-6} s^{-1} under the same conditions). From these results it is evident that the participation of intermediates more reactive than **7** in the transformation **6** → **4** are required.

We were not able to isolate any acetalic intermediates in the reactions under study. Instead, we obtained experimental evidence that the **7** → **4** rearrangement is faster in ethanol–dioxane mixtures than in ethanol–water mixtures with equal ethanol concentrations. Moreover, its velocity depends on the ethanol concentration in the ethanol–dioxane media, suggesting the participation of an ethyl acetal intermediate.

The probable pathway of the rearrangement **6** → **4** is shown in Scheme III, wherein the structures **6a** and **6b** represent the protonated forms of the substrate which are responsible for the formation of the reaction intermediates. A possible route for the rearrangement of **6** is the ring opening in the cation **6b** to form the resonance-stabilized cation **10**, which in turn leads to **4** through the formation of a C–C bond and elimination of morpholine in **12**. Alternatively, in aqueous media the cation **10** undergoes a nucleophilic attack on the C=N$^+$< moiety by water, yielding an intermediate α-amine alcohol that originates **7** through species **8**.

On the other hand, **6a** gives **7** and **11** by displacement of the nitrogenated group by the nucleophiles water and ethanol, respectively. The acid-catalyzed opening of the furan ring in **7** and **11** yields **4** through the resonance-stabilized cations **13** and **14**, respectively. Finally, the interconversion of **7** and **11** proceeds via the acid-catalyzed displacement of the group at C-2 in an analogous manner to its formation through **6a**.

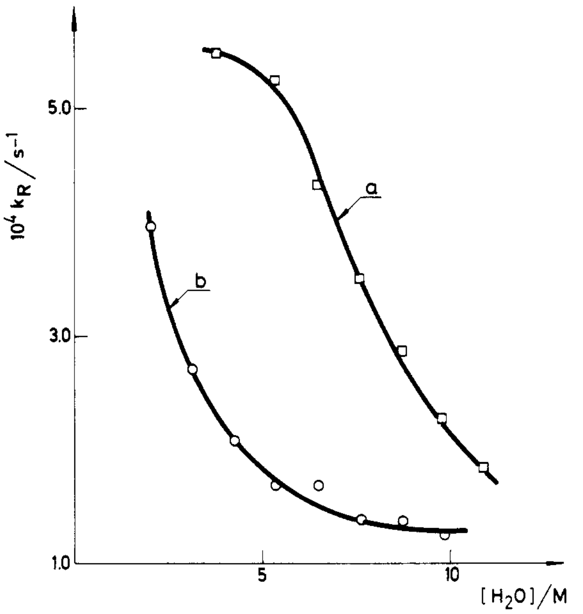


Figure 1. Variation of k_R with water concentration: (a) in dioxane–water mixtures, (b) in ethanol–water mixtures. [HCl] = 0.116 M.

The formation of the ethyl acetal **11** from **10** could be explained in terms of a nucleophilic attack of the alcohol on the C=N$^+$< group followed by an acid-catalyzed cyclization of the intermediate α-amine ether. However, this pathway for the formation of the acetalic intermediate **11** has not been considered in Scheme III because the kinetic study of the reaction indicates that its contribution to the macroscopic constants k_R and k_H is not significant.

The intermediates **10**–**14** of Scheme III were not detected in our reactions, and for this reason the rate constant equations were derived by applying the steady-state condition to these intermediates. On the other hand, the rearrangement **7** → **4** is very slow in comparison with the transformation **6** → **4** and was neglected in the derivation of the equations.

Rearrangement Rate Constants (k_R). The rearrangement rate constant (k_R) derived from Scheme III for dioxane–water mixtures by using the above conditions is represented by eq 1. Figure 1a shows the change in k_R

$$k_R = k_1k_2K_2[H^+](k_2 + k_3[H_2O])^{-1}(1 + K_1[H^+] + K_2[H^+])^{-1} \qquad (1)$$

as a function of solvent mixture composition. The change from dioxane to dioxane–water mixtures containing increasing water concentration showed a decrease in k_R, as predicted by eq 1. Furthermore, Figure 1a shows a tendency of k_R to reach a maximum value at low water concentration. This observation is again consistent with eq 1, which indicates that a maximum value corresponding to $k_R = k_1K_1[H^+](1 + K_1[H^+] + K_2[H^+])^{-1}$ should be obtained under these conditions if the rearrangement is the most important reaction of imonium cation **10** and the activation coefficient for protons is not affected markedly at such low concentrations of water.

The k_R rate constant equation derived for ethanol–dioxane mixtures is eq 2.

$$k_R = (k_1K_2 + K_1k_9[EtOH])[H^+](1 + K_1[H^+] + K_2[H^+])^{-1} \qquad (2)$$

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[8] Nielsen, A. T.; Houlihan, W. J. *Org. React.* (*N.Y.*) **1968**, *16*, 1.

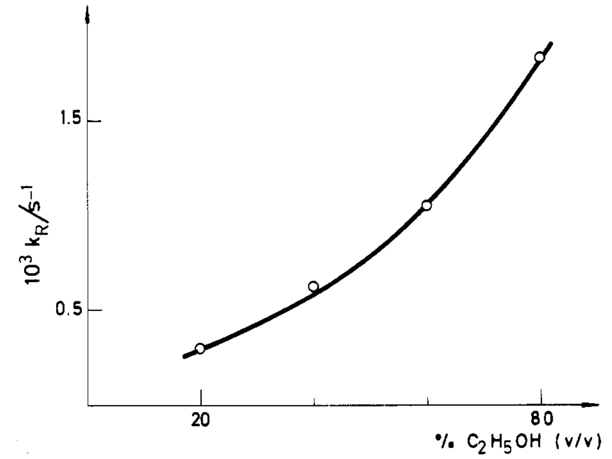

Figure 2. Variation of k_R with ethanol concentration in dioxane–ethanol mixtures. [HCl] = 0.100 M.

This equation suggests a linear dependence of k_R with the concentration of ethanol in the solvent mixture if the proton activity in the media is constant. Considering that the composition range covered is very wide (20–80% v/v of ethanol) and that the dielectric constants of the two solvents are so different, an increase in the activity coefficient for protons is expected as the concentration of ethanol is increased. This would lead to a positive deviation from linearity when k_R is plotted as a function of ethanol concentration. Figure 2 shows the experimental results obtained which confirm the predicted behavior.

Equation 3 is the rate equation derived from Scheme III when the reaction is carried out in ethanol–water mixtures.

$$k_R = (k_1k_2K_2(k_2 + k_3[H_2O])^{-1} + k_4k_9K_1[EtOH] \times (k_4 + k_{-5}[H_2O])^{-1})[H^+](1 + K_1[H^+] + K_2[H^+])^{-1} \quad (3)$$

This equation presents two terms, one due to the rearrangement from imonium cation **10** and other from the acetalic intermediate **11**.

At low water concentration, if the rearrangement reactions of **10** and **11** are more important than their hydrolysis reactions ($k_2 \gg k_3[H_2O]$ and $k_4 \gg k_{-5}[H_2O]$), eq 3 becomes eq 2 and we would expect a similar behavior for k_R. On the other hand, eq 3 suggests a decrease of k_R with an increase of water concentration in the media. Figure 1b shows the experimental behavior which is in agreement with the above discussion.

Hydrolysis Rate Constants (k_H). For dioxane–water mixtures the hydrolysis rate constant derived from Scheme III is eq 4. At low water concentration ($k_2 \gg k_3[H_2O]$),

$$k_H = (k_1k_3K_2(k_2 + k_3[H_2O])^{-1} + K_1k_{10})[H^+][H_2O] \times (1 + K_1[H^+] + K_2[H^+])^{-1} \quad (4)$$

eq 4 suggests an increase in k_H with water, which is in accordance with experimental behavior (Figure 3a). On the other hand, at high water concentration eq 4 leads to other straight line. This behavior cannot be checked in this work because to do so would require working at a high concentration of water. Under that condition very little **4** would form, which is our observable compound (see Experimental Section).

For ethanol–water mixtures, eq 5 was derived for k_H

$$k_H = (k_1k_3K_2[H_2O] \times (k_2 + k_3[H_2O])^{-1} + K_1k_{10}[H_2O] + k_{-5}k_9K_1[EtOH] \times (k_{-5}[H_2O] + k_4)^{-1})[H^+](1 + K_1[H^+] + K_2[H^+])^{-1} \quad (5)$$

from Scheme III. There are three terms in eq 5: one due to the hydrolysis of imonium cation **10**, one due to the direct hydrolysis on **6a**, and the other due to the hydrolysis of the acetal intermediate **11**. At low water concentration ($k_2 \gg k_3[H_2O]$ and $k_4 \gg k_{-5}[H_2O]$), eq 5 becomes eq 6.

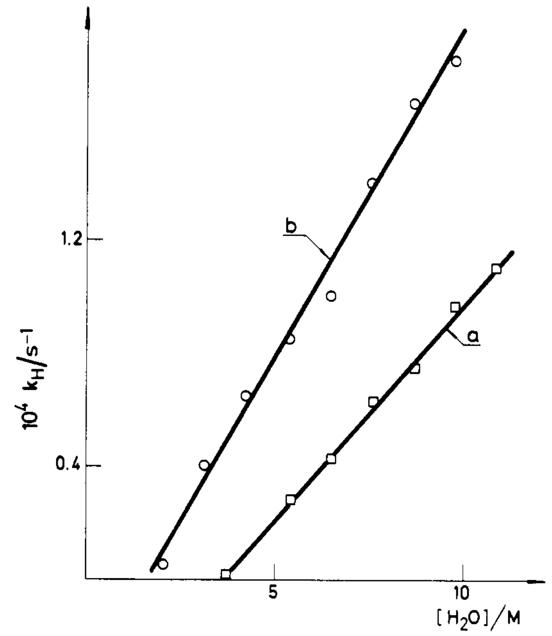

Figure 3. Variation of k_H with water concentration: (a) in dioxane–water, (b) ethanol–water. [HCl] = 0.116 M.

$$k_H = (k_1k_3K_2k_2^{-1} + K_1k_{10} + k_{-5}k_9K_1[EtOH]k_4^{-1}) \times [H_2O][H^+](1 + K_1[H^+] + K_2[H^+])^{-1} \quad (6)$$

From this, a water increase in the medium (decrease ethanol) should give a nonlinear k_H dependence on water concentration. The experimental behavior of k_H with the water concentration is shown in Figure 3b. A linear dependence is observed. This apparent discrepancy between the theoretical and experimental results can be explained by assuming that the third term in the first set of parentheses (eq 6) is not significant under these conditions. Consequently, the acetal intermediate is not important in the hydrolysis reaction at low water concentration.

At high water concentrations ($k_3[H_2O] \gg k_2$ and $k_{-5}[H_2O] \gg k_4$), the third term of eq 5 suggests a decreasing k_H value with increasing water concentration, while the second term predicts an increase of k_H. For the above-discussed reasons (dioxane–water mixtures), this cannot be checked experimentally.

The experimental behavior of the hydrolysis constants in water–dioxane and water–ethanol solutions (Figure 3) are linear for the different activities of the protons. This result is intriguing, but it can be explained by taking into account that for ethanol–water mixtures the activity coefficients of HCl change linearly within the range of concentrations of water that we have studied[9] and by assuming a similar behavior for the HCl activity coefficient in dioxane–water mixtures.

We can conclude, finally, that all the experimental results fit Scheme III.

Acknowledgment. We thank the Dirección de Investigación de la Pontificia Universidad Católica de Chile (DIUC) for financial support. We also thank the Instituto de Química General (CSIC), Madrid, Spain for elemental analyses.

Registry No. **4**, 68085-25-6; **6**, 86436-29-5; **7**, 86436-30-8.

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[9] Scatchard, G. *J. Am. Chem. Soc.* **1925**, *47*, 2098.