Acknowledgment. One of us (F.W.S.) thanks Dr. A. Weller for an interesting discussion.

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Proton Exchange in the Lowest Excited Singlet State of 2-Naphthol-6,8-disulfonate. Demonstration of the Establishment of Prototropic Equilibrium in the Excited State

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Abstract: The pH dependences of the fluorescence spectra of 2-naphthol-6,8-disulfonate were evaluated in terms of the kinetics of excited-state proton transfer. Deviations from ideal fluorometric titration behavior were compensated by a simple Brønsted kinetic activity factor which accounted for the primary kinetic salt effect. Criteria for the establishment of prototropic equilibrium in the lowest excited singlet state are stated and when applied to 2-naphthol-6,8-disulfonate, it is found that equilibrium prevails over most of the inflection region in the fluorometric titration.

The variations of the relative fluorescence efficiencies of hydroxy aromatics and their conjugate bases with pH are known to depend upon the kinetics of proton-transfer in the lowest excited singlet state.[1] Under the assumption of steady-state proton transfer in the lowest excited singlet state, the relative fluorescence efficiencies of the excited phenolic species have been shown to vary, approximately according to

$$\phi/\phi_0 = \frac{1 + \overleftarrow{k}\tau_0'[\mathrm{H_3O^+}]}{1 + \vec{k}\tau_0 + \overleftarrow{k}\tau_0'[\mathrm{H_3O^+}]} \tag{1}$$

while those of the excited conjugate base, phenolate species vary according to

$$\phi'/\phi_0' = \frac{\vec{k}\tau_0}{1 + \vec{k}\tau_0 + \overleftarrow{k}\tau_0'[\mathrm{H_3O^+}]} \tag{2}$$

where $[\mathrm{H_3O^+}]$ is the molar concentration of hydrogen ions, τ_0 and τ_0' are the actual lifetimes of excited acid and conjugate base in the absence of proton transfer (i.e., in the low and high pH limits, respectively), and $\vec{k}$ and $\overleftarrow{k}$ are the rate constants for dissociation of the excited phenolic species and protonation of the excited phenolate species, respectively. More refined treatments have corrected eq 1 and 2 for transient reprotonation of the phenolate species prior to the establishment of the steady state and for the effect of ionic strength on the "equilibrium" between the reactants and the activated complex in the transition state.[2,3] At higher pH the probability of protonation of the excited phenolate is negligibly small causing eq 1 and 2 to reduce to the pH-independent forms

$$(\phi/\phi_0)_{\mathrm{const}} = \frac{1}{1 + \vec{k}\tau_0} \tag{3}$$

$$(\phi'/\phi_0')_{\mathrm{const}} = \frac{\vec{k}\tau_0}{1 + \vec{k}\tau_0} \tag{4}$$

Because of the short duration of the lowest excited singlet state it is in order to question whether or not prototropic equilibrium can be fully established during the lifetime of the lowest excited singlet state and if so, under what conditions can equilibrium be realized and recognized? In order to answer these questions the pH dependences of the fluorescence spectra of 2-naphthol-6,8-disulfonate and its conjugate base were examined. This molecule was chosen for investigation because at near neutral pH it is extensively dissociated in the lowest excited singlet state (i.e., $(\phi/\phi_0)_{\mathrm{const}} \approx 0$, $(\phi'/\phi_0')_{\mathrm{const}} \approx 1$), a fact that suggested intuitively that at low pH, proton exchange in both directions might be considerably faster than fluorescence and nonradiative deactivation and might lead to the establishment of prototropic equilibrium in the lowest excited singlet state.

Experimental Section

The dipotassium salt of 2-naphthol-6,8-disulfonate was purchased from Pfaltz and Bauer, Inc. Stamford, Conn., and triply recrystallized from 50 vol % aqueous ethanol.

Fluorescence spectra were taken, at ambient temperature (25 °C), on a Perkin-Elmer MPF-2A fluorescence spectrophotometer whose output was corrected for wavelength variable response by means of a rhodamine B quantum counter and whose monochromators were calibrated against the xenon line emission spectrum. Fluorescence decay times were measured on a TRW instrument employing an 18-W deuterium lamp as its source. Absorption spectra were taken on a Beckman DB-GT spectrophotometer. Data analysis was performed on a digital computer.

Solutions of which spectra were taken were prepared by diluting

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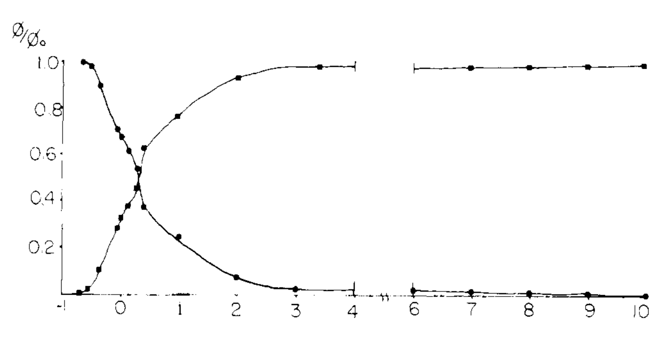

Figure 1. Relative fluorescence efficiencies of 2-naphthol-6,8-disulfonate (-■-■-■-) and 2-naphtholate-6,8-disulfonate (-●-●-●-) with molar hydrogen ion concentration in perchloric acid.

aqueous perchloric acid or sodium hydroxide in a 10-mL volumetric flask and then delivering 100 μL of 1.00×10^{-3} M dipotassium 2-naphthol-6,8-disulfonate with a micropipet, to the 10-mL flask. Each solution was prepared immediately before use, to minimize decomposition errors and errors caused by change in pH of the poorly buffered solutions in the mid-pH region.

Dilute perchloric acid and sodium hydroxide solutions were employed in preference to fairly concentrated buffer solutions, because buffer ions are known to react with excited aromatic acids and bases during the lifetime of the lowest excited singlet state.[3] This reaction often affects the mechanism and therefore the kinetics of excited-state proton transfer. It was deemed desirable to avoid this added complication.

All solutions were purged for 5 min with dry nitrogen, before the measurement of fluorescence lifetimes, to minimize the effect of oxygen quenching which may affect the longer lifetimes.

Fluorescence, in each case, was excited at an isosbestic point at 325 nm in the absorption spectrum. This makes the fluorometric titration correspond to variation of relative fluorescence efficiency with pH.

The lifetimes of the lowest excited singlet states of 2-naphthol-6,8-disulfonate and its conjugate base were measured at H_0 −2.1 and pH 11.0, respectively.

Results

2-Naphthol-6,8-disulfonate and its conjugate base fluoresce maximally at 388 and 458 nm, respectively. The variations of the fluorescence spectra with pH are shown in Figure 1.

In the pH region 6–10, the extremely small variations of the fluorescence spectra are due primarily to the ground-state ionization of the aromatic hydroxy group. The variations of the absorption spectra in this region permitted the calculation of $pK_a = 7.89 \pm 0.04$. From pH 6–2.5, the fluorescence spectra are constant in intensity, the quantum yield of the naphtholate at pH 5.75 being 98.2 ± 0.1% of that at pH 11.0. From pH 2.5 to H_0 −2.1 (4.7 M $HClO_4$) the violet fluorescence of the naphthol rises to a maximum and the blue-green fluorescence of the naphtholate vanishes, with decreasing pH (or H_0).

The ratio of $(\phi'/\phi_0')_{\mathrm{const}} = 0.982$ to $(\phi/\phi_0)_{\mathrm{const}} = 0.018$ yields $\vec{k}\tau_0 = 55 \pm 3$. Utilizing the value $\tau_0 = 14.5 \pm 0.3$ ns, determined at $H_0 = -2.1$, the rate constant for dissociation of the naphthol in the lowest excited singlet state was found to be $\vec{k} = 3.8 \pm 0.2 \times 10^9\ \mathrm{s}^{-1}$. Since the data from which $\vec{k}\tau_0$ was determined were taken in essentially pure water of ionic strength $\mu < 1 \times 10^{-3}$, this value of $\vec{k}$ is essentially the limiting value for zero ionic strength.

The rate constant for excited-state protonation of the naphtholate anion can be determined by dividing eq 1 by eq 2 to yield

$$\frac{\phi/\phi_0}{\phi'/\phi_0'} = \frac{1}{\vec{k}\tau_0} + \frac{\overleftarrow{k}\tau_0'}{\vec{k}\tau_0}[H_3O^+] \qquad (5)$$

A plot of $(\phi/\phi_0)/(\phi'/\phi_0')$ against $[H_3O^+]$ should yield a straight line of slope $\overleftarrow{k}\tau_0'/\vec{k}\tau_0$ and an ordinate intercept of $1/\vec{k}\tau_0$. However, in this case, because of the charged nature of the reactants, eq 5 should be modified to

$$\frac{\phi/\phi_0}{\phi'/\phi_0'} = \frac{1}{\vec{k}\tau_0} + \frac{\overleftarrow{k}\tau_0'}{\vec{k}\tau_0}F[H_3O^+] \qquad (6)$$

where F is the Brønsted kinetic activity factor[4,5] which, for H_3O^+ and the trinegative conjugate base studied here, is given by

$$-\log F = \frac{3.06\sqrt{\mu}}{1 + 3.3 \times 10^7 a\sqrt{\mu}} \qquad (7)$$

In eq 7 μ is the ionic strength of the solution and a is, to a first approximation, taken to be a mean ionic size parameter for all participants in the reaction. The factor F corrects the rate constants at each value of μ to the value corresponding to reaction at zero ionic strength. A plot of $(\phi/\phi_0)/(\phi'/\phi_0')$ against $F[H_3O^+]$ then should yield a straight line of slope $\overleftarrow{k}\tau_0'/\vec{k}\tau_0$ and ordinate intercept $1/\vec{k}\tau_0$. If $\vec{k}\tau_0$ is already known $[(\phi/\phi_0)/(\phi'/\phi_0')] - (1/\vec{k}\tau_0)$ may be plotted against $F[H_3O^+]$ to yield a straight line of slope $\overleftarrow{k}\tau_0'/\vec{k}\tau_0$ which passes through the origin. However, inclusion of $1/\vec{k}\tau_0$ as an unknown parameter in eq 6 was employed here, because the agreement of the value of $\vec{k}\tau_0$ obtained from the intercept with that evaluated from the relative quantum yields at near-neutral pH serves as a useful check on the accuracy of the linear plot, especially insofar as the selection of the value of the ionic size parameter a, used to calculate F, is concerned. Employing the data of Figure 1, the best least-squares line representing eq 6 was obtained using $a = 1.43 \times 10^{-7}$ cm. This line, shown in Figure 2, has a slope of $\overleftarrow{k}\tau_0'/\vec{k}\tau_0 = 7.3 \pm 0.1$ and an ordinate intercept of 0.018 ± 0.001. The intercept is in agreement with the value of $\vec{k}\tau_0$ obtained from the ratio of eq 3 and 4 within experimental error. From the slope and the intercept of the line shown in Figure 2, $\overleftarrow{k}\tau_0'$ was found to be $4.1 \pm 0.2 \times 10^2$. Using the value of τ_0' measured at pH 11, 26.2 ± 1.1 ns, the rate constant for protonation of the excited naphtholate trianion was found to be $\overleftarrow{k} = 1.6 \pm 0.1 \times 10^{10}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. The dissociation constant pK_a^* is given by $-\log(\vec{k}/\overleftarrow{k}) = 0.60 \pm 0.04$ (a Förster cycle calculation, using the shift of the absorption and fluorescence spectra upon dissociation, gave $pK_a^* = 0.7 \pm 0.4$). It should be noted that the portion of the fluorometric titration corresponding to $H_0 < -1.0$ ($[H_3O^+] > 2.3$ M) could not be fit linearly to eq 6. Rather, the values of $(\phi/\phi_0)/(\phi'/\phi_0')$ tended to increase geometrically with increasing $F[H_3O^+]$. This appears to be the result of the breakdown of the Brønsted activity

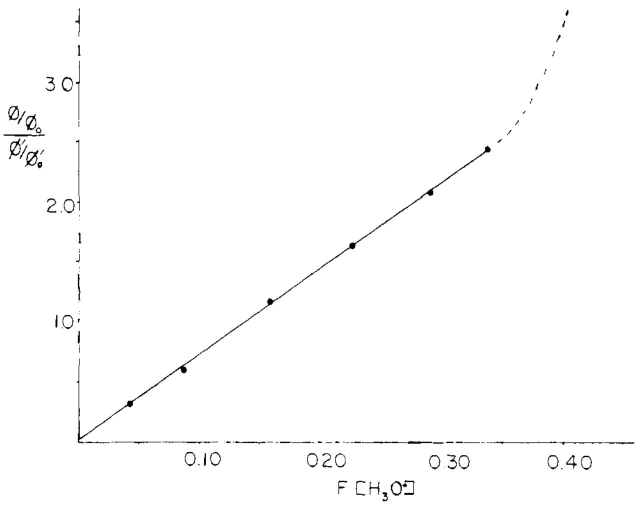

Figure 2. Variation of the ratio of the relative fluorescence efficiency of 2-naphthol-6,8-disulfonate with the product of the Brønsted activity factor, F, and the molar hydrogen ion concentration. The dashed portion of the curve represents the region of very high solution acidity ($[H_3O^+] > 2.3$ M) in which F is probably not accurately represented by an extended Debye–Hückel relationship.

factor based upon the extended Debye–Hückel treatment (eq 7) at high ionicities. Inclusion of an additional term, $b\mu$, where $b = 0.2$ or 0.3, at high ionicities, transforming eq 7 into

$$-\log F = \frac{3.06\sqrt{\mu}}{1 + 4.7\sqrt{\mu}} - b\mu \qquad (8)$$

as suggested by Davies[6] and Guggenheim[7] resulted in the data points corresponding to $[H_3O^+] > 2.3$ M falling closer to the straight line obtained for $[H_3O^+] < 2.3$ M. Alternatively, it is possible that the employment of the same ionic size parameter, a, for the hydronium ion, the naphtholate trianion, and the transition state dianion leads to erroneous results at high ionicities.[8]

Weller[2,3] has employed a correction to eq 6 for the non-steady-state protonation of the excited conjugate base. However, when this treatment was applied to the system under study here, no straight line could be obtained. Moreover, the plot obtained had a negative derivative, which is physically impossible. It appears that either non-steady-state protonation is not a problem in 2-naphthol-6,8-disulfonate, or the activity correction employed fortuitously and improbably corrects for the transient phenomenon. It is also possible that the encounter distance of 7.5 Å suggested by Weller[9] for the calculation of the diffusion volume and ultimately the fraction of molecules participating in the steady-state reaction is too small for the system studied here, leading to inaccurate results at low hydronium ion concentrations.

Discussion

The condition for the attainment of prototropic equilibrium in the lowest excited singlet state, between 2-naphthol-6,8-disulfonate (N*) and its conjugate acid (A*), is

$$\vec{k}[N^*(t)] = \overleftarrow{k}[H_3O^+][A^*(t)] \qquad (9)$$

In order to express eq 9 in terms of measurable relative fluorescence efficiencies it is necessary to integrate with respect to time:

$$\vec{k}\int_{t=0}^{\infty}[N^*(t)]\mathrm{d}t = \overleftarrow{k}[H_3O^+]\int_{t=0}^{\infty}[A^*(t)]\mathrm{d}t \qquad (10)$$

or

$$\vec{k}\tau_0\phi/\phi_0 = \overleftarrow{k}\tau_0'[H_3O^+]\phi_0'/\phi_0' \qquad (11)$$

At high ionic strengths, the activity factor F must be included, so that

$$\frac{\phi/\phi_0}{\phi'/\phi_0'} = \frac{\overleftarrow{k}\tau_0' F[H_3O^+]}{\vec{k}\tau_0} \qquad (12)$$

Comparison of eq 12 with eq 6 shows that a principal requirement for the occurrence of prototropic equilibrium in the lowest excited singlet state in a reaction of the type

$$HA^* + H_2O \rightleftharpoons H_3O^+ + A^{-*}$$

where HA* is directly excited, is $\overleftarrow{k}\tau_0' F[H_3O^+] \gg 1$. If it is taken that equilibrium occurs when $\overleftarrow{k}\tau_0' F[H_3O^+] \geq 20$ (since $\overleftarrow{k}\tau_0'$ is known to within about 5%), it may be concluded that prototropic equilibrium occurs in the lowest excited singlet state of 2-naphthol-6,8-disulfonate when $F[H_3O^+] \geq 4.9 \times 10^{-2}$ M. (pH $\leq$1.31) or over most of the inflection region of the fluorometric titration curve. It is interesting that the changeover from nonequilibrium proton exchange (at pH 1.31) to equilibrium proton exchange is unaccompanied by any change in form of the fluorometric titration and the condition of equilibrium is therefore not at all obvious to the casual observer. It should be noted that in any acid which dissociates in the lowest excited singlet state, it should always be possible to find some range of solvent acidity ($F[H_3O^+]$) where prototropic equilibrium prevails. However, the smaller $\overleftarrow{k}\tau_0'$, the more strongly acidic the solvent medium must be to effect excited-state equilibrium. This means that in short-lived and very weak conjugate bases equilibrium may only be possible in concentrated mineral acid or superacid (e.g., CF_3SO_3H) media. Moreover, even if equilibrium prevails above some value of $F[H_3O^+]$ it may occur beyond the observable inflection region of the fluorometric titration and therefore be unobservable.

Even if $\overleftarrow{k}\tau_0' F[H_3O^+] \geq 20$, the actual observation of equilibrium proton exchange within the inflection region of the fluorometric titration still depends upon $\vec{k}\tau_0$. For purposes of calculation, the inflection region may be defined as that region of $F[H_3O^+]$ where ϕ'/ϕ_0' varies between 5 and 95% of $(\phi'/\phi_0')_{\mathrm{const}}$ and therefore ϕ/ϕ_0 varies between $1 - 0.05(\phi'/\phi_0')_{\mathrm{const}}$ and $1 - 0.95(\phi'/\phi_0')_{\mathrm{const}}$. Since $(\phi'/\phi_0')_{\mathrm{const}} = \vec{k}\tau_0/(1 + \vec{k}\tau_0)$, the inflection region corresponds to values of $(\phi/\phi)/(\phi'/\phi_0')$, between $(1.025 + 5.25 \times 10^{-2}\vec{k}\tau_0)/\vec{k}\tau_0$, at high pH to $(20 + 19\vec{k}\tau_0)/\vec{k}\tau_0$, at low pH. The actual inflection points (they are not identical for acid and conjugate base unless $(\phi'/\phi_0')_{\mathrm{const}} = 1$) occur at $(\phi'/\phi_0')_{\mathrm{infl}} = \frac{1}{2}(\phi'/\phi_0')_{\mathrm{const}}$ and $(\phi/\phi_0)_{\mathrm{infl}} = 1 - \frac{1}{2}(\phi'/\phi_0')_{\mathrm{const}}$ and correspond to $[(\phi/\phi_0)/(\phi'/\phi_0')]_{\mathrm{infl}} = (2 + \vec{k}\tau_0)/\vec{k}\tau_0$. According to the condition of equilibrium imposed upon eq 6, equilibrium in the lowest excited singlet state will occur when $[(\phi/\phi_0)/(\phi'/\phi_0')] > (21/\vec{k}\tau_0)$. In order for the entire inflection region to represent excited-state equilibrium it would be necessary to have $(\phi/\phi_0)/(\phi'/\phi_0')$ for the high pH limit of the inflection region greater than 21, or $\vec{k}\tau_0 > 3.8 \times 10^{2}$.

This criterion is satisfied only by the longest lived and strongest acids in the lowest excited singlet state. On the other hand, in order for equilibrium to occur at some point within the inflection region, it is necessary to have $(\phi/\phi_0)/(\phi'/\phi_0')$ for the low pH limit of the inflection region greater than 21, or $\vec{k}\tau_0 > 5.3 \times 10^{-2}$. Probably, the majority of acids that exhibit excited-state dissociation fall into this category. In order for equilibrium to be present at the inflection points in the fluorometric titrations of acid and conjugate base, it is necessary to have $\vec{k}\tau_0 \geq 19$ which can be recognized quickly if it is noted that $(\phi'/\phi_0')_{\mathrm{const}} \geq 0.95$ (or $(\phi/\phi_0)_{\mathrm{const}} \leq 0.05$). In the event that equilibrium is present at the inflection points, the equilibrium constant K_a^* may be estimated from

$$K_a^* = \frac{\tau_0'}{\tau_0} F_{\mathrm{infl}}\,[H_3O^+]_{\mathrm{infl}}\left(\frac{\phi'/\phi_0'}{\phi/\phi_0}\right)_{\mathrm{infl}} \qquad (13)$$

or in logarithmic form

$$\mathrm{p}K_a^* = -\log\,(F[H_3O^+])_{\mathrm{infl}} - \log\frac{\tau_0'}{\tau_0} - \log\left(\frac{\phi'/\phi_0'}{\phi/\phi_0}\right)_{\mathrm{infl}} \qquad (14)$$

where $(F[H_3O^+])_{\mathrm{infl}}$ and $[(\phi'/\phi_0')/(\phi/\phi_0)]_{\mathrm{infl}}$ correspond to the values of F, $[H_3O^+]$, ϕ'/ϕ_0', and ϕ/ϕ_0 at the inflection points. The pK_a^* of 2-naphthol-6,8-disulfonate, obtained in this manner, from the inflection points $(\phi'/\phi_0')_{\mathrm{infl}} = 0.49$, $(\phi/\phi_0)_{\mathrm{infl}} = 0.51$, and $[H_3O^+]_{\mathrm{infl}} = 0.48$ M, was found to be 0.57, in excellent agreement with the value calculated from the rate constants.

Finally, it is in order to point out that, although the magnitude of $\overleftarrow{k}\tau_0'$ plays a major role in determining in which region of the acidity scale prototropic equilibrium may occur, it is actually $\vec{k}\tau_0$ that determines whether or not it occurs at all; for if $\vec{k}\tau_0 = 0$, there is no value of $\overleftarrow{k}\tau_0' F[H_3O^+]$ large enough to cause the occurrence of equilibrium.

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Formation of Isomeric Benzylidenecyclobutenones and 5-Phenylpent-2-en-4-ynals by the Gas-Phase Pyrolysis of α-Phenylfurfuryl Acetate[1]

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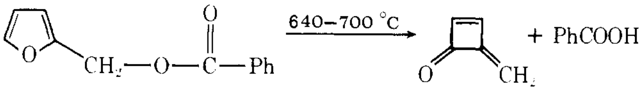
Abstract: Products of low-pressure (~10^{-4} Torr) gas-phase pyrolysis of α-phenylfurfuryl acetate at various temperatures are reported. The major oxygen-containing products, each produced in ca. 10% yield, are (*E*)- and (*Z*)-benzylidenecyclobutenones and (*E*)- and (*Z*)-5-phenylpent-2-en-4-ynals. Evidence for production of the hydrocarbons (*E*)- and (*Z*)-1-phenylbuten-3-ynes, naphthalene, and azulene is also presented. Under the pyrolysis conditions the stereoisomeric enynals are converted to the stereoisomeric cyclobutenones. The deuterium content of the four major oxygen-containing products obtained from the pyrolysis of α-phenylfurfuryl-α-d_1 acetate are reported. The d_1 species make up 54 ± 4% of the enynals and 75% of the cyclobutenones. Deuterium scrambling in the d_1-furfuryl acetate is shown to be unimportant. To account for these results a mechanistic scheme is presented which consists of both a route that involves formation of a carbene by α-elimination and a route that involves migration of the acetate group. A reversible 1,5-hydrogen shift between 5-phenylallenylketene and the (*Z*)-enynal permits species to cross from one route to the other and both sets of stereoisomeric products arise from each pathway.

A few years ago we reported that methylenecyclobutenone (**1**) can be obtained in fair yield by the low-pressure gas-phase pyrolysis of furfuryl benzoate (**2**).[2] This is a truly remarkable transformation which makes available the previously unknown parent compound of a class of compounds that is difficult to synthesize. The only other simple member of this class of compounds that has been reported is isopropylidenecyclobutenone,[3] which was also obtained by a flash pyrolysis route, one which involved a retro-Diels–Alder reaction.



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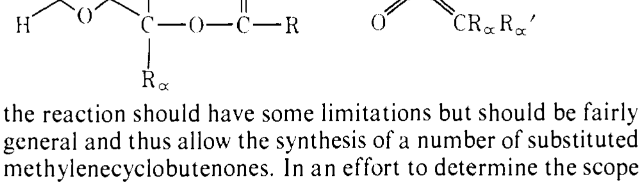
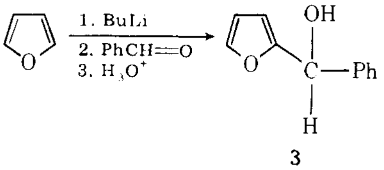
1 (40%)

The parent compound (**1**) was one of the few missing cyclobutadiene derivatives[4] and is a potentially useful synthetic intermediate since it is a cyclobutane derivative and is highly functionalized. We proposed a mechanism for the conversion of **2** to **1** based on the results of a deuterium-labeling experiment and a study of the products obtained from the pyrolysis of 5-methylfurfuryl benzoate.[2] If our mechanism is correct, the reaction should have some limitations but should be fairly general and thus allow the synthesis of a number of substituted methylenecyclobutenones. In an effort to determine the scope of this reaction and to define better its mechanism, we initiated a study of the pyrolysis of appropriately substituted furfuryl esters. α-Phenylfurfuryl acetate was selected as one of the first substituted esters to be studied because inductively the phenyl group is neither strongly electron withdrawing or electron donating and cannot lead to β-elimination reactions since it has no appropriate hydrogen atoms. Thus it was anticipated that the phenyl group should be an innocuous substituent unless it could perturb the conversion by resonance or steric interactions. The acetate was used instead of the benzoate since apparently increased steric congestion of the benzoate group resulted in a labile ester that could not be prepared and handled easily.



Results

α-Phenylfurfuryl alcohol (**3**) was prepared in high yield and purity from benzaldehyde and furfuryllithium as described by Ramanathan and Levine.[5] Alcohol **3** was converted to the benzoate by the method used for the preparation of **2**,[2] but rapid discoloration proved the ester to be labile and repeated attempts at purification were unsuccessful. The acetate (**4**) was much less reactive and could be obtained in high yield and purity by treating **3** with acetyl chloride and triethylamine in benzene.



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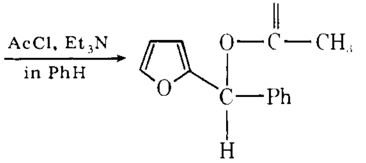

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The low-pressure (~10^{-4} Torr) gas-phase pyrolysis of **4** at various temperatures[6] produced a yellow band of products in the cold trap at 77 K. Polymerization was observed when the amorphous solid was allowed to warm to room temperature

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