

Direct Measurement of the Rates of Reketonization of Dienolates Produced by Photochemical Enolization of β -Alkyl α,β -Unsaturated Ketones in Aqueous Basic Solution^{1,2}

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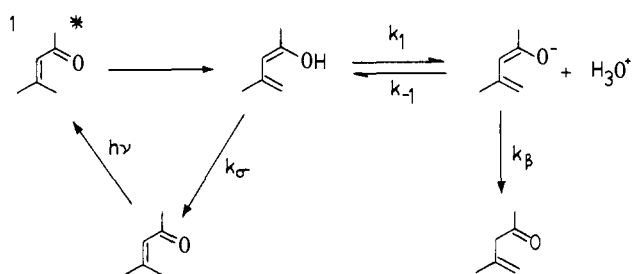
Abstract: The transient dienols produced by irradiation of five α,β -unsaturated ketones possessing γ -hydrogen atoms were observed as the corresponding dienolates in aqueous basic solution by using the technique of flash photolysis. The transients reketonize by protonation of the dienolate at carbon or via a 1,5-hydrogen shift in the dienol. The rates of both processes were measured; protonation by water at carbon of the dienolates occurs at room temperature at pseudo-first-order rates at ambient temperature in the range 375–1400 s⁻¹, depending upon the structure of the dienolate. The temperature dependencies of these rates for two of the ketones were measured and indicate that the activation enthalpy, ΔH^\ddagger , for the protonation step is ca. 50 kJ mol⁻¹ and the activation entropy, ΔS^\ddagger , is ca. -26 J mol⁻¹ K⁻¹. Reketonization of the dienols via the 1,5-shift mechanism occurs at room temperature at a rate in water of ca. 50 s⁻¹ or slower, depending upon the structure of the dienol. The pK_a for the dienol–dienolate equilibrium was measured for each ketone and was in the range 10.42–12.01 for the five systems examined.

Ultraviolet light irradiation of β -alkyl α,β -unsaturated ketones or esters possessing hydrogen atoms oriented syn with respect to the carbonyl group has been shown to yield (*Z*)-dienols via a photoenolization reaction from the singlet excited state³⁻¹¹ (Scheme I). Indirect evidence^{4,9} indicates that the dienols produced by the photochemical enolization process rapidly reketonize by two competing pathways. One route involves equilibration with the corresponding dienolate, which then reprotonates at carbon to give, predominantly, the β,γ -unsaturated carbonyl compound (k_β process in Scheme I). The other pathway involves a 1,5-hydrogen shift in the dienol to give the conjugated carbonyl compound (k_σ process in scheme I). Described here are the results of a series of experiments in which dienols were generated photochemically from a number of unsaturated ketones and the rates of the competing modes of decay determined by direct observation of the transient absorption spectra of the dienolates. The dienols were generated in aqueous solution by flash photolysis, and the rates of reketonization of the corresponding dienolates were measured as a function of pH and temperature.¹²

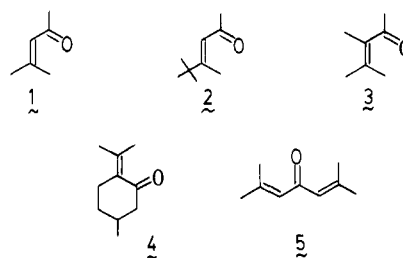
Results

Excitation with a UV flash of 20- μ s duration of aqueous basic solutions of ketones 1–5 resulted in the production of transients absorbing in the UV at longer wavelengths than the parent ketones. The absorption spectra of the transients were recorded for each ketone by measuring the initial absorbance, A° , of the solution at different wavelengths immediately after the lamp flash. Transients derived from ketones 1–4 had virtually identical spectra with the maxima appearing at ca. 290 nm, while the maximum for 5 was at a slightly longer wavelength (310 nm). No transients

Scheme I



could be observed at wavelengths lower than 270 nm for ketones 1–4 and below 300 nm for ketone 5, because of absorption by the residual ketones at these wavelengths. The absorption spectrum of the transient derived from ketone 1 is shown in Figure 1.



For each ketone it was found that the absorbance, A , of the transients decayed according to the first-order rate law $A = A^\circ e^{-\lambda t}$; half-lives were of approximately 70 μ s or longer, depending upon the ketone and the pH of the solution. A lowering of the pH of the solution resulted in a reduction in the rate constant λ for decay of the transient. The variation of the rate constant with pH for ketone 1 is shown in Figure 2. The curve has the appearance of a titration curve, and similar curves were obtained for the other ketones examined, except that the "end point" occurred at a different pH for each ketone. The initial absorbance, A° , of the transients also varied with pH, becoming smaller as the pH was lowered. Thus no transients were observed when the pH was less than ca. 9.5. The variation of A° with pH is shown in Figure 3 for ketone 1 and also has the appearance of a titration curve. Again, similar curves were obtained for the other ketones examined, and the end point occurred at a different pH for each ketone. The variation with pH of the rate constants for decay of the transients derived from ketones 1 and 2 was also measured over a range of temperatures. These results will be presented in the Discussion section below.

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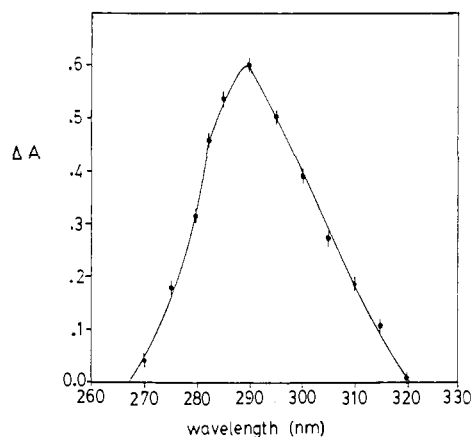


Figure 1. Absorption spectrum of the transient produced from ketone 1 upon flash excitation in water at pH 12.0.

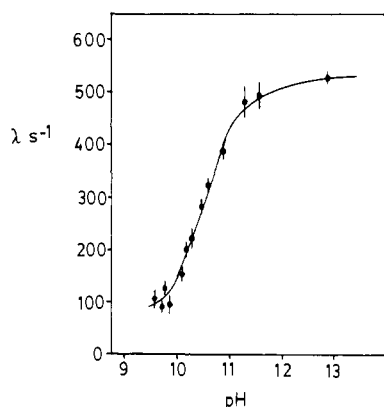


Figure 2. Plot of first-order-decay rate constant λ for disappearance of the absorbance of the transient produced by flash excitation of ketone 1 in water at various values of pH.

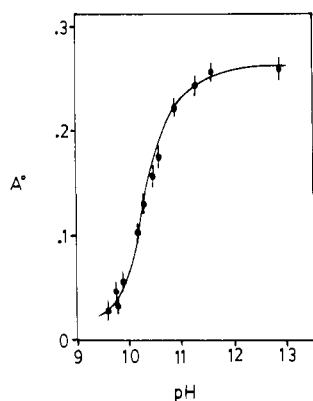


Figure 3. Plot of initial absorbance A^0 for the transient produced by flash excitation of ketone 1 in water at various values of pH.

Discussion

The transients observed following flash photolysis of ketones 1–5 are assigned to the dienolates resulting from photoenolization of the ketones followed by deprotonation of the dienols in the basic solution. The transients derived from ketones 1–4 were observed to absorb maximally at 290 nm and that from 5 at 310 nm, in aqueous basic solution. In comparison, the enolate of acetone absorbs at 245 nm in aqueous basic solution¹³ while that from acetophenone absorbs at 295 nm.¹⁴ The corresponding enols are reported to absorb at somewhat shorter wavelengths.^{15,16} The

absorption spectra of silyl dienol ethers have been measured,¹¹ and those corresponding to the dienols of ketones 1–4 absorb at ca. 230 nm. Taking this as a model for the dienol itself, the dienols from 1–5 should absorb in the same region as the π - π^* transition of the ketone precursors and so should not be seen (in the flash photolysis experiment not all of the ketone is converted to dienol because the maximum quantum yield of photoenolization is known¹⁰ to be ca. 10%). The assignment of the transients to absorption by the dienolates is also supported by the fact that they are only seen in basic solution.

The variation of the rate of decay of the transients with pH, which is illustrated for ketone 1 in Figure 2, can be understood if it is the dienolate which is being observed, if it is in rapid equilibrium with the dienol, and if the dienol and dienolate decay by independent routes represented by k_o and k_β in Scheme I. Thus at high pH all of the transients exist in the deprotonated form as the dienolate, and the rate of decay therefore corresponds to reketonization by protonation at carbon by water (protonation by hydronium ion can be ignored at high values of pH). As the pH is lowered the transient exists to a greater extent as the dienol which is not observed because its absorption is masked by unconverted ketone. The fact that the rate of decay of the residual dienolate does not remain constant but drops with the pH as more of the dienol is formed is evidence that the dienol and dienolate are in rapid equilibrium and that equilibration is faster than the rates of reketonization k_o and k_β . Thus the measured rate of decay is an average of the two competing rates k_o and k_β , weighted according to the relative amounts of dienol and dienolate present. The observation that the decay rate falls rather than increases as the pH is lowered implies that the dienol decay rate is slower than that of the dienolate.

The observed change in the initial absorbance of the transient with pH, shown for ketone 1 in Figure 3, is also consistent with the sequence proposed in Scheme I. As the pH drops the amount of the dienolate present in the dienol–dienolate mixture is reduced because the equilibrium shifts toward the dienol, and so its absorbance also drops.

The curves in Figures 2 and 3 are therefore true titration curves since they trace the change in the dienol–dienolate equilibrium ratio with pH, and accordingly the pK of the dienols can be crudely estimated from their midpoints.

The pK of the dienol, and also the rates of the decay of the dienolate and the dienol, can be estimated more accurately from the data such as that shown for 1 in Figures 2 and 3 by considering quantitatively the kinetics of the dienol and dienolate decays, and assuming the applicability of the sequence shown in Scheme I. The decay kinetics of the dienol and dienolate are identical with those of a reversibly formed exciplex¹⁷ or of an excited state formed by reversible energy transfer.¹⁸ The decay rates of the dienol (DOH) and dienolate (DO⁻) generated in the flash photolysis experiment are given by eq 1 and 2, respectively, where k_β is the

$$-\frac{d[\text{DOH}]}{dt} = k_o[\text{DOH}] + k_1[\text{DOH}] - k_{-1}[\text{DO}^-][\text{H}_3\text{O}^+] \quad (1)$$

$$-\frac{d[\text{DO}^-]}{dt} = k_\beta[\text{DO}^-] + k_{-1}[\text{DO}^-][\text{H}_3\text{O}^+] - k_1[\text{DOH}] \quad (2)$$

rate constant for protonation of the dienolate by water, k_o is the rate constant for the 1,5-hydrogen-shift mechanism of reketonization of the dienol, and k_1 and k_{-1} are the rate constants for proton transfer in the dienol–dienolate equilibrium. If equilibration of the dienol–dienolate is rapid relative to k_o and

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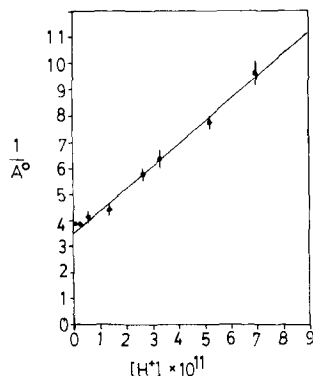


Figure 4. Plot of reciprocal of initial absorbance A^0 for the transient produced by flash excitation of the ketone **1** in water against hydrogen ion concentration.

k_β , then solution of eq 1 and 2 gives the integrated rate equation, eq 3, for the decay of the dienolate, where $[\text{DOH}]^0$ is the initial

$$[\text{DO}^-] = [\text{DOH}]^0 \left[\frac{K}{K + [\text{H}^+]} \right] e^{-\lambda t} \quad (3)$$

concentration of the dienol produced by the photoflash prior to equilibration with the dienolate, K is equal to k_1/k_{-1} and so is the acid dissociation constant for the dienol, and λ is a rate constant for decay given by eq 4. Equation 4 indicates that the dienol and dienolate decay at a common rate which is an average of the rate constants k_σ and k_β weighted according to the proportion of each present in the equilibrium. Thus $K/(K + [\text{H}^+])$ represents the

$$\lambda = k_\beta \left[\frac{K}{K + [\text{H}^+]} \right] + k_\sigma \left[\frac{[\text{H}^+]}{K + [\text{H}^+]} \right] \quad (4)$$

fraction of dienolate present in the dienol–dienolate mixture, and $[\text{H}^+]/(K + [\text{H}^+])$ represents the fraction present as dienol. The proportions of dienol and dienolate will be governed by the pH of the solution; at high pH the dienolate will predominate and $K/(K + [\text{H}^+])$ will tend to unity, while at low pH the dienol dominates and $K/(K + [\text{H}^+])$ will tend to zero and $[\text{H}^+]/(K + [\text{H}^+])$ will tend to unity. Therefore at high pH the dienolate–dienol mixture will decay with rate constant k_β , and at low pH it will decay with rate constant k_σ . The preexponential term in eq 3 corresponds to the concentration of the dienol after equilibration with the dienolate but before any reketonization has occurred and takes the form of the initial concentration of the dienol (before equilibration with the dienolate) multiplied by the proportion of the dienol–dienolate mixture present as the dienolate (i.e., $K/(K + [\text{H}^+])$).

In the flash photolysis experiment it is the absorbance of the transient species which is monitored, and consequently eq 3 takes the form shown in eq 5, where A is the transient dienolate's

$$A = [\text{DOH}]^0 \epsilon \ell \left[\frac{K}{K + [\text{H}^+]} \right] e^{-\lambda t} = A^0 e^{-\lambda t} \quad (5)$$

absorbance, ϵ is the extinction coefficient of the dienolate, and ℓ is the path length of the cell. Equation 5 predicts that the magnitude of the initial absorbance of the transient, A^0 , varies with $[\text{H}^+]$ and should drop to zero at low pH and become a maximum at high pH. This is what is observed for ketones **1–5** and accounts for the shape of the curve shown in Figure 3. Equation 5 predicts that a plot of the reciprocal of the initial absorbance, A^0 , against $[\text{H}^+]$ should yield a straight line and allows determination of the acid dissociation constant K for the dienol–dienolate equilibrium in water from the intercept and gradient. A plot of the data for ketone **1** is shown in Figure 4, and the value of K derived is $(4.2 \pm 0.3) \times 10^{-11} \text{ mol}^{-1}$.

More accurate values of K can be obtained from the rate constant λ for decay of the transient. Equation 4 indicates that

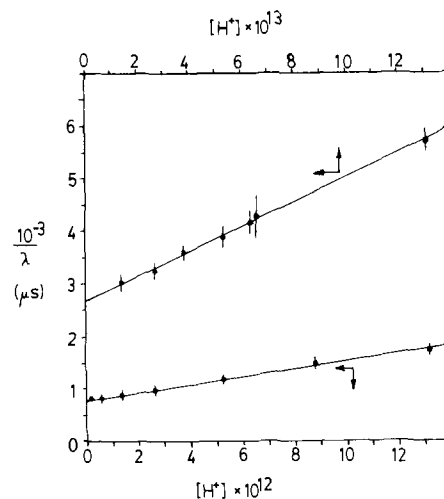


Figure 5. Plot of reciprocal of the first-order rate constant λ for disappearance of the absorbance of the transient produced by flash excitation of the ketones **2** (lower line) and **4** (upper line) in water against hydrogen ion concentration.

Table I. Dissociation Constants, K , for Dienols and Rate Constants k_σ and k_β for Reketonization of Dienols and Dienolates Derived from Ketones **1–5**^a

ketone	k_β, s^{-1}	k_σ, s^{-1}	K, mol^{-1}	pK
1	534 ± 8	8 ± 9	$(3.8 \pm 0.1) \times 10^{-11}$	10.42 ± 0.01
2	1270 ± 18	36 ± 14	$(1.08 \pm 0.04) \times 10^{-11}$	10.97 ± 0.02
3	1376 ± 55	56 ± 24	$(9.6 \pm 0.6) \times 10^{-13}$	12.01 ± 0.02
4	375 ± 6	14 ± 2	$(1.13 \pm 0.06) \times 10^{-12}$	11.95 ± 0.03
5	395 ± 14	1 ± 4	$(1.42 \pm 0.08) \times 10^{-11}$	10.85 ± 0.03

^a Determined at ambient temperature in aqueous basic solution of ionic strength 0.1.

λ depends upon $[\text{H}^+]$; at higher pH, eq 4 should simplify to eq 6, corresponding to the case where most of the dienol–dienolate

$$\lambda = k_\beta \left[\frac{K}{K + [\text{H}^+]} \right] \quad (6)$$

mixture is decaying via the dienolate. Equation 6 predicts that a plot of $1/\lambda$ against $[\text{H}^+]$, at sufficiently low $[\text{H}^+]$, should be linear with an intercept of $1/k_\beta$, and combination of the intercept with the gradient allows a value of K to be determined. The data for ketones **2** and **4** are shown in Figure 5. The plots shown in Figure 5 are linear and confirm that eq 6 holds in the pH ranges indicated. Inclusion of data for lower values of pH results in the appearance of curvature in the plots indicating that $k_\sigma[\text{H}^+]/(K + [\text{H}^+])$ in eq 4 is not negligible and that the simplification to eq 6 is not justified at these higher values of $[\text{H}^+]$. By use of the data in the regions where eq 6 holds, values of k_β and K were calculated for the dienolates derived from ketones **1–5**; these are summarized in Table I.

It should be noted that the values of k_β derived here are the sum of two rate constants for protonation of the dienolates by water because protonation can occur at either of two sites to give either the conjugated ketone originally irradiated or a deconjugated ketone as shown in Scheme 1. Previous work in this laboratory has shown that the rate of protonation to give the deconjugated ketone is approximately 10 times faster than the rate of protonation to give the conjugated ketone, so k_β closely approximates the rate of production of the deconjugated ketone as is implied in Scheme 1.

The values of K for the dienol–dienolate equilibria of ketones **1–5** are similar to those determined by a similar technique for the enols of acetone,¹³ isobutyraldehyde,¹⁶ and acetophenone;¹⁴ the pK values reported for these compounds are 10.94, 11.63, and 10.34, respectively. The rates of protonation of the enolates by water (i.e., the process designated k_β here) are $7.22 \times 10^3 \text{ s}^{-1}$ for acetophenone enolate¹⁵ and $5.01 \times 10^4 \text{ s}^{-1}$ for acetone enolate.¹³

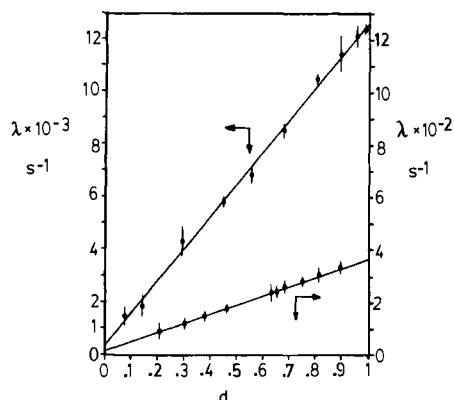


Figure 6. Plot of first-order-decay rate constant λ for decay of the absorbance of the transients produced by flash excitation of ketones **2** (upper line) and **4** (lower line) in water against parameter d defined by eq 7.

The fact that the pK values for dienol-derived ketones **1–5** are similar to those reported for the enols of acetophenone, isobutyraldehyde, and acetone suggests that the extra conjugative stabilization present in the dienols, as compared with the simple enols, is felt equally by both the dienols and dienolates so that their relative free energies remain constant. The larger pK values possessed by the dienols from ketones **3** and **5** relative to the dienols from ketones **1**, **2**, and **4** must reflect the effect of the extra methyl group at the ketone 3-position and its destabilization of the dienolate relative to the dienol. The origin of the destabilization may be in the inductive effect of the methyl group, or it may be due to a steric effect upon the conformation adopted by the dienol–dienolate.

As would be expected, the extra stabilization arising from the conjugated double bond present in the dienolates derived from ketones **1–5**, as compared with the simple enolates of acetone and isobutyraldehyde, considerably slows their rates of protonation at carbon by water; however, the stabilizing effect of the phenyl group, which slows k_{β} from approximately 50 000 to 7 000 in going from the enolate of acetone to that of acetophenone, is not seen for the dienolates of **1** and **5**, which have similar values of k_{β} , even though the latter has an extra double bond cross conjugated with the dienolate.

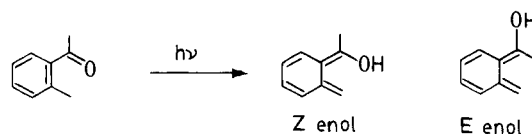
When the substitution $d = K/(K + [H^+])$ in eq 4 is made, eq 7 is obtained. The magnitude of d varies from zero to unity and

$$\lambda = (k_{\beta} - k_{\sigma})d + k_{\sigma} \quad \text{where } d = K/(K + [H^+]) \quad (7)$$

corresponds to the fraction of the dienolate–dienol mixture present as the dienolate. By use of the values of K obtained from the data fitted to eq 6 it is possible to determine the magnitude of k_{σ} for the 1,5-sigmatropic hydrogen shift by plotting λ against d . The data for ketones **2** and **4** are shown in Figure 6. The values of k_{σ} so derived for all of the ketones examined are given in Table I. For ketones **2**, **3**, and **4** the value of k_{σ} is finite, while for ketones **1** and **5** it is indistinguishable from zero. This does not mean that k_{σ} is, in fact, zero for these ketones, because it is known that if these ketones are irradiated in the absence of base, then they do not isomerize to their deconjugated isomers but do so when base is present to intercept the dienol. This can only be interpreted in terms of a 1,5-shift mechanism for reketonization and hence a finite value of k_{σ} .

The values of k_{σ} determined are all slower than ca. 50 s^{-1} , which corresponds to a dienol lifetime ($1/k$) of 20 ms or longer at room temperature in water. In contrast, simple enols such as those from acetone, while much higher in energy than the parent ketones, are long-lived species in the absence of acids and bases, and stable solutions of simple enols have been generated both thermally and photochemically with the enols characterized spectroscopically.¹⁷ The large difference in lifetimes of simple enols and the dienols generated here is a reflection of the fact that the only route available for thermal reketonization of simple enols in the absence of a catalyst is via a thermal 1,3-sigmatropic hydrogen shift. Such

Scheme II



a shift would have to proceed antarafacially for orbital symmetry to be conserved and so does not occur because the antarafacial transition state is too strained for a four-centered system involving only first-row elements. In contrast, noncatalyzed reketonization of the dienols described here can occur via a thermal 1,5-sigmatropic hydrogen shift suprafacially, and the transition state for this process is readily accessible. This interpretation is supported by observations which have been reported for the enols obtained by UV irradiation of *o*-alkyl aromatic ketones,²⁰ in these cases, because the enols are formed from both the triplet and singlet excited states, both the (*E*)- and (*Z*)-enols are formed as shown in Scheme II. In polar solvents the (*Z*)-enol is the shorter lived (lifetime ca. $1 \mu\text{s}$ in water at ambient temperature) and is presumed to revert to the ketone precursor via a 1,5-hydrogen shift. However, the (*E*)-enol cannot attain the required geometry and so is longer lived (lifetime of seconds) and must reketonize by a catalytic process. The much faster rate of the k_{σ} process for the aromatic enol as compared with the dienols derived from ketones **1–5** presumably arises from the fact that the former are regaining aromaticity and also because the system is held in the requisite geometry, whereas the dienol may be in a transoid conformation unsuitable for the 1,5-shift.

Attempts to trap the dienols formed photochemically from ketones such as **5** by using Diels–Alder dienophiles have been described.²¹ These attempts were unsuccessful, and other products derived from thermal ene reactions with the ketone were obtained instead. The failure of the Diels–Alder addition may be due to the relatively short lifetimes of the dienols. In the case of photoenolized *o*-alkyl aromatic carbonyl compounds, it is only the long-lived (*E*)-enols (with a lifetime of seconds) which have been trapped with dienophiles,²² whereas the rapidly decaying (*Z*)-enol has not. The rate constant for maleic anhydride addition to (*E*)-1-methoxy-1,3-butadiene has been measured;²³ assuming the same value for the Diels–Alder reaction of a dienol would require that it should have a lifetime longer than a second for it to be trapped efficiently. In fact, this is probably an underestimate given that the dienol is generated as the *Z* isomer, which is less likely to adopt the required cisoid conformation than (*E*)-1-methoxy-1,3-butadiene, and also because in a typical nonpolar Diels–Alder solvent hydrogen-bonding interactions would be absent, and these are known to extend enol lifetimes in the case of the aromatic (*Z*)-enols.²⁰

In previously reported work in this laboratory,^{5–7,9} semiquantitative studies using methods relying on steady-state kinetic and quantum yield measurements, as well as product studies, have indicated that the efficiency of the k_{σ} process depends in some degree on the preferred conformation adopted by the dienol. In nonpolar solvents such as diethyl ether, evidence suggests that k_{σ} is much faster for dienols derived from ketones such as **2** because the *tert*-butyl group holds the dienol in the cisoid conformation necessary for the 1,5-shift to occur and conversely that dienols derived from ketones possessing large γ -substituents do not reketonize via the 1,5-hydrogen-shift mechanism at all because the substituent holds the dienol in a transoid conformation. Such effects are not observed here; k_{σ} for the dienol derived from ketone **2** is no different, within error, from the values found for the dienol

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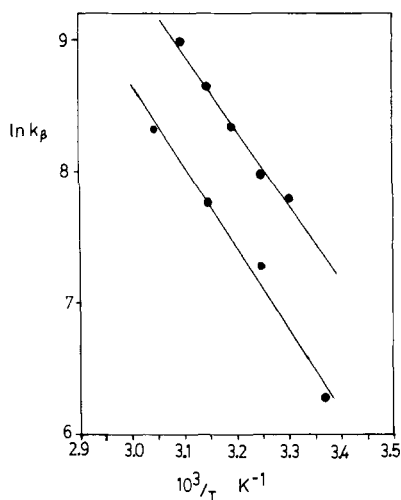


Figure 7. Arrhenius plot for rate constants for protonation by water, k_{β} , of the dienolates produced by flash excitation of ketones **1** (lower line) and **2** (upper line) in aqueous base.

Table II. Arrhenius Preexponential Factors and Activation Energies and Eyring Plot-Derived Activation Entropies and Enthalpies for Protonation by Water of the Dienolates from Ketones **1** and **2**

ketone	$\ln A$	E_a , kJ mol ⁻¹	ΔS^* , J K ⁻¹ mol ⁻¹	ΔH^* , kJ mol ⁻¹
1	27.4 ± 1.3	52 ± 3	-26 ± 10	50 ± 3
2	27.5 ± 0.9	50 ± 2	-26 ± 7	47 ± 2

from **3** and little different from the value determined for the dienol from **4**, even though the steric factors which might be expected to result in a higher value of k_{β} for the dienol from **2** are present. It is possible that hydrogen bonding between water and the dienol may account for the slower than expected rate of reketonization of the dienol derived from **2**; this effect has been observed for the (*Z*)-enols derived from *o*-alkyl aromatic ketones.²⁰

An attempt was made to obtain more accurate values of k_{β} by raising the temperature of the solution prior to generation of the transients. It was hoped that this would increase the magnitude of k_{β} so that it could also be measured for ketones **1** and **5**. The elevated temperatures necessary could not be maintained with sufficient accuracy with the apparatus used, and so the results did not allow reliable values of k_{β} to be obtained. However, the rate of protonation of the dienolate by water, k_{β} , was accessible with reasonable accuracy from the data obtained at higher values of pH where eq 6 holds, and this allowed the activation parameters for the protonation of the dienolates to be estimated. From the plots of λ against $[H^+]$, at low $[H^+]$, the values of k_{β} were obtained

at a variety of temperatures for ketones **1** and **2**; the Arrhenius plot of the data for ketones **1** and **2** is shown in Figure 7. The values of the A factors and the activation energies are given in Table II, as are the activation parameters obtained from the corresponding Eyring plots. The activation parameters are, as far as we are aware, the first to have been reported for the protonation of an enolate by water. The activation energies for the dienolates examined are identical within error and are quite high; their magnitude may reflect a large degree of hydrogen bonding between the solvent and the dienolate.

Experimental Section

Ketones **1**, **4**, and **5** were commercial samples. Ketone **2** was prepared from ethyl 3,4,4-trimethyl-2-pentenoate,⁶ the ester was hydrolyzed to the acid with ethanolic KOH, and the acid was converted to the ketone with methylolithium by using the procedure of Theus et al.²⁴ Ketone **3** was prepared from 4-chloro-3,4-dimethyl-2-pentanone by the previously reported procedure.²⁵ The ketones were all purified by distillation followed by preparative gas chromatography prior to use.

Flash photolysis experiments were performed by using a Photochemical Research Associates FP 1000 conventional flash photolysis system equipped with Xe flash lamps and an unfiltered 75-W high-pressure Xe monitoring lamp. The monitoring beam was focused through the quartz sample cell (10-cm path) into a model 1700-II Czerny-Turner monochromator (slits set for 2-nm resolution). The monochromator output was detected by an RCA 1P28 photomultiplier, and the transient signals were stored in a Nicolet 209-III A digital oscilloscope prior to transfer to an HP 9816 computer for analysis of the decays by a least-squares program. In variable-temperature experiments a jacketed quartz cell was used, and the cell solution was kept at constant temperature by using a thermostated heating bath to recirculate water through the cell's jacket. The temperature of the cell solution was measured by direct insertion of a glass-coated copper-constantan thermocouple, and the temperature was kept constant within ±0.2 °C.

All solutions for flash photolysis were prepared with triply distilled water which prior to use was freshly boiled to expell dissolved CO₂ and purged with nitrogen during cooling. In all cases the solutions were 10⁻⁵ M in ketone, and an appropriate quantity of KCl was present to maintain a constant ionic strength of 0.1. The base used was KOH free of carbonate. Values of pH were calculated from the known analytical concentration of KOH and corrected for activities. In variable-temperature experiments, pH, activities, and K_w were corrected for temperature and the volume change of water. Nitrogen purging of the solutions prior to flashing had no effect upon the decays of the transients; the same results were obtained with oxygen-saturated solutions. Solutions were made up immediately prior to use, and each solution was flashed once only. The energy of the flash was 50 J, and each flash was of 20-μs duration (width at half-height).

Registry No. 1, 141-79-7; **2**, 23732-21-0; **3**, 684-94-6; **4**, 15932-80-6; **5**, 504-20-1.

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