

Treatment of the tris(diisopropylammonium) salt of **8** (0.4 mmol) in dichloromethane (10 mL) with methyl iodide (1 mmol) at room temperature in the presence of 2-*O*-benzyl-(*S*)-propane-1,2-diol (8-fold excess) gave [ $^{16}\text{O}$ ,  $^{17}\text{O}$ ,  $^{18}\text{O}$ ] isotopically labeled 2-*O*-benzyl-1-phospho-(*S*)-propanediol (**4c**) in ca. 50% yield. The stereochemical analysis of the resulting 1- [ $^{16}\text{O}$ ,  $^{17}\text{O}$ ,  $^{18}\text{O}$ ]phospho-(*S*)-propane-1,2-diol following removal of the benzyl group by hydrogenolysis is shown in Figure 1B. The pattern expected for total inversion of configuration at phosphorus can be predicted on the basis of the usual assumptions.<sup>11</sup> Comparison of the two spectra in Figure 1 clearly shows that the phosphoryl transfer from  $\text{P}^{\text{I}}, \text{P}^{\text{I}}$ -disubstituted pyrophosphates to alcohols in *aprotic* solvents must proceed with considerable *racemization* of configuration at phosphorus. The amount of phosphoryl transfer proceeding with *retention* of configuration required to account for the observed ratios appears to be ca. 35% which would correspond to ca. 70% proceeding through a pathway involving *racemization*. The excess of the  $S_{\text{p}}$  configuration (ca. 30%) at phosphorus would arise from phosphoryl transfer occurring with inversion of configuration.

The observation that the phosphoryl-transfer reaction for which there is good evidence in favor of a metaphosphate-like intermediate occurs with significant racemization of configuration at phosphorus may indicate a relatively "free" metaphosphate but could also accord with a preassociation mechanism<sup>1,2,12</sup> if the nucleophile is not constrained to approach in line with the leaving group in a preassociation reaction. The contrast of this result with the previous studies in aqueous methanol may indicate a significant difference in reactivity in protic and aprotic solvents. Furthermore, it should be stressed that these studies have been conducted in comparatively dilute solution of both metaphosphate precursor and trap.

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### Direct Observation of a Photochemically Produced Dienol: Evidence for a Noncatalyzed Reketonization Pathway Unavailable to Simple Enols<sup>1,2</sup>

Randy M. Duhaime and Alan C. Weedon\*

*The Photochemistry Unit, The University of Western Ontario, London, Ontario, Canada N6A 5B7*

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Chemical trapping studies have shown<sup>3</sup> that ultraviolet light irradiation of  $\alpha, \beta$ -unsaturated ketones such as **1a** yields a *Z* dienol (e.g., **2a**). In the absence of a trap **2a** reverts to **1a** so that the ketone appears to be photochemically inert, as do aromatic ketones such as **5** which produce<sup>4</sup> transient photoenols **6a** and **6b**. Generation of **2a** in the presence of a base<sup>5</sup> produces the dienolate **3a** which can be reprotonated at carbon to yield the  $\beta, \gamma$ -unsaturated isomer **4a**. It has been proposed<sup>5,6</sup> by analogy<sup>4</sup> with the aromatic systems such as **6** that the noncatalyzed reketonization pathway of **2a** leading exclusively to **1a** is a 1,5-sigmatropic hydrogen shift occurring from the syn conformer of **2a**. This paper reports the results of a study in which the *Z* dienols were generated

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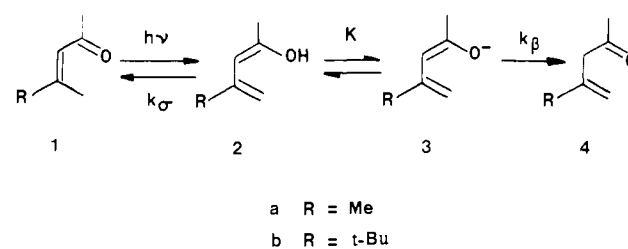
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### Scheme I



from **1a** and **1b** and the decays of the corresponding dienolates were monitored by using the technique of flash photolysis, thus enabling an estimate to be made of the rates of the noncatalyzed and base-catalyzed processes for reketonization and also of the  $k_{\text{K}}$ 's of the dienols.

Flash photolysis<sup>7</sup> of **1a** and **1b** in basic aqueous solution produced transient species with absorption maxima at 290 nm, assigned by analogy with the spectra of enolates<sup>8</sup> to the dienolate chromophore. First-order decay of the transients was observed; the rate constants increased with increasing pH and were too small for the transients to be assigned to the triplet excited states of the ketones. The initial intensities of the transients' absorptions declined as the pH was lowered and no absorption was seen below pH 9.5. These results are consistent with the generation of a dienol which rapidly equilibrates during the lamp flash with a dienolate; the observed initial intensities of the transients reflect the proportion of dienol and dienolate present at equilibrium, and the variation of the decay rate constant reflects competition between the processes designated  $k_{\sigma}$  (noncatalyzed reketonization of the dienol) and  $k_{\beta}$  (protonation of the dienolate by water) in Scheme I.

It can be shown<sup>9</sup> for the system in Scheme I that the dienolate **3** should decay according to eq 1, where  $[2]^0$  is the initial con-

$$[3] = \frac{K[2]^0}{K + [H^+]} e^{-\lambda t} \quad (1)$$

$$\lambda = k_{\beta} \frac{K}{K + [H^+]} + k_{\sigma} \frac{[H^+]}{K + [H^+]} \quad (2)$$

at low  $[H^+]$

$$\lambda = \frac{k_{\beta} K}{K + [H^+]} \quad (3)$$

at any  $[H^+]$

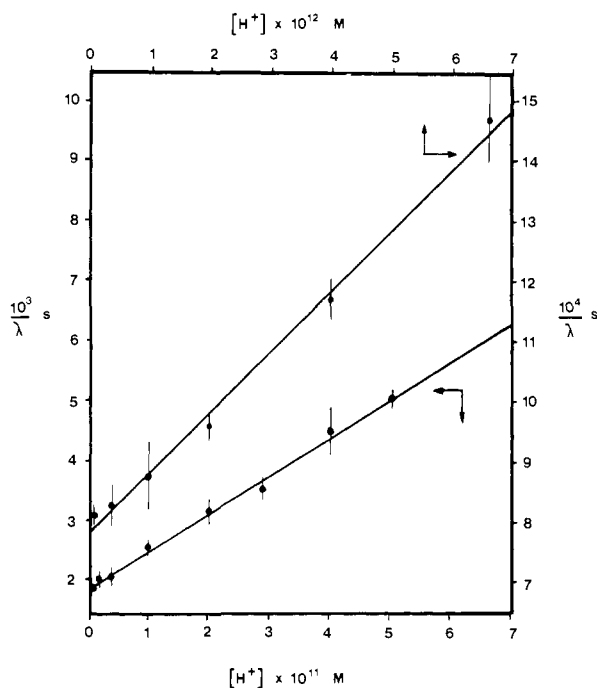
$$\lambda = (k_{\beta} - k_{\sigma})d + k_{\sigma} \quad (4)$$

centration of the dienol prior to equilibration with the dienolate, and  $K$  is the dienol-dienolate equilibrium constant. The parameter  $\lambda$  is defined by eq 2. If equilibration of the dienol with the dienolate is rapid relative to  $K_{\beta}$  and  $k_{\sigma}$ ,  $\lambda$  corresponds to decay of the dienolate and dienol with a common lifetime whose magnitude is governed by the proportions of the dienol and dienolate present. This is determined by the pH of the medium. At higher pH eq 2 reduces to eq 3; thus measurement of  $\lambda$  as a function of  $[H^+]$  at high pH allows an estimate of the values of  $K$  and  $k_{\beta}$ . Once  $K$  is known,  $k_{\sigma}$  can be determined by using eq 4, which is obtained from eq 2 by the substitution  $d = K/(K + [H^+])$ .

(7) Solutions were  $0.5 \times 10^{-4}$  M in ketones **1a** or **1b** and contained potassium hydroxide as the base and sufficient KCl to maintain an ionic strength of 0.10. The water used was triply distilled and boiled under  $\text{N}_2$  to remove dissolved  $\text{CO}_2$ . Fresh solutions were used for each flash; purging with  $\text{N}_2$  or use of oxygen-saturated solutions gave identical results. The photoflash was of 20- $\mu\text{s}$  duration and 50-J energy. Values of  $\lambda$  are the averages of at least three determinations in all cases. All determinations were made at 23  $^{\circ}\text{C}$ .

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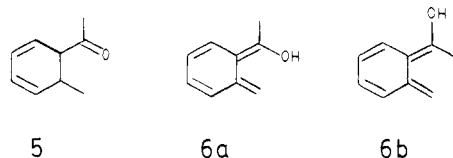
**Figure 1.** Plot of reciprocal of first-order decay rate constants for the dienolates **3a** and **3b** in water against proton concentration. Upper line **3b**; lower line **3a**.

Fitting values of  $\lambda$  measured at low  $[H^+]$  to eq 3 for both **1a** and **1b** (Figure 1) yields values of  $K$  and  $k_\beta$  of  $(3.80 \pm 0.17) \times 10^{-11}$  and  $539 \pm 17 \text{ s}^{-1}$  for **1a** and  $(1.07 \pm 0.5) \times 10^{-11}$  and  $1184 \pm 21 \text{ s}^{-1}$  for **1b**, respectively. The values of the constants corresponding to  $K$  and  $k_\beta$  for acetophenone enolate are  $4.6 \times 10^{-11}$  and  $7 \times 10^3$ , respectively.<sup>8</sup>

By use of the values of  $K$  obtained, the values of  $d$  were calculated and plotted against  $\lambda$  according to eq 4 (Figure 2) to yield  $k_\sigma$  and a further estimate of  $k_\beta$ . For **1a**,  $k_\sigma$  obtained from the intercept is indistinguishable from zero within error, corresponding to an upper limit of ca.  $5 \text{ s}^{-1}$ , while for **1b**  $k_\sigma$  is  $40 \pm 13 \text{ s}^{-1}$ . The gradients of the lines yield values of  $k_\beta$  identical with those determined at high pH from eq 3.

The magnitude of  $k_\sigma$  for **1b** indicates a dienol lifetime in water at room temperature of ca. 0.02 s, while the value for **1a** is at least an order of magnitude greater.<sup>10</sup> The lifetime of **1b** is in contrast to the lifetimes of simple enols which are stable, observable species in the absence of catalysts.<sup>11</sup> This difference supports the proposition that dienols can reketonize by a noncatalyzed pathway (the proposed 1,5-sigmatropic hydrogen shift) whereas for simple enols no noncatalyzed pathway is available (the necessary antarafacial transition state for a 1,3-hydrogen shift is unattainable for first-row elements).

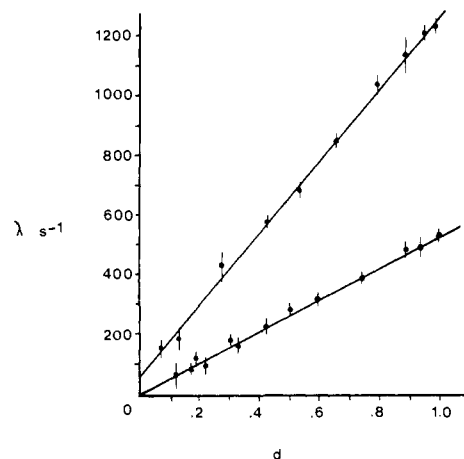
The values of  $k_\sigma$  for **2a** and **2b** are much slower than those for the analogous process of the dienols produced photochemically from *o*-alkyl aromatic ketones. In the case of **6a** this process occurs



at a rate of  $10^6 \text{ s}^{-1}$  in water.<sup>5</sup> The large difference presumably reflects two factors: in **2a** and **2b** the dienol is free to adopt a transoid conformation unfavorable for the 1,5-hydrogen shift,

(10) It could be argued that  $k_\sigma$  for **2a** is infinite—i.e., there is no 1,5-shift mechanism for this dienol; however, **1a** photodeconjugates only if base is present, confirming that an uncatalyzed reketonization pathway exists.

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**Figure 2.** Plot of first-order decay rate constants for the dienolates **3a** and **3b** in water against fraction of dienolate present in the dienol-dienolate equilibrium. Upper line **3b**; lower line **3a**.

whereas in the aromatic system the dienol is held in a cisoid orientation; also, in the aromatic system the reketonization reaction of the dienol is much more exothermic than is the case with **2** as the system is also rearomatizing. Application of Hammond postulate arguments predict that **6a** should therefore reketonize faster than **2**.

The larger value of  $k_\sigma$  for **1b** as compared with **1a** suggests that the sterically hindering methyl groups in **1b** encourage the adoption of a cisoid conformation of the dienol and implies that the dienol **1a** is more stable in the transoid orientation. This is supported by the observed effects of substitution upon the efficiency of photochemical deconjugation of unsaturated esters<sup>6</sup> and by the experimentally observed preferential adoption of transoid conformations<sup>12</sup> by dienes.

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### Nanosecond Flash Photolysis Studies of Intersystem Crossing Rate Constants in Biradicals: Structural Effects Brought About by Spin-Orbit Coupling

Matthew B. Zimmt, Charles Doubleday, Jr.,\* Ian R. Gould, and Nicholas J. Turro

Department of Chemistry, Columbia University  
New York, New York 10027

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This paper concerns the structural effects of spin-orbit coupling (SOC) as a mechanism of intersystem crossing (isc) in triplet-derived biradicals. First we show that SOC is strongly enhanced in biradicals with an acyl terminus relative to biradicals with only hydrocarbon termini. Second, we present evidence that, even for long chains, biradicals containing an acyl terminus prefer to undergo isc in conformers with small end-to-end distances. This appears to be a direct result of the dominance of SOC over electron-nuclear hyperfine coupling (HFC) in the isc process.

We have measured lifetimes ( $\tau$ ) of the biradicals in eq 1-3 by monitoring their nanosecond transient UV absorption at 320 nm.<sup>1</sup> All biradicals were characterized by their transient UV absorption

(1) Excitation sources were either a Lambda Physik excimer laser operating at 248 or 308 nm (base-line pulse width 20 ns) or a Quanta-Ray Nd-YAG laser, frequency-quadrupled to 266 nm (fwhm 6 ns). The transient absorption apparatus utilizing the excimer laser has been described: Turro, N. J.; Aikawa, M.; Butcher, J. J. *Quant. Electron.* **1980**, QE-16, 1218.