The Photo-Favorskii Reaction of p-Hydroxyphenacyl Compounds is Initiated by Water-Assisted, Adiabatic Extrusion of a Triplet Biradical

Journal:	*Journal of the American Chemical Society*
Manuscript ID:	ja-2007-109579.R1
Manuscript Type:	Communication
Date Submitted by the Author:	n/a
Complete List of Authors:	Givens, Richard; University of Kansas Lawrence, Department of Chemistry Heger, Dominik; University of Basel, Department of Chemistry Hellrung, Bruno; University of Basel, Chemistry Kamdzhilov, Yavor; University of Basel, Department of Chemistry Mac, Marek; Jagiellonian University, Department of Chemistry Conrad, Peter; University of Kansas Lawrence, Chemistry Cope, Elizabeth; University of Kansas Lawrence, Department of Chemistry Lee, Jong; University of Kansas Lawrence, Department of Chemistry Mata-Segreda, J.; University of Costa Rica, School of Chemistry Schowen, Richard; University of Kansas, Chemistry, Pharm Chem Wirz, Jakob; University of Basel, Department of Chemistry

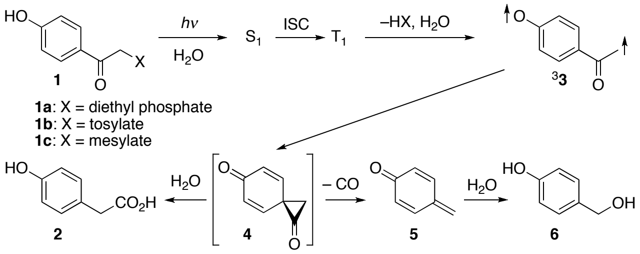
The Photo-Favorskii Reaction of *p*-Hydroxyphenacyl Compounds is Initiated by Water-Assisted, Adiabatic Extrusion of a Triplet Biradical

Richard S. Givens,*[‡] Dominik Heger, Bruno Hellrung, Yavor Kamdzhilov, Marek Mac,[§] Peter G. Conrad, II,[‡] Elizabeth Cope,[‡] Jong I. Lee,[‡] Julio F. Mata-Segreda,[†] Richard L. Schowen[‡] and Jakob Wirz*

Department of Chemistry, University of Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland, [§]Jagiellonian University, Ingardena 3, 30-060 Krakow, Poland, [‡]Department of Chemistry, University of Kansas Lawrence, Kansas 66045, and [†]Department of Chemistry, University of Costa Rica, 2060 Costa Rica

RECEIVED DATE (automatically inserted by publisher); givensr@ku.edu, J.Wirz@unibas.ch

p-Hydroxyphenacyl is an effective photoremovable protecting group, not least due to the fast release of its substrates, accompanied by a photo-Favorskii rearrangement of compounds **1** to *p*-hydroxyphenylacetic acid (**2**) that is transparent down to 300 nm. First used for the release of ATP from **1** (X = ATP) a decade ago,[1] the reaction has been employed in a variety of fields as diverse as neurobiology,[2] enzyme catalysis,[3] and biochemistry.[4] The nature and timing of the bond-making and bond-breaking events have not been fully elucidated despite extensive experimental and theoretical efforts by our group[5] and others.[6,7] We now report observation of the primary photoproduct, the triplet biradical ^{3}**3**, and of a new side product, *p*-hydroxybenzyl alcohol (**6**), that is formed by decarbonylation of the putative spirodione intermediate **4** at moderate water concentrations (Scheme 1). Solvent kinetic isotope effect (SKIE) studies by nanosecond laser flash photolysis (LFP) provide significant information on the role of water in the photo-Favorskii rearrangement of *p*-hydroxyphenacyl diethyl phosphate **1a** to *p*-hydroxyphenylacetic acid (**2**).



Scheme 1. Mechanism of the photo-Favorskii rearrangement **1**→**2**.

Anderson and Reese first reported the intriguing photoreaction **1**(X = Cl) → **2** + HCl and suggested that the skeletal rearrangement may proceed via a spirodione intermediate **4**,[8] which has yet to be detected. Intersystem crossing (ISC) of diethyl phosphate **1a** is very fast, $k_{\mathrm{ISC}} = 4 \times 10^{11}\ \mathrm{s}^{-1}$,[5] and we have established that the rearrangement proceeds from the triplet state, T_1.[1,4b,5] This was confirmed by Phillips et al.[7a–c] Hydroxylic solvents play a major role in the rearrangement. The lifetime of T_1 decreases from several µs in degassed, dry CH_3CN to about 0.4 ns in aqueous CH_3CN (50% by vol).[5,7c,d]

The lifetime of T_1 of **1a** is further reduced to 100 ± 10 ps in 87% aqueous CH_3CN (Figure 1), and to 63 ± 10 ps in wholly aqueous solution. This was the key to revealing that the decay of T_1 left weak absorptions at 445, 420 and 330 nm, which decayed with a somewhat longer lifetime of ca. 0.6 ns. Pump–probe spectra obtained with other derivatives of **1** with good leaving groups (**1b**,**c**: X = tosylate, mesylate) also displayed the transient species possessing the same weak, but characteristic bands, and the same lifetime. Kinetic analysis of sequential reactions A → B → C is generally difficult when the rate constants of the two processes are similar, unless independent information is available regarding one of the two rate constants.[9] Such information was available from recent work by Phillips and coworkers.[7c] Time-resolved resonance Raman spectroscopy of **1a** in 50% aqueous CH_3CN proved that the final product **2** appears with a rate constant of $2.1 \times 10^9\ \mathrm{s}^{-1}$ following pulsed excitation of **1**. The appearance of **2** followed a biexponential rate law, $T_1 \rightarrow M \rightarrow$ **2**, i.e., the formation of **2** was slightly delayed with respect to the decay of T_1, $k = 3.0 \times 10^9\ \mathrm{s}^{-1}$, which had been determined independently by optical pump–probe spectroscopy in the same solvent. A water-associated spirodione species **4**•$2H_2O$ was proposed for the intermediate M, which was said to be optically transparent in the 300–700 nm range.

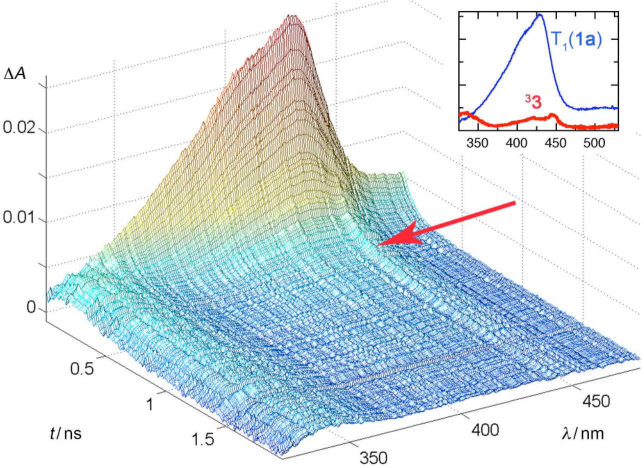


Figure 1. Pump–probe spectroscopy of **1a** in 87% aqueous CH_3CN. The sample was excited with a pulse from a Ti/Sa–NOPA laser system (266 nm, 150 fs pulse width, pulse energy 1 µJ).[10] The inset shows the species spectra of T_1 and ^{3}**3** that were determined by global analysis of the spectra taken with delays of 10–1800 ps using a biexponential fit.

Our observations are consistent with those of Phillips et al.,[7c] except that we have now detected weak absorption by the intermediate M, which we assign to the triplet biradical ^{3}**3**.[11] The position and shape of its absorption bands are similar to those of the phenoxy radical, which are also weak.[12] MP2 calculations (6-31G*, PCM acetonitrile, Supporting Information) predict that the biradical ^{3}**3** is twisted by 27° around the C_{ar}–CO bond, but there are two low-frequency modes involving this twist. Thus, reliable predictions for the geometry and, hence, the absorption spectrum of ^{3}**3** are difficult. If the twist of the C_{ar}–CO bond in fact is closer to 90°, then the absorption spectrum of ^{3}**3** should be nearly identical to that of the phenoxy radical. TDFT as well as open-shell PPP SCF CI calculations[13] predict that ^{3}**3** (twisted by 27°) and the phenoxy radical should have rather similar absorption spectra. We could not locate a stationary point for the singlet biradical ^{1}**3**. Both planar and vertical initial trial structures for ^{1}**3** converged to the spirodione **4**, suggesting that cyclization to **4** immediately follows ISC of ^{3}**3** (Figure 2).

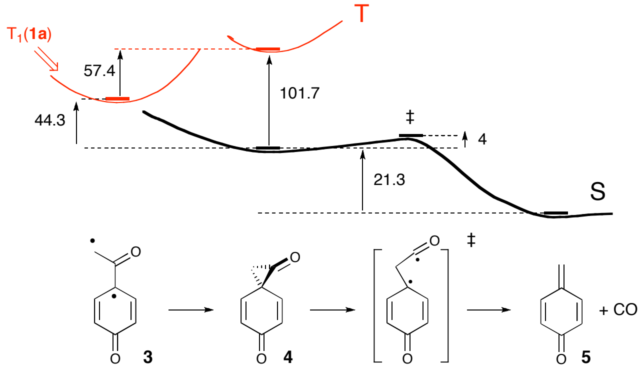


Figure 2. Ab initio calculations (MP2/6-31G*, PCM: acetonitrile). Solid lines (—) indicate stationary points. Energy differences in kcal mol^{-1}.

Our attempts to detect the elusive spirodione **4** by step–scan FTIR failed, and, with the wisdom of hindsight,[7c] this is no surprise. The C=O stretch vibration of cyclopropanone lies at 1813 cm^{-1},[14] and DFT calculations (Supporting Information) predict 1880 cm^{-1} for **4**. No transient signal was discovered in that region upon excitation (266 nm with 4-ns, 5-mJ pulses from a Nd/YAG laser) of **1a** in mixtures of D_2O (2–20% by vol) and CD_3CN. However, transient bands at 1450 and 1300 cm^{-1} appeared within the 50-ns rise time of our setup. Their first-order decay was accompanied by the rise of another band at 1647 cm^{-1}, $k = (8.5 \pm 1.0) \times 10^6$ s^{-1} in 2% D_2O (Figure 3). The rate increased while the amplitude of this band decreased with higher amounts of water. The prominent bands of the first intermediate are similar to those of triplet acetophenone[15] and are assigned to the triplet state T_1.

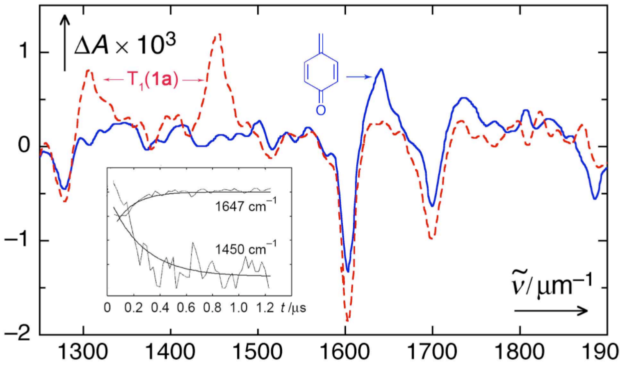


Figure 3. FTIR difference spectra at 50 ns (red, dotted) and 1 µs delay (blue, solid line) of **1a** in acetonitrile with 2% D_2O. The spectra were reconstructed after factor analysis of 50 spectra using two factors.

The same intermediates were detected by nanosecond laser flash photolysis of **1a** in wet CH_3CN. The first-order decay of the triplet–triplet absorption by T_1, λ_{max} = 395 nm, left a broad absorption, λ_{max} = 276 nm, which was sufficiently long-lived to be monitored on a conventional spectrophotometer. Its decay was accelerated by water, $k \approx 0.01$ s^{-1} in 5% and 0.05 s^{-1} in 10% H_2O, and particularly by acid. The initial amount of the 276-nm transient decreased with increasing water content. *p*-Hydroxybenzyl alcohol (**6**) was discovered to be a byproduct of the photoreaction in wet CH_3CN, and its relative yield also decreased with increasing water content.[16] These observations suggested that the 276-nm transient is *p*-quinone methide (**5**). Weak metastable NMR signals were detected shortly after irradiation of **1a** in a mixture of D_2O (2.5% by vol) and CD_3CN at –25 °C, also indicating the formation of **5** (Supporting Information).

Definitive identification of *p*-quinone methide (**5**) was possible by comparison with recent work of Kresge and coworkers, who reported rate constants for the hydrolysis of **5** that was generated by flash photolysis of *p*-hydroxybenzyl acetate in wholly aqueous solution, k_{unc} = 3.3 s^{-1} and $k_{H^+} = 5.3 \times 10^4$ M^{-1} s^{-1}.[17] Using the same method to generate authentic **5** in wet CH_3CN we obtained satisfactory agreement for the rate of hydrolysis of **5** formed from the two precursors. Taken together, these observations strongly support the assignment of the second transient (1647 cm^{-1}, λ_{max} = 276 nm)[18] to *p*-quinone methide (**5**), which is formed by decarbonylation of **4**, eq 1, at moderate water content. Ab initio calculations (Figure 2) indeed show that decarbonylation of **4** to *p*-quinone methide (**5**) is a very facile process with an activation energy of only 4 kcal mol^{-1}.

To characterize the role of water on the primary photoreaction and, in particular, the number of water molecules involved in the transition state for the release of HX, we studied the SKIE on the decay rate constants of T_1(**1a**) by LFP. Degassed 10% aqueous CH_3CN was chosen as a solvent, because accurate lifetimes of T_1(**1a**) could be obtained under these conditions with D/H mole fractions $n = n_D/(n_D + n_H)$ varying from 0 to 1. The resulting rate constants k_n are given in Table 1 and are plotted in Figure 4.

Table 1. Rate constants for the decay of T_1 (k_{obs}) as a function of the D/H mole fraction *n* obtained by LFP excitation at 248 nm and monitored at 395 nm at 25 °C in 10% aqueous CH_3CN.

n	$k_{obs}/(10^6\ s^{-1})$	average	k_H/k_n
0.00	11.2, 11.5, 11.5, 11.4, 11.6	11.4 ± 0.14	1.00
0.20	9.46, 9.62, 9.54, 9.50	9.53 ± 0.07	1.20 ± 0.02
0.40	8.33, 8.38, 8.31, 8.41	8.36 ± 0.04	1.36 ± 0.02
0.60	7.26, 7.21, 7.21, 7.26	7.24 ± 0.03	1.57 ± 0.02
0.80	6.31, 6.30, 6.31, 6.25	6.29 ± 0.03	1.81 ± 0.02
1.00	5.20, 5.31, 5.25	5.25 ± 0.06	2.17 ± 0.03

The *proton inventory* method[19] has rarely been applied to excited state processes.[20] It has proven to be a powerful method to determine the number of protons being transferred in the rate-determining step for ground state reactions. Our total SKIE is large, $k_H/k_D = 2.17 \pm 0.03$, and the proton inventory plot is clearly curved, indicating that the transition state involves at least two weakly bonded protons "in flight". The relationship between the k_n–n data pairs is commonly analyzed by the Kresge–Gross–Butler (KGB) relation, eq. 1,[21,22] where the parameters $\varphi_i^\ddagger = (D/H)_i/(D/H)_{L_2O}$ are the isotopic fractionation factors for the exchangeable positions i = 1 ·· ν in the transition complex.

$$k_n/k_H = \prod_{i}^{\nu}\left(1 - n + n\varphi_i^\ddagger\right) \qquad (1)$$

It is here assumed that isotopic fractionation in the reactant state is negligible. Then the fractionation factor for the ith transition-state site, $\varphi_i^\ddagger$, becomes equal to the reciprocal isotope effect $(k_H/k_D)^{-1}$ generated at that site. It is significantly less than 1 only for protons being transferred in the transition state or bonded to positively charged oxygen as in H_3O^+. Eq. 2 then reduces to some simplified limiting cases: (a) a single site generates the entire isotope effect of 2.17, as in a single proton-transfer reaction (eq. 2, $\nu = 1$ and $k_H/k_D = 2.17$); (b) two sites generate roughly equal effects as in a double proton-transfer reaction (eq. 2, $\nu = 2$; $k_H/k_D = 2.17^{1/2} = 1.47$); (c) three sites generate roughly equal effects as in general-base catalysis by water[19c] (eq. 2, $\nu = 3$; $k_H/k_D = 2.17^{1/3} = 1.30$); (d) a large number ν of sites generate the effect as in a large change in solvation, so that each effect is small and thus the dependence of k_n on n becomes exponential, eq. 3.

$$k_n/k_H = (1 - n + n[k_H/k_D]^{-1})^{\nu} \tag{2}$$

$$k_n/k_H = (1 - n[1 - \varphi^{\ddagger}])^{\nu} \approx (1/2.17)^{n} \tag{3}$$

The comparison of the data with these models in Figure 4 appears to exclude the one-proton model, and to require at least two protons to generate the observed isotope effect. It is worth noting that the decay rate constants of T_1(**1a**) in CH_3CN depend in a quadratic fashion on water concentration, $k_{obs} = k_0 + k_w[H_2O]^2$.[5]

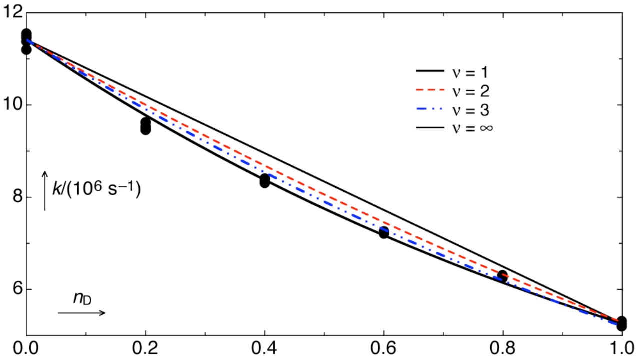


Figure 4. Decay rate constants k_n of T_1(**1a**) in degassed 10% (by vol) aqueous CH_3CN at 25 ± 0.1 °C at various atom fractions of deuterium n in the aqueous part of the solvent. The upper solid line shows the expectation (eq. 2, $\nu = 1$) for a single-site isotope effect of 2.17, the lower solid line the expectation (eq. 3) for a generalized solvation effect from many sites. The intermediate dashed lines correspond to a two-site effect (red, isotope effect of 1.5 at each site; eq. 2, $\nu = 2$) and a three-site effect (blue, isotope effect of 1.3 at each site; eq. 2, $\nu = 3$).

The acidity of the phenolic proton of **1a** increases by ~10^4 upon excitation to the triplet state, whereas the carbonyl group becomes much more basic.[5] The observed isotope effects show that H-bonding or H-transfer phenomena involving at least two protic sites accompanies the expulsion of phosphate from T_1(**1a**). Reasonable mechanisms that include such interactions include general base catalysis by water (removal of a proton from *p*–OH) in concert with general acid catalysis (proton transfer from the solvent to the phosphate leaving group and/or the excited carbonyl), or a water-molecule chain carrying a proton from the acidic *p*-OH site to the leaving phosphate group. Phillips[7] and Wan[6] have suggested such mechanisms, and Phillips has shown that protonation of the leaving phosphate is important.[7e] A sequential reaction, deprotonation of *p*-OH followed by general acid catalysis on phosphate expulsion from the anion, can be excluded, because the elimination reaction is faster than the deprotonation of T_1(**1a**).[5,7]

In conclusion, the sequence of intermediates occurring in the photo-Favorskii rearrangement of *p*-hydroxyphenacyl derivatives **1** in aqueous solutions is now established (Scheme 1). The proton inventory data indicate that diethyl phosphate release from T_1(**1a**) proceeds in concert with deprotonation and requires the assistance of at least two water molecules.[7c] The primary biradical ^{3}**3** has hitherto escaped detection by optical spectroscopy, because its absorption is so weak and its lifetime is similar to or, at low water concentrations, shorter than that of its strongly absorbing precursor, T_1(**1**). The formation of ^{3}**3** from T_1(**1**) amounts to release of the substrates HX; the lifetimes of T_1(**1**) thus define the release rate. Formation of *p*-hydroxybenzyl alcohol (**6**) has not been previously reported. It is a signature of the elusive spirodione **4**, the lifetime of which must be shorter than its rate of formation under the reaction conditions. Nevertheless, the spirodione **4** must be a real intermediate, because it is trapped at high water concentrations, yielding *p*-hydroxyphenylacetic acid (**2**).

Acknowledgments. This work was supported by the Swiss National Science Foundation (J.W.), and by NIH grants P50 GM069663 and R01 GM72910 (R.S.G.).

Supporting Information Available: Step–scan FTIR spectra, NMR of **5**, details of the calculations.

REFERENCES

1 Park, C.-H.; Givens, R. S. *J. Am. Chem. Soc*. **1997**, *119*, 2453–2463.

2 Sul, J-Y.; Orosz, G.; Givens, R. S.; Haydon, P. G. *Neuron Glia Biology* **2004**, *1*, 3–10.

3 Zou, K.; Cheley, S.; Givens, R. S.; Bayley, H. *J. Amer. Chem. Soc*. **2002**, *124*, 8220–8229. Zou, K.; Miller, T. W.; Givens, R. S.; Bayley, H. *Angew. Chem., Int. Ed*. **2001**, *40*, 3049–3051. Geibel, S.; Barth, A.; Amslinger, S.; Jung, A. H.; Burzik, C.; Clarke, R. J.; Givens, R.; Fendler, K. *Biophys. J*. **2000**, *79*, 1346–1357. Arabaci, G.; Gou.; X.-C.; Beebe, K. D.; Coggeshall, K. M.; Pei, D. *J. Am. Chem. Soc*. **1999**, *121*, 5085–5086. Du, X.; Frei, H.; Kim, S. H. *J. Biol. Chem*. **2000**, *275*, 8492–8500.

4 a. Givens, R. S.; Goeldner, M.; Eds. *Dynamic Studies in Biology*, Wiley-VCH, Weinheim, 2005. b. Givens, R. S.; Weber, J. F. W.; Jung, A. H.; Park, C-H. *Methods in Enzymology* **1998**, *291*(Caged Compounds), 1–29.

5 Conrad II, P. G.; Givens, R. S.; Hellrung, B.; Rajesh, C. S., Ramseier, M.; Wirz, J. *J. Am. Chem. Soc*. **2000**, *122*, 9346–9347.

6 Zhang, K.; Corrie, J. E. T.; Munasinghe, V. R. N.; Wan, P. *J. Am. Chem. Soc*. (**1999**), *121*, 5625-5632.

7 a. Ma, C.; Zuo, P.; Kwok, W. M.; Chan, W. S.; Kan, J. T. Z.; Toy, P. H.; Phillips, D. L. *J. Org. Chem*. **2004**, *69*, 6641-6657. b. Ma. C.; Kwok, W. M.; Chan, W. S.; Zuo, P.; Kan, J. T. W.; Toy, P. H.; Phillips, D. L. *J. Am. Chem. Soc*. **2005**, *127*, 1463–1427. c. Ma, C.; Kwok, W. M.; Chan, W. S.; Du, Y.; Kan, J. T. W.; Phillips, D. L. *J. Am. Chem. Soc*. **2006**, *128*, 2558–2570. d. Chan, W. S.; Kwok, W. M.; Phillips, D. L.; *J. Phys. Chem. A* **2005**, *109*, 3454–3469. e. Zuo, P.; Ma. C.; Kwok, W. M.; Chan, W.; Phillips, D. L. *J. Org. Chem*. **2005**, *70*, 8661–8675. f. Chen, X. B.; Ma, C.; Kwok, W. M.; Guan, X.; Du, Y.; Phillips, D. L. *J. Phys Chem. A* **2006**, 11*0*, 12406–12413.

8 Anderson, J. C.; Reese, C. B. *Tetrahedron Lett*., **1962**, *1*, 1–4.

9 Bonneau, R.; Wirz, J.; Zuberbühler, A. D. *Pure Appl. Chem*. **1997**, *69*, 979–992. Andraos, J.; Lathioor, E.C.; Leigh, W. J. *J. Chem. Soc. Perkin Trans. 2* **2000**, 365–373.

10 Müller, M. A.; Gaplovsky, M.; Wirz, J.; Woggon, W.-D. *Helv. Chim. Acta* **2006**, *89*, 2987–3001.

11 Radicals such as a phenoxy radical formed by hydrogen abstraction or a phenacyl radical formed by Norrish Type I cleavage of **1** can be excluded because of the short lifetime of intermediate M. Compounds **1** with poor leaving groups did, however, give some long-lived transient absorption at 330 nm that may be attributed to the formation of phenacyl radicals.

12 Radziszewski, J. G.; Gil, M.; Gorski, A.; Spanget-Larsen; J.; Waluk, J.; Mroz, B. J. *J. Chem. Phys*. **2001**, *115*, 9733–9738.

13 Gisin, M.; Wirz, J. *Helv. Chim. Acta* **1983**, *66*, 1556–1568.

14 Turro, N. J.; Hammond, W. B. *J. Am. Chem. Soc*. **1966**, *88*, 3672–3673.

15 Srivastava, S.; Young, E.; Toscano, J. P. *J. Am. Chem. Soc*. **1998**, *120*, 6173–6174.

16 The molar ratio of products **2**:**6** was 0.44 in 5% D_2O and decreased to 0.14 in 60% D_2O as determined by H-NMR.

17 Chiang, Y.; Kresge, A. J.; Zhu, Y. *J. Am. Chem. Soc*. **2002**, *124*, 6349–6356.

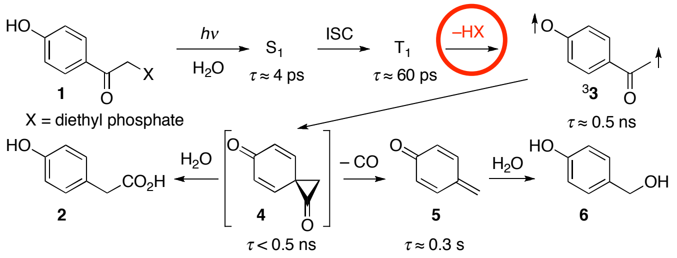
18 Lasne, M. C.; Ripoll, J. L.; Denis, J. M. *Tetrahedron Lett*. **1981**, *37*, 503–508.

19 a. Alvarez, F. J.; Schowen, R. L. In: *Isotopes in Organic Chemistry*, **1987**, *Vol. 7*, Buncel, E.; Lee, C. C.; Eds., p. 1–59. b. Kresge, A. J.; More O’Ferrall, R. A.; Powell, M. F. In: *Isotopes in Organic Chemistry*, **1987**, *Vol. 7*, Buncel, E.; Lee, C. C.; Eds., p. 177–273. c. Hegazi, M.; Mata-Segreda, J. F.; Schowen, R. L., *J. Org. Chem*. **1980**, *45*, 307–310.

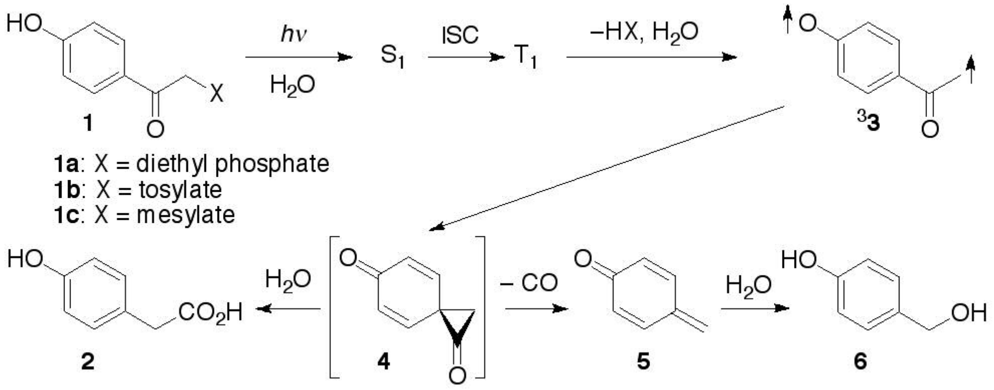
20 a. Chen, Y.; Gai, F.; Petrich, J. W. *J. Am. Chem. Soc*. (**1993**), 115, 10158-66. b. Gai, F.; Rich, R. L.; Chen, Y.; Petrich, J. W. *ACS Symposium Series* (**1994**), 568 Structure and Reactivity in Aqueous Solution, 182–95. c. Janz, J. M.; Farrens, D. L. *J. Biological Chem*. (**2004**), 279, 55886–55894. d. Kuehne, H.; Brudvig, G. W. *J. Phys. Chem*. B (**2002**), 106, 8189–8196.

21 Chang, T. K.; Chiang, Y.; Guo, H.-X.; Kresge, A. J.; Mathew, L.; Powell, M. F.; Wells, J. A. *J. Am. Chem. Soc*. **1996**, *118*, 8802–8807.

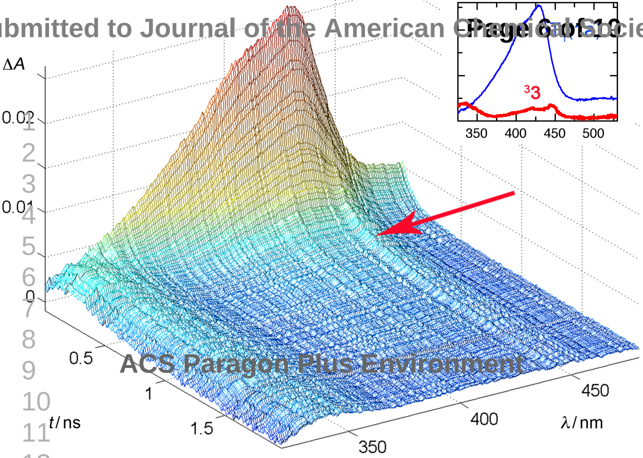
22 Quinn, D. M. In: Isotope Effects in Chemistry and Biology, Kohen, A.; Limbach, H.-H., Eds., Taylor and Francis, 2006, p 995-1018.



ABSTRACT FOR WEB PUBLICATION. The *p*-hydroxyphenacyl group **1** is an effective photoremovable protecting group, because it undergoes an unusual photo-Favorskii rearrangement concomitant with the fast release (<1 ns) of its substrates in aqueous solution. The reaction mechanism of the diethyl phosphate derivative **1a** was studied by picosecond pump–probe spectroscopy, nanosecond laser flash photolysis and step–scan FTIR techniques. The primary photoproduct is a triplet biradical, ^{3}**3**, with a lifetime of about 0.6 ns. The release of diethyl phosphate determines the lifetime of the triplet state T_1(**1a**), $\tau(T_1)$ = 60 ps in wholly aqueous solution. Formation of a new photoproduct, *p*-hydroxybenzyl alcohol (**6**), was observed at moderate water concentrations in acetonitrile. It is formed by CO elimination from the elusive spirodione intermediate (**4**), followed by hydration of the resulting *p*-quinone methide (**5**). Computational studies show that CO elimination from the spirodione is a very facile process.



Scheme 1. Mechanism of the photo-Favorskii rearrangement 1→2.
84x33mm (300 x 300 DPI)


ΔA
0.02
0.01
0
0.5
1
1.5
t / ns
350
400
450
λ / nm
350
400
450
500
³3

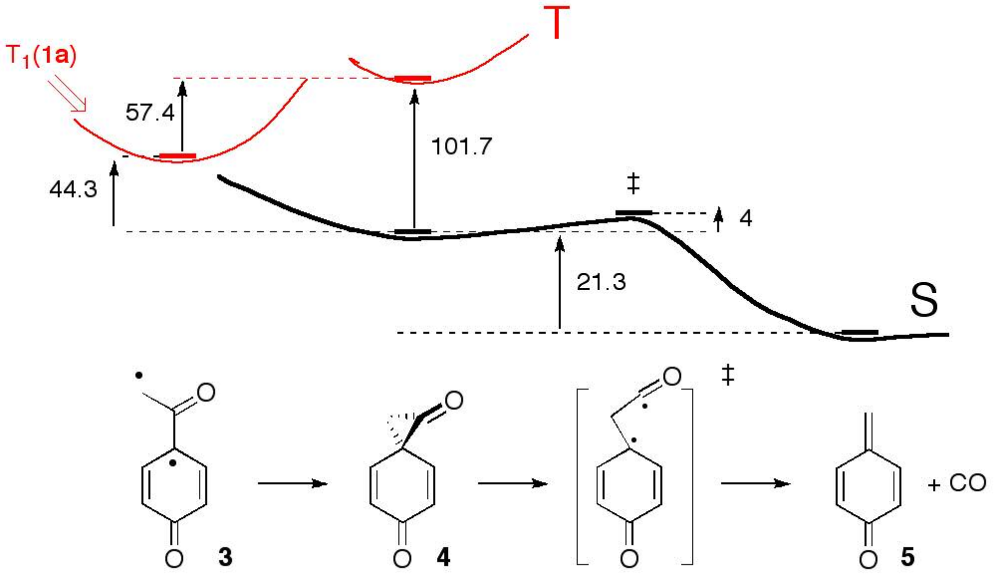
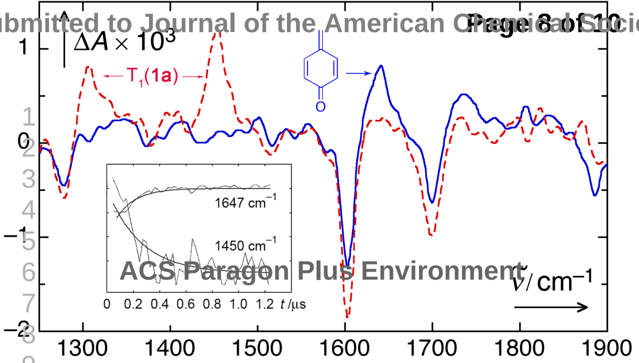
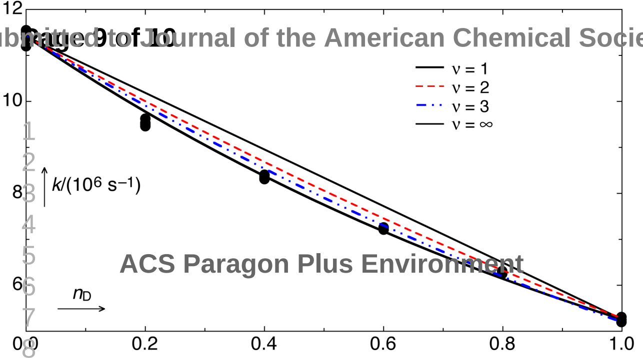
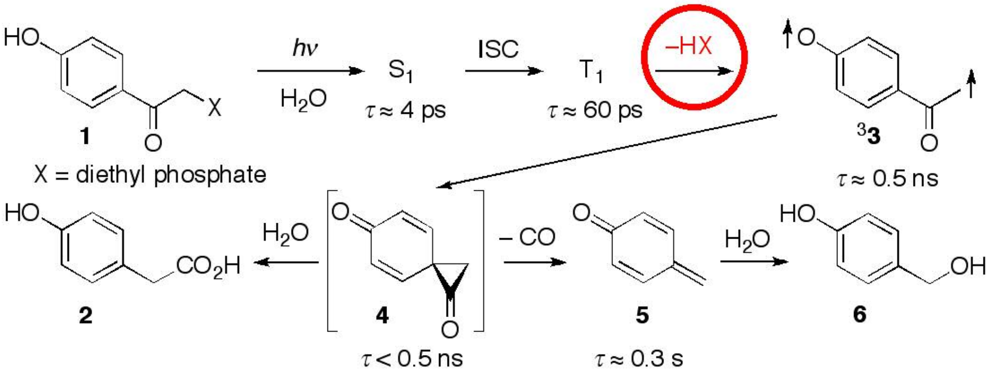


Figure 2. Ab initio calculations (MP2/6-31G*, PCM: acetonitrile). Solid lines (□) indicate stationary points. Energy differences in kcal mol□1.
85x50mm (300 x 300 DPI)


$\Delta A \times 10^3$
1
0
−1
−2
T_1(**1a**)
O
1647 cm^{-1}
1450 cm^{-1}
0
0.2
0.4
0.6
0.8
1.0
1.2
t/μs
$\tilde{\nu}$/ cm^{-1}
1300
1400
1500
1600
1700
1800
1900


12
10
8
6
0.0
0.2
0.4
0.6
0.8
1.0
$k/(10^6\ \mathrm{s}^{-1})$
n_D
ν = 1
ν = 2
ν = 3
ν = ∞



89x35mm (300 x 300 DPI)