

Photochemistry of 4-Pyrones in Water.
Formation of Dihydroxycyclopentenones and Furan Derivatives

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Irradiation of aqueous solutions of alkyl substituted 4-pyrones leads to the formation of dihydroxycyclopentenones. These primary products are also photolabile and in certain cases are photochemically converted to furan derivatives.

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The photodimerization of 2, 6-dimethyl-4-pyrone **1a** was first reported by Paterno in 1914 (1). Later, Yates and colleagues elucidated the structure of the dimeric product (2) and also observed that irradiation of **1a** in dilute aqueous solution also results in the formation of low yields of 4, 5-dimethyl-2-furaldehyde **3a**. Since that time the photochemistry of **1a** has been studied in various solvents and found to yield a variety of products including a ring contracted 4-hydroxycyclopentenone solvent adduct and 4, 5-dimethyl-2-pyrone upon irradiation in 2, 2, 2-trifluoroethanol (TFE) (4). Although the mechanistic origins of the latter products seem adequately rationalized, no satisfactory mechanism for furaldehyde formation has been established.

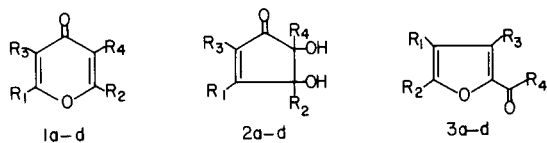
We now wish to report that furaldehyde **3a** does not appear to be a primary product in this photoreaction. Instead, irradiation of 2, 6-dimethyl-4-pyrone **1a** in dilute aqueous solution leads to the formation of dihydroxycyclopentenone **2a** which in turn is photochemically con-

verted to furaldehyde **3a**. Furthermore, we also report that photohydration leading to dihydroxycyclopentenones is general to a variety of other substituted 4-pyrones (5).

Irradiation (6) of a $1 \times 10^{-2} M$ aqueous solution of **1a** led to the detection of an unidentified dimeric product, 4, 5-dimethyl-2-furaldehyde **3a**, and to the isolation of a white, crystalline, non-gc-volatile product that was identified as 3, 4-dimethyl-4, 5-dihydroxycyclopent-2-enone in 41 percent yield. Similarly, irradiation of aqueous solutions of 4-pyrones **1b-1d** led to the isolation of dihydroxycyclopentenones **2b-2d** as the major or only primary products observed.

The structural assignments of **2a-2d** follow from their spectroscopic properties summarized in Table I. Addition of a water molecule is indicated by the mass spectrum of each compound which exhibits a parent ion 18 mass units larger than that of the starting 4-pyrone. Hydration is also supported by the strong OH stretching absorption in the infrared and by the deuterium oxide exchangeable signals in their nmr spectra. As expected for **2b-2d** both OH proton resonances appear as singlets whereas the C-4 and C-5 OH protons in **2a** appear as a singlet and a doublet, respectively, due to the latter's coupling with the proton at C-5. As demanded by the structure, upon addition of deuterium oxide, both OH proton resonances disappeared while the C-5 proton doublet collapsed to a singlet.

The spectroscopic data also confirm that hydration has been accompanied by ring contraction. Thus, the infrared



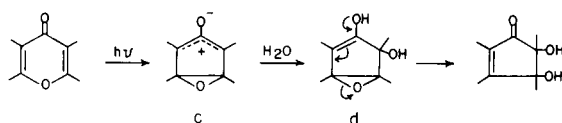
- a, $R_1 = R_2 = CH_3; R_3 = R_4 = H$
 b, $R_2 = R_4 = CH_3; R_1 = R_3 = H$
 c, $R_1 = R_2 = R_4 = CH_3; R_3 = H$
 d, $R_1 = R_2 = R_3 = R_4 = CH_3$

Table I
Spectroscopic Properties of Dihydroxycyclopentenones

Compound	M*	ν C=O	60 MHz NMR (δ in DMSO- d_6)					
			R ₁	R ₂	R ₃	R ₄	C ₄ and	C ₅ OH
2a	142	1700	1.97, 3H, d (1 Hz)	1.10, 3H, s	5.73, 1H, q (1 Hz)	3.87, 1H, d (6 Hz)	5.20, 1H, s	5.43, 1H, d (6 Hz)
2b	142	1710	7.13, 1H, d (6 Hz)	1.12, 3H, s	5.77, 1H, d (6 Hz)	1.03, 3H, s	5.02, 1H, s	5.03, 1H, s
2c	156	1710	1.97, 3H, d (1 Hz)	1.15, 3H, s	5.70, 1H, q (1 Hz)	1.07, 3H, s	4.97, 2H, s	
2d	170	1700	1.95, 3H, s	1.18, 3H, s	1.59, 3H, s	1.10, 3H, s	4.88, 1H, s	4.98, 1H, s

spectra exhibit C=C and C=O absorptions between 1600 and 1750 cm^{-1} as observed for other 4-hydroxycyclopentenone derivatives (7). In addition, the two one-proton doublets at 5.77 and 7.13 ppm, $J = 6$ Hz, in the nmr spectrum of **2b** are consistent with protons in the α and β position of this ring system (8). Furthermore, since **2a** and **2c** each show single α -vinyl proton absorptions coupled to a methyl group in the β -position, R-2 and R-4 in the original 4-pyrones have not interchanged during ring contraction. Finally, the nmr data for **2b** and **2c** reveal that water has added to the more highly substituted side of the unsymmetrically substituted 4-pyrones **1b** and **1c**.

Formation of these dihydroxycyclopentenones is mechanistically analogous to the formation of other 4-hydroxycyclopentenone solvent adducts (4, 9). In the



present case, the photochemically generated oxabicyclohexenyl zwitterion **c** is effectively trapped by addition of water to yield **d**. The observed products thus arise *via* subsequent thermal rearrangement of bicyclic enols of type **d** (10).

Of the 4-pyrones studied, only 2, 6-dimethyl-4-pyrone (**1a**) and 2, 3, 6-trimethyl-4-pyrone **1c** were observed to also yield furan derivatives upon irradiation in aqueous solution. Thus, in addition to the formation of furaldehyde **3a** from 4-pyrone **1a** (11), 4,5-dimethyl-2-acetylfuran **3c** was formed upon irradiation of trimethyl-4-pyrone **1c**. This latter furan derivative was isolated by preparative gc and identified by direct comparison of its spectroscopic and chromatographic properties with those of an authentic sample synthesized in this laboratory (12).

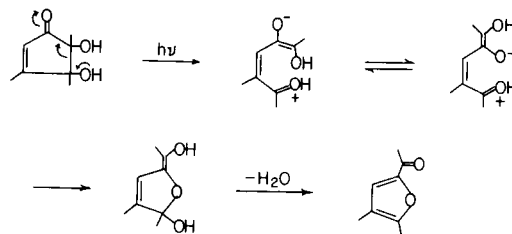
Both gc and hplc analyses (14) also revealed that furan derivatives **3a** and **3c** are also formed by direct irradiation of 1×10^{-2} M aqueous solutions of dihydroxycyclopentenones **2a** and **2c**, respectively. Quantitative gc, for example, showed that the yield of **3c** from **2c** reached a maximum of 25% and then slowly decreased upon continued irradiation without formation of any additional gc-volatile products. This decrease in concentration of **3c** upon prolonged irradiation is consistent with our observation that aqueous solutions of other 2-acetylfurans are also photolabile.

These results clearly show that furan derivatives are formed from dihydroxycyclopentenones and do not necessarily arise by direct photoisomerization of 4-pyrones or from dihydroxycyclopentenone precursors of type **d**. Although it is difficult to determine if any portion of furan derivatives **3a** or **3c** originate from these latter sources, several observations indicate that dihydroxycyclo-

pentenones **2a** or **2c** are their sole precursors.

First hplc analyses of aqueous solutions of 4-pyrones **1a** or **1c** as a function of irradiation time showed that **2a** and **2c** were clearly observable after conversion of 5% of either reactant 4-pyrone. Conversely, furan derivatives **3a** or **3c** could not be detected until after 22 or 15 percent of **1a** or **1c** had been consumed and substantial quantities of **2a** or **2c** were already present in the solution. Second, neither furan derivative **3a** nor **3c** could be detected by gc or hplc analyses upon irradiation of 4-pyrones **1a** or **1c** in either methanol or TFE solvent. If furans **3a** or **3c** were formed directly by photoisomerization of 4-pyrones **1a** or **1c**, their formation should be particularly enhanced in solvent such as TFE where minimal solvent trapping of photochemically generated intermediates occur (4, 9). Finally, although all of the 4-pyrones studied undergo photohydration and thus proceed *via* intermediates analogous to **c** and **d**, furan formation is only observed in the case of **1a** and **1c**. This further suggests that intermediate species such as **c** and **d**, common to all photohydration reactions, do not lead to furan derivatives.

Although the photophysical details of the conversion of dihydroxycyclopentenones are not known, the gross structural change can be rationalized by reverse aldol-type fission of the C-4 - C-5 bond, rotation, ring closure, and dehydration as shown below. Further studies of dihydroxy-



cyclopentenone photochemistry directed toward understanding the effect of the methyl substitution pattern on reactivity are in progress.

REFERENCES AND NOTES

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- (4) E. B. Keil and J. W. Pavlik, *J. Heterocyclic Chem.*, **13**, 1149 (1976).
- (5) Photohydration of 4-pyrones was previously reported by J. W. Pavlik and A. P. Spada, *Tetrahedron Letters.*, 4441, (1979) and J. A. Barltrop, A. C. Day, and C. J. Samuel, *J. Am. Chem. Soc.*, **101**, 7521 (1979).
- (6) All irradiations were carried out under nitrogen in a water-cooled quartz tube using an 8w 2537 Å low pressure Hg lamp.
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- (8) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden and Day, San Francisco, 1964, p. 54.

(9) J. W. Pavlik and L. T. Pauliukonis, *Tetrahedron Letters.*, 1939 (1976).

(10) Although direct evidence for the stereochemistry of **2a-2d** is lacking, it is expected that water would attack *anti* to the epoxide ring in **c** resulting in a *trans*-configuration at C-4 and C-5 as previously established for other solvent adducts (4).

(11) Furaldehyde **3a** was isolated by preparative gc. Its spectroscopic properties were essentially identical those previously reported in ref. 3: M^+ (124); ir (carbon tetrachloride): 2990, 2820, 1690, 1620, 1310, 1160, cm^{-1} ; 60-MHz nmr(carbon tetrachloride): δ 1.99 (s, 3H), 2.29 (s, 3H), 6.82 (s, 1H), 9.45 (s, 1H).

(12) 4,5-Dimethyl-2-acetylfuran was prepared by treating 2,3-dimethylfuran (13) with acetic anhydride in the presence of phosphoric acid: M^+ (138); ir (carbon tetrachloride): 2930, 2875, 1675, 1500, 1295, 1195 cm^{-1} ; 60-MHz nmr (carbon tetrachloride): δ 1.88 (s, 3H), 2.18 (s, 3H), 2.22 (s, 3H), 6.71 (s, 1H).

(13) 2,3-Dimethylfuran was prepared by the lithium aluminum hydride

reduction of 2-methyl-3-chloromethylfuran according to the procedure given by E. Wenkert, A. A. Craveiro, and E. L. Sanchez, *Synth. Commun.*, **7**, 85 (1977). The latter compound was synthesized according to the procedure of H. E. Winberg, F. S. Fawcett, W. E. Mochel, and C. W. Theobald, *J. Am. Chem. Soc.*, **82**, 1428 (1960).

(14) Gc analyses were carried out on a 6' \times 1/8 in column packed with 2% carbowax 20M-TPA on 80/100 Chromasorb G. At 160°, the retention of **1c** relative to **1a** is 0.27. Under programed conditions [130° (16 minutes) 4° minute⁻¹ to 170° (4 minutes)] the retention of **3c** relative to **3a** is 0.29. Hplc analyses (15) were performed on C₁₈ reverse phase columns. On a Waters RCM-100 Radial Pak column using water/methanol (1:1), 1 ml minute⁻¹, the retentions of **1b** and **1c** relative to **1a** are 0.4 and 1.5. On an Altrex Ultrasphere-ODS column using water (68%)/acetonitrile (32%), 1 ml minute⁻¹, the retentions of **3b** and **3c** relative to **3a** are 0.5 and 2.4.

(15) We would like to thank the National Science Foundation for Grant CDP-8017459 for the purchase of the hplc instrumentation used in this study.