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Photochemistry of 4-Hydroxypyrylium Cations in Aqueous Sulfuric Acid

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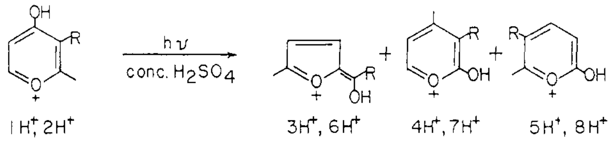
4-Hydroxypyrylium cations that are known to undergo phototransposition to 2-hydroxypyrylium cations in concentrated sulfuric acid were observed to undergo photo-ring contraction in 50% sulfuric acid. The initial products observed when the irradiations are carried out at 0 °C are 4,5-dihydroxycyclopent-2-enones that can be isolated. At higher temperatures these initial products undergo secondary acid catalyzed thermal reactions to yield substituted acetylfurans.

A variety of 4-hydroxypyrylium cations are known to undergo photoisomerization in concentrated H_2SO_4 to yield 2-hydroxypyrylium cations.[1] In the case of 2,3-dialkyl-4-hydroxypyrylium cations, however, this phototransposition reaction was accompanied by a photo-ring contraction. Thus, we have previously reported that irradiation of 2,3-dimethyl- or 2-methyl-3-ethyl-4-hydroxypyrylium cation (**1H$^+$** or **2H$^+$**) in concentrated H_2SO_4 leads to the formation of furyl cations **3H$^+$** or **6H$^+$** in addition to **4H$^+$** and **5H$^+$** or **7H$^+$** and **8H$^+$** as the principal 2-hydroxypyrylium cations.[1e]

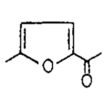


(**1**, **3**, **4**, **5**, R = CH_3; **2**, **6**, **7**, **8**, R = CH_2CH_3)

Although the phototransposition reaction of 4-hydroxypyrylium cations has received considerable attention, less information has been reported concerning the generality and mechanistic details of the photo-ring contraction reaction. Accordingly, in this paper we report the results of our studies concerning the effects of acid concentration and temperature on this photoreaction.

Results and Discussion

Table I gives the relative yields of **3**, **4**, and **5** after irradiation of 2,3-dimethyl-4-hydroxypyrylium cation (**1H$^+$**) in various concentrations of H_2SO_4 followed by neutralization.[2] Although no new products were observed upon changing the acid concentrate, the data do show that whereas 3,4-dimethyl-2-pyrone (**4**) and 5,6-dimethyl-2-pyrone (**5**) constitute over 97% of the product mixture after irradiation in 100% H_2SO_4, 5-methyl-2-acetylfuran (**3**) is essentially the sole product observed when the irradiation is carried out in 50% H_2SO_4.



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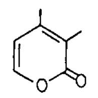

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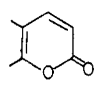

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Table I. Production Distribution as a Function of Acid Concentration

% H_2SO_4	% 3	% 4	% 5
100	3	51	46
93	59	18	23
75	96	2	2
50	~100	*a*	0

[a] Trace.

In order to investigate the general dependence of acid concentration on this photo-ring contraction reaction, other 4-hydroxypyrylium cations, known to undergo photoisomerization to 2-hydroxypyrylium cations in concentrated H_2SO_4,[1h] were irradiated in more dilute acid solution.

The photolysis of 2,3,6-trimethyl-4-hydroxypyrylium cation (**9H$^+$**) in 50% H_2SO_4 at room temperature was monitored by NMR spectroscopy. The spectra revealed that irradiation was accompanied by the disappearance of the signals at δ 2.6 and 2.1 due to the methyl groups of **9H$^+$** and the formation of a photochemically and thermally stable product with methyl groups absorbing at δ 2.42, 2.18, and 1.95. Examination by gas chromatography (GC) of an ether extract of this neutralized solution showed one major product and a much smaller quantity of a second product which was identified as 4,5,6-trimethyl-2-pyrone (**10**), the conjugate base of the phototransposition product, by direct comparison with an authentic sample of this compound.

The major product, which accounted for 94% of the product mixture, was isolated by preparative GC. The mass spectrum, which exhibited a parent ion at *m/e* 138, confirmed that the major product is isomeric with the reactant. In addition, the infrared spectrum, which possessed a carbonyl stretching absorption at 1673 cm^{-1} and C–O stretching doublets at 1290 and 1282 cm^{-1} and 918 and 907 cm^{-1} (very similar to the infrared spectra of 2-acetylfuran and 5-methyl-2-acetylfuran[3,4]), and the UV-absorption maximum at 293 nm provide excellent evidence that the isolated product is a dimethyl-2-acetylfuran. Furthermore, the NMR spectrum exhibits three three-proton signals at δ 1.92, 2.23, and 2.31 and a one-proton signal at δ 6.95 that is weakly coupled ($J < 1$ Hz) to the three-proton resonance at δ 1.92. This indicates that the ring proton absorbing at δ 6.95 is adjacent to only one of the two ring methyl groups and suggests that the isolated product is either 4,5-dimethyl- or 3,4-dimethyl-2-acetylfuran. A distinction was unambiguously made by direct comparison of the isolated product with an authentic

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[1] (a) Pavlik, J. W.; Clennan, E. L. *J. Am. Chem. Soc.* **1973**, *95*, 1697. (b) Pavlik, J. W.; Kwong, J. *Ibid.* **1973**, *95*, 7914. (c) Barltrop, J. A.; Day, A. C. *J. Chem. Soc., Chem. Commun.* **1975**, 177. (d) Barltrop, J. a.; Carder, R.; Day, A. C.; Harding, J. R.; Samuel, C. *Ibid.* **1975**, 729. (e) Pavlik, J. W.; Bolin, D. R.; Bradford, K. C.; Anderson, W. G. *J. Am. Chem. Soc.* **1977**, *99*, 2816. (f) Pavlik, J. W.; Dunn, R. M. *Tetrahedron Lett.* **1978**, 5071. (g) Barltrop, J. A.; Barrett, J. C.; Carder, R. W.; Day, A. C.; Harding, J. R.; Long, W. E.; Samuel, C. J. *J. Am. Chem. Soc.* **1979**, *101*, 7510. (h) Pavlik, J. W.; Patten, A. D.; Bolin, D. R.; Bradford, K. C.; Clennan, E. L. *J. Org. Chem.* **1984**, *49*, 4523.

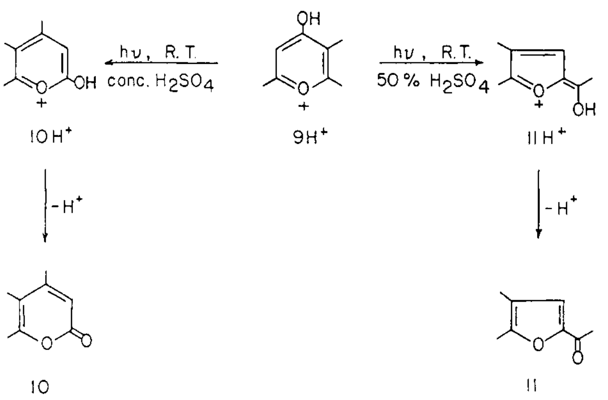
[2] Pavlik, J. W.; Spada, A. P. *Tetrahedron Lett.* **1979**, 4441.

[3] 2-Acetylfuran and 5-methyl-2-acetylfuran both exhibit carbonyl absorptions at 1675 cm^{-1}.

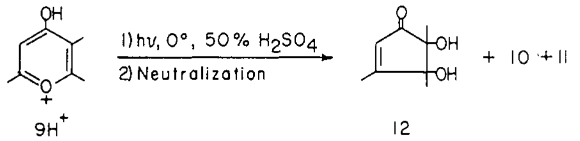
[4] Cross, A. H. J.; Stevens, S. G. E.; Watts, T. H. E. *J. Appl. Chem.* **1957**, *7*, 562.

0022-3263/85/1950-3046$01.50/0

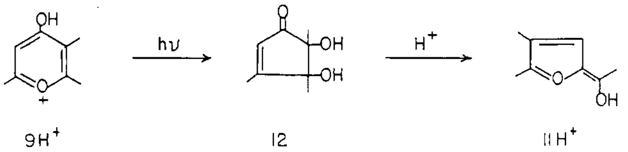
sample of 4,5-dimethyl-2-acetylfuran (11), prepared by acetylation of 2,3-dimethylfuran. These results confirm that whereas irradiation of **9H**$^+$ in concentrated H_2SO_4 leads exclusively to the phototransposition product **10H**$^+$,[1h] photo-ring contraction leading to **11H**$^+$ is the major pathway upon irradiation in 50% H_2SO_4 at room temperature.



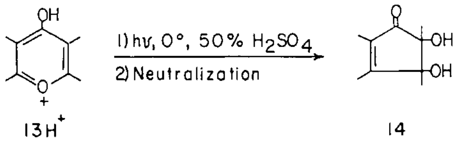
When **9H**$^+$ was irradiated in 50% H_2SO_4 at 0 °C, however, NMR spectra revealed the formation of a different product. Thus, after 4 h of irradiation, although there was a complete absence of signals at δ 2.42, 2.18, and 1.95 due to **11H**$^+$, a new set of signals was clearly visible at δ 2.15, 1.35, and 1.30. If this solution was allowed to warm to room temperature, the new signals decreased in intensity with concomitant formation of signals at δ 2.42, 2.18, and 1.95 due to **11H**$^+$. If instead of warming, the solution containing the photochemically generated transient species was neutralized immediately after irradiation at 0 °C, GC examination of an ether extract showed only small quantities of 2-pyrone **10** and acetylfuran **11**. From the aqueous layer, however, a white crystalline compound was isolated in greater than 60% yield, which was identified as 4,5-dihydroxy-3,4,5-trimethylcyclopent-2-en-1-one (**12**). The structural assignment follows from the spectroscopic properties. Addition of a water molecule is indicated by the mass spectrum of the compound, which exhibits a parent ion at *m/e* 156, 18 mass units higher than that of the 4-pyrone reactant, and a prominent signal at *m/e* 138 due to loss of water. Hydration and ring contraction are also supported by the strong OH stretching absorption in the infrared spectrum and by the D_2O-exchangeable two-proton singlet at δ 4.97 in the NMR spectrum, which confirms the presence of two hydroxyl groups located at tertiary ring carbons. The NMR spectrum also shows a one-proton signal at δ 5.91 which is weakly coupled to a three-proton signal at δ 2.17 consistent with an α-proton coupled to the methyl group in the β-position of an α,β-unsaturated system. As further demanded by the structure, two methyl singlets were also observed in the NMR spectrum at δ 1.31 and 1.21, reflecting their similar environments in which they are bonded to saturated carbon atoms. Finally, ring contraction is also supported by the infrared spectrum which exhibits C=C and C=O absorptions at 1620 and 1710 cm^{-1} as observed for other 4-hydroxycyclopentenone derivatives.[5,6]



In 50% H_2SO_4, the NMR spectrum of purified **12** was identical with the spectrum of the major product formed upon irradiation of **9H**$^+$ at 0 °C, confirming that gross structural changes did not occur during neutralization and isolation of this product. Furthermore, after the solution of **12** in 50% H_2SO_4 was allowed to stand overnight at room temperature, NMR spectral analysis of the acid solution and GC analysis of an ether extract of the neutralized solution showed essentially quantitative conversion of **12** to 4,5-dimethyl-2-acetylfuran (**11**). This indicates that 4-hydroxypyrylium cation **9H**$^+$ is photochemically converted into dihydroxycyclopentenone **12**, which undergoes acid-catalyzed isomerization to furyl cation **11H**$^+$. These data also show that 4,5,6-trimethyl-2-pyrone (**10**), a minor product formed upon direct photolysis of **9H**$^+$, does not arise from **12** but originates from **9H**$^+$ via a second pathway.



Tetramethyl-4-hydroxypyrylium cation (**13H**$^+$) behaved similarly upon irradiation in 50% H_2SO_4 at 0 °C. Thus, NMR spectral analysis showed that signals at δ 2.70 and 2.23 due to **13H**$^+$ decrease during irradiation with formation of new signals at δ 2.15, 1.78, 1.43, and 1.40. Neutralization of this solution led to the isolation of 2,3,4,5-tetramethyl-4,5-dihydroxycyclopent-2-enone (**14**), which exhibited spectral properties very similar to those observed for trimethyl diol **12** (see Experimental Section).



If the partially irradiated solution of **13H**$^+$ was allowed to warm, however, monitoring of it by NMR spectroscopy confirms the thermal lability of **14** and the formation of a new product with NMR signals at δ 5.59, 5.50, 2.18, 1.83, and 1.40. These signals are clearly not consistent with the formation of the trimethyl-2-acetylfuran analogous to **11**.

This product, isolated by preparative gas chromatography, exhibited a parent ion in the mass spectrum at *m/e* 152, corresponding to the dehydration of **14**. The infrared spectrum, however, revealed a carbonyl absorption at 1712 cm^{-1} and a C=C absorption at 1640 cm^{-1}, more characteristic of the cyclopentenone ring structure of **14** than an acetylfuran ring system, and an additional C=C absorption at 1610 cm^{-1}, suggestive of a terminal alkene. It thus appears that acid-catalyzed loss of water from **14** has not been accompanied by rearrangement of the ring system as it was in the case of **12**. Indeed, in addition to showing the presence of only three methyl signals at δ 1.15, 1.71, and 2.01, the NMR spectrum of the product in anhydrous Me_2SO-d_6 revealed two one-proton signals at δ 5.25 and 5.29, characteristic of a terminal methylene unit formed from one of the original methyl groups, and also a 1-proton, D_2O-exchangeable resonance at δ 5.20, confirming that **14** has undergone dehydration and that the second oxygen of the isolated product is still present in the structure as a hydroxyl group.

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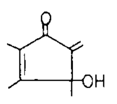
(5) Van Hooland, J.; DeClerco, P.; Vandewalle, M. *Tetrahedron Lett.* **1974**, 4343.

(6) Although direct evidence for the stereochemistry of **12** is lacking, the configuration at C-4 and C-5 is assumed to be trans by analogy with the structurally similar 4-hydroxy-5-alkoxycyclopentenones.[7]

(7) Pavlik, J. W.; Pauliukonis, L. T. *Tetrahedron Lett.* **1976**, 1939.

Taken together, these spectral properties are consistent with either structures **15** or **16**, formed by acid-catalyzed dehydration of **14**. Although the latter structure **16** is more likely on mechanistic considerations, the spectral properties do not allow unambiguous distinction between the two possibilities. This distinction was made possible, however, by analysis of the corresponding product isolated from irradiation of 2,6-di(methyl-d_3)-3,5-dimethyl-4-hydroxypyrylium cation (**14H$^+$-d_6**) in 50% H_2SO_4. In this case, NMR spectral analysis of the isolated product revealed the presence of signals at δ 1.15 and 1.71, for the methyl groups located α to the carbon function, the absence of the β-methyl signal at δ 2.01, and the methylene unit absorptions at δ 5.25 and 5.29, confirming that the latter group is located at C-4 as in **16-d_5**.



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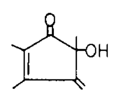
or



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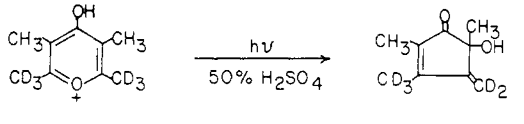
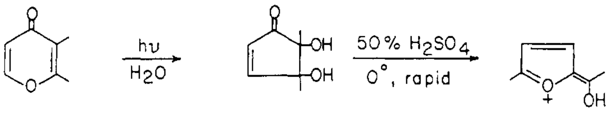


14 H$^+$-d$_6$ 16-d$_5$

When purified tetramethyl diol **14** was allowed to react in 50% H_2SO_4 at room temperature, spectroscopic and chromatographic analysis of the neutralized solution confirmed the formation of methylenecyclopentenone **16** but also revealed that tetramethyl-2-pyrone (**17**) is a minor product. Thus, GC analysis showed that **16** and **17** are formed from **14** in an 8:1 ratio.

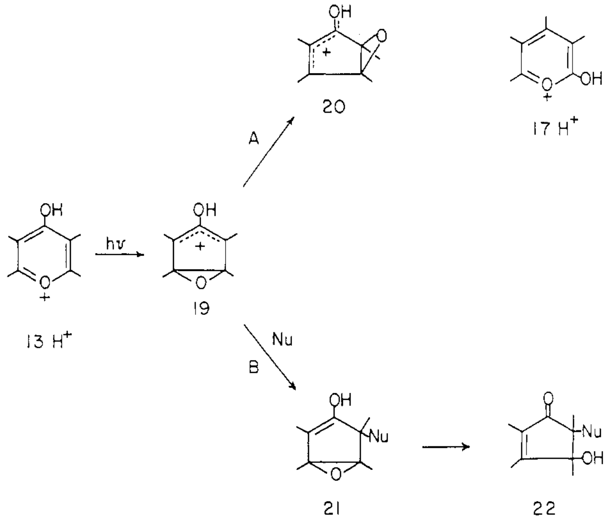
The intermediacy of dihydroxycyclopentenones **12** and **14** in the photo-ring contraction reactions of tri- and tetramethyl-4-hydroxypyrylium cations **9H$^+$** and **13H$^+$** suggests that an analogous intermediate is present in the conversion of 2,3-dimethyl-4-hydroxypyrylium cation (**1H$^+$**) into 5-methyl-2-acetylfuran (**3**). Although no such intermediate was detected by NMR spectroscopy, even when the irradiation was carried out at 0 °C, the anticipated diol **18** was formed when 2,3-dimethyl-4-pyrone (**1**) was irradiated in neutral aqueous solution.[8] Furthermore, **18** was rapidly converted into **3H$^+$** when dissolved in 50% H_2SO_4 at 0 °C. This observation lends credibility to the suggestion that dihydroxycyclopentenones are general intermediates in the photo-ring contraction reactions of 4-hydroxypyrylium cations.



1 18 3H$^+$

The change from photo-ring contraction to phototransposition upon increasing the acid concentration might indicate a change in the extent of 4-pyrone protonation and, hence, different photochemically active species at different acid concentrations. Several facts, however, indicate that this is not the case. First, the proton chemical shifts of all 4-pyrones studied were constant over the range of H_2SO_4 concentrations studied. This indicates that there is no significant change in the charge distribution and, hence, in the degree of protonation. Furthermore, the measured pK_{BH^+} for 2,6-dimethyl-4-pyrone is −0.28, indicating that 4-pyrones in general are completely protonated in 50% H_2SO_4.[9]

Scheme I



Both photo-ring contraction and phototransposition can be explained in terms of an intermediate 4-hydroxyoxabicyclohexenyl cation photochemically generated by π,π^*-excitation of the 4-hydroxypyrylium cation reactant. This species would be expected to undergo rapid inter- or intramolecular nucleophilic attack. At high H_2SO_4 concentrations, i.e., in the absence of high concentrations of a suitable external nucleophile, it is reasonable that intermolecular attack (path A in Scheme I using tetramethyl-4-hydroxypyrylium cation (**13H$^+$**) as an example) of the epoxide oxygen on the oxyallyl system resulting in migration of the epoxide ring and formation of the more stable 3-hydroxyoxabicyclohexenyl cation **20** would take place. This latter cation is the conjugate acid of an epoxycyclopentenone. Such compounds are known to undergo acid-catalyzed rearrangement to 2-pyrones via a second epoxide ring migration.[10,11]

Alternatively, the rate of intermolecular nucleophilic attack on the oxyallyl system to yield **21** (path B in Scheme I) would be greatly increased as the nucleophilicity of the medium is increased by decreasing the acid concentration. Subsequent rapid epoxide ring opening and proton transfer would lead to cyclopenteneone derivative **22**.

On the basis of the structures of the isolated diols and their increased yield with increased concentration of added water, it appears that water is trapping the photochemically generated oxabicyclohexenyl cation **19** to give **21** (Nu = OH), which leads directly to diol **22** (Nu = OH), i.e., **14**. Alternatively, considering the activities of water in aqueous H_2SO_4[12] and the increase in the concentration of $^-OSO_3H$ upon addition of water to pure H_2SO_4,[13] it is also possible that the oxabicyclohexenyl cation **19** is trapped by this anion to yield a cyclopentenone sulfate ester **21** (Nu = OSO_3H) that is converted into the observed diol **14** by hydrolysis.

Barltrop, Day, and colleagues have observed such a sulfate ester **24** upon photolysis of 3,5-dimethyl-4-

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[8] Pavlik, J. W.; Snead, T. E.; Tata, J. R. *J. Heterocycl. Chem.* **1981**, *18*, 1481.

[9] Rordam, H. N. K. *J. Am. Chem. Soc.* **1915**, *37*, 557.

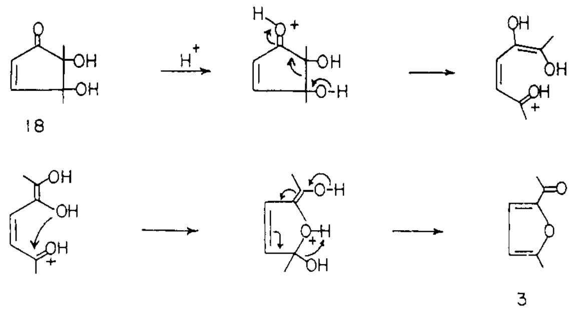
[10] Pütter, R.; Dilthey, W. *J. Prakt. Chem.* **1937**, *119*, 183; **1938**, *150*, 40.

[11] Ullman, E. F. *J. Am. Chem. Soc.* **1963**, *85*, 3529.

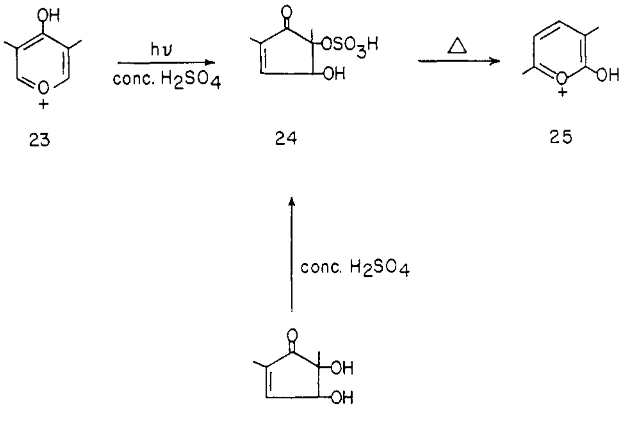
[12] Giauque, W. F.; Hornung, E. W.; Kunzler, J. E.; Rubin, T. R. *J. Am. Chem. Soc.* **1960**, *82*, 62.

[13] Yound, T. F.; Maranville, L. F.; Smith, H. M. "The Structure of Electrolyte Solutions"; Hamer, W. J., Ed.; Wiley: New York, 1959.

Scheme II



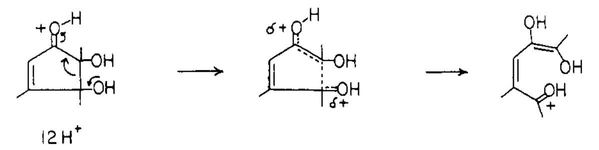
hydroxypyrylium cation (**23**) in concentrated H_2SO_4.[14] We have observed that a spectroscopically identical species is formed when 2,5-dimethyl-4,5-dihydroxycyclopentenone (**26**) is dissolved in concentrated H_2SO_4.[15] Furthermore, regardless of its origin, this species undergoes thermal conversion to 3,6-dimethyl-2-hydroxypyrylium cation (**25**).

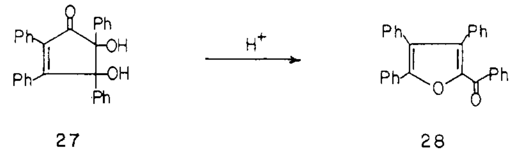


The NMR spectrum of the species formed in 50% H_2SO_4 either photochemically from 3,5-dimethyl-4-hydroxypyrylium cation (**23**) or thermally from dimethyldihydroxycyclopentenone **26** is similar to the spectrum of **24**, but the signals are shifted upfield. For example, the C-2 and C-5 methyl groups in the sulfate ester **24** absorb at approximately δ 2.0 and 1.8, respectively, in either concentrated H_2SO_4 or neutral solvent.[14] Conversely, the species formed in 50% H_2SO_4 has methyl signals at δ 1.7 and 1.2, very similar to the positions of the methyl absorptions of diol **26** in neutral solvent. Further, in 50% H_2SO_4 the species in solution is thermally stable. Accordingly, since the NMR spectra shifts are not due to solvent acidity, it appears that the species formed in 50% H_2SO_4 is different from that formed in concentrated H_2SO_4. We suggest that in 50% H_2SO_4 the species is the diol rather than the sulfate ester.

Both the reactivity and fate of the dihydroxycyclopentenones are dependent on the extent of substitution. In 50% H_2SO_4, dimethyl diol **18** undergoes rapid conversion into 5-methyl-2-acetylfuran (**3**) even at 0 °C. Presumably this conversion involves protonation of the carbonyl oxygen followed by reverse aldol ring opening, bond rotation, ring closure, and loss of H_2O as shown in Scheme II. This reaction is similar to the acid-catalyzed conversion of 4,5-dihydroxy-2,3,4,5-tetraphenylcyclopentenone (**27**) into 2,4,5-triphenyl-2-benzoylfuran (**28**) observed by Yates and Stout.[17]

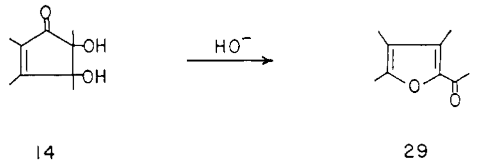
Scheme III

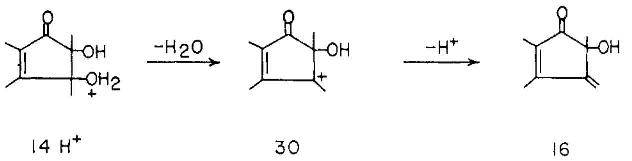




Although trimethyl diol **12** undergoes an analogous reaction in 50% H_2SO_4, the reaction is far slower at room temperature and does not occur at 0 °C. This reduced reactivity is reasonable since methyl substitution at C-3 would be expected to stabilize the protonated reactant **12H**$^+$ relative to the transition state for the reverse aldol ring opening and results in a lower reaction rate (Scheme III).

Additional methyl substitution stabilizes the carbonyl protonated species even further to the extent that tetramethyl diol **14** does not react via the reverse aldol pathway. Thus, whereas we have observed the clean conversion of **14** into trimethylacetylfuran **29** under conditions of base catalysis, in 50% H_2SO_4 methyl substitution at C-2 favors formation of allylic cation **30**, the precursor of the methylene cyclopentenone derivative **16**. In the absence of methyl substitution at C-2, this pathway is not observed due to the destabilizing effect of the carbonyl group α to the allyl system.





Experimental Section

General Procedures. Nuclear magnetic resonance spectra were recorded at 60 MHz with a Hitachi-Perkin-Elmer (PE) R-24B spectrometer. In neutral solution, chemical shifts were measured relative to Me_4Si, whereas in acid solution the chemical shifts were measured with methylene chloride (δ 5.30) as a secondary standard. Infrared spectra were recorded on a PE-397 spectrometer. Gas chromatography was performed on a PE-3920 FID instrument equipped with 6 ft or 10 ft × $^1/_8$ in. (analytical) and 6 ft × $^1/_4$ in. (preparative) columns packed with 2% Carbowax 20M-TPA on Chromosorb G. Mass spectra were recorded on a Du Pont 21-491 spectrometer. Elemental analyses were determined by MicAnal, Tucson, AZ.

Preparation of 4-Hydroxypyrylium Cations. All 4-hydroxypyrylium cations were prepared by dissolving the corresponding 4-pyrone in H_2SO_4 of the desired concentration. Aqueous sulfuric acid solutions were prepared by dilution of 100% H_2SO_4 with distilled water. For analytical reactions, 20 mg of the 4-pyrone was dissolved in 0.35 mL of acid, while for preparative scale irradiations approximately 240 mg of the 4-pyrone was

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[14] Barltrop, J. A.; Day, A. C.; Samuel, C. J. *J. Chem. Soc., Chem. Commun.* **1976**, 823.

[15] Dihydroxycyclopentenone **26** was prepared by irradiation of 3,5-dimethyl-4-pyrone in aqueous solution.[16]

[16] Barltrop, J. A.; Day, A. C.; Samuel, C. J. *J. Am. Chem. Soc.* **1979**, *101*, 7521.

[17] Yates, P.; Stout, G. H. *J. Am. Chem. Soc.* **1954**, *76*, 1954.

dissolved in 8.0 mL of acid. The preparation and spectral properties of the 4-pyrones used in this study have been previously described.[1h]

Irradiation and Analyses Procedures. Acid solutions were placed in a quartz tube that was suspended in a quartz Dewar flask and irradiated with six 8-W low-pressure Hg lamps arranged in a circular array of diameter 1.5 in. around the Dewar flask. The samples were cooled by passing a stream of dry N_2 through a heat exchanger coil immersed in a dry ice–acetone bath and through the quartz Dewar flask holding the sample. The temperature of the sample was monitored with a potentiometer and a glass-coated thermocouple immersed in the sample solution. NMR spectra were recorded at ambient temperature immediately after irradiation. Irradiated mixtures were neutralized by dropwise addition to a rapidly stirred aqueous suspension of sodium bicarbonate and extracted with ether.

2,3-Dimethyl-4-hydroxypyrylium Cation (1H$^+$). After irradiation in 100%, 93%, 75%, or 50% H_2SO_4 at room temperature, the acid solutions were neutralized and the ether extracts analyzed by GC on the 10 ft × $^1/_8$ in. column. At 140 °C, the retentions of 5-methyl-2-acetylfuran (**3**), 3,4-dimethyl-2-pyrone (**4**), and 5,6-dimethyl-2-pyrone (**5**) relative to 2,3-dimethyl-4-pyrone (**1**) are 0.23, 0.94, and 1.27, respectively. Products were identified as previously discussed.[1e,h]

2,3,6-Trimethyl-4-hydroxypyrylium Cation (9H$^+$). (a) Irradiation at Room Temperature. After irradiation in 50% H_2SO_4 at room temperature, the acid solution was neutralized and the ether extract analyzed by GC on the 6 ft × $^1/_8$ in. column. At 150 °C, the retentions of 4,5-dimethyl-2-acetylfuran (**11**) and 4,5,6-trimethyl-2-pyrone (**10**) relative to 2,3,6-trimethyl-4-pyrone (**9**) are 0.32 and 2.23, respectively.

Products **10** and **11** were collected by preparative GC. **10** was identified by comparison of its chromatographic and spectroscopic properties with those of an authentic sample of 4,5,6-trimethyl-2-pyrone that was previously synthesized in this laboratory.[1h]

Product **11** exhibited the folowing spectroscopic properties: IR (CCl_4) 2930, 2875, 1673, 1500, 1290, 1282, 1195, 918, 907 cm^{-1}; NMR (CCl_4) δ 1.92 (br s, 3 H), 2.23 (s, 3 H), 2.31 (s, 3 H), 6.95 (br s, 1 H); mass spectrum, *m/e* (relative intensity) 138 (65), 128 (12), 124 (24), 123 (100), 95 (16), 67 (41), 66 (15), 65 (16), 63 (12), 52 (19), 43 (47). Anal. Calcd for $C_8H_{10}O_2$: C, 69.55; H, 7.30. Found: C, 69, 37; H, 7.01. These properties were identical with those of 4,5-dimethyl-2-acetylfuran [bp 90–92 °C (18 torr) (Kugelrohr)] prepared by acetylation of 2,3-dimethylfuran[18,19] according to the method previously described for the acetylation of 2-methylfuran.[20]

(b) Irradiation at 0 °C. After irradiation (0.240 g, 1.74 mmol of **9**) in 8.0 mL of 50% H_2SO_4 at 0 °C, the acid solution was immediately neutralized. GC analysis of the ether extract showed only small quantities of **10** and **11**. The aqueous layer was concentrated to dryness and the residual white solid extracted with absolute ethanol. The mixture was filtered to remove inorganic salts and the filtrate concentrated to leave a white solid that was recrystallized from ether to give 4,5-dihydroxy-3,4,5-trimethylcyclopentenone (**12**) as fine white needles [mp 139–140 °C; yield 0.171 g (1.10 mmol, 63%)]; IR (KBr) 3340 (br) 1706, 1624, 1181, 1126, 1064, 951, 696 cm^{-1}; NMR (Me_2SO-d_6) δ 1.07 (s, 3 H), 1.15 (s, 3 H), 1.97 (d, 3 H, J = 1 Hz), 5.70 (q, 1 H, J = 1 Hz), 4.97 (s, 2 H, D_2O exchangable); mass spectrum, *m/e* (relative intensity) 156 (6), 141 (10), 138 (29), 124 (16), 113 (20), 110 (10), 85 (12), 67 (13), 43 (100), 41 (22). Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.74. Found: C, 61.23; H, 7.66.

2,3,5,6-Tetramethyl-4-hydroxypyrylium Cation (13H$^+$). (a) Irradiation at Room Temperature. After irradiation in 50% H_2SO_4 at room temperature, the acid solution was neutralized and the ether extract analyzed by GC on the 6 ft × $^1/_8$ in. column. At 165 °C, the retentions of 2,3,5-trimethyl-4-methylene-5-hydroxycyclopentenone (**16**) and 3,4,5,6-tetramethyl-2-pyrone (**17**) relative to 2,3,5,6-tetramethyl-4-pyrone (**13**) are 1.12 and 1.77, respectively.

Products **16** and **17** were collected by preparative GC. **17** was identified by comparison of its chromatographic and spectroscopic properties with those of an authentic sample of 3,4,5,6-tetramethyl-2-pyrone that was previously synthesized in this laboratory.[1h]

Product **16** exhibited the following spectroscopic properties: IR (CCl_4) 3390 (br), 1705, 1635, 1605, 1405, 1195, 1120, 965, 955 cm^{-1}; NMR Me_2SO-d_6) δ 1.15 (s, 3 H), 1.71 (s, 3 H), 2.01 (s, 3 H), 5.20 (m, 3 H, one of these protons is exchangeable with D_2O, leaving two one-proton singlets at δ 5.25 and 5.29); mass spectrum, *m/e* (relative intensity) 152 (8), 151 (36), 124 (16), 123 (13), 109 (54), 93 (10), 91 (11), 81 (52), 79 (20), 77 (13), 53 (23), 51 (17), 43 (100).

(b) Irradiation at 0 °C. After irradiation (0.240 g, 1.58 mmol of **13**) in 8.0 mL of 50% H_2SO_4 at 0 °C, the acid solution was immediately neutralized and the aqueous solution washed with ether. The aqueous layer was concentrated to dryness and the residual white solid extracted with absolute ethanol. The mixture was filtered to remove inorganic salts and the filtrate concentrated, leaving a white solid that was recrystallized from ether to give 2,3,4,5-tetramethyl-4,5-dihydroxycyclopentenone (**14**) as fine white needles [mp 142–143 °C; yield 0.185 g (1.09 mmol, 69%)]: IR (KBr) 3040 (br), 1712, 1640, 1610, 1452, 1332, 1225, 1150, 1070, 1020, 950 cm^{-1}; NMR (Me_2SO-d_6) δ 1.10 (s, 3 H), 1.18 (s, 3 H), 1.59 (s, 3 H), 1.95 (s, 3 H), 4.88 (s, 1 H, D_2O exchangeable), 4.98 (s, 1 H, D_2O exchangeable); mass spectrum, *m/e* (relative intensity) 170 (2.4), 155 (36), 153 (16), 152 (40), 137 (29), 127 (12), 109 (21), 43 (100). Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.54; H, 8.28.

Reaction of 4,5-Dihydroxy-3,4,5-trimethylcyclopentenone (12) in 50% H_2SO_4. Diol **12** (0.025 g, 0.160 mmol) was dissolved in 0.30 mL of 50% H_2SO_4, and the reaction was monitored by NMR spectroscopy. After 2 days at room temperature the signals at δ 1.44 (3 H), 1.48 (3 H), 2.28 (3 H), and 6.6 (1 H) due to **12** had disappeared and signals at δ 2.02 (3 H), 2.37 (3 H), 2.52 (3 H), and 5.84 (1 H) due to **11**H$^+$ were the only observable signals. The resulting solution was added dropwise to a rapidly stirred suspension of 2.0 g of $NaHCO_3$ in 10 mL of water. The resulting aqueous solution was extracted with 5 × 3 mL of ether. The combined ether extract was dried over $MgSO_4$ and concentrated to ~0.5 mL. Gas chromatographic analysis of this solution showed that 4,5-dimethyl-2-acetylfuran (**11**) was the only GC volatile product formed in ~85% yield.

Reaction of 4,5-Dihydroxy-2,3,4,5-tetramethylcyclopentenone (14) in 50% H_2SO_4. Diol **14** (0.025 g, 0.147 mmol) was dissolved in 0.30 mL of 50% H_2SO_4, and the reaction was monitored by NMR spectroscopy. After 9 days at room temperature the signals at δ 1.43 (3 H), 1.46 (3 H), 1.82 (3 H), and 2.21 (3 H) due to **14** had disappeared and signals at δ 1.41 (3 H), 1.83 (3 H), 2.18 (3 H), 5.48 (1 H), and 5.56 (1 H) due to **16** were the only observable signals. The resulting solution was neutralized, extracted, and concentrated as previously described for diol **12**. Gas chromatographic analysis showed that 4-hydroxy-2,3,5-trimethyl-4-methylenecyclopentenone (**16**) and 4,5,6-trimethyl-2-pyrone (**10**) were the only volative products formed in a ratio of 8:1.

3,4,5-Trimethyl-2-acetylfuran (29). 2,3,4,5-Tetramethyl-4,5-dihydroxycyclopentenone (**14**) (0.051 g, 0.30 mmol) was dissolved in 2.0 mL of water and treated with 5 drops of 40% NaOH in water. After 30 min at room temperature, the slightly yellow solution was heated on a steam bath for 5 min, diluted to 10 mL with water, and conntinuously extracted with ether for 24 h. The ether extract was dried over $MgSO_4$ and concentrated. Kugelrohr distillation gave 3,4,5-trimethyl-2-acetylfuran (**29**) as a colorless liquid [bp 145–148 (23 torr); 0.033 g (0.22 mmol, 73% yield)]: Ir (neat) 2910, 2830, 1660, 1620, 1540, 1415, 1375, 1355, 1305, 1255, 1105, 920, 710 cm^{-1}; NMR ($CDCl_3$) δ 1.90 (s, 3 H), 2.25 (s, 6 H), 2.40 (s, 3 H); mass spectrum, *m/e* (relative intensity) 152 (2), 127 (8), 126 (13), 125 (9), 99 (15), 55 (10), 54 (16), 43 (100).

Registry No. 1H$^+$, 62968-76-7; **3**, 1193-79-9; **4**, 62968-83-6; **5**, 4209-44-3; **9H$^+$**, 73761-43-0; **10**, 14818-31-6; **11**, 73761-44-1; **12**, 97072-95-2; **13H$^+$**, 51595-74-5; **14**, 97072-97-4; **16**, 73761-47-4; **17**, 51595-76-7; **29**, 73761-50-9.

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