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PHOTO-RING CONTRACTION REACTIONS OF 4-HYDROXYPYRYLIUM CATIONS

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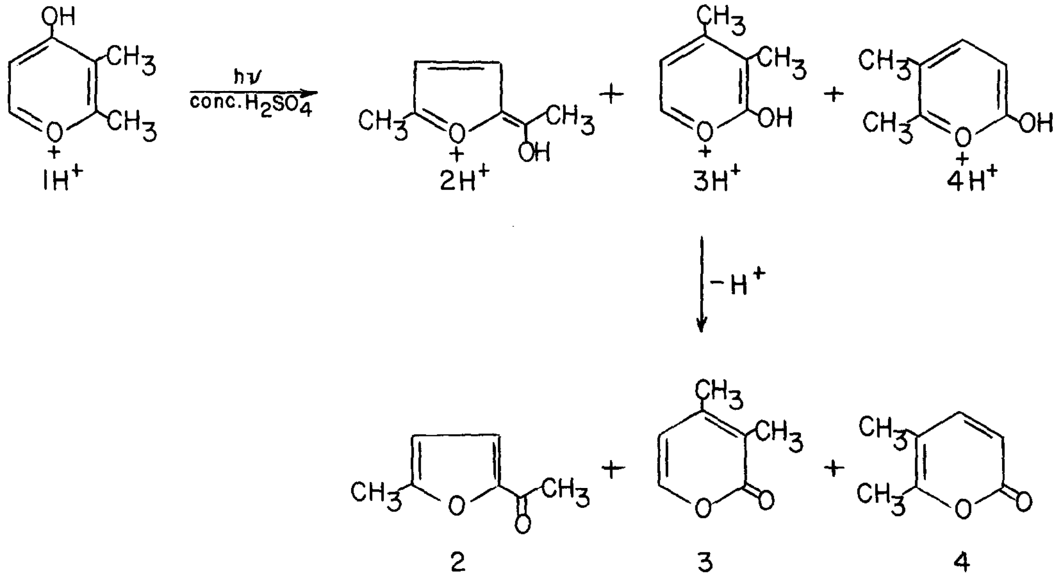
SUMMARY: 4-Hydroxypyrylium cations undergo photo-ring contraction upon irradiation of 50 percent H_2SO_4. Dihydroxycyclopentenones are intermediates in these reactions.

A variety of 4-hydroxypyrylium cations are known to undergo photoisomerization in concentrated H_2SO_4 to yield 2-hydroxypyrylium cations.[1a-f] In one example, however, this photo-transposition reaction was accompanied by a photo-ring contraction. Thus, irradiation of 2,3-dimethyl-4-hydroxypyrylium cation **1H**$^+$ in concentrated H_2SO_4 leads to the formation of furyl cation **2H**$^+$ in addition to both mechanistically expected 2-hydroxypyrylium cations **3H**$^+$ and **4H**$^+$.[1e]



We now wish to report that the relative yields of products in the latter reaction is markedly dependent on acid concentration. Table 1 gives the relative yields of **2**,**3**, and **4** after irradiation of **1H**$^+$ in various concentrations of H_2SO_4 followed by neutralization.[2]

Although no new products were observed upon changing the acid concentration, the data does show that whereas 3 and 4 constitute over 97 percent of the product mixture after irradiation in 100 percent H_2SO_4, 5-methyl-2-acetylfuran 2 is essentially the sole product observed when the irradiation is carried out in 50 percent acid.

Table 1. Product Distribution as a Function of Acid Concentration

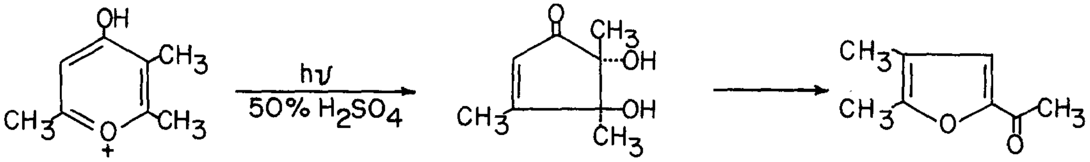
$\%H_2SO_4$	2,%[a]	3,%	4,%
100	2.4	51.3	46.3
93	59.0	18.1	22.8
75	96.0	2.0	2.0
50	99.5	.5	0

a. Analyses were performed by glpc on a 10 ft. x 1/8 in. column packed with 2% Carbowax 20M-TPA on Chromosorb G. Yields given refer to the relative percent of volatiles recovered after neutralization and ether extraction.

In order to investigate the generality of the dependence of acid concentration on this photo-ring contraction reaction, 2,3,6-trimethyl-and 2,3,5,6-tetramethyl-4-hydroxypyrylium cations $5H^+$ and $6H^+$, both known to undergo photoisomerization to 2-hydroxypyrylium cations in concentrated H_2SO_4, were irradiated in more dilute acid solution.

Changes in the nmr spectrum after irradiation of $5H^+$ in 50 percent H_2SO_4 at room temperature revealed the clean conversion of this cation to a photochemically and thermally stable product with methyl groups absorbing at δ 2.42, 2.18, and 1.95ppm. Gas chromatographic examination of an ether extract of the resulting neutralized solution showed one major product (~95%) and a much smaller quantity (~5%) of a second product which were isolated by preparative gc. These major and minor products were identified on the basis of their spectroscopic properties and independent syntheses as 4,5-dimethyl-2-acetylfuran 7 and 4,5,6-trimethyl-2-pyrone 8.[3]

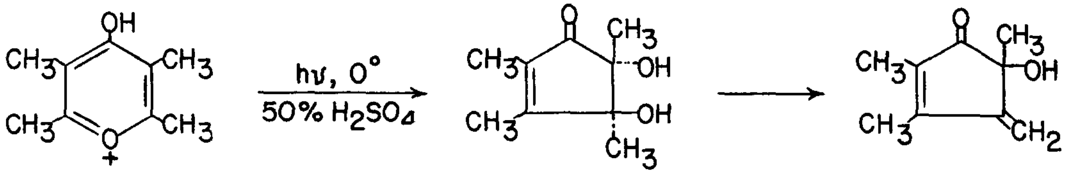
When cation $5H^+$ was irradiated in 50 percent H_2SO_4 at 0°, however, changes in the nmr spectrum showed the formation of a different product with methyl groups absorbing at δ 2.15, 1.35, and 1.30ppm. If the irradiated solution was allowed to warm to room temperature this new product was thermally converted to 4,5-dimethyl-2-acetylfuran 7. If instead of warming, the solution was neutralized immediately after irradiation at 0°, gc examination of an ether extract showed only small quantities of acetylfuran 7 and 2-pyrone 8. From the aqueous layer, however, <u>trans</u>-4,5-dihydroxy-3,4,5-trimethylcyclopent-2-enone 9 was isolated as a white crystalline solid. In 50 percent H_2SO_4 the nmr spectrum of 9 is identical to the spectrum of the major product formed upon irradiation of $5H^+$ at 0°, and upon standing in 50 percent H_2SO_4 at room temperature, 9 was slowly converted to 7. These results confirm that 9 is an intermediate in



$5H^+$ 9 7

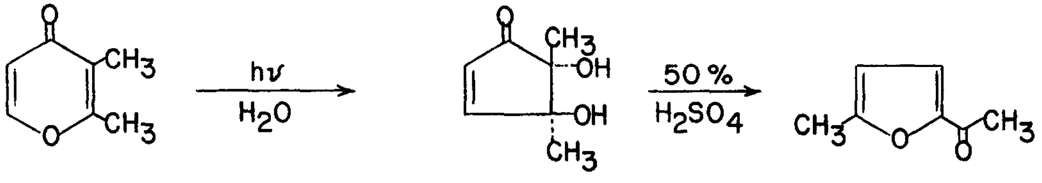
the photo-ring contraction of 2,3,6-trimethyl-4-hydroxypyrylium cation to 4,5-dimethyl-2-acetylfuran 7.

Tetramethyl-4-hydroxypyrylium cation 6H$^+$ behaved similarly. Thus dihydroxycyclopentenone 10 was the only product observed by nmr after irradiation of 6H$^+$ at 0°. The diol 10, did not, however, rearrange to the acetylfuran analogous to 7. Rather, upon prolonged standing in 50 percent H_2SO_4 at room temperature, 10 was converted to cyclopentenone derivative 11.



6H$^+$ 10 11

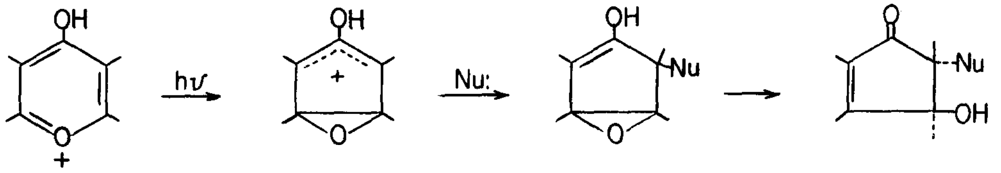
The intermediacy of diols 9 and 10 in the photo-ring contraction reactions of 5H$^+$ and 6H$^+$ implies that an analogous intermediate is present in the conversion of 1H$^+$ to 2. Although no such intermediate was detected, even after irradiation of 1H$^+$ at 0°, we have observed that the anticipated diol 13 is formed when 2,3-dimethyl-4-pyrone is irradiated in neutral aqueous solution.[4] Furthermore, 13 is rapidly converted to 5-methyl-2-acetylfuran when dissolved in 50 percent H_2SO_4. This observation lends credibility to the suggestion that dihydroxycyclopentenones are general intermediates in the photo-ring contractions of 4-hydroxypyrylium cations.



1 13 2

Whereas the change in product distribution with H_2SO_4 concentration might indicate a change in the extent of 4-pyrone protonation, the proton chemical shifts of all 4-pyrones studied were constant over the range of H_2SO_4 concentrations employed. This indicates that there is no significant change in the degree of 4-pyrone protonation over this acid concentration range. 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 percent H_2SO_4.[5]

The formation of a dihydroxycyclopentenone is consistent with nucleophilic trapping of a photochemically generated 4-hydroxyoxabicyclohexenyl cation followed by epoxide ring opening and proton transfer as shown below. Although based on the structure of the diol and its increasing yield with increased concentration of added water it is tempting to suggest that water is acting as the trapping agent, the activities of water in aqueous H_2SO_4 over the concentration range shown in Table 1 do not suggest that neutral water is available to act in this



capacity.[6] Addition of water to 100 percent H_2SO_4 is, however, accompanied by a substantial increase in the concentration of HSO_4^{-1} and it seems likely that the oxabicyclohexenyl cation is trapped by this latter anion.[7] The isolated diol would thus result from hydrolysis of the initially formed bisulfate adduct.

Both the reactivity and fate of the dihydroxycyclopentenone in 50 percent H_2SO_4 are dependent on the extent of methyl substitution. Thus although trimethyldiol **9** is more stable than dimethyl homologue **13**, both are converted to acetylfuran derivatives--most probably *via* acid-catalyzed reverse aldol ring opening, bond rotation, ring closure, loss of water, and deprontonation. In contrast, tetramethyldiol **10** is considerably more stable in 50 percent H_2SO_4. Interestingly, although we have observed its clean conversion to 3,4,5-trimethyl-2-acetylfuran under conditions of base catalysis, in 50 percent H_2SO_4 it apparently undergoes protonation at the C-4 hydroxyl group with subsequent elimination to yield the observed methylene cyclopentenone derivative **11**.

References and Notes

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2. Irradiations were carried out at 2537A in quartz nmr tubes.

3. All products were characterized by their unambiguous synthesis and/or spectroscopic properties.

4. The details of 4-pyrone photochemistry in water will be reported in a separate communication.

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