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PHOTOISOMERIZATION OF 2,6-DI-t-BUTYL-4-HYDROXYPYRYLIUM CATION EVIDENCE FOR A DEWAR-TYPE INTERMEDIATE

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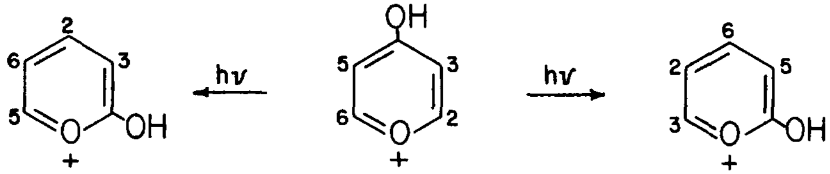
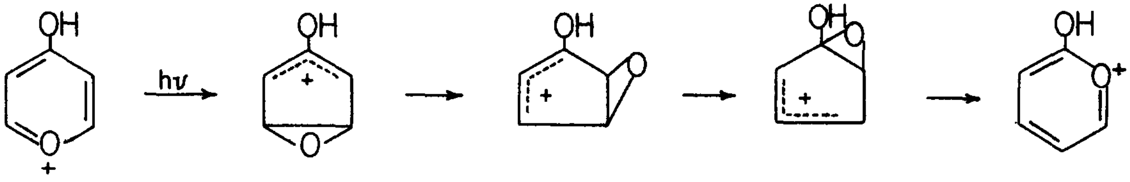
All previously reported examples of 4-hydroxypyrylium cation photoisomerizations have been shown to follow the phototransposition patterns shown below in which substituents in the 2 and 6 positions of the reactants are found in the 4 or 5 positions of the products.[1-5]

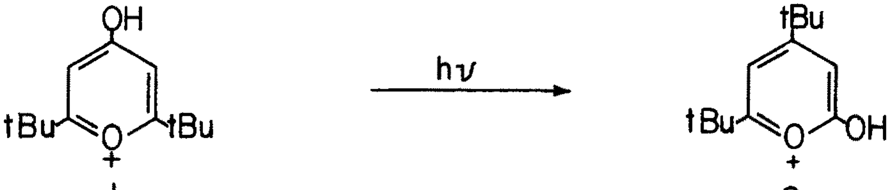


These phototransposition patterns are consistent with the mechanism shown below. Thus, initial 2,6-bridging, symmetry allowed in the first excited state



of the 4-hydroxypyrylium cation, is followed by a series of epoxide ring migrations and final collapse of the 2-hydroxyoxobicyclohexenyl cation to yield the observed 2-hydroxypyrylium cation product.

We now wish to report that photoisomerization of 2,6-di-t-butyl-4-hydroxypyrylium cation $\underset{\sim}{1}$ does not lead to 4,5-di-t-butyl-2-hydroxypyrylium cation--the product from the previously established phototransposition pattern--but to inefficient formation of 4,6-di-t-butyl-2-hydroxypyrylium cation 2. This is



1

2

the first reported example of a 4-hydroxypyrylium cation photoisomerization which does not follow the previously established phototransposition pattern.

Irradiation[6] of a 0.24 molar solution of 2,6-di-t-butyl-4-hydroxypyrylium cation[7] in 96 percent H_2SO_4 [UV: λmax 265nm (ε7860) and 240nm (ε7400); ^{1}Hnmr: 1.4 ppm,s,18H; 7.1 ppm,s,2H; ^{13}Cnmr: 27.767 ppm,q,J=123.15Hz(CH_3); 36.286 ppm, s,(quarternary t-butyl carbons); 109.453 ppm,d,J=164.2Hz(C-3 and C-5 ring carbons), 175.233 ppm,s,(C-2 and C-6 ring carbons); 182.272 ppm,s,(C-4 ring carbon)] was accompanied by the formation of a new cation with λmax 296nm, characteristic of 2-hydroxypyrylium cations, and ^{1}Hnmr singlets at 1.4 ppm (9H), 1.5 ppm (9H), 7.05 ppm (1H), and 7.3 ppm (1H). Lack of coupling between the ring protons indicates a 2-hydroxypyrylium cation photoproduct with non-adjacent ring protons. Inspection of the nmr spectra of a variety of 2-hydroxypyrylium cations reveals that protons at the C-4 and C-6 positions absorb between 8 and 8.5 ppm, whereas those at C-3 and C-5 absorb close to 7 ppm. Indeed, the C-3 and C-5 ring protons of 4,6-dimethyl-2-hydroxypyrylium cation appear at 6.9 and 7.1 ppm. The observed chemical shifts at 7.05 and 7.3 ppm thus indicate ring protons at C-3 and C-5 and accordingly place the t-butyl substituents at C-4 and C-6 of the 2-hydroxypyrylium cation ring.

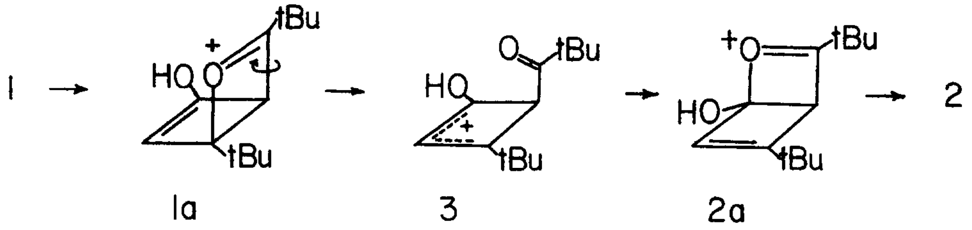
Gas chromatographic analysis of the neutralized reaction mixture revealed the presence of a single volatile product, which was isolated by preparative gas chromatography and was shown, by re-solution in 96 percent H_2SO_4, to be the conjugate base of the photoproduct.

The mass spectrum of the neutralized product exhibited major fragment peaks at m/e 208 (71%), 180 (29%), 166 (21%), 165 (96%), 152 (21%), 151 (100%), 95 (29%), 57 (25%), and 41 (32%). Studies of the mass spectral properties of 2-pyrones have established that loss of a substituent at the C-6 ring position initiates a prominent fragmentation pathway.[9] Inspection of the mass spectral data reveals that, whereas an M-1 peak at m/e 207, corresponding to a loss of hydrogen, is not observed, loss of a t-butyl group, as evidenced by the base peak at m/e 151, does constitute the major fragmentation reaction. Furthermore, loss of a C-6 substituent is reportedly followed by elimination of two molecules of carbon monoxide. In agreement with this, a major peak was also observed in the mass spectrum at m/e 95. A second well-established fragmentation pathway for 2-pyrones involves initial loss of carbon monoxide yielding an M-28 species. As required by this pathway, a major peak at m/e 180 was also observed in the mass spectrum of the neutralized photoproduct. Taken together, these mass spectral data constitute excellent evidence that the conjugate base of the photoproduct is indeed a di-t-butyl-2-pyrone with one of the substituents at the C-6 position.

The infrared spectrum of this neutral product exhibited carbonyl absorption at 1730 cm^{-1} and ^{1}Hnmr singlets at 6.1 ppm (2H), 1.4 ppm (9H), and 1.3 ppm (9H). Thus, whereas the mass spectral data places one of the t-butyl groups in the C-6 position, the nmr data, which shows two equivalent ring protons, requires that the other t-butyl group is in the 4 position confirming that the neutralized photoproduct is 4,6-di-t-butyl-2-pyrone. By comparison, 4-6 dimethyl-2-pyrone shows carbonyl absorption also at 1730 cm^{-1} and equivalent ring protons absorbing at 5.9 ppm.

The photoisomerization of 2,6-di-t-butyl-4-hydroxypyrylium cation 1 to 4,6-di-t-butyl-2-hydroxypyrylium cation 2 is clearly inconsistent with a mechanism involving 2,6 bridging as the primary photochemical reaction. Inspection of molecular models reveals that this reaction should be sensitive to the size of the C-2 and C-6 substituents since these groups move closer together during electrocyclic ring closure. Thus, in the present case it appears that the very large t-butyl groups sterically preclude 2,6-bridging and force photoisomerization to occur via an alternate mechanistic route.

When 2,6-bridging is sterically precluded, we suggest that the primary photoreaction is 2,5-bridging to yield transient 4-hydroxy-Dewar pyrylium cation 1a which undergoes subsequent thermal isomerization to yield 2-hydroxy-Dewar pyrylium cation 2a.[10] This latter rearrangement requires rotation about the



C-2:C-3 bond in 1a and could involve the intermediacy of the homoaromatic cyclobutenyl cation 3. Ring opening of the Dewar cation 2a leads directly to 4,6-di-t-butyl-2-hydroxypyrylium cation 2, the observed photoproduct.

References and Notes

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6. Irradiations were carried out at 2537Å in quartz NMR tubes at ambient temperature under a continuous fine stream of nitrogen.
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10. Dewar-pyrylium cations have also been suggested as intermediates in the photoisomerization of 2-hydroxypyrylium cations. See reference 1.

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