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HETEROCYCLODIENEONE PHOTOCHEMISTRY I. PHOTO-2-PYRIDONE (2-AZA-3-OXOBICYCLO/‾2.2.0_7HEX-5-ENE)

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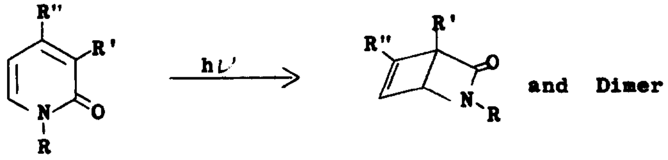
About ten years ago the photodimerization of 2-pyridones was described (1,2,3). More recently the photoisomerization of N-methyl-2-pyridone (1b) was accomplished by low-temperature photolysis and workup of dilute solutions of the latter (4). This mode of preparation of the photoisomer (2b) as well as the reported great instability of the related photo-2-pyrone /‾pyrophoric and explosive in air (4)_7, Dewar benzene /‾$t_{1/2}$ approx. 2 days at room temperature (5)_7, and Dewar pyridine /‾$t_{1/2}$ approx. 2.5 min. at room temperature (6)_7 has left the impression that the whole series of unsubstituted photoisomers, while capable of finite existence, is relatively labile. In part, this has led to a complete lack of activity in this area.



(1) (2) (3)

a) R=R'=R"=H (isolated yield, 15%; 60 hr irradiation; m.p. 65.5-66.5°)

b) R=Me, R'=R"=H (11%; 72 hr; b.p. 24°/0.08 mm)

c) R=i-Pr; R'=R"=H (75%; 46 hr; b.p. 42°/0.1 mm)

d) R=$CH_2C_6H_5$, R'=R"=H (20%; 18 hr; b.p. 120-130°/0.1mm)

e) R=C_6H_5, R'=R"=H (17%; 24 hr; m.p. 68-70°)

f) R=Me; R'=OMe; R"=H (36%; 24 hr; b.p. 58-63°/0.07mm)

g) R=Me; R'=CN; R"=OMe (89%; 44 hr; m.p. 69.0-69.5°)

We now report on the facile preparations and relatively high degree of stability of the photo-2-pyridones (2) including the parent, photo-2-pyridone (2-aza-3-oxobicyclo/¯2.2.0_7hex-5-ene)(2a).

Syntheses were carried out by irradiating 0.002 to 0.2 *M* methanolic solutions (other transparent solvents can be used) with a Pyrex-filtered Hanovia 450 W source, Products were isolated by fractional distillation or sublimation of the concentrated residues (7). The products 2 were characterized and distinguished from the starting materials (1) and the photodimers (3) (1,2,3) as follows: i) 2 are all liquids or low melting solids whereas 3 are all solids melting above 200°. ii) 2a-e all have mass spectral base or major peaks at m/e = 52 corresponding to the cyclobutadiene cation. 2f and 2g have base peaks at m/e = 82 and 107, respectively, corresponding to the appropriately substituted cyclobutenium ion. In the mass spectra of the corresponding 1 and 3 these ions are either extremely minute or nonexistent. iii) 2 all showed infrared absorptions at 1720 to 1750 and 1535 to 1550 cm^{-1} characteristic of the *β*-lactam carbonyl and fused cyclobutene double bond, respectively, with the single exception of an enhanced C=C absorption shifted to 1640 cm^{-1} for 2g. iv) The pmr spectra of 2a-e all had absorptions for two olefinic and two bridgehead protons similar to those shown for 2a in Fig. 1 while those for 2f and 2g were reduced by substituents at the corresponding positions. A detailed analysis of the pmr spectrum of 2c using shift reagents and decoupling gave $J_{1,4} = 2.2$, $J_{5,6} = 2.3$, and $J_{1,5} \cong J_{1,6} \cong J_{4,5} \cong J_{4,6} \cong 1$. These coupling constants are quite different from those of 3 (1,2,3). The chemical shifts easily differentiate 1.

The photoisomers (2) appear to be indefinitely stable at room temperature and below. However, thermolysis of 2b above 100° or irradiation through quartz at 2537 Å causes reversion to 1b. The kinetics of the thermal reversion of 2b (10% w/w in *o*-dichlorobenzene) were studied using pmr spectroscopy. Clean first-order rates of 3.29×10^{-5} (130.0°), 1.56×10^{-4} (145.0°), and 6.22×10^{-4} sec^{-1} (160.0°) yielded $\Delta H^{\ddagger} = 33.2$ kcal/mole, $\Delta S^{\ddagger} = + 2.7$ e.u. (130.0°), and log A = 14.0. At 130°, 2a reverts to 1a with a rate approximately 10 times that of the 2b reversion. This may reflect some assistance by the lactim tautomer.

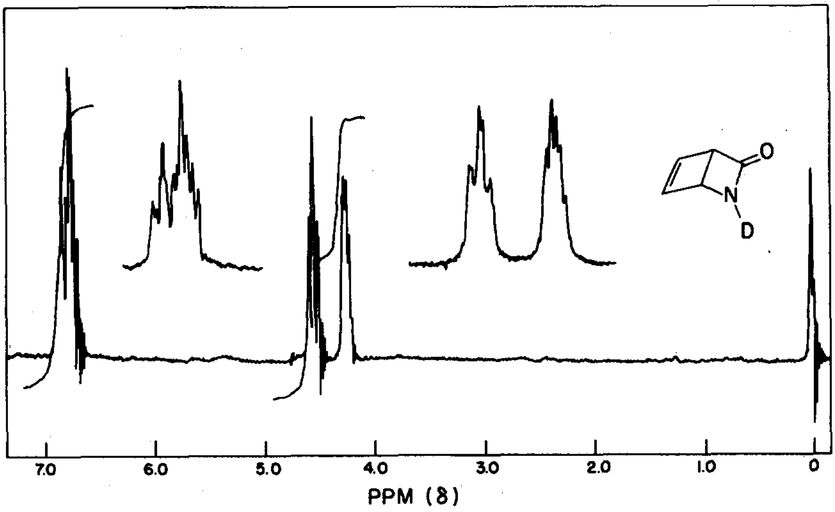


Figure 1. The 60-MHz pmr spectrum of photo-2-pyridone (2a) in $CDCl_3$ after D_2O exchange (Varian T-60). Inserts are expansions at 250 Hz sweep width.

Having now established the generality of the 2-pyridone photoisomerization (8) and the relatively high degree of stability of the photoisomers (9), our further efforts will be directed toward elucidation of the mechanism of the photoisomerization, possible extension to other ring systems and particularly investigation of the reactions of the photoisomers and their derivatives.

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References and Footnotes

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7. From similar concentrated residues, the authors of ref. 3 crystallized the less soluble photodimers **3a-c** but apparently recycled or discarded the photoisomers **2a-c**.
8. It is interesting to speculate that the extraordinary facility with which ricinine (**1g**) is converted to "photoricinine" (**2g**) with no dimer detected might have some significance in phytological photosynthesis.
9. We suggest that the stability of the photo-2-pyridones (**2**) relative to, for instance, Dewar pyridine (6) is mainly an effect of the relatively lower ground state energies expected for **2**. It has recently been shown that the amide group in 14.1 ± 3.5 kcal/mol more stable than the isomeric imidate: P. Beak, J. Bonham, and J. T. Lee, Jr., *J. Amer. Chem. Soc.*, **90**, 1569 (1968). Additionally removal of the second double bond as in **2** should favor stability: *cf.* H. M. Frey, J. Metcalfe, and J. M. Brown, *J. Chem. Soc.* (B), 1586 (1970).