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THE PHOTOCHEMICAL [4+4] CYCLODIMERIZATION OF 2-PYRAZINONE IN THE SOLID STATE

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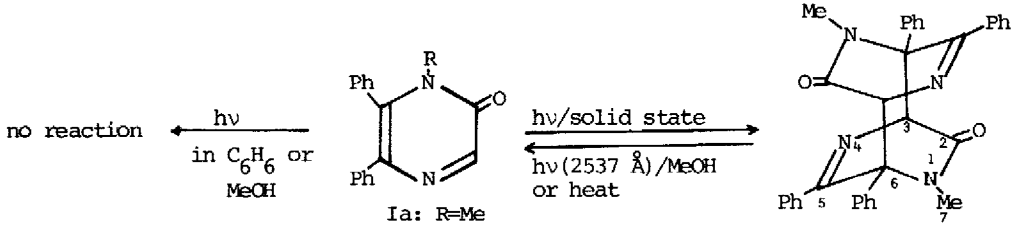
Summary: Irradiation of 1-methyl-5,6-diphenyl-2-pyrazinone (Ia) in the solid state gave the [4+4] anti dimer (II) in 100% yield, while (Ia) in a solution phase was inert upon irradiation.

The photochemical cyclodimerization of aromatic compounds is a well-established photoreaction. The most common type of reaction in this class is the [4+4] cyclodimerization of naphthalenes and anthracenes involving inter- and intramolecular reactions.[1] However, those of heteroaromatic compounds draw little attention. The photochemical [4+4] cyclodimerization of 2-pyridones and 2-pyrones in solution was reported by Taylor and Paquette et al.[2] and de Mayo et al.[3] Recently, a similar photochemical [4+4] cyclodimerization of 4,6-diphenyl-2-pyrone in both solution and solid state was reported by Rieke et al.[4] We wish to report here the photochemical [4+4] cyclodimerization of 1-methyl-5,6-diphenyl-2-pyrazinone (Ia) in the solid state.

1-Methyl-(Ia)[5] and 1-ethyl-5,6-diphenyl-2-pyrazinone (Ib)[5] were inert to the photolysis in benzene and methanol solution.[6] However, irradiation of (Ia) in the solid state[7] with a high pressure mercury lamp (400 W) at room temperature for 20 min gave the [4+4] anti dimer (II), mp. 148-150°C, in 100% yield based on recovered starting pyrazinone (Ia). Similar irradiation of (Ia) in the solid state[8] at 2537 Å for 4 h gave also the [4+4] anti dimer (II) in 86% yield, but at slower rate.



Ia: R=Me
Ib: R=Et

II

The structure of the dimer (II) was confirmed on the basis of the spectral data and elemental analysis. The infrared spectrum of (II) showed a carbonyl stretch at 1660 cm^{-1}, versus 1640 cm^{-1} for the starting pyrazinone (Ia). One would expect the carbonyl of syn isomer to come at higher value due to dipole-dipole interaction. The ultraviolet spectrum showed λ_{max}(EtOH) at 261 (ε=3.6 x 10^3) and 351 nm (ε=4.5 x 10^2). The ^{1}H-NMR spectrum showed a singlet at δ 2.58, a singlet at δ 6.35, and the multiplet at δ 6.85-7.35 assignable to methyl, methine, and aromatic protons in the ratio of 3 : 1 : 10, respectively, while that of (Ia) showed a singlet at δ 3.31(3H), a singlet at δ 8.30(1H), and the multiplet at δ 7.1-7.45(10H), respectively. Furthermore, ^{13}C-NMR spectrum of (II) showed peaks at 31.9(q), 70.1(d), 76.7(s), 169.8(s), and 178.5(s) ppm due to carbons at 7-, 3-, 6-, 5-position, and carbonyl carbon, respectively, in addition to aromatic carbon peaks.

Mass spectrum of (II) showed the parent peak m/e 524 (M$^+$: Field disorption mass). The [4+4] anti dimer (II) was stable at room temperature. However, heating of the dimer (II) at reflux temperature in benzene for 16 h or its melting point produced the starting pyrazinone (Ia) in both 100 % yields. Furthermore, irradiation of the dimer (II) in methanol through a quartz tube at 2537 Å for 30 min causes reversion to the starting pyrazinone (Ia) in almost quantitative yield. On the other hand, irradiation of 1-ethyl-5,6-diphenyl-2-pyrazinone (Ib) in the solid state did not give any photoproducts and (Ia) was recovered quantitatively. To our knowledge, this represents the first case of the photochemical [4+4] cyclodimerization in the solid state photochemistry of monocyclic heteroaromatic compounds containing nitrogen atom.[9] We are determining to what this process may be general in the solid state photochemistry.

References and notes

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2. L.A. Paquette and G. Slomp, J. Am. Chem. Soc., 85, 765 (1963). E.C. Taylor and R.O. Kan, ibid., 85, 776 (1963).
3. P. de Mayo and R.W. Yip, Proc. Chem. Soc., 1964, 84.
4. R.D. Rieke and R.A. Copenhafer, Tetrahedron Lett., 1971, 879.
5. The starting pyrazinones (Ia-b) were prepared by modifying the method of Jones (R.G. Jones, J. Am. Chem. Soc., 71, 78 (1949)). Ia: mp. 165-167°C; UV(EtOH) (ε) 266 (1.2 x 10^4) and 347 nm (7.3 x 10^3). Ib: mp. 159-161°C; UV(EtOH) (ε) 264 (1.1 x 10^4) and 345 nm (6.4 x 10^3); IR (KBr) 1650 cm^{-1}; δ(CDCl$_3$) 1.15 (t, 3H), 3.90 (q, 2H), 7.1-7.6 (m, 10H), and 8.33 (s, 1H). Satisfactory elemental analyses have been obtained for all new compounds.
6. In the solution photochemistry of 2-pyrazinones, Furrer reported that 1,3,5,6-tetramethyl-2-pyrazinone gave an unstable intramolecular [2+2] cyclization product, 1,2,4,6-tetramethyl-3-oxo-2,5-diazabicyclo[2,2,0]hex-5-ene, which could not be isolated, and was identified a reduced derivative by hydrogenation. H. Furrer, Chem. Ber., 105, 2780 (1972). We could not detect the corresponding intramolecular [2+2] cyclization product when 2-pyrazinone (Ia and b) was irradiated in a solution phase and the starting pyrazinone was recovered in almost quantitative yield.
7. The recrystallized 2-pyrazinone (Ia) (100 mg) was sandwiched between a pair of Pyrex plates (thickness 2 mm) and the solid sample thus obtained was irradiated.
8. The solid sample, which was sndwiched between a pair of quartz plates, was irradiated with a low pressure mercury lamp.
9. In the solid state photochemistry of 2-pyrone, which is one of heteroaromatic compounds containing oxygen atom, and acridizinium salt, the formation of intermolecular [4+4] dimer was reported by Rieke et al.[4] and Bradsher et al. (C.K. Bradsher, L.E. Beaves, and J.H. Jones, J. Org. Chem. 22, 1740 (1957)).

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