

## Photorearrangement of 5,6-Dichloro-1,4-dihydro-1,4-dimethylpyrazine-2,3-dione and its Further Reactions<sup>†</sup>

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**Summary** On u.v. irradiation the title dione (**4**) rearranges to 2-(dichloromethylene)-1,3-dimethylimidazolidine-4,5-dione (**7**) (with thermal reversibility); however, in the presence of moisture dimethylimidazolidinetrione (**5**) is formed, *via* (**6**).

FOLLOWING our studies on the photochemistry of heterocycles containing electron-poor, vicinally dihalogenated

double bonds<sup>2</sup> such as the 5,6-dihalogeno-1,3-dimethyluracils (**1**)<sup>3</sup> and 4,5-dihalogeno-1,2-dihydro-1,2-dimethylpyrazine-3,6-diones (**2**)<sup>4</sup> we have now investigated the photochemistry of the title pyrazinedione (**4**).

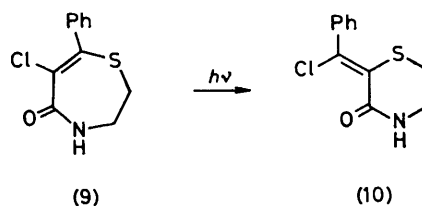
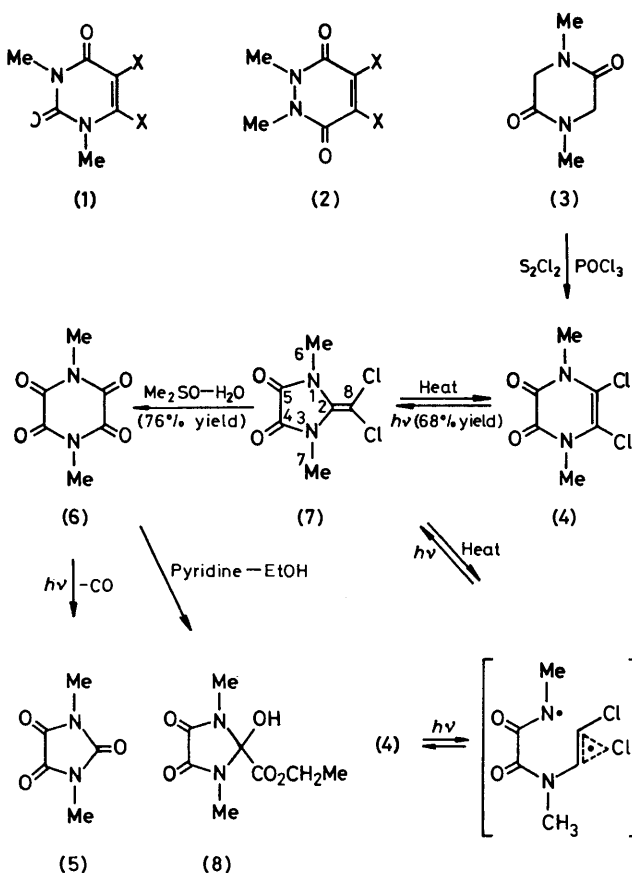
Compound (**4**)<sup>†</sup> was prepared by the method of Hino and Sato<sup>5</sup> by treatment of the dione (**3**) with phosphorus trichloride oxide–disulphur dichloride and obtained in moderate yield; the mechanism of this reaction is as yet

<sup>†</sup> Compound (**4**) shows a weak and unresolved phosphorescence emission band at  $\lambda_{\text{max}}$  490–495 nm (corr. values); lifetime  $\tau < 1 \mu\text{s}$ ; estimated  $E_T$  ca. 58 kcal/mol. (1 cal = 4.184 J). We thank Prof. G. Kaupp for the measurements.

unclear. Long-wavelength u.v. irradiation [Pyrex filter;  $\lambda > 313$  nm; 0.01 M tetrahydrofuran (THF) solution; 11 h; room temperature] results in a total disappearance of (4) (t.l.c.). Compound (7) was obtained in 68% yield by high-

shows that it contains remarkable amounts of (4). These results, as well as the almost identical mass spectra of (4) and (7), indicate the photoisomerization (4)  $\rightarrow$  (7) to be thermally reversible.

In the presence of moisture dimethylimidazolidinetrione (5)<sup>†</sup> was obtained in varying quantities (t.l.c.). Control experiments showed that (7) is hydrolysed slowly in the presence of water, but rapidly in dimethyl sulphoxide-water, to afford 1,4-dimethylpiperazine-2,3,5,6-tetrone (6), which in turn, upon u.v. irradiation, is decarbonylated to give (5) via a double  $\alpha$ -cleavage. As a constitutional isomer of alloxan,<sup>6</sup> compound (6) can be rearranged in pyridine to give the imidazolinecarboxylate (8), m.p. 82–82 °C [<sup>1</sup>H n.m.r. (CDCl<sub>3</sub>):  $\delta$  3.00 (s, 2  $\times$  NMe), 6.11 (s, OH), 4.41 (q, CH<sub>2</sub>Me), and 1.36 (t, CH<sub>2</sub>Me)].



The ring contraction reaction (4)  $\rightleftharpoons$  (7) obviously proceeds with a simultaneous 1,2-chlorine shift, and, by analogy with the photolactonization of dimedone,<sup>7</sup> a diradical intermediate can be postulated. However, in view of the similarity to the work of Schultz *et al.*<sup>8</sup> and the photo-methanolysis of vinyl sulphides, an ionic mechanism is also possible. Attempts to elucidate the mechanism are in progress. A similar photoinduced ring contraction reaction with a simultaneous 1,2-halogen shift was observed previously for the conversion of (9) into (10).<sup>9</sup>

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vacuum sublimation. The n.m.r. spectra (CD<sub>3</sub>SOCD<sub>3</sub>) are typical: <sup>1</sup>H  $\delta$  3.24 (s, 2  $\times$  Me); <sup>13</sup>C:  $\delta$  33.3 (C-6,7), 113.0 (C-8), 153.9 (C-2 or C-4,5), and 154.4 p.p.m. (C-4,5 or C-2); m.p. 167–168 °C. Examination of the sublimation residue

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<sup>†</sup> Dialkyl-imidazolidinetriones are frequently formed as stable photoproducts upon u.v. irradiation of appropriate substrates; cf. ref. 1.

<sup>1</sup> For Part 12 of the series 'Photochemistry of Heterocycles,' see H. Wamhoff, W. Kleimann, G. Kunz, and C. H. Theis, *Angew. Chem.*, 1981, **93**, 601; this work was taken in part from the Diplomarbeit of W. Kleimann, University of Bonn, 1979.

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<sup>3</sup> H. Wamhoff, G. Szilágyi, and J. Keuler, unpublished work.

<sup>4</sup> Diplomarbeit of V. Müller von Bacsko, University Bonn, 1979; (1) and (2) proved to be photostable.

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<sup>7</sup> H. Nozaki, Z. Yamaguti, T. Okada, R. Noyori, and M. Kawanisi, *Tetrahedron*, 1967, **23**, 3993.

<sup>8</sup> A. G. Schultz and R. H. Schlessinger, *Tetrahedron Lett.*, 1973, 4787, 4791.

<sup>9</sup> H. Wamhoff and C. H. Theis, unpublished work.