

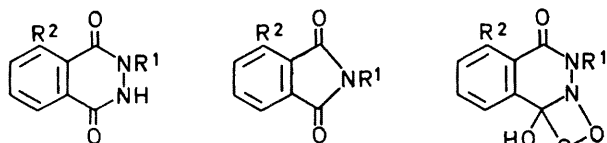
Photochemical Ring Contraction of Luminol, 5-Amino-2,3-dihydrophthalazine-1,4-dione

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Summary The irradiation of luminol (1) in dimethylformamide affords 3-aminophthalimide (4), the 2,3-dihydrophthalazine-1,4-dione ring being contracted.

IN the course of a survey of the fluorescent spectra of luminol, 5-amino-2,3-dihydrophthalazine-1,4-dione (1), we found that the fluorescent spectrum in dimethylformamide changed with time.¹ We have further investigated the photoreaction of (1).



- (1) R¹ = H, R² = NH₂ (4)
 (2) R¹ = H, R² = H (5)
 (3) R¹ = Ph, R² = H (6)
 R¹ = NH₂, R² = NH₂ (7)

A solution of (1) in dimethylformamide (1 g/350 ml) was irradiated with a high-pressure mercury lamp through a

Pyrex filter in the presence of bubbling oxygen (2.5 ml/min) for 20 h at 35°. After the evaporation of dimethylformamide under reduced pressure, the reaction mixture was chromatographed on silica gel with benzene-ethyl acetate (10:3). The product (0.245 g) was identified as 3-aminophthalimide (4);² λ_{max}(EtOH) nm (ε), 224 (20,000), 236 (17,700), 258 (7300), and 386 (4700); fluorescence λ_{max} (dimethylformamide) 477 nm.

In spite of the fact that (1) is easily formed from its isomer (7)³ through ring expansion, the ring contraction of (1) has not been reported. Since the irradiation of (7) did not give (4), (7) could not be an intermediate of the ring contraction. When the solution of 2,3-dihydrophthalazine-1,4-dione (2) in dimethylformamide was irradiated in the same way as (1), phthalimide (5) was obtained in a 29.0% yield. In the case of 2,3-dihydro-2-phenylphthalazine-1,4-dione (3), *N*-phenylphthalimide (6) was obtained (33.2%). Since this reaction was retarded *in vacuo* or in an atmosphere of nitrogen, the participation of oxygen must be essential. Although the structure of the nitrogen moiety is not clear at present, the above facts give some support to the tentative mechanism of the photoreaction as being: (1) → enol form of (1) → (8) → (4).

(Received, May 18th, 1970; Com. 756.)

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