Photochemical Oxidation of Pyrazolidinones

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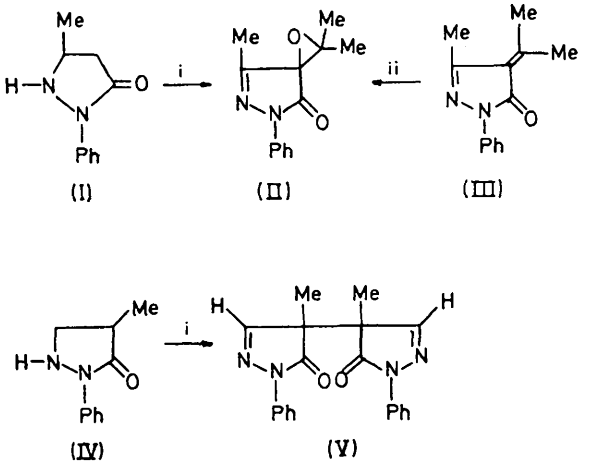
Summary Pyrazolidinone (I) gives the novel spiro-epoxide (II) on irradiation in acetone; the isomeric pyrazolidinone (IV) undergoes oxidative dimerization to (V).

The easy oxidation of pyrazolidinones by reagents such as phenylhydrazine, nitrous acid, and ferric chloride is well known.[1] In a study of the photochemistry of pyrazolidinones,[2] we have found that they also undergo oxidative reactions when irradiated in the presence of ketones. Irradiation of the pyrazolidinone (I) in acetone with a Hanovia 450 W medium-pressure mercury arc lamp through a Pyrex filter gave a white, crystalline compound, isolated by chromatography on alumina with benzene, m.p. 74·5—75° [ν_{max} ($CHCl_3$) 1725 cm^{-1}; δ (CCl_4) 1·65 (3H, s), 1·75 (3H, s), 2·15 (3H, s), and 7·2 and 7·7 (5H, m) p.p.m.; *m/e* 230], which was shown by analysis to have the empirical formula $C_{13}H_{14}N_2O_2$ and assigned structure (II). The same compound was synthesized by the reaction of *m*-chloroperoxybenzoic acid with the pyrazolinone (III).[3]



Reagents: i, Me_2CO, $h\nu$; ii, *m*-chloroperoxybenzoic acid.

Irradiation of the isomeric pyrazolidinone (IV) in acetone under the same conditions gave another white, crystalline substance, m.p. 131·5—132° [ν_{max} ($CHCl_3$) 1720 cm^{-1}; δ ($CDCl_3$) 1·25 (s), 1·65 (s), 7·2, and 7·7 (m) p.p.m.; *m/e* 346, base peak 173] which was shown by analysis to have the empirical formula $C_{20}H_{18}N_4O_2$. The area of the two n.m.r. singlets varied in different samples but the total area was always half that of the low-field multiplets. The mass spectrum showed clearly that the first and most prevalent fragmentation was cleavage in half. On the basis of these data, we assigned structure (V) to this substance, which was apparently isolated as a mixture of *meso*- and (±)-forms which do not separate easily on chromatography and recrystallization.

A similar reaction does not take place when 4,4-dimethyl-2-phenylpyrazolidin-3-one, which cannot be oxidized to a pyrazolinone, is irradiated in acetone. An interesting feature of the reaction which may have a bearing on the mechanism is the fact that the spiro-epoxide (II) was isolated in small quantities (among many other products difficult to separate and characterize) and identified spectrally when the pyrazolidinone (I) was irradiated in the presence of acetophenone, and acetone was subsequently added to the mixture as soon as the lamp was turned off. The nature of the reactive intermediate which survives and adds to acetone in the dark is under investigation.

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[2] S. N. Eğe, *J. Chem. Soc.* (*C*), 1969, 2624.

[3] L. Knorr *Annalen.*, 1888, **238**, 137; G. Westöö, *Acta Chem. Scand.*, 1957, **11**, 1285.