

The Photolysis of *N*-2,4-Dinitrophenylamino-acids, a Route to 2-Substituted 5-Nitrobenzimidazole 3-Oxides

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THE photolysis of most *N*-2,4-dinitrophenyl- α -amino-acids in solution at pH 6 or above gives, as the major product, 4-nitro-2-nitrosoaniline.¹ The photolytic reactions at lower pH have previously been little investigated. Between pH 5 and pH 2, *N*-2,4-dinitrophenylglycine gives a virtually colourless solution on photolysis (tungsten filament bulbs) though the presence of traces of the yellow 4-nitro-2-nitrosoaniline can be demonstrated by thin-layer chromatography. Below pH 2, the yield of 4-nitro-2-nitrosoaniline increases until in 1*N*-hydrochloric acid it is nearly 70% of that at pH 8.0. It is unlikely, then, that the initial step in the formation of 4-nitro-2-nitrosoaniline involves decarboxylation of the ionized carboxyl group as suggested by Russell.¹

The main product of photolysis of *N*-2,4-dinitrophenylglycine between pH 2 and pH 5 has,

in aqueous solution below pH 2, λ_{\max} 230 and 278 $m\mu$, between pH 3 and pH 6 λ_{\max} 258 and 300 (sh) $m\mu$, and above pH 7, λ_{\max} 271 and 325 $m\mu$. This compound has been isolated and shown to be 5-nitrobenzimidazole 3-oxide, identical with an authentic sample prepared by the partial reduction of *N*-formyl-2,4-dinitroaniline.² Similarly *N*-2,4-dinitrophenyl- α -alanine on photolysis in 0.5% acetic acid gave 2-methyl-5-nitrobenzimidazole 3-oxide, isolated in 79% yield. Spectroscopic studies indicate that most *N*-2,4-dinitrophenyl- α -amino-acids decompose similarly when photolysed at pH 3. Thus this reaction provides a convenient route to 5-nitrobenzimidazole 3-oxides with a considerable variety of 2-substituents.

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¹ D. W. Russell, *Biochem. J.*, 1963, **87**, 1; *J. Chem., Soc.*, 1963, 894; 1964, 2829.

² S. Takahashi and H. Kano, *Chem. and Pharm. Bull. (Japan)*, 1964, **12**, 282.