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THE MECHANISM OF THE PHOTOCHEMICAL TRANSFORMATIONS OF N-2,4-DINITROPHENYL-α-AMINO-ACIDS

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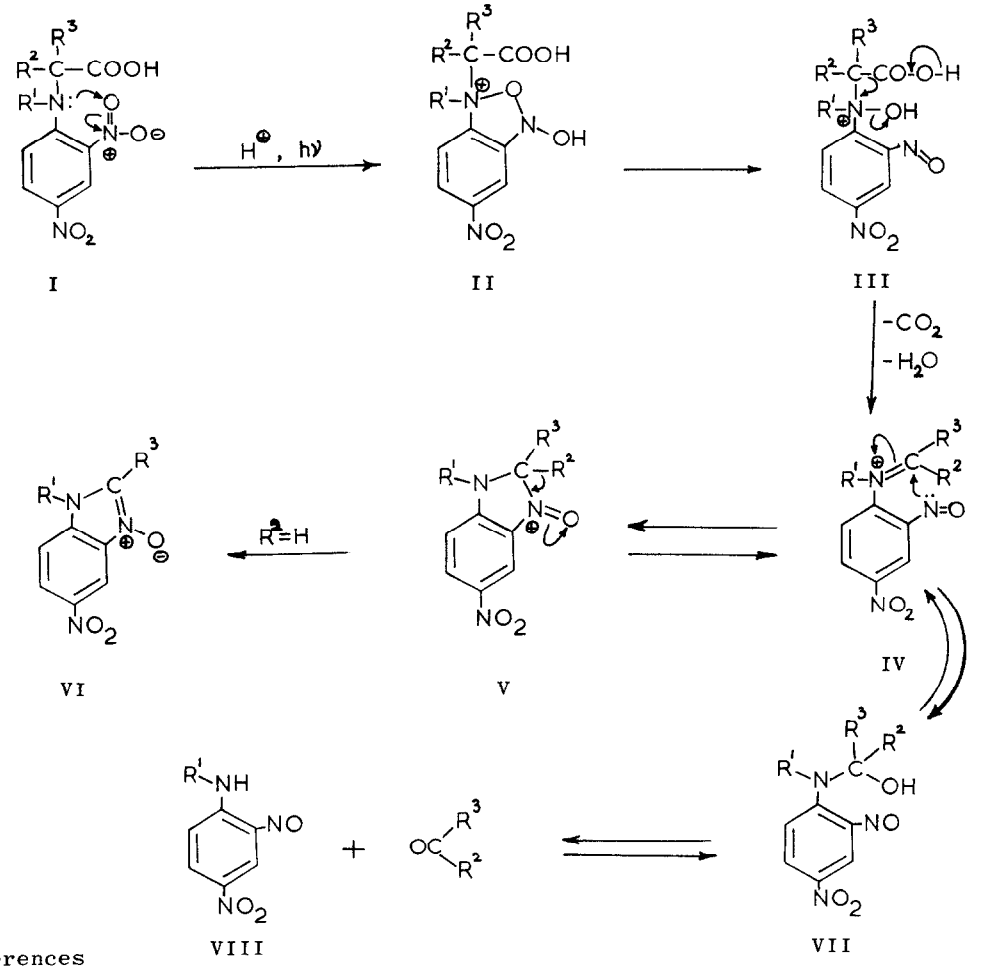
The photolability of N-2,4-dinitrophenyl derivatives of α-amino-acids (I) has been known to protein chemists for some time[1], and was observed to involve loss of carbon dioxide. More recently Russell[2] and Needle and Pollitt[3] have demonstrated that the nature of products from this photoreaction depend upon pH, low pH favouring the formation of a 6-nitro-benzimidazole-N-oxide (VI) while higher pH gives the 2-nitroso-4-nitro anilines (VIII) and an aldehyde. The nitroso anilines (VIII) have been shown to react with aldehydes under acid-catalysis to give benzimidazole-N-oxides (VI)[2e,f]. However, the details of the mechanism of the photolysis reaction are still unclear.

It is now proposed that the reaction proceeds by way of the key intermediate (II), an analogue of the intermediate indicated in the preceeding paper as responsible for the related reactions of o-nitro-t-anilines. The subsequent decarboxylation (III-IV) is then reminiscent of the reactions of a β-keto acid and yields the immonium ion (IV) which is the reasonable precursor of the N-oxide (VI) or the nitroso amine (VIII). In the case of primary amino-acid derivatives (I; R^1=H) this intermediate (IV) is a protonated anil. Any proposed mechanism must take into account: (a) The reaction proceeds with R^1=H or alkyl. (b) Oxygen transfer can still occur with R^2 and R^3 = alkyl groups, resulting in the nitroso aniline (VIII) but no benzimidazole. (c) The photoreaction is acid-catalysed. (d) The rate of reaction as measured by loss of carbon dioxide evolution is very similar for a range of 2,4-dinitrophenyl-amino-acids. All these factors are accomodated in the above mechanism.



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