Formation of a 1,2,4-Oxadiazoline from an Aziridine: Mechanism of the Reaction and Photochemical Conversion into a Benzimidazole Derivative

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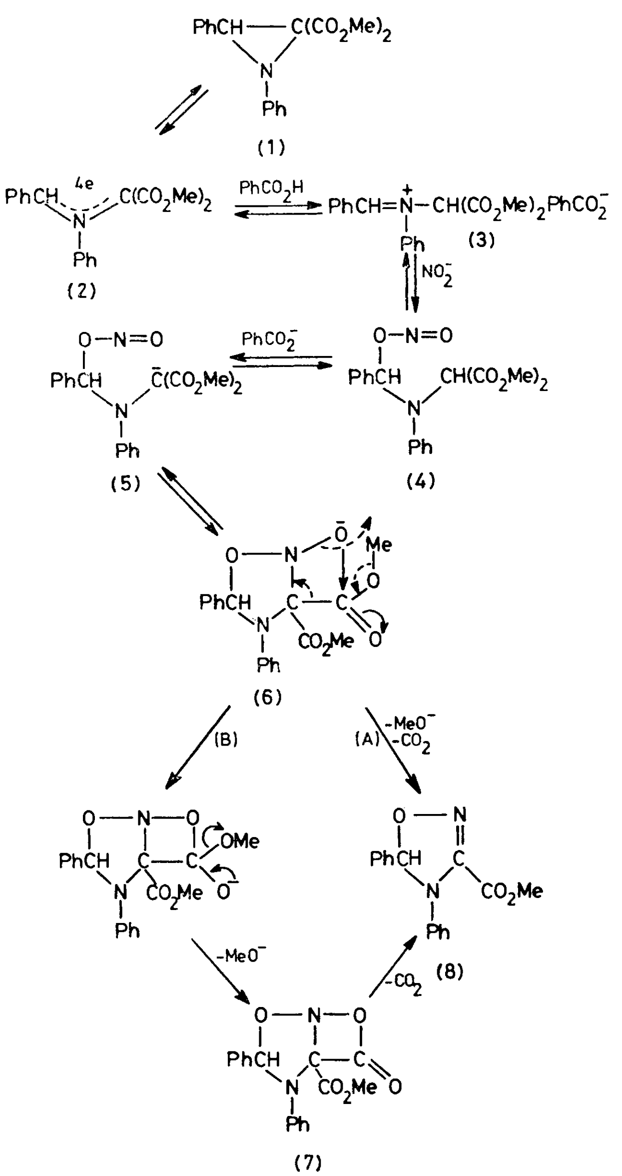
Summary Reaction of sodium nitrite with the aziridine (**1**) in the presence of benzoic acid leads to the formation of the 1,2,4-oxadiazoline (**8**), photolysis of which in benzene provides methylbenzimidazole-2-carboxylate (**9**).

We have previously shown that the aziridine (**1**) is a potential azomethine ylide and reacts with both electrophiles and nucleophiles.[1] Under nitrogen, addition of benzoic acid to a solution of the aziridine (**1**) in 1,2-dimethoxyethane at room temperature leads to the iminium salt (**3**) *via* the azomethine ylide (**2**) (characterized by ^{1}H[2] and ^{13}C[3] n.m.r. spectroscopy). Reaction of sodium nitrite with (**3**) gives the 1,2,4-oxadiazoline (**8**), carbon dioxide, and methanol.



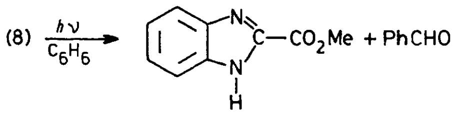
SCHEME

A possible route to (**8**) is given in the Scheme. Addition of nitrite to the iminium salt (**3**) would be expected to give the nitrite (**4**) and hence the anion (**5**). Assuming that (**5**) cyclises to give (**6**), there are then two possibilities which could account for the formation of the oxadiazoline (**8**). It was suggested that a good way of distinguishing between the two possibilities would be to carry out this reaction sequence with ^{18}O labelled potassium nitrite, and we have now studied this reaction. Analysis of the reaction products by g.l.c. and g.l.c.–mass spectrometry clearly shows that the CO_2 produced is labelled and the methanol is not. This evidence supports the β-lactam pathway (B).

The oxadiazoline (**8**) was obtained pure from methanol [m.p. 95—96 °C; yield 75%; satisfactory elemental analyses were obtained; n.m.r., δ ($CDCl_3$) 6·51 (s, 5H) and 3·83 (s, Me ester); ν_{max} (Nujol), 1732 (C=O) and 1576 (C=N) cm^{-1}].

When a degassed solution of (**8**) in anhydrous benzene was irradiated with a high-pressure mercury arc lamp (Hanau HQ 81) for 16 h under nitrogen, the benzimidazole (**9**) was obtained quantitatively, together with benzaldehyde (*cf.* photolysis of 1,2,4- and 1,3,4-oxadiazolin-5-one).[4]

Compound (**9**) was obtained pure from $CHCl_3$ [m.p. 213—214 °C,[5] 86% yield; satisfactory elemental analyses were obtained; n.m.r. δ (C_5D_5N) 12·53br (s, 1H, exchangeable with D_2O), 3·89 (s, Me ester), and 7·25—8·02 (2 multiplets, aromatic A_2B_2 system); ν_{max} (Nujol) 2500—2800 (associated NH) and 1735 (C=O) cm^{-1}].



(9)

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