

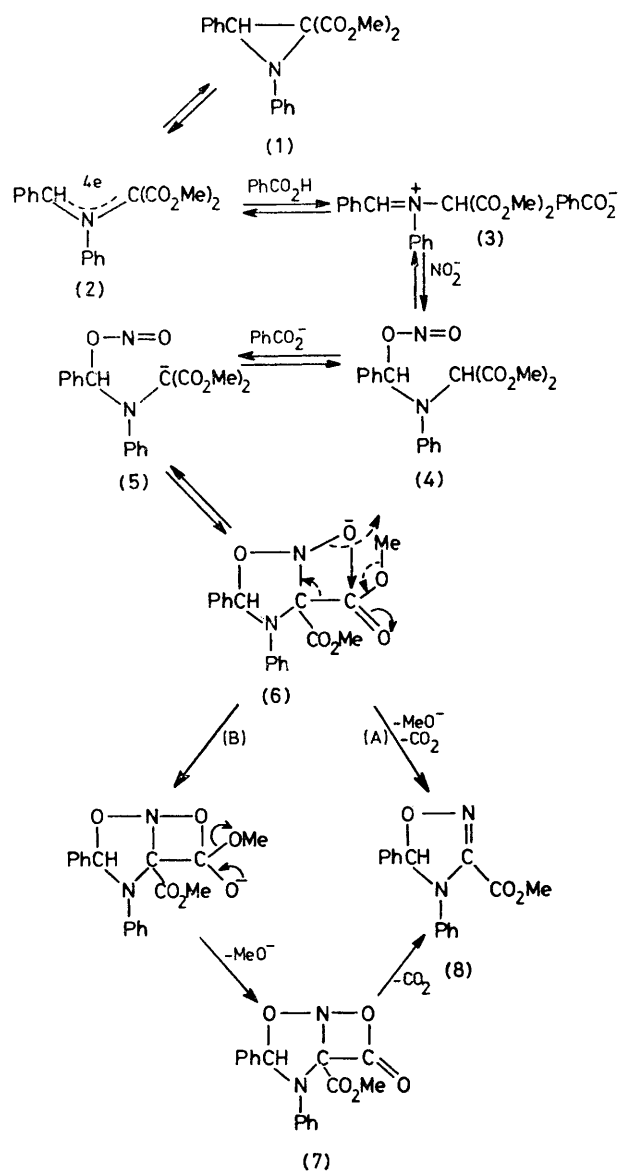
Formation of a 1,2,4-Oxadiazoline from an Aziridine: Mechanism of the Reaction and Photochemical Conversion into a Benzimidazole Derivative

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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-dimeth-



SCHEME

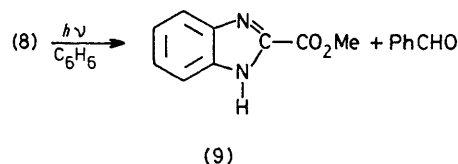
oxyethane at room temperature leads to the iminium salt (3) via the azomethine ylide (2) (characterized by $^1\text{H}^2$ and $^{13}\text{C}^3$ n.m.r. spectroscopy). Reaction of sodium nitrite with (3) gives the 1,2,4-oxadiazoline (8), carbon dioxide, and methanol.

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. $95-96^\circ\text{C}$; 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. $213-214^\circ\text{C}$,⁵ 86% yield; satisfactory elemental analyses were obtained; n.m.r. δ ($\text{C}_6\text{D}_5\text{N}$) 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}].



We thank a referee for suggestions on the mechanism of formation of (8).

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⁵ B. C. Ennis, G. Halan, and E. L. Samuel, *J. Chem. Soc. (C)*, 1967, 30.