

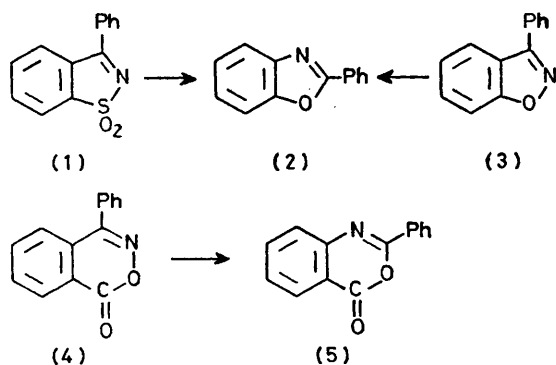
Ring Transpositions in the Pyrolysis of Benzisoxazoles and 2,3-Benzoxazin-1-ones

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Summary On flash vacuum pyrolysis 3-phenylbenzothiazole 1,1-dioxide (1) and 3-phenyl-1,2-benzisoxazole (3) give 2-phenylbenzoxazole (2) and 4-phenyl-2,3-benzoxazin-1-one (4) gives 3-phenyl-2,4-benzoxazin-1-one (5) by reactions involving C-N transposition; however this rearrangement does not occur in the conversion of 1,2,3-benzotriazines into benzazetes.

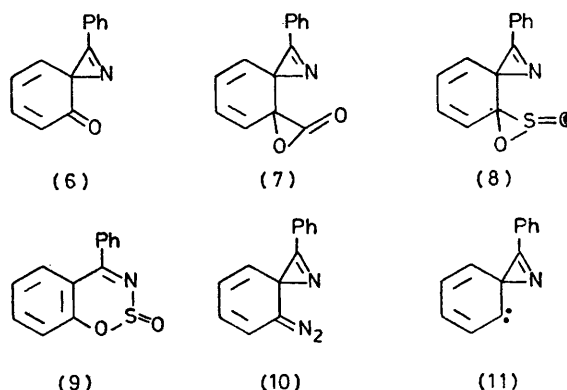
ABRAMOVITCH and WAKE recently reported the formation of benzoxazoles (2) in the flash vacuum pyrolysis of 3-aryl-1,2-benzisoxazole 1,1-dioxides (1).¹ As part of our systematic search for routes to benzazetes we have also studied this pyrolysis in the hope that extrusion of SO₂ would lead to the benzazete. Our pyrolyses were carried out at lower pressure (0.1–1 Torr) but our findings agree with those of Abramovitch and Wake, the major product at 800 °C being the benzoxazole (2). Furthermore we have established that under these pyrolysis conditions 3-phenyl-1,2-benzisoxazole (3) is transformed in 80% yield into the benzoxazole (2).



In both of these reactions interchange of C and N in the benzo-fused heterocycle has taken place. The generality of this type of scrambling process is further revealed in the

pyrolysis of the 2,3-benzoxazin-1-one (4), again a potential benzazete precursor. At 625 °C, biphenylene (7%)[†] is produced by complete fragmentation to give benzyne, and unchanged oxazinone (60%) is recovered. However, in addition the isomeric 2,4-benzoxazin-1-one (5) is also formed (11%).

The conversion of the benzisoxazole (3) into the benzoxazole (2) most reasonably involves the azirine intermediate (6). Analogous intermediates have been proposed for the thermal rearrangement of unfused isoxazoles to oxazoles;² the additional energy barrier imposed by benzo-fusion can be overcome by means of the flash vacuum pyrolysis technique. The benzoxazinone rearrangement, (4) → (5), could involve the related azirine α -lactone (7)[‡] and the conversion of benzisothiazole dioxides into benzoxazoles can be accounted for by the analogous azirine (not aziridine¹) (8)



which extrudes SO. However alternative mechanisms for the last reaction such as ring expansion to the six-membered heterocycle (9) followed by extrusion are also possible.

Clearly this type of C-N transposition in thermolysis of benzofused heterocycles has some generality and is to be

[†] Biphenylene formation has been reported in the pyrolysis of 4-substituted 2,3-benzoxazin-1-ones but isomerisation to the 2,4-benzoxazin-1-one was not noted; M. P. David and J. F. W. McOmie, *Tetrahedron Letters*, 1973, 1361.

[‡] Alternative mechanisms are possible, for example an intramolecular *syn* Beckmann rearrangement.

expected in other flash vacuum pyrolyses. However it does not occur in the vapour phase pyrolysis of 4-aryl-1,2,3-benzotriazines to give benzazetes³ where azirine intermediates (**10**) and (**11**) are also feasible. 1,2,4-Benzotriazines are not observed in these pyrolyses and a careful search using 6- and 7-methyl-4-phenyl-1,2,3-benzotriazines has

revealed no evidence for C-N scrambling in the benzazetes produced.

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¹ R. A. Abramovitch and S. Wake, *J.C.S. Chem. Comm.*, 1977, 673.

² G. L. Aldous, J. H. Bowie, and M. J. Thompson, *J.C.S. Perkin I*, 1976, 16.

³ B. M. Adger, C. W. Rees, and R. C. Storr, *J.C.S. Perkin I*, 1975, 45.