

Novel Benzyne Additions to the 1,2,5-Thiadiazole and 1,2,5-Selenadiazole Ring Systems

Martin R. Bryce,^a Peter Hanson,^b and John M. Vernon^{*b}

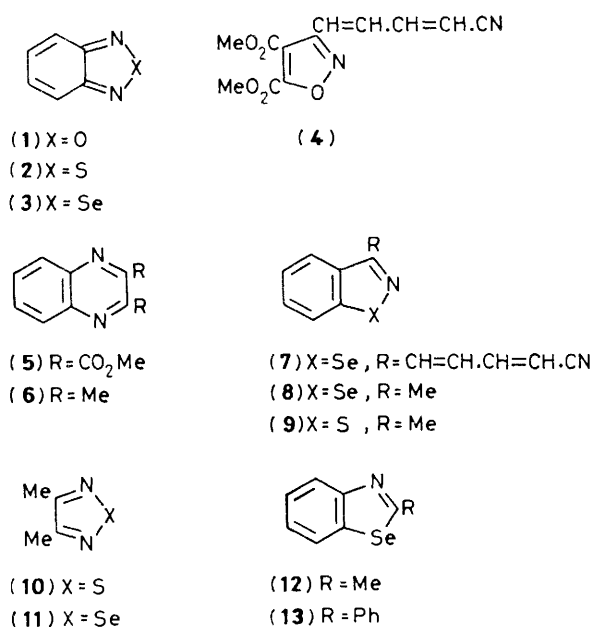
^a Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, U.K.

^b Department of Chemistry, University of York, Heslington, York YO1 5DD, U.K.

Novel modes of benzyne addition to 3,4-dimethyl-1,2,5-thiadiazole and 3,4-dimethyl-1,2,5-selenadiazole afford methyl derivatives of three heterocyclic systems: quinoxaline, 1,2-benzisothiazole, and 1,3-benzoselenazole respectively.

The photochemical addition of dimethyl acetylenedicarbonylate to 2,1,3-benzoxadiazole (1) gives stereoisomeric adducts (4) by trapping of a nitrile oxide intermediate.¹ In contrast, thermal or photochemical reaction of the acetylene-ester with 2,1,3-benzoselenadiazole (3) gives the quinoxaline (5) and selenium, presumably *via* an unusual cycloaddition to the heterocyclic N=C-C=N diene.² 2,1,3-Benzothiadiazole (2) similarly gives (5) but in only trace amounts. Benzyne and (3) afford 1:1 adducts (7) in high yield; they are structurally similar to (4) but their mechanism of formation is quite different.² Again (2) reacts analogously but in low yield. We now report additions of benzyne to the monocyclic systems (10) and (11).

Benzyne (generated from preformed benzenediazonium-2-carboxylate in refluxing tetrahydrofuran) and 3,4-dimethyl-1,2,5-thiadiazole (10) gave four products: 2,3-dimethylquinoxaline (6) (13%), sulphur (19%), 3-methyl-1,2-benzisothiazole (9) (49%), and acetonitrile (53% by g.l.c.). The quinoxaline (6) and sulphur are complementary products presumably derived from attachment of benzyne at both nitrogen atoms of (10) and decomposition of the intermediate adduct. The reluctance of benzyne to add across other heterocyclic N=C-C=N dienes (including 3,4-dimethyl-1,2,5-oxadiazole) has been clearly shown;³ the only reported



case is reaction with 2-methylbenzotriazole to give phenazine.² The other products, (9) and acetonitrile, are also complementary and correspond to the heterocyclic and nitrile parts of adduct (7), respectively. Their formation can be rationalised by initial attack of benzyne at the sulphur atom of (10), in accord with the mechanism proposed previously.²

The corresponding products to be expected from benzyne and 3,4-dimethyl-1,2,5-selenadiazole (11) are acetonitrile and 3-methyl-1,2-benzisoselenazole (8). However, instead of the latter product, the isomeric 2-methyl-1,3-benzoselenazole (12) (2%) was isolated from a tarry mixture, and acetonitrile (7%) was detected by g.l.c. Identification of the unexpected product (12) was confirmed by an independent synthesis,⁴ and its properties are decisively different from those of its isomer (8).⁵ Similarly 3,4-diphenyl-1,2,5-selenadiazole with benzyne afforded benzonitrile (20% by g.l.c.) and 2-phenyl-1,3-benzoselenazole (13) (1%).

Formation of the 1,3-benzoselenazoles (12) and (13) is the

result of a novel pattern of benzyne addition, as yet unexplained. The difference in behaviour of the closely related heterocycles (10) and (11) towards benzyne is remarkable.

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