

Preparation of Disubstituted 1,2,5-Selenadiazole *N*-Oxides from 1,2-Diketone Dioximes and Diselenium Dichloride. Thermolysis and Photolysis of 2,1,3-Benzoselenadiazole *N*-Oxide

By CHRISTIAN L. PEDERSEN

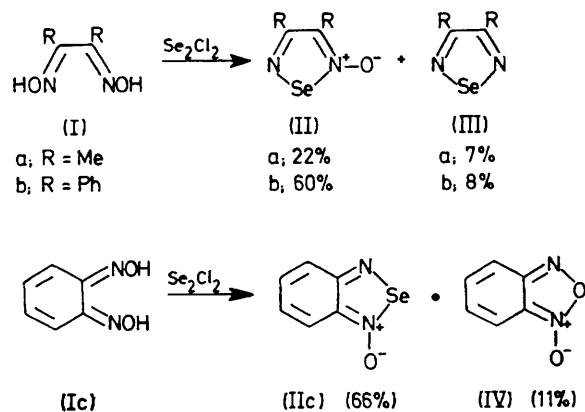
(Department of General and Organic Chemistry, The H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark)

Summary Reaction of 1,2-diketone dioximes with diselenium dichloride in dimethylformamide gives disubstituted 1,2,5-selenadiazole *N*-oxides; the thermal and photochemical behaviour of 2,1,3-benzoselenadiazole *N*-oxide is described.

The only observed by-product from *o*-benzoquinone dioxime (Ic) was benzofuroxan (IV). By contrast, phenylglyoxime merely underwent dehydration to give α -oximinobenzyl cyanide.³ The results are summarized in the Scheme.

1,2,5-Oxadiazole *N*-OXIDES (furoxans) have been intensively investigated,¹ but the corresponding 1,2,5-thiadiazole *N*-oxides were not identified until a few years ago² and have not yet been investigated in detail. The thiadiazole *N*-oxides were prepared in low yields from 1,2-diketone dioximes with either SCl_2 in benzene or S_2Cl_2 in dimethylformamide, so we examined whether this reaction could be extended to preparation of the selenium analogues.

The reactions were performed with a 1 mol. excess of Se_2Cl_2 in dimethylformamide. After 18 h the mixtures were hydrolysed and extracted with chloroform. Compounds (IIa–c) crystallized on concentration. Preparative t.l.c. on silica gel (eluant: benzene–light petroleum–acetone, 7:7:1) of the oily residues gave minor amounts of compounds (IIa–c) and the parent selenadiazoles (IIIa,b).



SCHEME

Compounds (IIa—c) [m.p.s. (uncorr.; decomp.) *ca.* 125°, 131—132°, and 180—182°, respectively] showed satisfactory analytical data and their molecular weights were confirmed by mass spectrometry. In addition, the presence of an *N*-oxide function was established by i.r. spectroscopy⁴ [(IIa) 1350, (IIb) 1345, and (IIc) 1360 cm⁻¹].

Thermolysis of (IIc) in decalin gave two compounds identified as 2,1,3-benzoselenadiazole (51%) and benzofurazan (32%), whereas photolysis[†] in CH₂Cl₂ (10⁻³ M) gave benzofurazan (96%). The thermal degradation is probably

best explained by assuming the existence of two competing pathways, *viz.* reduction of the *N*-oxide to the parent amine⁴ and ring opening followed by reclosure and loss of selenium to give benzofurazan.[‡] A photochemical analogue of the latter pathway obviously dominates in the photolysis of compound (IIc). Light-induced deoxygenation, a common side reaction in the photolysis of aromatic amine *N*-oxides,⁵ was not detected.

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[†] Hanovia Q-700 immersion lamp, with a saturated solution of anthracene in acetone as filter.

[‡] Reversible ring opening to dinitroso-compounds is a well established reaction of furoxans.^{1b}

¹ See for example (a) J. V. R. Kaufman and J. P. Picard, *Chem. Rev.*, 1959, **59**, 429; (b) A. J. Boulton and P. B. Ghosh, *Adv. Heterocyclic Chem.*, 1969, **10**, 1.

² K. Pilgram, *J. Org. Chem.*, 1970, **35**, 1165.

³ A. R. Gagneux and R. Meier, *Helv. Chim. Acta*, 1970, **53**, 1883.

⁴ E. Ochiai, 'Aromatic Amine Oxides,' Elsevier, Amsterdam, 1967, pp. 114, 184.

⁵ G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, 1970, **70**, 231.