942. 3-*Nitro*-o-*phenylenediamines: a New Route*

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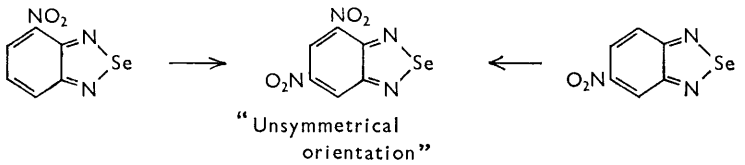
3-Nitro-*o*-phenylenediamine has previously been synthesised by a five-stage method.[1] Boyer and Schoen [2] prepared 3,5-dinitro-*o*-phenylenediamine by reducing 4,6-dinitrobenzofuroxan with hydriodic acid. The ease of preparing 2,1,3-benzoselenadiazoles [3-5] and their nitration at the 4(or 7)-position suggested that the selective reduction of the nitro-derivatives using hydriodic acid would give a simple route to the less accessible 3-nitro-*o*-phenylenediamines. This was found to be so. In earlier work 4-nitro-2,1,3-benzoselenadiazole has been reduced with iron and acetic acid to 4-amino-2,1,3-benzoselenadiazole [4] and with zinc and hydrochloric acid to 1,2,3-triaminobenzene.[6] Recently Brizzi *et al.*[7] obtained 4-nitro-1,2,3-triaminobenzene by treating 4-amino-5-nitro-2,1,3-benzoselenadiazole with hydrogen sulphide.

2,1,3-Benzoselenadiazole on nitration gave 4-nitro-2,1,3-benzoselenadiazole.[4,6] Treatment of the latter with hydriodic acid gave 3-nitro-*o*-phenylenediamine in good yield. Nitration of 5-nitro-2,1,3-benzoselenadiazole was claimed by Cheeseman *et al.*[5] to give the 4,5-dinitro-2,1,3-benzoselendiazole. However, we have found the nitration product to be the 4,6-dinitro-derivative, as this compound on reduction with hydriodic acid gave the known 3,5-dinitro-*o*-phenylenediamine.[2] The alleged structure of 4,5-dinitro-2,1,3-benzoselenadiazole was based on the following results. Firstly, nitration of 4- or 5-nitro-2,1,3-benzoselenadiazole gave the same dinitro-2,1,3-benzoselenadiazole and secondly, the dipole

[1] E. C. Fischer and M. M. Joullie, *J. Org. Chem.*, 1958, **23**, 1944.
[2] J. H. Boyer and W. Schoen, *J. Amer. Chem. Soc.*, 1956, **78**, 423.
[3] O. Hinsberg, *Ber.*, 1889, **22**, 862.
[4] L. S. Efros and Z. V. Todres Selektor, *J. Gen. Chem.* (*U.S.S.R.*), 1957, **27**, 1064.
[5] C. W. Bird, G. W. H. Cheeseman, and A. A. Sarsfield, *J.*, 1963, 4767.
[6] E. Sawicki and A. Carr, *J. Org. Chem.*, 1957, **22**, 503.
[7] C. Brizzi, D. Dal Monte Casoni, and E. Sandri, *Ann. Chim.* (*Italy*), 1964, **54**, 476.

moment of the latter was $3{\cdot}9 \pm 0{\cdot}2$ D, supporting the unsymmetrical orientation. Obviously the structure of the 4,6-isomer agrees with these results:



The 4,6-dinitro-2,1,3-benzoselenadiazole structure has been confirmed as follows. The proton magnetic resonance spectrum of the dinitrobenzoselenadiazole consists of two doublets, of equal intensity, constituting an AB quartet in the low-field aromatic region of the spectrum, the origin positions being at 0·97 and 0·78 τ (for a 10% solution in dimethyl sulphoxide at 38°). The doublet splittings, measured on a scale of 5 mm./c./sec., give $J = 2{\cdot}2$ c./sec. These results show that the two benzene-ring protons are *meta*-orientated and therefore that the nitro-groups in the dinitrobenzoselenadiazole have the 4,6-orientation. The lower-field doublet signal is perceptibly broadened, so this is assigned to H-7, being nearest to a ring nitrogen atom.

4,6-Dinitro-2,1,3-benzothiadiazole can be reduced by the hydrogen iodide method to 3,5-dinitro-*o*-phenylenediamine in lower yield than its selenium analogue.

Experimental.—*3-Nitro-o-phenylenediamine.*[1,8-10] 4-Nitro-2,1,3-benzoselenadiazole [6] (11·4 g., 0·05M) was added to 54% hydriodic acid (*d* 1·7; 125 ml.) and the mixture was heated at 50° for 1½ hr. The cooled mixture was treated with sodium hydrogen sulphite solution to remove iodine and was basified with 30% sodium hydroxide solution. The dark red precipitate was filtered off, washed with water, and dried. Recrystallisation from water (charcoal) gave 3-nitro-*o*-phenylenediamine as bright red needles 5·1 g. (66·7%), m. p. 158—159° (lit.,[9] 159°) (Found: C, 47·05; H, 4·8; N, 27·7. Calc. for $C_6H_7N_3O_2$: C, 47·05; H, 4·6; N, 27·45%).

4,6-Dinitro-2,1,3-benzoselenadiazole. 5-Nitro-2,1,3-benzoselenadiazole [4] (20 g.) was dissolved in concentrated sulphuric acid (160 ml.) and fuming nitric acid (*d* 1·5; 120 ml.) was added. The solution was heated slowly to 90° and, after 15 min., cooled and poured on to crushed ice. The precipitate was filtered off, washed thoroughly with water, dried, and recrystallised from acetic acid to give pale yellow needles of 4,6-dinitro-2,1,3-benzoselenadiazole (17·6 g.), m. p. 211—213° (Found: C, 26·65; H, 1·05; N, 20·7. $C_6H_2N_4O_4Se$ requires C, 26·4; H, 0·75; N, 20·5%).

3,5-Dinitro-o-phenylenediamine.[2,11] This compound was prepared according to the above procedure for 3-nitro-*o*-phenylenediamine using 4,6-dinitro-2,1,3-benzoselenadiazole (6·83 g.) and 54% hydriodic acid (63 ml.). The crude product was recrystallised from acetic acid to give red needles of 3,5-dinitro-*o*-phenylenediamine (3·8 g., 77%), m. p. 214—217° (lit.,[2] 214—215°) (Found: C, 36·5; H, 3·15; O, 32·3. Calc. for $C_6H_6N_4O_4$: C, 36·35; H, 3·05; O, 32·15%).

3,5-Dinitro-o-phenylenediamine. A mixture of 4,6-dinitro-2,1,3-benzothiadazole [12] (19 g.) and 54% hydriodic acid (*d* 1·7; 150 ml.) was heated at 40° for 2 hr., treated with sodium hydrogen sulphite solution to remove iodine, basified with 10% sodium hydroxide solution, and extracted with ether. The ethereal extract was dried (Na_2SO_4) and evaporated, leaving a residue which was recrystallised from acetic acid to give red needles of 3,5-dinitro-*o*-phenylenediamine (5 g., 30%), m. p. 215—217°, identical with the above derivative.

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[8] H. I. X. Mager and W. Berends, *Rec. Trav. chim.*, 1959, **78**, 5.
[9] J. L. Rabinowitz and E. C. Wagner, *J. Amer. Chem. Soc.*, 1951, **73**, 3030.
[10] G. M. van der Want, *Rec. Trav. chim.*, 1948, **67**, 45.
[11] L. Horner, U. Schwenk, and E. Junghanns, *Annalen*, 1953, **579**, 212.
[12] V. G. Pesin, A. M. Khaletskü, and V. A. Sergeev, *Zhur. obshchei Khim.*, 1963, **33**, 1759.