912. 2,1,3-*Benzoselenadiazoles as Intermediates in* o-*Phenylenediamine Synthesis.*

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Substitution and subsequent reduction of 2,1,3-benzoselenadiazoles produces otherwise difficultly accessible *o*-phenylenediamines. For example, halogenation occurs at positions 4 and 7, and sulphonation at position 4. 5-Substituted 2,1,3-benzoselenadiazoles undergo further electrophilic substitution at position 4.

o-Phenylenediamines are important intermediates in heterocyclic synthesis but their preparation is often long and difficult. Although it is convenient to base the preparation of the derivatives on *o*-phenylenediamine itself, this usually leads only to 4-substituted or 4,5-disubstituted products. For example, the nitration of *NN'*-bistoluene-*p*-sulphonyl-*o*-phenylenediamine, followed by hydrolysis, affords 4,5-dinitro-*o*-phenylenediamine, and bromination leads to the 4,5-dibromo-derivative.[1] A route to the difficultly accessible 3-substituted *o*-phenylenediamines was suggested by the formation [2,3] of the 4-nitro-compound on nitration of 2,1,3-benzoselenadiazole, which is readily formed from *o*-phenylenediamine and selenium dioxide. This selenadiazole could be reduced with zinc and hydrochloric acid to 1,2,3-triaminobenzene dihydrochloride,[2] and with iron and acetic acid to, mainly, 4-amino-2,1,3-benzoselenadiazole,[3] which shows the normal reactivity of an aromatic amine [4] and is thus a possible intermediate for numerous *o*-phenylenediamine syntheses. We have investigated further substitution reactions of 2,1,3-benzoselenadiazoles, as well as alternative methods of reductive ring cleavage.

When 2,1,3-benzoselenadiazole was treated with two equivalents of bromine and silver sulphate in sulphuric acid at room temperature, 4,7-dibromo-2,1,3-benzoselenadiazole was obtained. Neither chlorination nor iodination occurred readily at room temperature; at 100° mixtures of 4-chloro- and 4,7-dichloro-2,1,3-benzoselenadiazole and 4-iodo- and 4,7-di-iodo-2,1,3-benzoselenadiazole were formed. 4-Chloro-2,1,3-benzoselenadiazole was converted into the 4,7-dichloro-compound under these conditions. The relatively low yields of chloro- and iodo-derivatives may be due to competitive sulphonation. The infrared spectra of 4,7-dichloro-, 4,7-dibromo-, and 4,7-di-iodo-2,1,3-benzoselenadiazole are closely similar and the presence of adjacent ring hydrogen atoms is revealed by strong absorption at 845, 836, and 829 cm.$^{-1}$, respectively. The structures of the dichloro- and dibromo-compound were confirmed by reduction with stannous chloride and hydrochloric

[1] Cheeseman, *J.*, 1962, 1170.
[2] Sawicki and Carr, *J. Org. Chem.*, 1957, **22**, 503.
[3] Efros and Todres Selektor, *J. Gen. Chem.* (*U.S.S.R.*), 1957, **27**, 1064.
[4] Efros and Todres Selektor, *J. Gen. Chem.* (*U.S.S.R.*), 1957, **27**, 3165.

acid to the known 3,6-dichloro-[5] and 3,6-dibromo-*o*-phenylenediamines.[6] This method of reductive ring cleavage gave better yields of diamine than reduction with zinc and hydrochloric acid. 3,6-Dichloro-*o*-phenylenediamine was converted into 5,8-dichloroquinoxaline for comparison with an authentic specimen, and the dichloro- and dibromo-diamines were further characterised by formation of their 2,3-diphenylquinoxaline derivatives.

2,1,3-Benzoselenadiazole-4-sulphonic acid was readily prepared by heating the benzoselenadiazole with oleum; its sodium salt was reduced with zinc and hydrochloric acid to 2,3-diaminobenzenesulphonic acid. 2,1,3-Benzothiadiazole, a less readily available intermediate, has similarly been converted into 2,3-diaminobenzenesulphonic acid.[7]

Some substitution reactions of 5-methyl-,[8] 5-chloro-,[2] and 5-nitro-2,1,3-benzoselenadiazole [2] were examined since these compounds can be prepared from commercially available *o*-phenylenediamines. All three compounds undergo nitration in the 4-position, and the infrared spectra of the products show strong absorption in the region 828—818 cm.$^{-1}$, attributable to the in-phase, out-of-plane CH bending of the adjacent ring hydrogen atoms at positions 6 and 7. This confirms the structure assigned to the product of nitration of 5-methyl-2,1,3-benzoselenadiazole on ultraviolet spectral evidence.[8] The same dinitro-2,1,3-benzoselenadiazole was obtained from either 4- or 5-nitro-2,1,3-benzoselenadiazole and must therefore be the 4,5-dinitro-derivative; this was further confirmed by its dipole moment (3·9 $\pm$ 0·2 D) which, since the dipole moment of 2,1,3-benzoselenadiazole is 0·94 D,[9] supports the unsymmetrical orientation. As expected, the 4-nitro-compound was less readily nitrated than the isomeric 5-nitro-compound; analogous to this reaction is the vigorous nitration of quinoxaline itself which produces 5,6-dinitroquinoxaline with a small amount of 5-nitroquinoxaline.[10] Chlorination of 5-chloro-2,1,3-benzoselenadiazole in sulphuric acid containing silver sulphate gives a dichloro-derivative which must be 4,5-dichloro-2,1,3-benzoselenadiazole, because it is not identical with the unambiguously synthesised 4,6- and 5,6-dichloro-derivatives, and its infrared spectrum shows the expected strong absorption at 810 cm.$^{-1}$.

The monochloromonomethyl-2,1,3-benzoselenadiazole obtained by warming 3,4-diaminotoluene and selenium dioxide in concentrated hydrochloric acid [11] was thought to be the 5,6-disubstituted compound because preformed 5-methyl-2,1,3-benzoselenadiazole is not chlorinated under these conditions. Infrared measurements confirm that the product is 5-chloro-6-methyl-2,1,3-benzoselenadiazole; it shows strong absorption at 858 cm.$^{-1}$ but no further strong absorptions in the region 850—800 cm.$^{-1}$ characteristic of compounds with adjacent ring hydrogen atoms.

Experimental

Preparation of 2,1,3-*Benzoselenadiazoles from* o-*Phenylenediamines.*—A filtered solution of selenium dioxide (0·011 mole) in water (5 ml.) was added to a solution of the diamine (0·01 mole) in the minimum volume of boiling 96% ethanol. The mixture was boiled for 5—10 min., cooled, and the 2,1,3-benzoselenadiazole filtered off in almost quantitative yield.

4-*Bromo*-2,1,3-*benzoselenadiazole*, from 96% ethanol (30 parts), had m. p. 158—159° (Found: Br, 30·2. $C_6H_3BrN_2Se$ requires Br, 30·5%). 5-*Bromo*-2,1,3-*benzoselenadiazole*, from 96% ethanol (20 parts), had m. p. 132—133° (Found: Br, 30·4%). 4,6-*Dichloro*-2,1,3-*benzoselenadiazole*, from benzene (30 parts), had m. p. 210—211° (Found: C, 28·5; H, 0·9; N, 11·4. $C_6H_2Cl_2N_2Se$ requires C, 28·6; H, 0·8; N, 11·1%). 5,6-Dichloro-2,1,3-benzoselenadiazole, from nitromethane (12 parts), had m. p. 165—166° (Found: C, 28·7; H, 0·7; N, 11·35%).

[5] Macleod, *J. Amer. Chem. Soc.*, 1922, **44**, 2260.
[6] Calhane and Wheeler, *Amer. Chem. J.*, 1899, **22**, 452.
[7] Efros and Levit, *J. Gen. Chem.* (*U.S.S.R.*), 1955, **25**, 183.
[8] Sawicki and Carr, *J. Org. Chem.*, 1958, **23**, 610.
[9] Hill and Sutton, *J. Chim. phys.*, 1949, **46**, 244.
[10] Dewar and Maitlis, *J.*, 1957, 2518.
[11] Hinsberg, *Ber.*, 1890, **23**, 1393.

Bromination of 2,1,3-*Benzoselenadiazole.*—Bromine (3·2 g., 0·02 mole) was added to a solution of 2,1,3-benzoselenadiazole (1·83 g., 0·01 mole) and silver sulphate (3·12 g., 0·01 mole) in concentrated sulphuric acid (20 ml.). The mixture was shaken at room temperature for 1·25 hr., the precipitate of silver bromide filtered off, and the filtrate poured into ice–water. The precipitate, from ethyl acetate (450 ml.), gave 4,7-dibromo-2,1,3-benzoselenadiazole (2·12 g., 62%) as golden yellow needles, m. p. 285—287° (Found: C, 21·4; H, 0·9; Br, 46·9; N, 7·8. $C_6H_2Br_2N_2Se$ requires C, 21·1; H, 0·6; Br, 46·9; N, 8·2%).

Chlorination of 2,1,3-*Benzoselenadiazole.*—Chlorine was passed for 3 hr. through a solution of the benzoselenadiazole (1·83 g., 0·01 mole) and silver sulphate (3·12 g., 0·01 mole) in concentrated sulphuric acid (10 ml.). After cooling, the precipitate of silver chloride was filtered off and the filtrate poured into ice–water. Crystallisation of the precipitate from pyridine–water (2 : 1, 30 ml.) gave 4,7-*dichloro*-2,1,3-*benzoselenadiazole* (0·43 g., 17%), m. p. (mainly) 279—281° (Found: C, 28·7; H, 1·0; N, 11·4. $C_6H_2Cl_2N_2Se$ requires C, 28·6; H, 0·8; N, 11·1%); dilution of the mother-liquor with water (50 ml.) furnished 4-chloro-2,1,3-benzoselenadiazole (0·48 g., 22%), m. p. and mixed m. p. 158—161° (lit.,[4] 161—162°). A mixture of chlorinated products and unchanged 2,1,3-benzoselenadiazole was isolated from a parallel experiment in which only 0·005 mole of silver sulphate was used.

Chlorination of 4-*Chloro*-2,1,3-*benzoselenadiazole.*—Chlorine was passed for 4½ hr. through a solution of 4-chloro-2,1,3-benzoselenadiazole (0·72 g., 0·0033 mole) and silver sulphate (1·04 g., 0·0033 mole) in concentrated sulphuric acid (5 ml.). After cooling of the solution, the precipitate of silver chloride was filtered off, and the filtrate poured into ice–water. The precipitate (0·60 g.) had m. p. (mainly) 255—267°. Lower melting material was removed by sublimation at 140°/0·3 mm.; crystallisation of the residue from toluene (25 ml.) then gave 4,7-dichloro-2,1,3-benzoselenadiazole (0·22 g.), m. p. 273—276°, raised on admixture with an authentic specimen.

Chlorination of 5-*Chloro*-2,1,3-*benzoselenadiazole.*—The chlorination of the 5-chloro-compound (0·01 mole) was carried out similarly to the chlorination of the 4-chloro-compound. The product, 4,5-*dichloro*-2,1,3-*benzoselenadiazole* (0·75 g., 30%), had m. p. 204—215° (from benzene, 25 ml.), raised to 222—223° by successive crystallisation from ethanol (140 parts) and benzene (30 parts) (Found: C, 28·9; H, 1·1; N, 11·3%). Fractional sublimation of the benzene-soluble material yielded unchanged 5-chloro-2,1,3-benzoselenadiazole.

Iodination of 2,1,3-*Benzoselenadiazole.*—Powdered iodine (15·2 g., 0·06 mole) was added to a stirred solution of 2,1,3-benzoselenadiazole (3·66 g., 0·02 mole) and silver sulphate (9·36 g., 0·03 mole) in concentrated sulphuric acid (20 ml.). The mixture was stirred, heated at 105° for 3 hr., and then cooled, the precipitate of silver iodide filtered off, and the filtrate poured into ice–water. The precipitate was triturated with 2N-ammonium hydroxide and dried. Fractional sublimation of the residue (3·74 g.) at 0·3 mm. gave (a) unchanged 2,1,3-benzoselenadiazole (0·25 g.), m. p. 65—70°, (b) a fraction consisting mainly of 4-*iodo*-2,1,3-*benzoselenadiazole*, and (c) a residue containing 4,7-*di-iodo*-2,1,3-*benzoselenadiazole*. The 4-iodo-derivative (0·65 g., 11%), m. p. 148—151°, crystallised from a light petroleum (b. p. 60—80°) extract of the fraction from (b), and yellow needles of unchanged m. p. were obtained by further crystallisation from this solvent (50 parts) (Found: C, 23·0; H, 1·1. $C_6H_3IN_2Se$ requires C, 23·3; H, 1·0%). The infrared spectrum of 4-iodo-2,1,3-benzoselenadiazole was closely similar to that of the 4-chloro- and the 4-bromo-derivative. Soxhlet extraction of the fraction from (c) with ethyl acetate gave 4,7-di-iodo-2,1,3-benzoselenadiazole (0·88 g., 10%), golden yellow needles (from xylene, 120 parts), m. p. *ca.* 283—284° (Found: C, 17·2, 17·2; H, 0·5, 0·6; N, 6·3. $C_6H_2I_2N_2Se$ requires C, 16·6; H, 0·5; N, 6·4%).

3,6-*Dibromo*-o-*phenylenediamine.*—4,7-Dibromo-2,1,3-benzoselenadiazole (3·4 g., 0·01 mole) and stannous chloride dihydrate (4·5 g., 0·02 mole) were ground together in a mortar, then added gradually with stirring to concentrated hydrochloric acid (40 ml.). The mixture was heated, stirred at 70° for 2 hr., and then cooled, and the crystalline complex filtered off and decomposed with 50% sodium hydroxide solution. Crystallisation of the precipitate from 30% ethanol (70 ml.) gave 3,6-dibromo-*o*-phenylenediamine (2·04 g., 77%), m. p. 96—98° (lit.,[6] 94—95°). Treatment with benzil in ethanolic solution gave 5,8-*dibromo*-2,3-*diphenylquinoxaline*, m. p. 221—223° (from cyclohexane, 50 parts, or ethanol, 20 parts) (Found: C, 54·6; H, 2·6; N, 6·6. $C_{20}H_{12}Br_2N_2$ requires C, 54·6; H, 2·7; N, 6·4%).

3,6-*Dichloro*-o-*phenylenediamine.*—4,7-Dichloro-2,1,3-benzoselenadiazole was reduced similarly to the 4,7-dibromo-compound. The crude product was obtained in 90% yield and

gave the dichloro-diamine as needles, m. p. 96—98° (from aqueous ethanol) (lit.,[5] 98°). Treatment of the diamine with aqueous glyoxal sodium bisulphite gave 5,8-dichloroquinoxaline, m. p. and mixed m. p. 209—210°, and treatment with benzil in ethanolic solution gave 5,8-dichloro-2,3-diphenylquinoxaline, m. p. 218—219° (lit.,[5] 214°).

Sulphonation of 2,1,3-*Benzoselenadiazole*.—2,1,3-Benzoselenadiazole (2 g.) was heated in oleum (16 ml.; *d* 1·92) at 150—160° for 1 hr. The solution was cooled, poured slowly into cold water (200 ml.), and partially neutralised with sodium hydrogen carbonate (24 g.); sodium chloride (15 g.) was added and dissolved by heating. Crystallisation commenced immediately and after several hours *sodium* 2,1,3-*benzoselenadiazole*-4-*sulphonate* (2·6 g., 83%) was filtered off. A specimen was recrystallised from ethanol (Found: N, 9·8. $C_6H_3N_2NaO_3SSe$ requires N, 9·8%)

2,3-*Diaminobenzenesulphonic Acid*.—Sodium 2,1,3-benzoselenadiazole-4-sulphonate (2·5 g.) was dissolved in water (10 ml.) and concentrated hydrochloric acid (1·5 ml.), zinc dust (5 g.) was added portionwise, and the mixture was heated on the steam-bath for 1 hr., and filtered hot. Addition of concentrated hydrochloric acid (20 ml.) to the filtrate produced crystals of 2,3-diaminobenzenesulphonic acid (1·3 g., 79%), m. p. 275—277° (from water, 20 ml.) (lit.,[7] 276—278°) (Found: C, 38·2; H, 4·0; N, 14·8. Calc. for $C_6H_7N_2O_3S$: C, 38·5; H, 3·7; N, 15·0%).

Nitration of 5-*Chloro*-2,1,3-*benzoselenadiazole*.—The 5-chloro-compound (1 g.) in sulphuric acid (15 ml.) at 10° was treated with a mixture of concentrated nitric (1 ml.) and sulphuric acid (2 ml.). After 1 hr. the solution was poured on to ice and the yellow product filtered off. 5-*Chloro*-4-*nitro*-2,1,3-*benzoselenadiazole* (0·93 g., 77%) had m. p. 230—232° (from benzene, 50 ml.) (Found: C, 27·4; H, 0·84; N, 16·4. $C_6H_2ClN_3O_2Se$ requires C, 27·4; H, 0·76; N, 16·0%).

Nitration of 5-*Nitro*-2,1,3-*benzoselenadiazole*.—The 5-nitro-compound (1 g.) was dissolved in concentrated sulphuric acid (8 ml.) and fuming nitric acid (6 ml.) added. Gentle warming on the steam-bath resulted in an immediate colour change from red to yellow and the reaction was completed by warming for a further 15 min. The solution was cooled, and then poured into water, and the product was filtered off. 4,5-*Dinitro*-2,1,3-*benzoselenadiazole* (0·95 g., 79%) had m. p. 210—213° (from benzene, 60 ml.) (Found: C, 26·6; H, 0·65; N, 20·9. $C_6H_2N_4O_4Se$ requires C, 26·4; H, 0·73; N, 20·5%). The dipole moment in benzene at 25°, for a solution containing 0·000823 mole fraction of the compound, was 3·9 ± 0·2 D.

Nitration of 4-*Nitro*-2,1,3-*benzoselenadiazole*.—The 4-nitro-compound [2] (1 g.) was nitrated as for the 5-nitro-isomer. The colour change was not so rapid, and the mixture was heated on the steam-bath for 1 hr. The product was chromatographed on silica gel in benzene. Elution with benzene produced (a) 4,5-dinitro-2,1,3-benzoselenadiazole (0·29 g.), (b) a mixture (0·21 g.) of mainly 4,5-dinitro- with some 4-nitro-2,1,3-benzoselenadiazole, and (c) 4-nitro-2,1,3-benzoselenadiazole (0·1 g.).

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