INVESTIGATIONS IN THE FIELD OF 2,1,3-THIADIAZOLE AND 2,1,3-SELENADIAZOLE

L. The Nitration of Benzo-2,1,3-Selenadiazole and its Derivatives*

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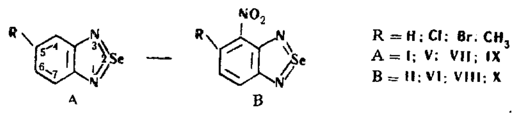
Benzo-2,1,3-selenadiazole and its derivatives readily undergo nitration with sodium nitrate in concentrated sulfuric acid with the formation, usually in high yield, of the corresponding mononitro and dinitro derivatives. The initial benzo-2,1,3-selenadiazoles were synthesized from selenium dioxide and o-diamines. The latter were obtained by reducing o-nitroaniline with sodium dithionite or by the reductive cleavage of the corresponding derivatives of benzo-2,1,3-thiadiazole.

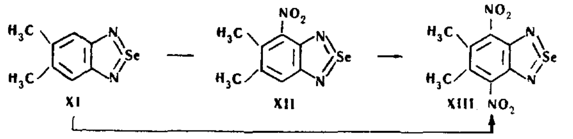
The nitration of benzo-2,1,3-selenadiazole (I) and its derivatives with a mixture of sodium nitrate and concentrated sulfuric acid has not been reported in the literature. Nevertheless, this method enables two nitro groups to be introduced simultaneously into the o- and p-positions of the benzene ring in some cases. This method is of considerable preparative advantage in working with small amounts of the starting materials.

In the present paper we give data on the nitration of compound I and some of its derivatives.

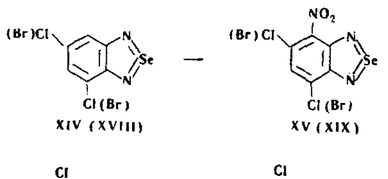
The nitration of compound I with an equimolecular amount of sodium nitrate in concentrated sulfuric acid gave 4-nitrobenzo-2,1,3-selenadiazole (II) in high yield [1,2]. Under similar conditions, 4-chloro- (III), 5-chloro- (IV), 5-bromo- (VII), and 5-methylbenzo-2,1,3-selenadiazoles (IX) gave high yields of, respectively, 4-chloro-7-nitro- (IV), 5-chloro-4-nitro- (VI) [4], 5-bromo-4-nitro- (VIII) [6], and 5-methyl-4-nitrobenzo-2,1,3-selenadiazoles (X) [3,5].

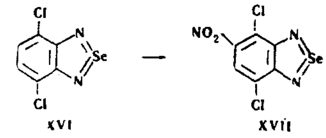


When the nitration of disubstituted benzoselenadiazoles was carried out, the influence of the nature of the substituent was shown. Thus, in the nitration of 5,6-dimethylbenzo-2,1,3-selenadiazole (XI) under the conditions customary for aromatic compounds, a 98% yield of 5,6-dimethyl-4-nitrobenzo-2,1,3-selenadiazole (XII) was formed. The action on the latter of a mixture of sodium nitrate and concentrated sulfuric acid gave an 81% yield of 5,6-dimethyl-4,7-dinitrobenzo-2,1,3-selenadiazole (XIII). Compound XIII can be obtained directly from XI by nitration with a mixture of sodium nitrate and concentrated sulfuric acid.

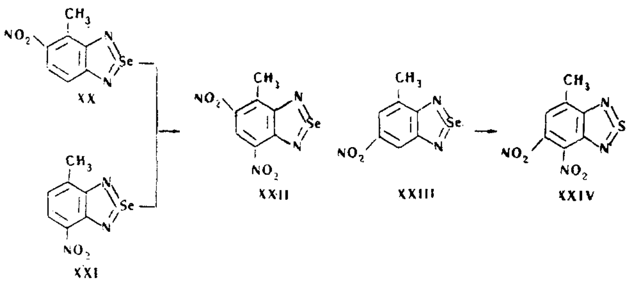


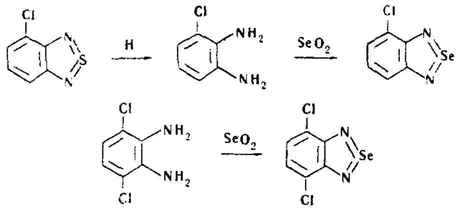
Under similar conditions, 4,6-dichloro- (XIV), 4,7-dichloro- (XVI), and 4,6-dibromobenzo-2,1,3-selenadiazoles (XVIII) formed, respectively, 4,6-dichloro-7-nitro- (XV), 4,7-dichloro-5-nitro- (XVIII), and 4,6-dibromo-7-nitrobenzo-2,1,3-selenadiazoles (XIX). It was impossible to introduce a second nitro group on further nitration.





The nitration of 4-methyl-5-nitrobenzo-2,1,3-selenadiazole (XX) and 4-methyl-7-nitrobenzo-2,1,3-selenadiazole (XXI) yielded 4-methyl-5,7-dinitrobenzo-2,1,3-selenadiazole (XXII). Under similar conditions, 4-methyl-6-nitrobenzo-2,1,3-selenadiazole (XXIII) formed, mainly, 7-methyl-4,5-dinitrobenzo-2,1,3-selenadiazole (XXIV). It was impossible to introduce a second nitro group. It was also impossible to nitrate 5-bromo-4-nitro- and 5-methyl-4-nitrobenzo-2,1,3-selenadiazoles under these conditions.





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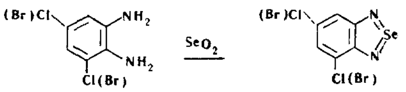
*For part XLIX, see [14].

Nitration with Sodium Nitrate in Concentrated Sulfuric Acid

Amount of compound (A), g	Amount of sodium nitrate, g (amount of concentrated H_2SO_4, g)	Amount of compound (B), g	Mp, • C (solvent for crystallization), color of the crystals	Empirical formula	N, % found	N, % calculated	Yield, %
I; 1.83	0.85 (9.2)	II; 1.80	220—221 (toluene), yellow				83.3
IX; 1.97	0.85 (9.2)	X; 2.32	192—194 (toluene), yellow				96.3
XI; 2.11	0.85 (9.2)	XII; 2.30	223—224 (acetic acid), yellow	$C_8H_7N_3O_2Se$	16.47; 16.80	16.41	80.9
XI; 2.11	2.00 (18.4)	XIII; 2.40	360 (acetic acid), yellow	$C_8H_6N_4O_4Se$	18.33; 18.47	18.60	73.0
XII; 4.00	3.20 (22.1)	XIII; 3.43					73.0
VII; 2.62	0.85 (9.2)	VIII; 2.90	226—230 (280[6]) (toluene), yellow	$C_6H_2BrN_3O_2Se$[1*]	14.19; 14.74	16.03	94.5
V; 0.54	0.21 (2.3)	VI; 0.60	230—232 (toluene), yellow				90.9
III; 0.54	0.21 (2.3)	IV; 0.65	269—270 (glycol), yellow	$C_6H_2ClN_3O_2Se$[2*]	16.69; 16.89	16.00	99.1
XIV; 0.50	0.25 (3.7)	XV; 0.57	202—203 (acetic acid), colorless	$C_6HCl_2N_3O_2Se$[3*]	14.00; 14.20	14.14	95.0
XVI; 0.80	1.40 (5.5)	XVII; 0.71	219—220 (acetic acid), colorless	$C_6HCl_2N_3O_2Se$[4*]	15.47; 15.50	14.14	75.0
XVIII; 3.41	0.25 (9.2)	XIX; 3.32	228—230 (acetic acid), light brown	$C_6HBr_2N_3O_2Se$[5*]	10.48; 10.49	10.88	86.0
XX; 1.80	1.50 (9.2)	XXII; 1.68	148—149 (acetic acid + water) (1:1), yellow	$C_7H_4N_4O_4Se$	18.90; 19.10	19.51	80.0
XXI; 1.80	1.50 (9.2)	XXII; 1.47					70.0
XXIII; 1.80	1.50 (9.2)	XXIV; 1.64	156—157 (acetic acid), bright yellow	$C_7H_4N_4O_4Se$	19.12; 19.61	19.51	78.0

[1*] Studied in more detail.
[2*] Found, %: Cl 13.22; 12.98%. Calculated, %: Cl 13.52%.
[3*] Found, %: Cl 23.88: 24.05%. Calculated Cl 23.91%.
[4*] Found, %: Cl 23.30; 23.46%. Calculated Cl 23.91%.
[5*] Found, %: Br 41.44%. Calculated Br 41.43%.



The starting materials for this study, derivatives of benzo-2,1,3-selenadiazole, were obtained by the reaction of selenium dioxide with the corresponding o-diamines [7].

5-Chloro-, 5-bromo-, 5-methyl-, 4-methyl-5-nitro-, 4-methyl-6-nitro-, and 4-methyl-7-nitrobenzo-2,1,3-selenadiazoles were obtained by published methods [4–6].

EXPERIMENTAL

Nitration with sodium nitrate in concentrated sulfuric acid. Sodium nitrate was added in portions to a hot solution of benzo-2, 1, 3-selenadiazole (A) in concentrated sulfuric acid at such a rate that the temperature of the reaction mixture did not exceed 100° C. The reaction product was kept at 100° C for 5 min, cooled, and poured onto ice. The precipitate of nitrobenzoselenadiazole (B) that deposited was filtered off, washed with water, dried, and crystallized from a suitable solvent (see table).

4-Chlorobenzo-2, 1, 3-selenadiazole (III). A mixture of 1 g of 4-chlorobenzo-2, 1, 3-thiadiazole [8, 9], 4 g of stannous chloride dihydrate, and 30 ml of hydrochloric acid (d 1. 19) was boiled with stirring until a solution had been formed (2 hr), and then the mass was evaporated to dryness, made alkaline with 10% sodium hydroxide solution, and extracted with dichloroethane. After the solvent had been distilled off, 0.65 g (81%) of 1, 2-diamino-3-chlorobenzene was obtained in the form of a dark brown oily liquid which crystallized on standing at 0° C; mp ~32° C. The crystalline mass was dissolved in 13 ml of 50% ethanol, 0. 65 g of selenium dioxide in 5 ml of 50% ethanol was added, the mixture was diluted with water, and the white precipitate that deposited was filtered off and washed with water. Yield 0. 98 g (98%); mp 160°–162° C. Literature data [4, 10]: mp 158°–161° C.

4, 6-Dichlorobenzo-2, 1, 3-selenadiazole (XIV). A solution of 4 g of selenium dioxide in 30 ml of 70% acetic acid was added to a solution of 5.9 g of 1, 2-diamino-3, 5-dichlorobenzene [13] in 30 ml of 70% acetic acid. The precipitate that deposited was filtered off and washed successively with a small amount of acetic acid and with water. The yield was quantitative. After crystallization from acetic acid it formed crystals with mp 205.5–206° C. Literature data |4|: mp 210–210°-211° C. Found, %: Cl 28.30; 28.19; N 10.80; 10.87%. Calculated for $C_6H_2Cl_2N_2Se$, %: Cl 28. 17; N 11. 11%.

4, 7-Dichlorobenzo-2, 1, 3-selenadiazole (XVI). This was obtained similarly to the preceding compound XIV from 0. 59 g of 1, 2-diamino-3, 6-dichlorobenzene [11] in 30 ml of 33% acetic acid and 0.4 g of selenium dioxide in 5 ml of water. The yield was quantitative. White crystals with mp 271°–272° C, sparingly soluble in water, more soluble in hot acetic acid. According to the literature [4]: mp 279°– 281° C. Found, %: Cl 27.78; 27.97; N 10.91; 10.89%. Calculated for $C_6H_2Cl_2N_2Se$, %: Cl 28.17; N 11.11%.

4, 6-Dibromobenzo-2, 1, 3-selenadiazole (XVIII). This was obtained similarly to XIV from 2.3 g of 1, 2-diamino-3, 5-dibromobenzene [12] in 10 ml of acetic acid and 1 g of selenium dioxide in 6 ml of 50% acetic acid. Yield 2.4 g (81.3%). White crystals with mp 217°–218° C (from ethanol), sparingly soluble in water, readily soluble in hot acetic acid. Found, %: Br 46.83; 46.75; N 8.58; 8.33%. Calculated for $C_6H_2Br_2N_2Se$, %: Br 46.92; N 8.21%.

5, 6-Dimethylbenzo-2, 1, 3-selenadiazole (XI). This was obtained similarly to XIV from 6.8 g of 1, 2-diamino-4, 5-dimethylbenzene in 20 ml of acetic acid and 6 g of selenium dioxide in 20 ml of water. Yield 8.8 g (83.4%). White crystals with mp 143°–144° C (from ethanol) readily soluble in acetic acid, sparingly soluble in water. Found, %: N 13.31, 13.53. Calculated for $C_8H_8N_2Se$, %: N 13.27.

5, 6-Dimethyl-4-nitrobenzo-2, 1, 3-selenadiazole (XII). With stirring, a mixture of 1 ml of nitric acid (d 1.52) and 2 ml of concentrated sulfuric acid was added dropwise to a solution of 1.7 g of XI in 10 ml of concentrated sulfuric acid at 0°–5° C, after which the mass was stirred at the given temperature for 30 min and at 20° C for another 30 min. Then it was poured onto ice and the precipitate that deposited was filtered off and washed with water. Yield 2.02 g (98%). After crystallization from acetic acid, bright yellow crystals with mp 223°–224° C.

4, 6-Dibromo-7-nitrobenzo-2, 1, 3-Selenadiazole (XIX). Similarly (compare the preparation of compound XII), 1.8 g of XVIII, 1 ml of nitric acid (d 1.52) and 12 ml of sulfuric acid (d 1.84) gave 1.38 g (67.5%) of substance. After crystallization from acetic acid, it formed light brown crystals with mp 228°–230° C.

4, 6-Dichloro-7-nitro-2, 1, 3-selenadiazole (XV). Similarly (see above) 2.52 g of XIV yielded 2.82 g (95%) of substance. After crystallization from acetic acid, colorless crystals with mp 202°–203° C.

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