INVESTIGATIONS OF 2,1,3-THIA- AND SELENADIAZOLES

LXVI.* AMINATION OF BENZO-2,1,3-SELENADIAZOLE AND ITS METHYL DERIVATIVES WITH HYDROXYLAMINE SULFATE IN CONCENTRATED SULFURIC ACID

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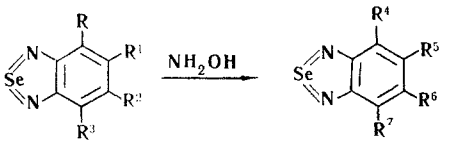
All of the possible isomeric monoaminobenzo-2,1,3-selenadiazoles are formed in the reaction of benzo-2,1,3-selenadizaole 4- or 5-methyl-, or 5,6-dimethylbenzo 2,1,3-selenadiazoles with hydroxylaminesulfate in concentrated sulfuric acid.

It has been previously shown [1, 2] that all of the possible isomeric monoaminobenzo-2,1,3-thiadiazoles are formed in the reaction of benzo-2,1,3-thiadiazole and its methyl derivatives with hydroxylamine sulfate in concentrated sulfuric acid (Turskii reaction).

In the present paper, we present the results of a study of the behavior of benzo-2,1,3-selenadiazole (I), and 4-methyl (IV), 5-methyl- (VIII), and 5,6-dimethylbenzo-2,1,3-selenadiazole (XII) under the conditions of the Turskii reaction in the presence of vanadium pentoxide as the catalyst.

When equimolecular amounts of I and hydroxylamine sulfate are heated at 100°C for 5 h, 4-amino- (II) and 5-aminobenzo-2,1,3-selenadiazoles (III) are isolated in almost equal amounts. Under similar conditions, IV forms 4-methyl-5-amino- (V), 4-methyl-6-amino- (VI), and 4-methyl-7-aminobenzo-2,1,3-selenadiazoles (VII), while VIII gives 5-methyl-6-amino- (IX), 5-methyl-4-amino- (X), and 4-amino-6-methylbenzo-2,1,3-selenadiazoles (XI). The amination of XII gives 5,6-dimethyl-4-aminobenzo-2,1,3-selenadiazole (XIII) (see Table 1).



I $R=R^1=R^2=R^3=H$

II $R^5=R^6=R^7=H$, $R^4=NH_2$
III $R^4=R^6=R^7=H$, $R^5=NH_2$

IV $R^1=R^2=R^3=H$, $R=CH_3$

V $R^6=R^7=H$, $R^4=CH_3$, $R^5=NH_2$
VI $R^5=R^7=H$, $R^4=CH_3$, $R^6=NH_2$
VII $R^5=R^6=H$, $R^4=CH_3$, $R^7=NH_2$

VIII $R=R^2=R^3=H$, $R^1=CH_3$

IX $R^4=R^7=H$, $R^5=CH_3$, $R^6=NH_2$
X $R^6=R^7=H$, $R^5=CH_3$, $R^4=NH_2$
XI $R^4=R^6=H$, $R^5=CH_3$, $R^7=NH_2$

XII $R=R^3=H$, $R^1=R^2=CH_3$

XIII $R^7=H$, $R^5=R^6=CH_3$, $R^4=NH_2$

*See [1] for communication LXV.

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TABLE 1. Aminobenzo-2,1,3-selenadiazoles

Start. benzo-2,1,3-selenadiazole	Chromatogram zones	Amine	Mp, °C	Yield, %
I	Upper, yellow	III	149—150[3]	25
	Lower, red	II	159—160[3, 4]	23
IV	Upper, light-yellow	V	166—167[5]	24
	Middle, light-yellow	VI*	192—193	14
	Lower, red	VII	132—133[5]	17
VIII	Upper, yellow-green	IX†	185—187[5]	9
	Lower, red‡	X+XI	90—110	37
XII	Red	XIII**	150—152	36

* The acetyl derivative was obtained as light-yellow crystals with mp 235-236° (from butanol). Found: N 16.8; 17.0%. $C_9H_9N_3OSe$. Calculated: N 16.5%.

† The acetyl derivative was obtained as gray crystals with mp 229-231°. Found: N 17.0; 17.0%. $C_9H_9N_3OSe$. Calculated: N 16.5%.

‡ Contains a mixture of X and XI, which were separated as the acetyl derivatives (see the Experimental section).

** Found: N 18.8; 18.9%. $C_8H_9N_3Se$. Calculated: N 18.6%. The acetyl derivative was obtained as light-yellow crystals with mp 231-233°. Found: N 15.5; 15.7%. $C_{10}H_{11}N_3OSe$. Calculated: N 15.7%.

All of the amines, except for X and XI, were separated by means of adsorption chromatography on aluminum oxide. Compounds X and XI were separated by means of chromatography as acetyl derivatives XIV and XV, respectively. The structures of the amines and their acetyl derivatives were proved by comparison of them with known substances and also by alternative synthesis.

EXPERIMENTAL

Benzo-2,1,3-selenadiazole (I). The reaction of 2.06 g (0.01 mole) of o-phenylenediamine sulfate in 20 ml of hot water and 1.63 g (0.01 mole) of ammonium selenite in 20 ml of water gave 1.55 g (85%) of a substance with mp 74-76° (see [7]).

4-Methylbenzo-2,1,3-selenadiazole (IV). The reaction of 3.1 g (0.025 mole) of 3-methyl-1,2-phenylenediamine in 30% of hot alcohol and 3.2 g (0.025 mole) of selenous acid in 10 ml of water gave 4.75 g (96%) of a substance with mp 110-111° (see [5]).

5-Methylbenzo-2,1,3-selenadiazole (VIII). This compound was similarly obtained in 95% yield and had mp 72-73° (see [5]).

5,6-Dimethylbenzo-2,1,3-selenadiazole (XII). The reaction of 13.6 g (0.1 mole) of 4,5-dimethyl-1,2-phenylenediamine in 40 ml of hot acetic acid and 12.9 g (0.1 mole) of selenous acid in 80 ml of 50% acetic acid gave 17.4 g (82%) of a substance with mp 143-144° (see [8]).

Amination. Hydroxylamine sulfate (0.0033 mole) and 0.02 g of vanadium pentoxide* were added at 100° to a solution of 0.0033 mole of the appropriate benzo-2,1,3-selenadiazole in 10 ml of concentrated sulfuric acid. The mass was stirred at this temperature for 5 h, cooled, and poured with stirring into 100 ml of water. The aqueous mixture was made alkaline in the cold with 20% sodium hydroxide solution and extracted with 300-600 ml of carbon tetrachloride in 20-ml portions. The combined extracts were dried with anhydrous sodium sulfate and passed through a column filled with activated aluminum oxide. (A mixture of 100 g of activity II aluminum oxide and 3 ml of water was used.) Carbon tetrachloride was then passed through the column until colored zones appeared; the contents of the column were extracted, and the zones were separated and eluted with acetone. The amines (Table 1) obtained after evaporation of the eluates did not depress the melting points of authentic samples.

Acetylation of a Mixture of Amines X and XI with mp 90-110°. A mixture of the amines was heated for 1-2 min with excess acetic anhydride on a boiling-water bath until a clear solution was obtained. A fivefold volume of water was added, and the mixture was exaporated to dryness with stirring. The residue (0.29 g) was dissolved in benzene and passed through a column filled with activated aluminum oxide. Ben-

* The yields of the amines were insignificant when vanadium pentoxide was not present.

zene was then passed through the column until colored zones appeared. The upper (yellow-green) and lower (yellow) zones were separated and eluted with acetone, and the eluates were evaporated to dryness. The yellow zone yielded 0.1 g of XIV as a pale-yellow powder with mp 221-221.5° (224-224.8°) [5]. Found: N 16.5, 16.8%. $C_9H_9N_3OSe$. Calculated: N 16.5%. The yellow zone yielded 0.15 g of yellow crystals with mp 211-212° that did not depress the melting point of XV obtained by alternative synthesis (see below).

Hydrolysis of XIV and XV. Acetyl derivatives XIV and XV were refluxed for 10 min with 5-10 ml of 20% sodium hydroxide solution. The mixtures were cooled, and the resulting crystals were removed by filtration, washed with water, dried, and dissolved in carbon tetrachloride. The carbon tetrachloride solutions were passed through a column filled with activated aluminum oxide. The red zone was separated and and eluted with acetone. The eluate was evaporated to dryness to give X or XI, respectively, with mp 125° (124-125°) [5] or 134-135°. Compound XI did not depress the melting point of a sample obtained by alternative synthesis (see below).

4-Amino-6-methylbenzo-2,1,3-selenadiazole (XI). A 3.9-g (0.02 mole) sample of 3,5-dinitro-4-aminotoluene [9] was added at 60° to a mixture of 35 g of stannous chloride dihydrate and 75 ml of hydrochloric acid (sp. gr. 1.19). The mixture was refluxed for 5 min, and the resulting dark solution was evaporated to dryness on a boiling-water bath. The residue was dissolved in water, and the aqueous solution was made alkaline with 20% sodium hydroxide solution and extracted with ether (five 100-ml portions). The ether extracts were dried with sodium sulfate, and the ether was removed to give 1 g (37%) of 3,4,5-triaminotoluene as a dark-brown powder with mp 94-96°, which was used without additional purification to obtain XI.

A solution of 0.43 g (0.003 mole) of selenous acid in 3 ml of water was added with stirring to a solution of 0.46 g (0.003 mole) of 3,4,5-triaminotoluene in 3 ml of warm alcohol, and the mixture was made alkaline with 20% sodium hydroxide solution. The resulting reddish-yellow crystals were removed by filtration, washed with water, dried (.063 g), and dissolved in carbon tetrachloride. The carbon tetrachloride solution was passed through a column filled with activated aluminum oxide. Carbon tetrachloride was then passed through the column until colored zones appeared. The red zone was separated and eluted with acetone, and the elutate was evaporated to dryness to give 0.31 g (44%) of orange crystals that were readily soluble in most organic solvents and less soluble in water. Found: N 19.9, 20.2%. $C_7H_7N_3Se$. Calculated: N 19.8%. The acetyl derivative (XV) was obtained as yellow crystals with mp 211-212°. Found: N 16.9, 17.0%. $C_9H_9N_3OSe$. Calculated: N 16.5%.

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