Russian Journal of Organic Chemistry, Vol. 39, No. 2, 2003, pp. 284–286. Translated from Zhurnal Organicheskoi Khimii, Vol. 39, No. 2, 2003, pp. 306–308.

SHORT COMMUNICATIONS

4-(2-Aminophenyl)-1,2,3-thia- and -selenadiazoles as a Source of 2-Indolechalcogenolates

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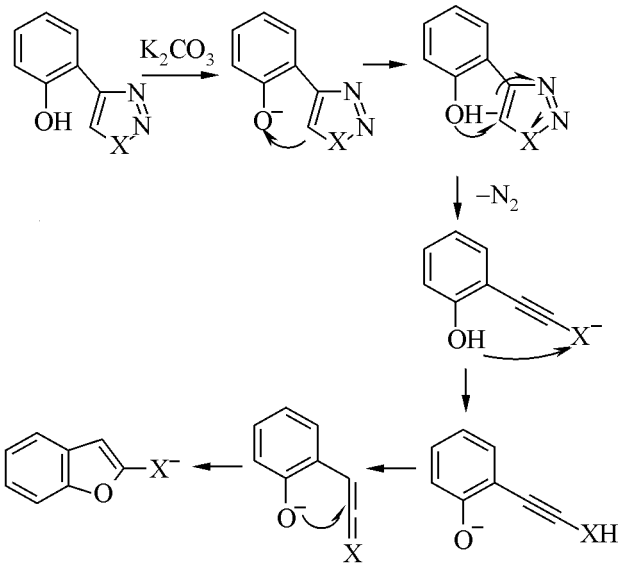
Received November 6, 2002

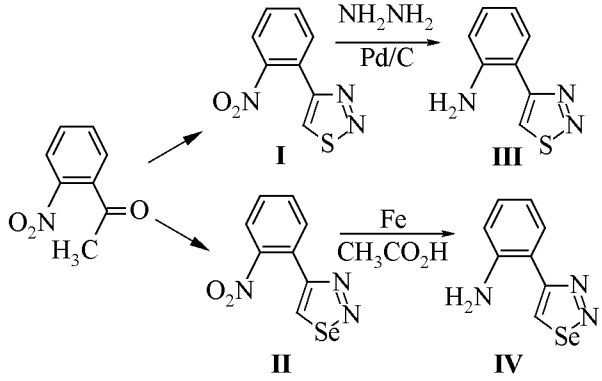
We recently developed a new preparation method for 2-benzofuranchalcogenolates by cascade decomposition reaction of 4-(2-hydroxyphenyl)-1,2,3-thia- and -selenadiazoles initiated by weak bases [1, 2]. The 4-substituted 1,2,3-thia- and -selenadiazoles treated with strong bases, as potassium ethylate, butyllithium etc., commonly readily decompose with nitrogen liberation affording alkynchalcogenolates [3]. However the 4-(2-hydroxyphenyl)-1,2,3-thia- and -selenadiazoles decomposed in the presence of so weak a base as potassium carbonate (see scheme). Therewith do not arise alkynchalcogenolates but forms a 2-chalcogenolatebenzofuran anion resulting from a cascade of reactions: starting with phenolate formation till intramolecular cyclization involving the hydroxy group and chalcogenoketene fragment.



X = S, Se.

Aiming at extension of this method to indole synthesis we reduced 4-(2-nitrophenyl)-1,2,3-thia- (**I**) and -selenadiazole (**II**) into 4-(2-aminophenyl-1,2,3-thia- (**III**) and -selenadiazole (**IV**). 4-(2-Nitrophenyl)-1,2,3-thiadiazole (**I**) was prepared by treating with thionyl chloride of o-nitroacetophenone ethylcarbazone [4], and 4-(2-nitrophenyl)-1,2,3-selenadiazole (**II**) was obtained by reaction of selenium(IV) oxide with o-nitroacetophenone semicarbazone [5].

However 4-(2-aminophenyl-1,2,3-thia- (**III**) and -selenadiazole (**IV**) did not decompose in the presence of potassium carbonate as the corresponding hydroxy derivatives [1, 2]. Only when treated with a strong base, potassium *tert*-butylate, these thia- and -selenadiazoles **III, IV** liberated nitrogen and transformed into potassium 2-(2-aminophenyl)-ethynylchalcogenolates (**V, VI**).



Potassium 2-(2-aminophenyl)ethynylthiolate underwent intramolecular cyclization under the action of ethanol and converted into potassium 2-indolethiolate. Formation of the latter was confirmed by alkylation with methyl iodide that furnished in good yield only 2-methylsulfanylindole (**VII**). Potassium 2-(2-aminophenyl)ethynylselenolate (**VI**) unlike the corresponding thiolate underwent the intramolecular cyclization only under treatment with acetic acid and immediately

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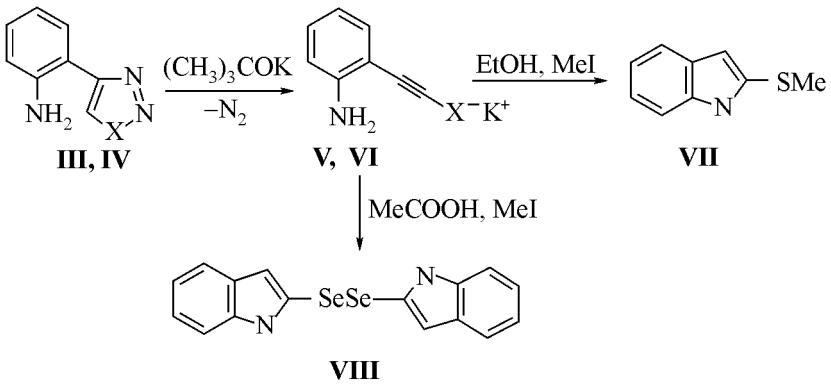

III, IV **V, VI** **VII**

VIII

X = S (**III, V, VII**), Se (**IV, VI, VIII**).

afforded in good yield bis(2-indolyl) diselenide (**VIII**) disregarding the presence of methyl iodide.

4-(2-Aminophenyl)-1,2,3-thiadiazole (III). To a dispersion of 2 g of 5% palladium on carbon in 160 ml of ethanol and 1.21 g (5.85 mmol) of 2-(2-nitrophenyl)-1,2,3-thiadiazole (**I**) was added 1.46 g (29.2 mmol) of hydrazine hydrate. The reaction mixture was boiled for 24 h. On cooling to 20–25°C the reaction mixture was filtered, and the solvent was removed under reduced pressure. The resinous residue was subjected to chromatography on a column 3×25 cm packed with silica gel Merck 70/230, eluent dichloromethane. On removing the solvent we obtained 0.81 g (78%) of thiadiazole **III**. Light-red plates, mp 84–85°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.53 s (NH_2), 6.78–6.84 m (H^3 and H^5), 7.21 t.d (H^4), 7.49 d.d (H^6), 8.62 s (H^5 Ht). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 114.4 (C^1), 117.2, 117.9, 129.5, 130.4 (C^5 Ht, CH, J_1 190 Hz), 130.8, 145.5 (C^2), 163.1 (C^4 Ht). Mass spectrum, *m/z* (I_{rel}, %): M^+ 177 (63), $[M–N_2]^+$ 149 (78), $[M–N_2–S]^+$ 117 (100), 89 (33), 77 (26), 49 (32). Found, %: C 54.41, 54.22; H 4.08, 4.23. $C_8H_7N_3S$. Calculated, %: C 54.23, H 3.95.

4-(2-Aminophenyl)-1,2,3-selenadiazole (IV). A dispersion of 0.63 g (2.45 mmol) of 4-(2-nitrophenyl)-1,2,3-selenadiazole (**II**), 10 ml of glacial acetic acid, and 0.69 g (12.32 mmol) of degreased iron powder was stirred for 2.5 h at heating to 50–60°C in a flask protected from light. On cooling to 20–25°C the reaction product was extracted into chloroform, and the extract was washed with water to remove the acetic acid, The chloroform was removed at reduced pressure, and the resinous residue was subjected to chromatography on a column 3× 20 cm packed with silica gel L 1000/1600, eluent tetrachloromethane–chloroform, 4:1,collecting the fraction with the product. On removing the solvent we obtained 0.3 g (55%) of selenadiazole (**IV**), red-green crystals with metallic luster, mp 58–60°C, R_f 0.25 (eluent chloroform). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.05 s (NH_2), 6.83–6.89 m (H^3 and H^4), 7.26 t.d (H^5), 7.51 d.d (H^6), 9.38 s (H^5 Ht, with satellites HSe, J_2 42 Hz). ^{13}C NMR spectrum ($CDCl_3$), δC, ppm: 116.9 (C^1), 117.5 (C^3), 118.5 (C^5), 130.4 (C^6), 130.6 (C^4), 139.4 (C^5 Ht, CH, J_1 190 Hz), 145.7 (C^2), 163.1 (C^4 Ht). Mass spectrum, *m/z* (I_{rel}, %): M^+ 225 (2), $[M–N_2]^+$ 197 (6), $[M–N_2–Se]^+$ 117 (100), 89 (48), 77 (16). Found, %: C 42.39, 42.45; H 3.29, 3.42. $C_8H_7N_3Se$. Calculated, %: C 42.67, H 3.11.

2-Methylsulfanylindole (VII). To a solution of 0.15 g (0.85 mmol) of 4-(2-aminophenyl)-1,2,3-thiadiazole (**III**) in 20 ml of anhydrous THF was added under argon 0.112 g (1 mmol) of potassium *tert*-butylate. The reaction mixture was stirred for 15 min till gas evolution completely stopped, and then 1 ml of ethanol was added. The reaction mixture was stirred for 10 min more, and then was added 0.18 g (1.275 mmol) of methyl iodide. After stirring of the reaction mixture for 1 h the solvent was removed under reduced pressure. The residue was subjected to chromatography on a column 3×30 cm packed with silica gel Merck 70/230, eluent hexane–dichloromethane, 1:3. On removing the solvent we obtained 0.12 g (85%) of indole (**VII**). Light-brown crystals, mp 47–48°C (mp 48–49°C [6]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.44 s (SCH_3), 6.52 s (H^3), 7.07–7.20 m (H^5–H^7), 7.50 d (H^4), 8.00 s (NH).

Bis(2-indolyl) diselenide (VIII). To a solution of 0.15 g (0.67 mmol) of 4-(2-aminophenyl)-1,2,3-selenadiazole (**IV**) in 20 ml of anhydrous THF was added under argon 0.09 g (0.8 mmol) of potassium *tert*-butylate. The reaction mixture was stirred for

15 min till gas evolution completely stopped, and then 2 drops of acetic acid were added. The reaction mixture was stirred for 10 min more, and then was added 0.143 g (1 mmol) of methyl iodide. After stirring of the reaction mixture for 1 h the solvent was removed under reduced pressure. The residue was subjected to chromatography on a column 3× 20 cm packed with silica gel L 100/160, eluent heptane–dichloromethane, 3:1. On removing the solvent we obtained 0.08 g (62%) of diselenide **VIII**. Light-orange crystals, mp 134–134.5°C, R_f 0.65 (eluent chloroform). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.76 s (H^3), 7.11–7.26 m (H^5 and H^6), 7.28 d (H^7), 7.59 d (H^4), 8.19 s (NH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 111.2 (C^7), 113.1 (C^2), 120.9 (C^5), 121.2 (C^4), 122.2 (C^3), 124.1 (C^6), 128.9 (C^8), 138.9 (C^1). Mass spectrum, *m/z* (I_{rel}, %): M^+ 392 (4), $[M–2H]^+$ 390 (9), $[M–Se]^+$ 312 (12), $[M–Se–2H]^+$ 310 (34), $[M–2Se]^+$ 232 (79), $[M–SeC_8H_7N]^+$ 196 (85), $[C_8H_7N]^+$ 117 (100), $[C_8H_7N–NHCH]^+$ 89 (51). Found, %: C 49.21, 49.31; H 3.15, 3.27. $C_{16}H_{12}N_2Se_2$. Calculated, %: C 48.98; H 3.06.

Melting points were measured on Boetius heating block. ^{1}H and ^{13}C NMR spectra were registered on spectrometers Bruker Avance 9300 and 75 MHz respectively) and Bruker AMX400 (400 and 100 MHz respectively, as internal references served the residual protons (^{1}H) and carbon nuclei (^{13}C) of deuterated solvents. Mass spectra were recorded on Kratos MS 890 instrument with direct admission of the sample into the ion source, ionizing electrons energy 70 eV, temperature of ionizing chamber 200°C. The mass of molecular ions in the mass spectra is given for the principal isotope ^{80}Se. The reaction progress was monitored by TLC on Silufol UV-254 plates, development under UV irradiation or in iodine vapor. All solvents used in the study were purified and dried by standard procedures.

The study was carried out under financial support of the Russian Foundation for Basic Research (grant no. 00-03-32740).

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