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# 4- (*ORTHO*-HYDROXYPHENYL) -1,2,3-SELENADIAZOLE AS A SOURCE OF 2-BENZOFURANSELENOLATE

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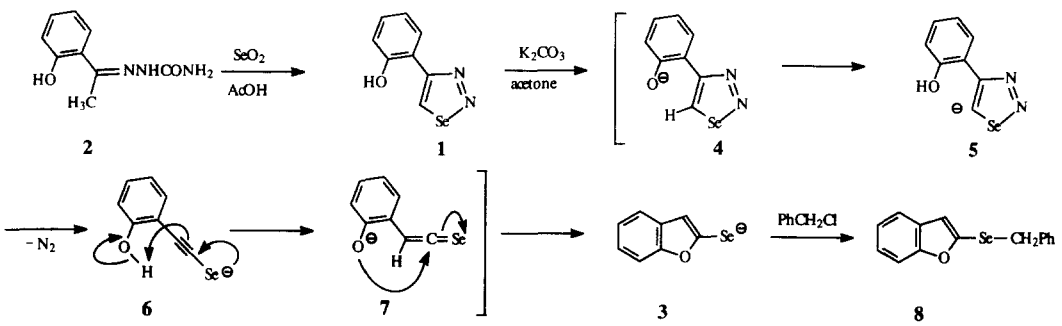
**Abstract**: The novel 4-(*ortho*-hydroxyphenyl)-1,2,3-selenadiazole smoothly transforms into 2-benzofuranselenolate through potassium carbonate catalyzed selenadiazole ring cleavage. The presence of alkyneselenolate is proved by the formation of methyl(*ortho*-methoxy-phenylethynyl)selenide in the presence of methyl iodide. Alkylation and oxidation reactions of 2-benzofuranselenolate are described.


4-Substituted 1,2,3-selenadiazoles, are usually easily decomposed with liberation of nitrogen and formation of alkyneselenolates[1] under the action of strong bases, such as organolithium reagents or potassium ethoxide. The acetylenic selenolates are widely used in organic synthesis for the synthesis of acetylenic selenides, in 1,3-anionic cycloaddition reactions and in other cyclization reactions or, after protonation, as a source of reactive selenoketenes.[2]

In order to obtain entry to 1,2,3-selenadiazoles, and hence alkyneselenolates, having a second functional group, we prepared the novel 4-(*ortho*-hydroxyphenyl)-1,2,3-selenadiazole (**1**).[4,5]




**2** **1** **4** **5**

**6** **7** **3** **8**

To this end, the semicarbazone of *ortho*-hydroxy-acetophenone (**2**) was treated with selenium dioxide[3] to give (**1**). However, attempted alkylation of the phenol (**1**) under weakly basic conditions ($K_2CO_3$) cleanly decomposed the selenadiazole ring with formation of benzofuran-2-selenolate (**3**).

The selenolate (**3**) apparently results from a multistep process involving the phenolate (**4**) which deprotonates the selenadiazole ring with formation of heteroanion (**5**), which immediately decomposes to the alkynethiolate (**6**). Intramolecular proton shift gives the reactive selenoketene (**7**), which cyclizes to give the selenolate (**3**). This sequence bears analogy to a reaction reported by one of us[6] involving 1,2,3-thiadiazoles, leading to benzofuran-2-thiolates.

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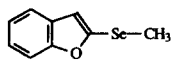

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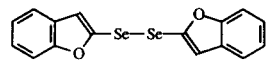

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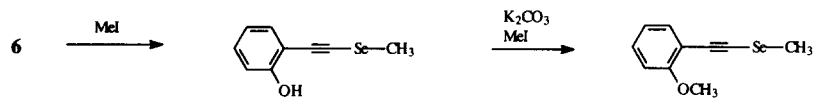
The formation of the benzofuran-2-selenolate (**3**) is confirmed by chemical experiments. Thus, the decomposition of the selenadiazole (**1**) in the presence of benzyl chloride affords the 2-benzylselenide (**8**) in good yield. On the other hand decomposition of the selenadiazole (**1**) with addition of methyl iodide after 30 min of stirring gives the 2-methylselenide (**9**). Finally, oxidation of selenolate (**3**) with iodine yields the interesting bis(2-benzofuranyl)diselenide (**10**).



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We followed the progress of the cyclization reaction of (**1**) by $^1$H NMR spectroscopy in DMSO-d$^6$ and 1 eq of tetrabutylammonium hydroxide. The formation of (**3**) was observed clearly, without the accumulation of intermediates (**4-7**). It is interesting to note that for the alkyne sulfides the correponding intermediates could be detected by $^1$H NMR spectroscopy.[6] Apparently, the alkyneselenolate (**6**) is too unstable to be observed under these conditions. Therefore, we decided to attempt chemical trapping of the selenolate (**6**) with methyl iodide. The product turned out to be 1-(*ortho*-methoxyphenyl)-2-methylselenoethyne (**11**), which is clearly formed by dimethylation of (**6**), probably *via* 1-(*ortho*-hydroxyphenyl)-2-methylselenoethyne (**12**). Methylation of the alkyneselenide is apparently faster than the ring closure to benzofuran, which is not the case for other alkylating agents.

**Acknowledgement**

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**References and notes**

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2. Review see: Petrov M.L., Petrov A.A. *Usp. Khim.* **1987**, *61*, 267;Zmitrovich N.I., Petrov M.L., Petrov A.A. *Zh. Org. Khim.* **1990**, 26, 179; Zmitrovich N.I., Petrov M.L. *Zh. Org. Khim.* **1996**, *32*, 1870;Terenteva N.A., Petrov M.L., Potekhin K.A., Galichev B.A.,Struchov Yu.T. *Zh. Org. Khim.* **1994**,*30*, 1471;Ishihara H., Yoshimi M., Kato S. *Angew. Chem.* **1990**, *102*, 572; Murai T., Kakami K., Hayashi A., Komuro T., Takuda H., Fujii M., Kanda K., Kato S. *J.Amer.Chem.Soc.* **1997**, *119*,8592; Murai T., Esaka T., Kato S. *Bull.Chem.Soc. Jpn.* **1998**,*71*, 1193
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4. All new compounds gave the correct analytical and mass-spectra data and suitable spectroscopic data (IR, NMR).
5. (**1**). Yield : 55 % after recrystallizion from a mixture of ethanol-water, light-brown plates, mp 103-105 °C, $R_f$ 0.4 (benzene, Silufol UV-254). $^1$H NMR spectrum (400 MHz, $CD_3SOCD_3$, ppm): 6.99 q (1H, H$^5$ arom), 7.08 d (1H, H$^3$arom), 7.28 q (1H, H$^4$ arom), 8.26 d (1H, H$^6$ arom), 10.09 s (1H, H$^5$ heterocycl., with satellites $^2$JHSe 42 Hz), 10.35 (1H, OH). $^{13}$C NMR (100 MHz, $CD_3SOCD_3$, ppm): 116.4, 119.5, 129.6, 130.1 (C$^3$, C$^4$, C$^5$, C$^6$ arom), 118.8 (C$^1$ arom), 142.1 d (H$^5$ heterocycle, 1JCC 196 Hz, satellites $^1$J CSe 133 Hz), 155.2 (H$^4$ heterocycle). Found, %: C 42.33; H 2.91. $C_8H_6N_2OSe$. Calculated, %: C 42.69; H 2.69.
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