Pergamon

Tetrahedron Letters 40 (1999) 3903–3904

TETRAHEDRON LETTERS

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

Michael L. Petrov [a]*, Michael A. Abramov[a], Wim Dehaen[b]*, and Suzanne Toppet[b]

[a] *St.Petersburg State Institute of Technology, Moskovskii pr. 26, 198013, St.-Petersburg, Russia*

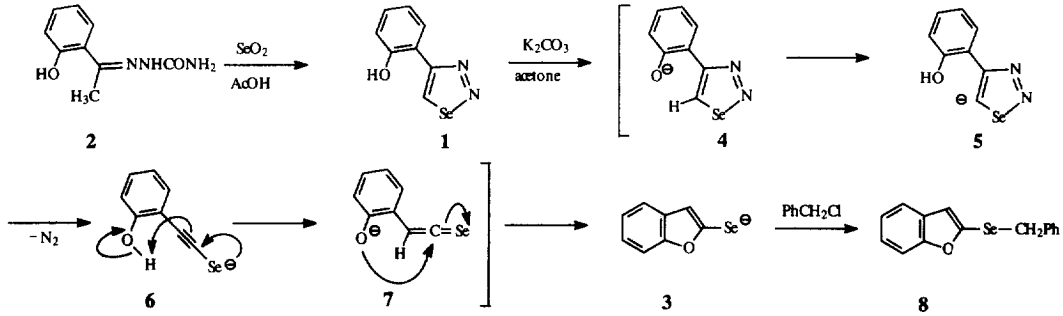
[b] *Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3001 Leuven (Heverlee), Belgium*

Received 8 February 1999; accepted 15 March 1999

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]

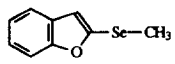


To this end, the semicarbazone of *ortho*-hydroxy-acetophenone (**2**) was treated with selenium dioxide[3] to give (**1**). However, attempted alkylation of the phenol (**1**) under weakly basic conditions (K_2CO_3) cleanly decomposed the selenadiazole ring with formation of benzofuran-2-selenolate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

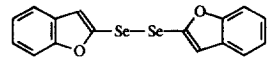
The selenolate (**3**) apparently results from a multistep process involving the phenolate (**4**) which deprotonates the selenadiazole ring with formation of heteroanion (**5**), which immediately decomposes to the alkynethiolate (**6**). Intramolecular proton shift gives the reactive selenoketene (**7**), 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.

E-mail: mlpetrov@tu.spb.ru; wim.dehaen@chem.kuleuven.ac.be

0040-4039/99/$ - see front matter
PII: S0040-4039(99)00565-1

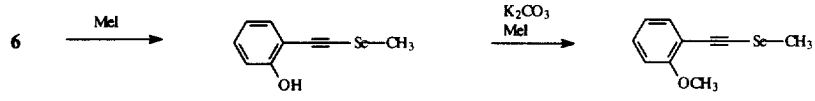


9



10

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**).



12 11

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

W.D. and S.T. thank the Ministerie voor Wetenschapsbeleid, the FWO-Vlaanderen and the Katholieke Universiteit Leuven for their financial support.

References and notes

1. Lalezari I., Shafiee A., Yalpani M. *J.Org.Chem.* **1973**, *38*, 338 ; Laithev V.Z., Petrov.M.L., Petrov A.A. *Zh. Org. Khim.* **1982**, *18*, 514.
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
3. Lalezari I., Shaffice A., Yalpani M.*Tetrahedron Lett.* **1969**, .*58*, 5105; Caplin A. *J.Chem.Soc., Perkin Trans.I* **1974**, 30; Lalezari I., Shaffice A., Yalpani M. *J. Org. Chem.* **1971**, *36*, 2836.
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.
6. B. D'hooge, S. Smeets, S. Toppet, W. Dehaen, *J. Chem. Soc., Chem. Commun.* **1997**, 1753-1754.