Russian Journal of Organic Chemistry, Vol. 40, No. 11, 2004, pp. 1691–1693. Translated from Zhurnal Organicheskoi Khimii, Vol. 40, No. 11, 2004, pp. 1737–1739.
Original Russian Text Copyright © 2004 by Petrov, Androsov, Lyakhovetskii.

SHORT COMMUNICATIONS

4,6-Bis(1,2,3-thiadiazol-4-yl)-1,3-benzenediol as a Source of Furo[3',2':4,5]benzo[*b*]furan-2,6-dithiolate

M.L. Petrov, D.A. Androsov, and Yu.I. Lyakhovetskii

St. Petersburg State Technological Institute, St. Petersburg, 190013 Russia
e-mail: mlpetrov@tu.spb.ru

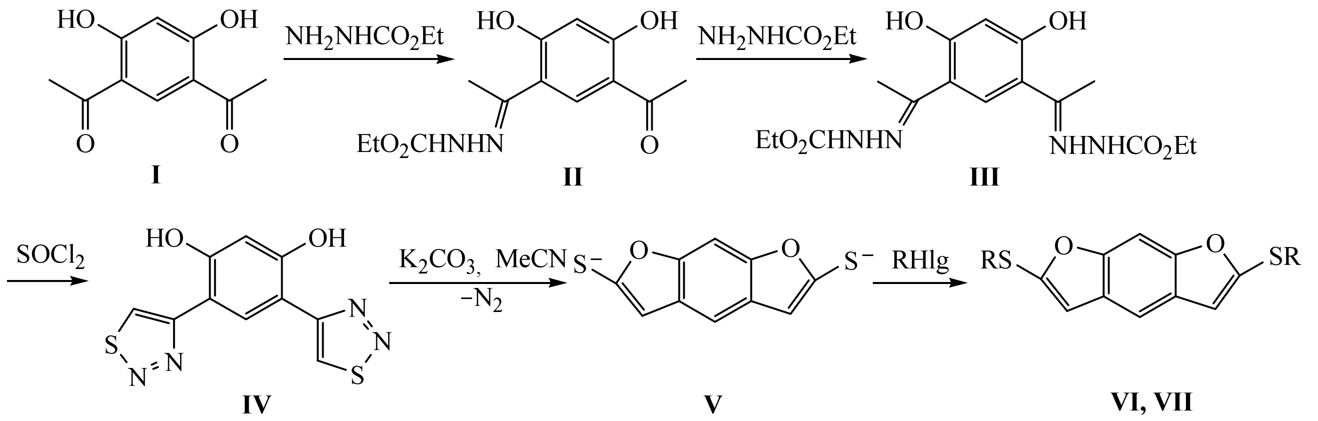
Received February 19, 2004

Compounds containing furo[3',2':4,5]benzo[*b*]-furan heterocyclic structure were found in some algae (so-called cyperaquinone [1]). As a rule these heterocycles can be synthesized from resorcinol [2] and have been first mentioned in the literature in 1932 [3]. We recently developed a new preparation procedure for 2-benzofuranchalcogenolates by treating 4-(2-hydroxyphenyl)-1,2,3-thia- and selenadiazoles with bases [4–10]. This method of benzo[*b*]furans synthesis is underlain by intramolecular addition of an *ortho*-hydroxy group to the products of 1,2,3-thia- and selenadiazoles decomposition, thioketenes and selenoketenes [5].

In an attempt to extend this method to the synthesis of furo[3',2':4,5]benzo[*b*]furans we prepared 4,6-di(1,2,3-thiadiazol-4-yl)-1,3-phenylenediol. Among benzene derivatives containing more than one 1,2,3-thiadiazol-4-yl substituent only the 4-[3,5-di(1,2,3-thiadiazol-4-yl)phenyl]-1,2,3-thiadiazole was known [11]. The initial compound for the synthesis of 4,6-di(1,2,3-thiadiazol-4-yl)-1,3-phenylenediol, 1-(5-acetyl-2,4-dihydroxyphenyl)-1-ethanone (**I**), was obtained via Fries rearrangement from the resorcinol diacetate [12]. Reaction of compound **I** with ethoxycarbonylhydrazine afforded successively its ethoxycarbonylhydrazone (**II**) and bis(ethoxycarbonylhydrazone) (**III**). Previously unknown 4,6-di(1,2,3-thiadiazol-4-yl)-1,3-phenylenediol (**IV**) was obtained by treating bis(ethoxycarbonylhydrazone) (**III**) with thionyl chloride.

Treated with potassium carbonate bis(thiadiazole) **IV** decomposed with nitrogen elimination giving rise to furo[3',2':4,5]benzo[*b*]furan-2,6-dithiolate (**V**). Dithiolate **V** formation was confirmed with the following experiments: The decomposition of dithiadiazole **IV** effected by potassium carbonate in the presence of butyl bromide furnished 2,6-di(butylthio)furo[3',2':4,5]benzo-[*b*]furan (**VI**), a similar reaction in the presence of benzyl chloride afforded 2,6-di(benzylthio)-furo[3',2':4,5]benzo[*b*]furan (**VII**).

1-(5-Acetyl-2,4-dihydroxyphenyl)-1-ethanone ethoxycarbonylhydrazone (II). A mixture of 1.28 g



1070-4280/04/4011-1691©2004 MAIK “Nauka/Interperiodica”

(6.6 mmol) of 1-(5-acetyl-2,4-dihydroxyphenyl)-1-ethanone (**I**) [13], 1.37 g (13.16 mmol) of ethoxycarbonylhydrazine, and 20 ml of toluene was boiled for 2 h while distilling off water into the Dean-Stark trap. The reagents first dissolved giving a light-yellow solution, and in 30 min a colorless precipitate of ethoxycarbonylhydrazone separated. On completion of the reaction the precipitate was filtered off, thoroughly washed with water, and dried. Yield of ethoxycarbonylhydrazone **II** 1.76 g (95%). Fine crystalline powder, mp. 245–247°C, R_f 0.44 (eluent chloroform–acetone, 5:1).

^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.26 t ($C\underline{H}_3CH_2$), 2.35 s ($CH_3C{=}N$), 2.62 s ($CH_3C{=}O$), 4.2 q ($C\underline{H}_2CH_3$), 6.32 s (H^6), 7.99 s (H^3), 10.72 s (OH^1), 12.56 s (NH), 14.03 s (OH^5). ^{13}C NMR spectrum (DMSO-d_6), *δ*, ppm: 13.7 ($\underline{C}H_3CH_2$), 14.8 ($\underline{C}H_3C{=}N$), 27.19 ($\underline{C}H_3C{=}O$), 61.59 ($\underline{C}H_2CH_3$), 104 (C^6), 112.2 (C^2), 113.24 (C^4), 132.93 (C^3), 154.38 (C=N), 164.23 (C^1), 165.79 (C^5), 203.1 (C=O). Mass spectrum, *m/z* (I_{rel}, %): M^+ 280 (100). Found, %: C 55.87, 55.64; H 5.82, 5.93. $C_{13}H_{16}N_2O_5$. Calculated, %: C 55.71; H 5.75.

1-(5-Acetyl-2,4-dihydroxyphenyl)-1-ethanone bis(ethoxycarbonylhydrazone) (III). A mixture of 2.8 g 10 mmol) of compound **II**, 5.2 g (50 mmol) of ethoxycarbonylhydrazine, 1 ml of acetic acid, and 200 ml of ethanol was boiled at vigorous stirring for 30 h. On completion of the reaction the light-greenish precipitate was filtered off, washed with ethanol (5×20 ml), and dried. Yield of bis(ethoxycarbonylhydrazone) (**III**) 3.26 g (89%). Fine crystalline greenish powder, mp 275°C (decomp.), R_f 0.36 (eluent chloroform–acetone, 3:1). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.26 t ($C\underline{H}_3CH_2$), 2.32 C ($CH_3C{=}N$), 4.19 q ($C\underline{H}_2CH_3$), 6.28 s (H^6), 7.59 s (H^3), 10.63 s (NH), 13.38 s (OH). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 13.75 ($\underline{C}H_3CH_2$), 14.83 ($\underline{C}H_3C{=}N$), 61.43 ($\underline{C}H_2CH_3$), 104.52 (C^6), 112.2 (C^2 and C^4), 128.68 (C^3), 154.42 (C=N and C=O), 161.31 (C^1 and C^5). Mass spectrum, *m/z* (I_{rel}, %): M^+ 366 (80). Found, %: C 52.36, 52.545; H 5.91, 5.79. $C_{16}H_{22}N_4O_6$. Calculated, %: C 52.45; H 6.05.

4,6-Di(1,2,3-thiadiazol-4-yl)-1,3-phenylenediol (IV). In a flask equipped with a magnetic stirrer, a reflux condenser, and a system for removal and absorption of gases was added to 1.76 g (4.81 mmol) of 1-(5-acetyl-2,4-dihydroxyphenyl)-1-ethanone bis(ethoxycarbonylhydrazone) (**III**) 30 ml of freshly distilled thionyl chloride. The mixture was heated at reflux and stirring for 5 h; the mixture became homogeneous about 5 min after the start of reaction turning into a brown solution that got somewhat darker to the end of the process. On cooling the reaction mixture to 20–25°C the excess thionyl chloride was distilled off in a vacuum. To the residue 30 ml of cold water was added to decompose the traces of thionyl chloride. The separated precipitate was filtered off, washed with water (5×20 ml), and dried. Yield of the crude reaction product 1.8 g. It was extracted with boiling benzene (3×15 ml), the substance precipitated from the extract was filtered off, washed with a little benzene, and dried. Yield of compound **IV** 0.7 g (52%). Light-yellow small crystals, mp 270°C (decomp), R_f 0.54 (eluent chloroform–acetone,5:1). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.83 s (H^2), 9.27 s (H^5), 9.33 s (H, Ht), 10.81 s (OH). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 103.43 (C^4, C^6), 110.13 (C^2), 130.23 (C^5, Ht), 132.83 (C^4, Ht), 156.37 (C^5), 158.07 (C^1, C^3). Mass spectrum, *m/z* (I_{rel}, %): M^+ 278 (95). Found, %: C 42.97, 43.21; H 2.24, 2.33. $C_{10}H_6N_4O_2S_2$. Calculated, %: C 43.16; H 2.16.

2,6-Di(butylthio)furo[3',2':4,5]benzo[*b*]-furan (VI). A dispersion of 0.46 g (1.66 mmol) of compound **IV**, 0.69 g (4.98 mmol) of freshly calcined potassium carbonate, 0.46 g (3.32 mmol) of butyl bromide, and 50 ml of dry acetonitrile was boiled for 2 h at vigorous stirring. Then the reaction mixture was filtered, and the filtrate was evaporated in a vacuum. The residue was subjected to chromatography on a column (3×10 cm) packed with silica gel of the grade L 100/160, eluent carbon tetrachloride. From the first fraction on removal of the solvent we obtained 0.23 g (42%) of viscous light-yellow oily compound **VI**, R_f 0.63 (eluent carbon tetrachloride). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.91 t (CH_3), 1.46 t. d ($SCH_2C\underline{H}_2$), 1.65 t.d ($SCH_2CH_2C\underline{H}_2$), 2.94 t.t ($SCH_2$), 6.81 s ($H^3$, H^5), 7.47 s (H^8), 7.51 s (H^4). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 13.35 (CH_3), 21.39 ($\underline{C}H_2CH_3$), 31.57 (SCH_2), 34.23 ($SCH_2\underline{C}H_2$), 93.67 (C^8), 109.48 (C^4), 110.61 (C^3, C^5), 125.19 (C^{3a}, C^{4a}), 150.6 (C^{7a}, C^{8a}), 154.36 (C^2, C^6). Mass spectrum, *m/z* (I_{rel}, %): M^+ 334 (27). Found, %: C 64.49, 64.67; H 6.45, 6.59. $C_{18}H_{22}O_2S_2$. Calculated, %: C 64.41, H 6.54.

2,6-Di(benzylthio)furo[3',2':4,5]benzo-[*b*]furan (VII). A dispersion of 0.09 g (0.324 mmol) of 4,6-di(1,2,3-thiadiazol-4-yl)-1,3-phenylenediol (**IV**), 0.134 g (0.971 mmol) of freshly calcined potassium carbonate, 0.082 g (0.647 mmol) of benzyl chloride, and 5 ml of dry acetonitrile was boiled for 2 h at vigorous stirring. Then the reaction mixture was filtered, and the filtrate was evaporated in a vacuum. The residue was subjected to chromatography on a column (3×10 cm) packed with silica gel of the grade L 100/160, eluent carbon tetrachloride. From the first fraction on removal of the solvent we obtained 0.05 g (39%) of 2,6-di(benzylthio)furo[3',2':4,5]-benzo[*b*]furan (**VII**). Fine crystalline powder, mp 95–96°C, R_f 0.52 (eluent carbon tetrachloride). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.16 s (CH_2), 6.69 s (H^3, H^5), 7.25 br.s (Ph), 7.43 s (H^8), 7.54 s (H^4). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 39.32 (CH_2), 93.74 (C^8), 110.16 (C^4), 111.89 (C^3, C^5), 125.15 (C^{3a}, C^{4a}), 127.21 (Ph, C_p), 128.37 (Ph, C_o), 128.67 (Ph, C_m), 137.05 (Ph, C_{ipso}), 149.58 (C^{7a}, C^{8a}), 154.65 (C^2, C^6). Mass spectrum, *m/z* (I_{rel}, %): M^+ 402 (69). Found, %: C 71.72, 71.56; H 4.31, 4.29. $C_{24}H_{18}O_2S_2$. Calculated, %: C 71.64; H 4.48.

Melting points were measured on a Boëtius heating block. ^{1}H and ^{13}C NMR spectra were registered on spectrometers Bruker Avance (300 and 75 MHz) and Bruker AMX-400 (400 and 100 MHz), as internal references served signals of residual protons (^{1}H) and carbon atoms (^{13}C) of deuterated solvents. Mass spectra were recorded on a mass spectrometer Kratos MS 890 at a direct admission of a sample into the ion source, ionizing electrons energy 70 eV, temperature in the ionization chamber 200°C. The reaction progress was monitored by TLC on Silufol UV-254 plates, spots were visualized by UV irradiation or 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 Ministry of Education of the Russian Federation (grant no. A03-2.11-3).

REFERENCES

1. MacLeod, J.K., Worth, B.R., and Wells, R.J., *Aust. J. Chem.,* 1978, vol. 31, p. 1553.
2. Worden, L.R., Burgstahler, A.W., Kaufman, K.D., Weis, J.A., and Schaaf, T.K., *J. Heterocyclic Chem.,* 1969, vol. 6, p. 191.
3. Algar, J., Barry, V.C., and Twomey, T.F., *Proc. Roy. Irish. Acad.*, 1932, 41B8.
4. Petrov, M.L., Abramov, M.A., Dehaen, W., and Toppet, S., *Tetrahedron Lett*., 1999, 40, 3903.
5. Abramov, M.L., Dehaen, W., D'hooge, B., Petrov, M.L., Smeets, S., Toppet, S., and Voets, M., *Tetrahedron,* 2000, vol. 56, p. 3933.
6. Petrov, M.L., Abramov, M.A., Androsov, D.A., and Dekhaen, V., *Zh. Obshch. Khim.,* 2000, vol. 70, p. 1755.
7. Petrov, M.L., Abramov, M.A., Abramova, I.P., Dekhaen, V., and Lyakhovetskii, Yu.I., *Zh. Org. Khim.,* 2001, vol. 37, p. 1713.
8. Petrov, M.L., Abramov, M.A., Androsov, D.A., Dekhaen, V., and Lyakhovetskii, Yu.I., *Zh. Obshch. Khim.,* 2002, vol. 72, p. 1365.
9. Petrov, M.L., Dekhaen, V., Abramov, M.A., Abramova, I.P., and Androsov, D.A., *Zh. Org. Khim.,* 2002, vol. 38, p. 1563.
10. Petrov, M.L., Abramov, M.A., Abramova, I.P., and Dekhaen, V., *Zh. Org. Khim.,* 2003, vol. 39, p. 283.
11. L'abbe, G., Haelterman, B., and Dehaen, W., *J. Chem. Soc., Perkin Trans.,* 1994, p. 2203.