SYNTHESIS OF THE PRECURSORS OF BIS(TRICHLORO-1,4-BENZOQUINONYL)TETRATHIAFULVALENES*

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In reaction with potassium butylxanthate and sodium tert-butyltrithionate, 2,5-dihydroxy-3,4,6,7-tetrachloro-2,3-dihydrobenzo[b]furan forms the products from nucleophilic substitution of a chlorine atom, i.e., O-butyl S-(2,5-dihydroxy-4,6,7-trichloro-2,3-dihydrobenzo[b]furan-3-yl) xanthate and S-tert-butyl S'-(2,5-dihydroxy-4,6,7-trichloro-2,3-dihydrobenzo[b]furan-3-yl) trithiocarbonate respectively. Recyclization of the xanthate in concentrated sulfuric acid gave 4-(2,5-dihydroxy-3,4,6-trichlorophenyl)-1,3-dithiol-2-one, which was oxidized by iron trichloride to the corresponding benzoquinone. Cyclization of the trithiocarbonate in the presence of trifluoroacetic and p-toluenesulfonic acid led to 7-hydroxy-5,6,8-trichloro-3a,8b-dithiolo[4,5-b]benzo[d]furan-2-thione.

The present work is a continuation of investigations [1-3] into the synthesis of heteroaryl-substituted trichloro-1,4benzoquinones based on the recyclization of derivatives of the universal synthon 2,5-dihydroxy-3,4,6,7-tetrachloro-2,3dihydrobenzo[b]furan (I) [4]. By this method it is easy to obtain 1,4-benzoquinones C-C-bonded with various heterocycles, the synthesis of which by direct methods of construction of the carbon-carbon bond between the indicated fragments is extremely complicated [5, 6]. In the molecules of such compounds intramolecular charge transfer is observed between the electron-donating heterocycle and the electron-withdrawing benzoquinone fragment, and this is reflected in their electronic spectra.

Earlier we obtained heteroaryl-substituted trichloro-1,4-benzoquinones containing a triazole, thiazoline, selenazole, 1,3,4-thiadiazine, or pyrazole ring [1, 2]. It seemed of great interest to study the possibilities of using the method for the construction of tetrathiafulvalene, C-C-bonded with two trichloro-1,4-benzoquinone residues. Tetrathiafulvalene derivatives are very strong organic electron donors and are widely used for the production of charge-transfer complexes and radical-ion salts [7-9]. The synthetic precursors of tetrathiafulvalene are 1,3-dithiol-2-ones and 1,3-dithiole-2-thiones [7-9]. The aim of the present work was to synthesize their derivatives containing the 2,5-dihydroxy-3,4,6-trichlorophenyl residue, which is easily oxidized to the corresponding 1,4-benzoquinone, as substituent.

The reaction of the benzofuran (I) with potassium butylxanthate gave the product from substitution of the chlorine atom at position 3 by the butylxanthate group, i.e., O-butyl-S-(2,5-dihydroxy-4,6,7-trichloro-2,3-dihydrobenzo[b]furan-3-yl) xanthate (II) (Scheme 1). The action of heat on compound (II) with concentrated sulfuric acid led to its cyclization with simultaneous opening of the dihydrofuran ring and the formation of 4-(2,5-dihydroxy-3,4,6-trichlorophenyl)-1,3-dithiol-2-one (III). The proposed mechanism of the transformation (II) \rightarrow (III) is shown in Scheme 2. Protonation of the hydroxyl group at position 2 probably occurs initially, and the cation formed after elimination of a water molecule enters into intramolecular recyclization with closure of the 1,3-dithiole ring and simultaneous opening of the dihydrofuran ring. Hydrolytic removal of the butoxy group led to the formation of compound (III). Oxidation of the latter with iron trichloride in aqueous ethanol gave 4-(3,5,6-trichloro-1,4-benzoquinon-2-yl)-1,3-dithiol-2-one (IV), while acetylation with acetic anhydride gave 4-(2,5-diacetoxy-3,4,6-trichlorophenyl)-1,3-dithiol-2-one (V).

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The method for the construction of the 1,3-dithiole-2-thione ring by the reaction of α -halogenocarbonyl compounds with sodium *tert*-butyl trithiocarbonate followed by cyclization in the presence of trifluoroacetic acid and p-toluenesulfonic acid is well known [10, 11].

The reaction of the benzofuran (I) with sodium *tert*-butyl trithiocarbonate gave S-*tert*-butyl S'-(2,5-dihydroxy-4,6,7-trichloro-2,3-dihydrobenzo[b]furan-3-yl) trithiocarbonate (VI). However, its cyclization in the presence of trifluoroacetic acid and p-toluenesulfonic acid led to the tricyclic product 7-hydroxy-5,6,8-trichloro-3a,8b-dihydro-1,3-dithiolo[4,5-b]benzo[d]furan-2-thione (VII) (see [12, 13]). During an attempt at the recyclization of the trithiocarbonate (VI) by heating in concentrated sulfuric acid, a difficultly separable mixture — the main component of which was the product (VII) — was obtained. We were unable to achieve the oxidative cleavage of the dihydrofuran ring and convert compound (VII) into the thio analog of the benzoquinone (IV).

The IR spectra of the crystalline compounds (II, IV) contain bands characteristic of the OH groups (about 3500 and 3400 cm⁻¹) and also of the stretching vibrations of the C-H bond of the butyl and *tert*-butyl groups respectively (in the region of 2990-2890 cm⁻¹).

In the PMR spectrum of compound (II), recorded in deuterochloroform solution, apart from the signals of the protons of the butyl group there are two broad singlets in the upfield region at 5.17 and 6.00 ppm for the 3-H and 2-H protons respectively. These protons are probably in the mutual *trans* position, and the instrument does not resolve their signals into two lines on account of the low spin-spin coupling constant (${}^{3}J = 0.5$ Hz) (see [12]). In addition to these signals the spectrum also contains two weak doublets with ${}^{3}J = 6$ Hz at 5.65 and 6.22 ppm, which can be attributed to a small amount of the *cis* isomer (10-12%) as impurity (see [4]). In the PMR spectrum of compound (VI) the signals of the likewise *trans*-arranged 3-H

Scheme 2



and 2-H protons are observed at 5.65 and 6.22 ppm. Spin coupling is observed here between the 2-H and 2-OH protons (${}^{3}J$ = 5 Hz). In the PMR spectrum of the tricyclic compound (VII) there are two doublets at 7.00 (3a-H) and 6.18 (8b-H) respectively with ${}^{3}J$ = 7.6 Hz, indicating that they are in the *cis* position. This spectrum agrees well with the data from the PMR spectra for known tricyclic analogs of compound (VII) [12].

In the IR spectrum of the crystalline compound (III) the band for the stretching vibrations of the C=O group of 1,3dithiol-2-one is observed at extremely low frequencies for carbonyl absorption — 1632 cm⁻¹ (increased to 1650 cm⁻¹ in dioxane solution) — but this agrees with published data [14]. The spectrum also contains broad bands in the region of 3490-3325 cm⁻¹, corresponding to the vibrations of the associated OH groups. In the PMR spectrum of compound (III) there is a singlet for the 5-H proton of the dithiole ring and a broad signal for the protons of the OH groups.

In the IR spectrum of the crystalline quinone (IV) there are two split bands for carbonyl absorption at 1682 and 1672 (quinone C=O) and 1644 and 1634 cm⁻¹ (dithiolone C=O), and there is no absorption for OH groups. In the spectrum recorded for a solution in dioxane the carbonyl absorption appears in the form of two distinct narrow bands at 1692 and 1652 cm⁻¹, respectively. Only one singlet for the 5-H proton of dithiolone is observed in the PMR spectrum of the quinone (IV). The UV spectrum contains a strong absorption band at 276, which can be assigned to the $\pi \to \pi^*$ transition in the benzoquinone system [15], and a weaker band at 350 nm, corresponding to the $\pi \to \pi^*$ in the dithiolone ring. In addition, the spectrum contains an intramolecular charge-transfer band at 465 nm with a hypsochromic shift compared with the analogous bands in the spectra of our previously synthesized trichloro-substituted 1,4-benzoquinones linked to nitrogen-containing heterocycles by a C-C bond [1-3].

In the IR spectrum of the diacetyl derivative (V) there are bands for the C=O group at 1785 (acetyl) and 1653 cm⁻¹ (dithiolone), but there is no absorption for the OH group. Its PMR spectrum contains two singlets, corresponding to the protons of the two nonequivalent acetyl groups, and a singlet for the proton at position 5 of dithiolone.

Our attempts to convert compounds (III) and (V) into bis(trichloro-1,4-benzoquinonyl)tetrathiafulvalenes (VIII) (two isomers) by deoxygenation [16] by the action of triethyl phosphite were unsuccessful.

EXPERIMENTAL

The IR spectra were recorded on a Specord M-80 instrument for suspensions in Nujol (1900-1500 cm⁻¹, sodium chloride prism) and hexachlorobutadiene (3800-2000 cm⁻¹, lithium fluoride prism) and for saturated solutions in dioxane. The electronic spectrum was obtained on a Specord M-40 instrument for a solution in ethanol (concentration $5 \cdot 10^{-5}$ M). The PMR spectra were obtained on a Bruker H-90 instrument (90 MHz) for solutions in deuterochloroform with TMS as internal standard.

The individuality of the compounds was monitored by TLC on plates with a fixed layer of Silufol UV-354 silica gel with ethyl acetate-carbon tetrachloride as eluant and development in UV light.

2,5-Dihydroxy-3,4,6,7-tetrachloro-2,3-dihydrobenzo[b]furan (I). Compound (I) was obtained by the method in [4].

O-Butyl S-(2,5-Dihydroxy-4,6,7-trichloro-2,3-dihydrobenzo[b]furan-3-yl) Xanthate (II). To a solution of 1.45 g (5 mmole) of benzofuran (I) in 25 ml of methanol while stirring with a magnetic stirrer at 20°C over 15-20 min we added dropwise a solution of 1 g (5.3 mmole) of potassium butylxanthate in 25 ml of methanol. The reaction mixture was stirred at 20°C for a further 6 h and was then poured into 200 ml of water. The precipitate was filtered off, washed with water, and dried. We obtained 1.9 g (95%) of colorless crystals of compound (II); mp 118-120°C. After recrystallization from carbon tetrachloride, mp 122-123°C, R_f 0.78 (2:3 ethyl acetate – carbon tetrachloride). IR spectrum, cm⁻¹: 3538 (OH), 3370 (OH), 2962, 2964, 2874 (CH of butyl group), 1612, 1586. PMR spectrum (δ , ppm): 0.91 (3H, t, ³J = 7 Hz, CH₃); 1.38 (2H, sextet, ³J = 7 Hz, CH₃CH₂); 1.72 (2H, q, ³J = 7 Hz, CH₂); 3.22 (1H, bs, 2-OH, disappears after the addition of D₂O); 4.58 (2H, t, ³J = 7 Hz, CH₂O); 5.17 (1H, s, 3-H); 5.56 (1H, bs, 5-OH, disappears after the addition of D₂O); 6.00 (1H, s, 2-H). Found %: C 38.43; H 3.02; Cl 26.63; S 15.90. C₁₃H₁₃Cl₃O₄S₂. Calculated %: C 38.67; H 3.25; Cl 26.35; S 15.88.

4-(2,5-Dihydroxy-3,4,6-trichlorophenyl)-1,3-dithiol-2-one (III). A mixture of 0.8 g (2 mmole) of compound (II) and 4 ml of concentrated sulfuric acid was kept at 60-65 °C for 1 h, cooled, and poured into 40 ml of water. The precipitate was filtered off, washed with water, and dried. We obtained 0.65 g (98%) of light-violet crystals of the unpurified product (III). For purification the crystals were boiled with 30 ml of benzene to which a small amount of silica gel was added. The hot solution was filtered, evaporated to 10 ml, and left to crystallize. After 20 h the colorless crystals of the product (III) were filtered off, washed with benzene, and dried. The yield was 76%; mp 176-177°C, R_f 0.73 (2:3 ethyl acetate – carbon tetrachloride). IR spectrum, cm⁻¹: Nujol, 3490, 3414, 3325 (OH), 1632 (C=O), 1608; dioxane, 1650 (C=O). PMR spectrum (δ , ppm): 5.62 (2H, bs, 2OH); 6.70 (1H, s, 5-H). Found %: C 33.06; H 0.89; Cl 32.66; S 19.55. C₉H₃Cl₃O₃S₂. Calculated %: C 32.79; H 0.92; Cl 32.27; S 19.46.

4-(3,5,6-Trichloro-1,4-benzoquinon-2-yl)-1,3-dithiol-2-one (IV). To a solution of 0.33 g (1 mmole) of compound (III) in 10 ml of ethanol with stirring (magnetic stirrer) at 20°C over 2-3 min we added dropwise 40 ml of a 20% aqueous solution of iron trichloride. The reaction mixture was stirred vigorously at 20°C for a further 1 h. The precipitate was then separated, washed with water, dried. We obtained 0.32 g (97%) of dark-red crystals of compound (IV); mp 165-166°C, R_f 0.78 (1:2 ethyl acetate – carbon tetrachloride). IR spectrum, cm⁻¹: Nujol, 3098, 1682, and 1672 (C=O of quinone), 1644 and 1634 (C=O of dithiolane), 1610, 1564 (C=C of quinone), 1518; dioxane, 1692 (C=O of quinone), 1652 (C=O of dithiolane), 1578 (C=C of quinone). UV spectrum, nm (log ε): 276 (4.20), 350 (3.12), 465 (3.06). PMR spectrum (δ , ppm): 7.16 (s, 5-H). Found %: C 33.00; H 0.27; Cl 31.94; S 19.58. C₉HCl₃O₃S₃. Calculated %: C 32.99; H 0.31; Cl 32.47; S 19.58.

4-(2,5-Diacetoxy-3,4,6-trichlorophenyl)-1,3-dithiol-2-one (V). A mixture of 0.33 g (1 mmole) of compound (III), 5 ml of acetic anhydride, and 3-4 drops of orthophosphoric acid was kept at 80°C for 1 h, cooled, and poured into 50 ml of water. After 20 h the precipitate was removed, washed with water, and dried. We obtained 0.4 g (98%) of the product; mp 144-145°C. After recrystallization from ethanol we obtained 0.35 g (82%) of pale-yellow needle crystals of compound (V); mp 145-146°C, R_f 0.73 (1:3 ethyl acetate-carbon tetrachloride). IR spectrum, cm⁻¹: 3104, 2940, 1785 (C=O of acetyl groups), 1653 (C=O of dithiolane). PMR spectrum (δ , ppm): 2.30 (3H, s, CH₃); 2.42 (3H, s, CH₃); 6.70 (1H, s, 5-H). Found %: C 37.52; H 1.55; Cl 25.55; S 15.69. C₁₃H₇Cl₃O₅S₂. Calculated %: C 37.74; H 1.71; Cl 25.71; S 15.50.

S-tert-Butyl-S'-(2,5-dihydroxy-4,6,7-trichloro-2,3-dihydrobenzo[b]furan-3-yl) Trithiocarbonate (VI). To a solution of 1.17 g (4 mmole) of benzofuran (I) in 30 ml of acetone with stirring at 0-5 °C we added dropwise a solution of 1.0 g (4.46 mmole) of sodium *tert*-butyl trithiocarbonate (dihydrate) at such a rate that the color of the solution remained yellow. (With too rapid addition the solution becomes brown.) The reaction mixture was stirred at 20 °C for a further 2 h, after which it was diluted with 100 ml of water and extracted with 100 ml of diethyl ether. The ether extract was dried over anhydrous magnesium sulfate and evaporated under vacuum. The residue was recrystallized from carbon tetrachloride, and 1.1 g (65%) of yellow crystals of compound (VI) were obtained; mp 160-162 °C (decomp.). IR spectrum, cm⁻¹: 3520 (OH), 3392 (OH), 2988, 2964, 2920, 2892, 1418, 1302, 1200, 1080. PMR spectrum (δ , ppm): 1.58 (9H, s, Bu-t); 3.42 (1H, d, ³J = 5 Hz, 2-OH, disappears after the addition of D₂O); 5.49 (1H, s, 5-OH, disappears after the addition of D₂O); 5.53 (1H, s, 3-H); 5.93 (1H, d, ³J = 5 Hz, 2-H). Found %: C 37.56; H 2.72; Cl 24.92; S 22.41. C₁₃H₁₃Cl₃O₃S₃. Calculated %: C 37.28; H 2.89; Cl 25.40; S 22.97.

7-Hydroxy-5,6,8-trichloro-3*a***,8***b***-dihydro-1,3-dithiolo**[**4,5***b*]**benzo**[*d*]**furan-2-thione** (VII). We suspended 0.42 g (1 mmole) of compound (VI) in a mixture of 6 ml of anhydrous acetic acid and 6 ml of trifluoroacetic acid. We added 0.02 g of p-toluenesulfonic acid and kept the reaction mixture at 100°C for 20 min, after which we boiled it for a further 20 min. The

lemon-yellow precipitate that separated after cooling was washed with 5 ml of a 1:1 mixture of acetic and trifluoroacetic acids and then with water. We obtained 0.28 g (81%) of compound (VII); mp 190-192°C. IR spectrum, cm⁻¹: 3300 (OH), 2976, 1420, 1354, 1202, 1190, 1070. PMR spectrum (δ , ppm): 6.18 (1H, d, ${}^{3}J$ = 7.6 Hz, 3a-H); 7.00 (1H, d, ${}^{3}J$ = 7.6 Hz, 8b-H). Found %: C 31.51; H 0.79; Cl 30.51; S 27.04. C₉H₃Cl₃O₂S₃. Calculated %: C 31.27; H 0.87; Cl 30.77; S 27.83.

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