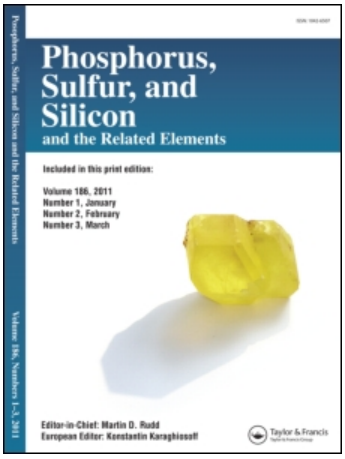

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New Bis(thio)-, Tris(thio)-, and Tetrakis(thio)-substituted Quinones from the Reactions of p-Chloranil with Some Thiols and Dithiols

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New Bis(thio)-, Tris(thio)-, and Tetrakis(thio)-substituted Quinones from the Reactions of p-Chloranil with Some Thiols and Dithiols

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*p-Chloranil (**1**), when reacted with different thiol compounds, namely 1-buthylthiol, cyclohexylthiol, and 2,2-oxydiethanethiol in ethanol in the presence of Na_2CO_3, yielded the corresponding S-substituted quinone derivatives.*

Keywords Chloranil; thiol; dithiol; quinones; oxydiethanethiol; disulphide

It is known that some mono(thio)-, bis(thio)-, tris(thio)-, and tetrakis (thio)-substituted quinones were produced from p-benzoquinone.[1–8] Previously, the reactions of p-chloranil with thiols have been studied.[4,9–12] It is known also that the tetra(thio)substituted-1,4-benzoquinones were prepared from p-chloranil with ethanedithiol HS-CH_2-CH_2-SH) and propanedithiol—(HS-CH_2-CH_2-CH_2-SH).[10]

Quinones are found in some anticancer, antibacterial, antifungal, and antimalarial agents.[13–16] It is also known that quinones are used in the preparation of superconducting materials.[6,10] Some metal complexes and oxidation products (such as sulfoxides and sulfones) of thioethers, crown ethers, and crown thioethers, were reported previously.

Our aim of this study is to prepare new thio-substituted quinones from the reactions of p-chloranil with some thiols and dithiols and identification of their structures.

The new bis(thio)- and tetrakis(thio)-substituted quinone compounds (**6**, **7**) were obtained from the reaction of haloquinone

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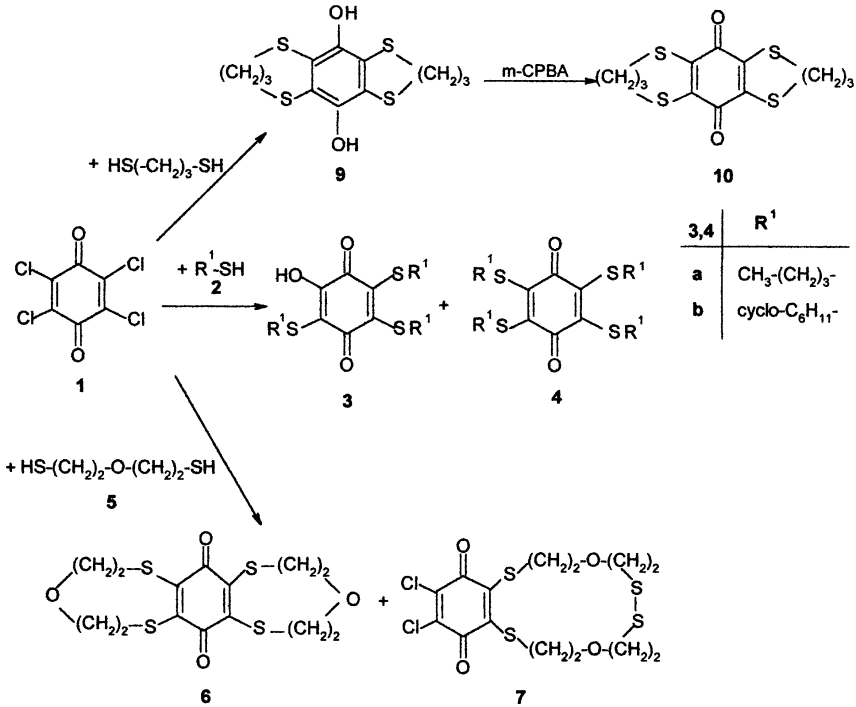
compound **1** with oxydiethanethiol **5** (Scheme 1). Compound **6** is a tetrakis(thio)substituted quinone and has an interesting structure; however, compound **7** is a disubstituted quinone. These interesting compounds, **6** and **7**, were obtained from the dithiol compound **5** simultaneously.



SCHEME 1

The ^{1}H-NMR spectrum of compound **6** gave a multiplet for the methylene groups at $\delta = 2.4$–4.3 ppm.

The IR spectrum of compound **7** showed a S—S-band at 500–400 cm^{-1}.

Chloranil gave tris(thio)- and tetrakis(thio)substituted thioethers (**3a–b**, **4b**) with thiols(R-SH). Compounds **6**, **7**, **3a–b**, and **4b** posses still quinoid structures. Compounds **3a**, **3b**, **4b**, **6**, and **7** are new compounds.

Compound **1** gave compound **9** with 1,3-propanedithiol **8** which has an aromatic structure. After oxidation of compound **9** with m-CPBA, we obtained compound **10**, which is a known compound.[10] Formation of compound **10** was probably via compound **9**.

IR spectra of compounds **3a–b**, **4b**, **6**, and **7** showed the characteristic >C=O group band. Compounds **3a** and **3b** also showed the OH group band (at 3500 cm^{-1}).

All of these compounds have interesting structures, a dark brown color, and are stable compounds. The structures of the new quinone compounds obtained were determined by elemental analysis and spectroscopic methods.

EXPERIMENTAL SECTION

Elemental analyses were carried out using a Thermo Finnigan Flash EA 1112 analyzer. UV spectra were recorded on a P. General TU-1901 Spectrometer. IR Spectra were recorded on a Perkin Elmer Spectrum ONE Systems spectrometer. The ^1H NMR spectra were recorded on a Varian Unity INOVA 500 MHz spectrometer and mass spectra were recorded on a VG-ZAB-SPEC-Spectrometer. Melting points were recorded on a Büchi SMP 20 melting point apparatus and are uncorrected. Products were isolated by column chromatography on SiO_2 (Fluka Kieselgel 60, particle size 63–200 μm).TLC plates silica: 60 F_{254} (Merck, Darmstadt), detection with ultraviolet light (254 nm).

Preparation of S-Substituted Quinones

Two pathways were used.

General Procedure I

Sodium carbonate was dissolved in ethanol and into the resulting solution, firstly thiol and then p-chloranil were added in small portions. The reaction mixture was refluxed for 5 h and concentrated in vacuo. The residue was extracted in a Soxhlet extractor with dichloromethane. After evaporation, the extract was crystallized or obtained as oil.[10]

General Procedure II

The solution of Na_2CO_3 in ethanol was added slowly to the mixture of p-chloranil and thiol. Without heating, the reactants gave the product and the color of the solutions quickly changed. The reaction was controlled by TLC. Then the reaction mixture was concentrated in vacuo and the residue extracted in a Soxhlet extractor. After the recovery of solvents, the crude products were purified by chromatographic methods.

In these experiments, mostly General Procedure I was used; but only with 2,2-oxydiethanethiol, General Procedure II was choosen, because

the reaction was very rapid and a color change was observed. The reaction mixtures had a strong tendency to form polymeric compounds.

*6-Hydroxy-2,3,5-tris(butylthio)-1,4-benzoquinone (**3a**).* Compound **3a** was synthesized from p-chloranil (0.5 g, 2 mmol) and 1-buthyltiol **2a** (0.21 mL, 2 mmol) according to General Procedure I. Purification (CC) gave 0.13 g (17%) of **3a.** $R_f = 0.53$ [EtAc-CCl_4 (1:1). Dark oil. —IR(film): $\nu = 2960$ cm^{-1} (C—H), 1650 (C=O), 1580 (C=C), 3400 (OH). ^{1}H-NMR ($CDCl_3$-TMS int.): $\delta = 0.6$–1.1 (m, 9 H, CH_3) , 1.1–1.8 (m, 12 H, 6 CH_2), 2.6–3.4 (m, 6 H, 3 S-C$\underline{H}_2$-$CH_2CH_2CH_3$), $C_{18}H_{28}O_3S_3$(388.614), MS m/z 390.1.

*6-Hydroxy-2,3,5-tris(cyclohexylhio)-1,4-benzoquinone (**3b**).* Compound **3b** was synthesized from p-chloranil (0.922 g, 3.75 mmol) and cyclohexylthiol (1.83 ml, 15 mmol) according to General Procedure I. Purification (CC) gave 0.59 g (33.5%) of **3b**. $R_f = 0.49$ [EtAc-CCl_4]. Dark brown crystals, m.p. 163–165°C, —IR (KBr): $\nu = 2990$ cm^{-1} (C—H), 1650 (C=O), 1550 (C=C), 3500 (OH). —^{1}H-NMR ($CDCl_3$ - TMS int.): $\delta = 0.7$–2.3 [m, 30 H (CH_2) , 3 H (—CH)]. $C_{24}H_{34}O_3S_3$ (466.72), MS m/z 468.5.

*2,3:5,6-Tetra(cyclohexythio)-1,4-benzoquinone (**4b**).* Compound **4b** was synthesized from **1** (0.922 g, 3.75 mmol) and cyclohexylthiol **2b** (1.83 mL, 15 mmol) according to General Procedure I. Purification (CC) gave 0.25 g (12%) of **4b**. $R_f = 0.58$ [EtAc-CCl_4 (1:1)]. Brown oil. —IR (film): $\nu = 2980$ cm^{-1} (C—H), 1650 (C=O), 1540 (C=C). —^{1}H-NMR ($CDCl_3$, TMS int.): $\delta = 1.0$–2.3 (m, 40 H, —CH_2), 3.9–4.5 (m, 4H, —CH). $C_{30}H_{44}O_2S_4$ (564.94), MS m/z 566.2.

*2,3:5,6_Bis(2,2-oxydiethanethio)-1,4-benzoquinone (**6**).* Compound **6** was synthesized from **1** (0.922 g, 3.75 mmol) and 2,2-oxydiethanethiol (0.45 mL, 3.75 mmol) according to General Procedure II. Purification (CC) gave 0.106 g (15%) of **6**. Brown oil. —IR(film): $\nu = 2980$ cm^{-1} (C—H), 1650 (C=O), 1580 (C=C). —^{1}H-NMR ($CDCl_3$ – TMS int.): $\delta = 2.4$–4.3 (m, 16 H, —CH_2). $C_{14}H_{16}O_4S_4$(376.54). MS m/z 377.9.

*2,3-(2,2-Oxydiethanedisulfide)-5,6-dichloro-1,4-benzoquinone (**7**).* Compound **7** was synthesized from **1** (0.922 g, 3.75 mmol) and 2,2-oxydiethanethiol (0.45 mL, 3.75 mmol) according to General Procedure II. Purification (CC) gave 0.216 g (19%) of **7.** $R_f = 0.68$ [CH_2Cl_2 – CCl_4(1:1)]. Dark-brown crystals, m.p. 196–198°C . —IR (KBr): $\nu = 2900$ cm^{-1} (C—H), 1680 (C=O), 1595 (C=C). —^{1}H-NMR ($CDCl_3$ – TMS int.): $\delta = 2.4$–4.7 (m, 16 H, —CH_2). $C_{14}H_{16}Cl_2O_4S_4$ (447.74) , MS m/z 448.3 .

*2,3:5,6-Bis(trimethylenedithio)-1,4-hydroquinone (**9**).* Compound **9** was synthesized from p-chloranil (1.845 g, 7.5 mmol) and 1,

3-propanedithiol (1.8 mL, 17.96 mmol), sodium carbonate (3.047 g, 28.75 mmol), ethanol (137.5 mL) mixture by refluxing for 5 h. Then the reaction mixture was concentrated in vacuo and extracted using a Soxlet extractor with dichloromethane as solvent. After extraction, the extract was recrystallized from chlorobenzene. Yield: 0.475 g (20%), yellow crystals from chlorobenzene; m.p. 306–308°C; $R_f = 0.46$ ($CHCl_3$). –IR(KBr): $\nu = 2980$ cm^{-1}(C–H), 3300(OH). ^{1}H-NMR($CDCl_3$): $\delta = 2.11$(4 H, C–C$\underline{H}_2$-C), 2.85 (8 H, S–C$\underline{H}_2$), 6.9(ArO$\underline{H}$).

*2,3:5,6-Bis(trimethylenedithio-1,4-benzoquinone (**10**).* 0.1 g, 0.32 mmol compound **9** was reacted with (0.22 g, 1.3 mmol) 3-CPBA in 25 mL $CHCl_3$ for 12 h. Then the mixture washed with 2 n NaOH and water, dried with $MgSO_4$ and $CHCl_3$, and was evaporated. Purification (CC) gave 0.01 g (9.75%) of **10**, m.p. 287–289°C of green crystals from chlorobenzene. The structure of compound **10** was characterized by melting point, elemental analysis, and spectroscopic methods (IR, ^{1}H-NMR, MS). $C_{12}H_{12}O_2S_4$ (316.48), MS m/z 316.0.

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