The Synthesis of Novel Mono(alkoxy)-, Tris(thio)- and Tetrakis(thio)-Substituted Quinones from the Reactions of *p*-Chloranil with Various S-Nucleophiles

Cemil Ibis,* Mahmut Yildiz,† and Cigdem Sayil*

Istanbul University, Faculty of Engineering, Department of Chemistry, 34320 Avcilar, Istanbul, Turkey
**E-mail: ibiscml@istanbul.edu.tr and sayil@istanbul.edu.tr*
†Istanbul University, Hasan Ali Yucel Faculty of Education, 34470 Beyazit, Istanbul, Turkey
Received July 7, 2009, Accepted September 4, 2009

The tetrakis(thio)-substituted-1,4-benzoquinone products **4a-e**, **6**, **7**, and the mono(alkoxy)-tris(thio)-substituted-1,4-benzoquinone products **5a-e** and **8a-e** were synthesized from the reactions of *p*-chloranil with some thiols and mixture of two different thiol compounds in alcohol in the presence of Na_2CO_3 at room temperature. The structures of the novel S,S,S,S- and S,S,S,O- substituted products, which were obtained by the reactions of *p*-chloranil as a starting compound with *n*-propanethiol, *n*-pentanethiol, *n*-decanethiol, *n*-dodecanethiol, 2-methyl-2-propanethiol, and mixture of *n*-decanethiol and *n*-cyclohexanethiol as S-nucleophiles, were characterized by spectroscopic methods.

Key Words: *p*-Chloranil, Tetrathiobenzoquinones, Thioquinone compounds, Quinone derivatives, *n*-Propanethiol

Introduction

Thioethers have become known as an important class of organic compounds. They have useful applications in organic reactions and synthesis, in agrochemicals and in bioorganic, medicinal, heterocyclic chemistry.[1] Thioethers can also be used in the synthesis of various sulphur compounds, which can act in many biological processes.[2]

Quinones are useful compounds for preparation of superconducting materials.[3,4] They also exhibit high biological activity as antimalarial, antifungal, antitumor and antibacterial agents.[5-9] The *p*-chloranil containing chlorine atoms and a pair of carbonyl groups is a quite reactive compound. Therefore a large number of *p*-benzoquinone derivatives are synthesized from *p*-chloranil.[4,10-14] *p*-Chloranil and its derivatives behave as electron acceptors in the reaction of charge-tranfer complexes.[4,15-20]

Thioethers which are synthesized from the reactions of thiols with quinones are known as thioquinones.[11-13] Tetrakis(thio)-substituted-1,4-benzoquinone compounds are used in the dye industry. Certain thioquinone dye molecules are known to have characteristics such as organic nonlinear optical materials,[21] organic photoconductors, and emitters for electroluminescence.[11] According to an US patent, mercapto quinones are valuable compounds for using oil-soluble fungicidal sprays on plants as fungicides.[22] It has been reported before that from the reactions of *p*-chloranil with difunctional thiols have been obtained the cyclic thioquinones,[11] their solid state spectrum and crystal structure have been investigated.[23,24]

Alkyl(thio)-substituted-*p*-benzoquinones were yielded from the reaction of 1,4-benzoquinones with *n*-ethanethiol[25] and *p*-chloranil with *n*-dodecanethiol, benzyl mercaptan, and *p*-methylthiophenol.[10] Tetraalkylthio-1,4-benzoquinones are used as additives in engine lubricants.[26,27]

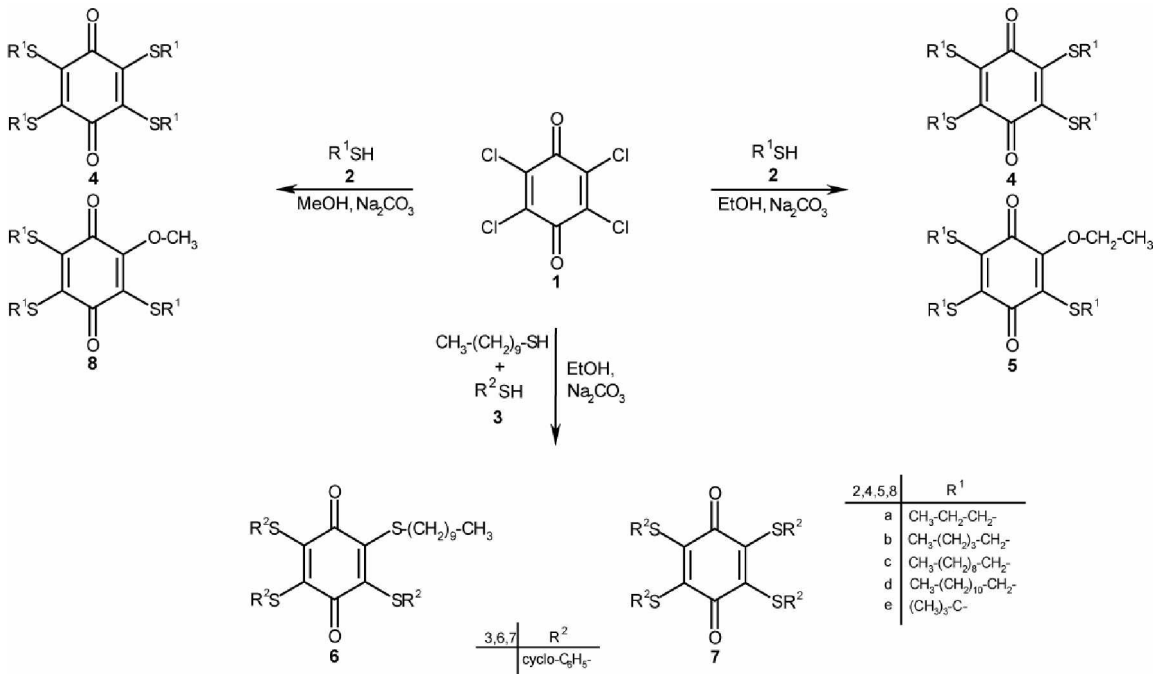
The main purpose of this paper is to synthesize novel thio-substituted-*p*-benzoquinones and identify of their structures.

Results and Discussion

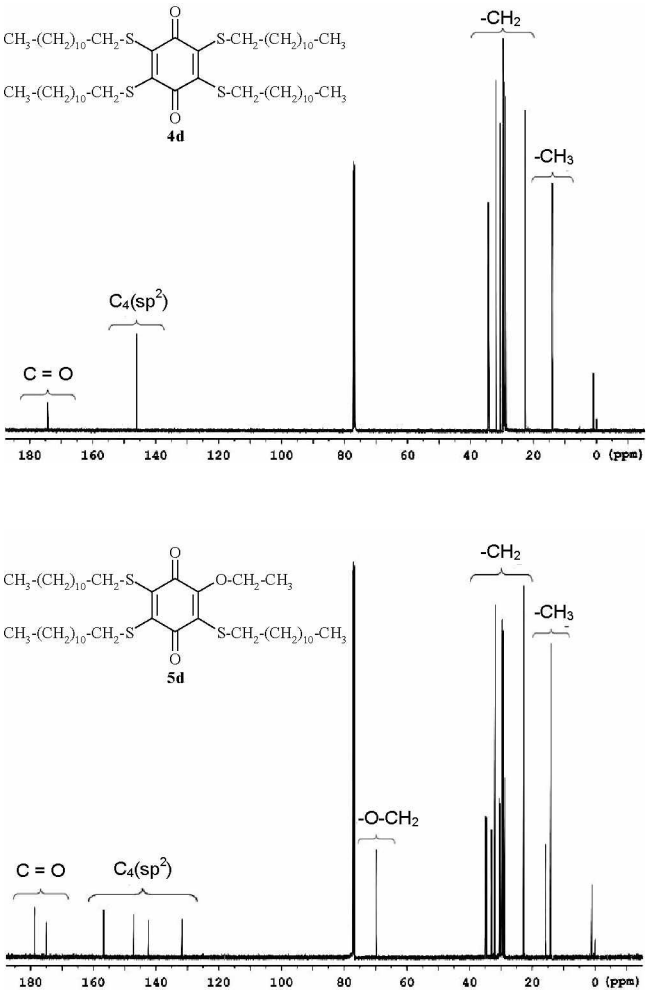
It is also known that reactions of quinones with thiols give thio-substituted derivatives or cyclic structures, a Michael-type addition reaction took place followed by elimination of NaCl to afford the thio-substituted quinonyl derivatives.[10,11,28,29] In this study, from the reactions of *p*-chloranil with **2c**, mixture of **2c** with **3**, **2d** and **2e** the compounds **4c**,[10] **7**,[12] **4d**[10] and **4e**[10] which have been published previously were respectively synthesized, but their spectroscopic properties weren't investigated intensely before. In addition, from the reactions of **1** with **2a-e** and mixture of **2c** with **3**, in ethanol in the presence of Na_2CO_3, **4a-b**, **5a-e**, **6** and the reaction of **1** with **2a-e** in methanol in the presence of Na_2CO_3, **4a-b** and **8a-e** were respectively synthesized. All of these products are new S,S,S,S- and S,S,S,O- substituted thioquinone compounds (Scheme 1). However, they are stable and coloured dyes. Their structures were characterized by microanalysis and spectroscopic data.

The reactions of **1** with three molar equivalents of thiol which are **2a-e** have been studied. Our investigation was to synthesize tetrakis(thio)-substituted products and tris(thio)-substituted products containing chlorine atom. As intented, the tetrakis (thio)-substituted compounds **4a-e** were obtained. In contrast to expectations by analogy to the molar ratios of the reactants, tris(thio)-substituted compounds containing chlorine atom derivatives were not observed potentially due to the decreased thiol amount in the medium of the reaction, while the alkoxy derivatives of tris(thio)-substituted compounds were obtained successfully. Various and interesting tris(thio)-substituted products were obtained as a by-product in addition.

Unexpectedly, these alkoxy derivatives of tris(thio)-substituted products containing an ethoxy group coming from the solvent ethanol or a methoxy group coming from the solvent methanol instead of chlorine atom were observed. In spite of the activity of thiol nucleophile, as a result of the inadequate thiol



Scheme 1



Scheme 2. The ^{13}C NMR Spectrum of Compounds **4d** and **5d**.

in the medium of the reaction. CH_3-CH_2-O- or CH_3-O- substitutes with one chlorine atom as an alcohol nucleophile at the position where intented one chlorine atom includes. The mono (alkoxy)-tris(thio)-substituted compounds **5a-e** and **8a-e** were synthesized in this way.

The ^{13}C-NMR shifts of the methylene carbon atoms of compound **5a** which are adjacent to the oxygen atoms (-O-CH_2-) have showed their resonances in the downfield at 68.7 ppm. The carbon atoms of CH- groups, which are adjacent to the sulphur atoms, are observed at 45.5 ppm in the spectra of compounds **6** and **7**.

The ^{13}C-NMR shifts of the four C (sp^2) atoms of compound **4d** have appeared at 146 ppm as one peak only, while the four C (sp^2) atom signals of compound **5d** have showed their resonances at 131.7, 142.3, 147.1, 156.6 ppm as four peaks. The spectra of compound **4d**, carbon atoms of carbonyl groups are observed at 174.3 ppm as one peak only while the carbon atom signals of carbonyl groups of **5d** have showed their resonances at 174.9, 178.7 ppm as two peaks (Scheme 2). Moreover, the ^{13}C-NMR spectrum of **4a-c**, **4e**, **5a-c**, **5e**, **6**, **7**, **8a-e** show similar characteristic shifts like **4d** and **5d**.

In the ^{1}H-NMR spectra of **5a**, protons in methylene group (-O-CH_2-) which situated in ethoxy group and which are adjacent to the oxygen atom are observed as multiplet at 4.30 ~ 4.34 ppm. However, these peaks are not observed in the spectra of **4a**. The methylene protons of **5b**, which are adjacent to the sulphur atoms, have appeared as multiplet at 3.0 ~ 3.1 ppm.

In the mass spectrum of the compounds **4a** and **5a** the accurate mass measurement of the molecular ion peak are noticed at m/z = 404.90 [M^+] and 374.90 [M^-], respectively. IR spectra of compounds **4c-d**, **5c**, **7** and **4a-b**, **5b**, **5d**, **6** showed the characteristic carbonyl group band at 1650 cm^{-1} and 1660 cm^{-1}, respectively.

Experimental Section

UV spectra were recorded in UV-Vis spectrophotometer TU-1901. IR spectra were recorded for liquids as film and for solids as KBr discs on a Shimadzu FT-IR 8101 spectrometry. Microanalyses were carried out with a Carlo Erba Elemental Analyzer 1106. Mass spectra were obtained on a Thermo Finnigan LCQ Advantage MAX MS/MS spectrometer according to either APCI or ESI techniques. ^{1}H-NMR and ^{13}C-NMR spectra were recorded with Varian^{UNITY} INOVA spectrometers with 500 MHz frequency for ^{1}H-NMR and 125 MHz frequency for ^{13}C-NMR. ^{1}H-NMR spectra and ^{13}C-NMR spectra in $CDCl_3$ refer to the solvent signal center at δ 7.26 and δ 77.0 ppm, respectively. Melting points were determined with a Buchi apparatus B-540 and uncorrected. All reagents and solvents were commercially available and used without further purification. Column chromatographic separations were carried out on silica gel 60 (Merck, particle size 63 ~ 200 μm). TLC was carried out on Merck DC-plates (aluminum based) silica gel (60 F_{254}) for monitoring reactions.

Standard Procedure I. Sodium carbonate was dissolved in ethanol and into the resulting solution, firstly *p*-chloranil and then thiol were added slowly in small portions. 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 with an appropriate solvent. After the recovery of solvents by means of evaporator, the crude products were purified by chromatographic methods.

Standard Procedure II. Sodium carbonate was dissolved in methanol and into the resulting solution, firstly *p*-chloranil and then thiol were added slowly in small portions. 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 with an appropriate solvent. After the recovery of solvents by means of evaporator, the crude products were purified by chromatographic methods.

Synthesis. ***Synthesis of 2,3,5,6-tetrapropylthio-1,4-benzoquinone (4a), 2-ethoxy-3,5,6-tripropylthio-1,4-benzoquinone (5a).*** Compounds **4a** and **5a** were synthesized by the reaction of 1 g (4.1 mmol) *p*-chloranil (**1**) with 0.9 g (12.2 mmol) *n*-propanethiol (**2a**) according to the standard procedure I.

2,3,5,6-Tetrapropylthio-1,4-benzoquinone (4a): Yield: 1.2 g, 70.5%; Dark brown oil; R_f (CCl_4): 0.24; IR (film, cm^{-1}): ν 2980 (C-H), 1660 (C = O), 1540 cm^{-1} (C = C); UV/vis ($CHCl_3$): λ_{max} 236, 403 nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.94 (t, ^3J = 7.32 Hz, 12H, C***H***$_3$), 1.51-1.59 (m, 8H, C***H***$_2$), 2.99 (t, ^3J = 7.32 Hz, 8H, SC***H***$_2$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.47, 24.13, 36.45, 146.30, 174.48; MS (APCI): *m/z* (%) 404.90 (100); $C_{18}H_{28}O_2S_4$ (404.68); Calcd.: C, 53.42; H, 6.97; S, 31.70. Found: C, 53.12; H, 5.72; S, 32.84.

2-Ethoxy-3,5,6-tripropylthio-1,4-benzoquinone (5a): Yield: 0.4 g, 24.3%; Dark brown oil; R_f (CCl_4): 0.15; IR (film, cm^{-1}): ν 2990 (C-H), 1670 (C = O), 1580 cm^{-1} (C = C); UV/vis ($CHCl_3$): λ_{max} 234, 399 nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.98-1.03 (m, 9H, C***H***$_3$), 1.40 (t, ^3J = 7.32 Hz, 3H, C***H***$_3$CH$_2$O-), 1.56-1.66 (m, 6H, C***H***$_2$), 2.98-3.14 (m, 6H, SC***H***$_2$), 4.31-4.35 (m, 2H, CH$_3$C***H***$_2$O-); ^{13}C NMR (125 MHz, $CDCl_3$): δ 12.24, 12.27, 12.29, 14.75, 22.59, 22.84, 22.89, 33.93, 35.48, 35.78, 68.76 (CH$_3$-*C*H$_2$-O-), 130.53, 141.38, 146.14, 155.77, 173.98, 177.72; MS (APCI): *m/z* (%) 374.90 (100); $C_{15}H_{26}O_3S_3$ (374.57); Calcd.: C, 54.51; H, 6.99; S, 25.68. Found: C, 54.13; H, 5.80; S, 23.42.

Synthesis of 2,3,5,6-tetrapentylthio-1,4-benzoquinone (4b), 2-ethoxy-3,5,6-tripentylthio-1,4-benzoquinone (5b). Compounds **4b** and **5b** were synthesized by the reaction of 1 g (4.1 mmol) *p*-chloranil (**1**) with 1.3 g (12.2 mmol) *n*-pentanethiol (**2b**) according to the standard procedure I.

2,3,5,6-Tetrapentylthio-1,4-benzoquinone (4b): Yield: 0.7 g, 33.8%; Dark brown oil; R_f (CCl_4): 0.40; IR (film, cm^{-1}): ν 2980 (C-H), 1660 (C = O), 1510 cm^{-1} (C = C); UV/vis ($CHCl_3$): λ_{max} 234, 406 nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.89 (t, ^3J = 7.32 Hz, 12H, C***H***$_3$), 1.28-1.62 (m, 24H, C***H***$_2$), 3.08 (t, ^3J = 7.32 Hz, 8H, SC***H***$_2$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.10, 22.42, 30.40, 31.06, 34.54, 146.25, 174.05; MS (APCI): *m/z* (%) 517.05 (100); $C_{26}H_{44}O_2S_4$ (516.89); Calcd.: C, 60.41; H, 8.58; S, 24.81. Found: C, 60.09; H, 7.85; S, 26.36.

2-Ethoxy-3,5,6-tripentylthio-1,4-benzoquinone (5b): Yield: 0.3 g,15%; Dark brown oil; R_f (CCl_4): 0.32; IR (film, cm^{-1}): ν 2980 (C-H), 1660 (C = O), 1590 cm^{-1} (C = C); UV/vis ($CHCl_3$): λ_{max} 231, 401 nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.89 (t, ^3J = 7.32 Hz, 9H, C***H***$_3$), 1.27-1.63 (m, 24H, C***H***$_2$; 3H, C***H***$_3$CH$_2$O-), 3.00-3.16 (m, 6H, SC***H***$_2$), 4.30-4.34 (m, 2H, CH$_3$C***H***$_2$O-); ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.92, 15.79, 22.23, 29.89, 30.15, 30.18, 30.85, 30.87, 30.88, 33.02, 34.55, 34.88, 69.77 (CH$_3$-*C*H$_2$-O-), 131.69, 142.36, 147.18, 156.71, 175.02, 178.76; MS (APCI): *m/z* (%) 459.01 (100); $C_{23}H_{38}O_3S_3$ (458.73); Calcd.: C, 60.22; H, 8.35; S, 20.97. Found: C, 60.25; H, 6.35; S, 22.25.

Synthesis of 2,3,5,6-tetradecylthio-1,4-benzoquinone (4c),[10] ***2,3,5-tridecylthio-6-ethoxy-1,4-benzoquinone (5c).*** Compounds **4c**[10] and **5c** were synthesized by the reaction of 0.5 g (2.0 mmol) *p*-chloranil (**1**) with 1.0 g (6.1 mmol) *n*-decanethiol (**2c**) according to the standard procedure I.

2,3,5,6-Tetradecylthio-1,4-benzoquinone (4c):[10] Yield: 0.3 g, 21.6%; Red crystal; R_f (CCl_4): 0.75; mp 43 ~ 44 °C (lit.[10] 45 °C); IR (KBr, cm^{-1}): ν 2920 (C-H), 1650 (C = O), 1510 cm^{-1} (C = C); UV/vis ($CHCl_3$): λ_{max} 243, 405 nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, ^3J = 7.32 Hz, 12H, C***H***$_3$), 1.26-1.61 (m, 64H, C***H***$_2$), 3.08 (t, ^3J = 7.32 Hz, 8H, SC***H***$_2$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.07, 21.67, 27.76, 28.20, 28.31, 28.54, 28.56, 29.55, 30.89, 33.37, 145.04, 173.28; MS (ESI): *m/z* (%) 797.38 (100); $C_{46}H_{84}O_2S_4$ (797.34); Calcd.: C, 69.28; H, 10.61; S, 16.08. Found: C, 69.74; H, 9.62; S, 17.70 (lit.[10] C, 69.6; H, 10.7).

2,3,5-Tridecylthio-6-ethoxy-1,4-benzoquinone (5c): Yield: 0.1 g, 10.3%; Dark brown oil; R_f (CCl_4): 0,66; IR (film, cm^{-1}): ν 2920 (C-H), 1650 (C = O), 1530 cm^{-1} (C = C); UV/vis ($CHCl_3$): λ_{max} 242, 335 nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, ^3J = 7.32 Hz, 9H, C***H***$_3$), 1.26-1.62 (m, 48H, C***H***$_2$; 3H, C***H***$_3$CH$_2$O-), 3.00-3.16 (m, 6H, SC***H***$_2$), 4.29-4.34 (m, 2H, CH$_3$-C***H***$_2$-O-); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.09, 15.79, 22.68, 28.72, 28.74, 28.76, 29.18, 29.20, 29.23, 29.31, 29.48, 29.52, 29.53, 29.54, 29.56, 29.57, 30.23, 30.48, 30.52, 31.91, 33.04, 34.58, 34.92, 69.76 (CH$_3$-*C*H$_2$-O-), 131.70, 142.34, 147.19, 156.68, 174.99, 178.74; MS (ESI): *m/z* (%) 669.30 (100); $C_{38}H_{68}O_3S_3$ (669.12); Calcd.: C, 68.21, H, 10.24; S, 14.38. Found: C, 67.20; H, 9.70; S, 15.40.

Synthesis of 2,3,5,6-tetradodecylthio-1,4-benzoquinone (4d),*[10] *2,3,5-tridodecylthio-6-ethoxy-1,4-benzoquinone (5d). Compounds **4d**[10] and **5d** were synthesized by the reaction of 1 g (4.1 mmol) *p*-chloranil (**1**) with 2.45 g (12.2 mmol) *n*-dodecanethiol (**2d**) according to the standard procedure I.

2,3,5,6-Tetradodecylthio-1,4-benzoquinone (4d):[10] Yield: 1.1 g, 29.2%; Orange crystal; R_f (CCl_4): 0.77; m.p. 47 ~ 48 °C (lit.[10] 48 ~ 49 °C; IR (KBr, cm^{-1}): ν 2920 (C-H), 1650 (C = O), 1540 cm^{-1} (C = C); UV/vis ($CHCl_3$): λ_{max} 248, 406 nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, ^3J = 6.83 Hz, 12H, CH_3), 1.22-1.61 (m, 80H, CH_2), 3.08 (t, ^3J = 7.32 Hz, 8H, SCH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.10, 22.70, 28.79, 29.23, 29.38, 29.58, 29.64, 29.68, 29.70, 30.58, 31.95, 34.39, 146.08, 174.32; MS (ESI): *m/z* (%) 909.46 (100); $C_{54}H_{100}O_2S_4$ (909.64); Calcd.: C, 71.30; H, 11.08; S, 14.10. Found: C, 71.80; H, 10.79; S, 15.4 (lit.[10] C, 71.2; H, 11.4).

2,3,5-Tridodecylthio-6-ethoxy-1,4-benzoquinone (5d): Yield: 0.7 g, 21.9%; Black crystal; R_f (CCl_4): 0.63; m.p. 40 ~ 41 °C; IR (KBr, cm^{-1}): ν 2950 (C-H), 1660 (C = O), 1580 cm^{-1} (C = C); UV/vis ($CHCl_3$): λ_{max} 248, 400 nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, ^3J = 7.32 Hz, 9H, CH_3), 1.21-1.60 (m, 60H, CH_2; 3H, CH_3CH_2O-), 3.00-3.15 (m, 6H, SCH_2), 4.30-4.34 (m, 2H, CH_3CH_2O-); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 14.10, 15.80, 22.70, 28.72, 28.74, 28.77, 29.19, 29.21, 29.36, 29.37, 29.53, 29.55, 29.61, 29.63, 29.66, 29.67, 29.69, 30.23, 30.49, 30.53, 31.94, 33.04, 34.58, 34.91, 69.76 (CH_3-CH_2-O-), 131.71, 142.35, 147.19, 156.68, 174.99, 178.73; MS (ESI): *m/z* (%) 753.38 (100); $C_{44}H_{80}O_3S_3$ (753.26 g); Calcd. C, 70.15; H, 10.70; S, 12.77. Found: C, 70.67; H, 11.78; S, 10.31.

Synthesis of 2,3,5,6-tetra(2-methyl-2-propyl)thio-1,4-benzoquinone (4e),*[10] *2-ethoxy-3,5,6-tri(2-methyl-2-propyl)thio-1,4-benzoquinone (5e). Compounds **4e**[10] and **5e** were synthesized by the reaction of 1 g (4.7 mmol) *p*-chloranil (**1**) with 1.1 g (12.2 mmol) 2-methyl-2-propane thiol (**2e**) according to the standard procedure I.

2,3,5,6-Tetra(2-methyl-2-propyl)thio-1,4-benzoquinone (4e):[10] Yield: 0.4 g, 19.2%; Red crystal; R_f (petroleum ether/$CHCl_3$(2:1)): 0.23; m.p.141 ~ 142 °C (lit.[10] 141 ~ 143 °C; IR (KBr, cm^{-1}): ν 1670 (C = O), 1540 (C = C), 1370 cm^{-1}(C-H); UV/vis ($CHCl_3$): λ_{max} 263, 399 nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.39 (s, 36H, CH_3); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 32.72, 52.60, 152.64, 178.97; MS (ESI): *m/z* (%) 461.60 (100); $C_{22}H_{36}O_2S_4$(460.79); Calcd.: C, 57.35; H, 7.87; S, 27.83. Found: C, 57.18; H, 7.89; S, 27.70 (lit.[10] C, 57.3; H,7.9).

2-Ethoxy-3,5,6-tri(2-methyl-2-propyl)thio-1,4-benzoquinone (5e): Yield: 0.1 g, 8.3%; Black powder; R_f [petroleum ether/$CHCl_3$(2:1)]: 0.19; m.p. 41.5 ~ 42.5 °C; IR (KBr, cm^{-1}): ν 1670 (C = O), 1580 (C = C), 1370 cm^{-1}(C-H); UV/vis ($CHCl_3$): λ_{max} 244, 352 nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.29-1.39 (m, 27H, CH_3; 3H, CH_3CH_2O-), 4.40-4.44 (m, 2H, CH_3CH_2O-); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.87, 31.03, 31.47, 31.55, 49.23, 50.76, 51.65, 69.33 (CH_3CH_2O-), 124.05, 145.39, 155.12, 162.98, 177.34, 180.02; MS (APCI): *m/z* (%) 416.80 (100); $C_{20}H_{32}O_3S_3$ (416.67); Calcd.: C, 57.65; H, 7.74; S, 23.09. Found: C, 57.45; H, 7.28; S, 23.01.

Synthesis of 2,3,5-tricyclohexylthio-6-decylthio-1,4-benzoquinone (6), 2,3,5,6-tetracyclohexyl thio-1,4-benzoquinone (7),[12] Compounds **6** and **7**[12] were synthesized by the reaction of 1 g (4.1 mmol) *p*-chloranil (**1**) with 1.4g (8.1 mmol) *n*-decanethiol (**2c**) and 1.0 g (8.1 mmol) cyclohexanethiol (**3**) according to the standard procedure I.

2,3,5-Tricyclohexylthio-6-decylthio-1,4-benzoquinone (6): Yield: 0.3 g, 13.6%; Dark brown oil; R_f (CCl_4): 0.47; IR (film, cm^{-1}): ν 2930 (C-H), 1540 (C = C), 1660 cm^{-1} (C = O); UV/vis ($CHCl_3$): λ_{max} 252, 406 nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, ^3J = 6.83 Hz, 3H, CH_3), 1.18-1.92 (m, 16H, CH_2; 30H, $CH_{2cyclohex}$), 3.07 (t, ^3J = 7.81 Hz, 2H, SCH_2), 3.68-3.73 (m, 3H, SC*H*); ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.07, 21.65, 24.50, 24.51, 24.90, 24.99, 25.01, 27.71, 27.73, 28.17, 28.29, 28.51, 28.54, 29.20, 29.35, 29.48, 30.87, 33.06, 33.12, 33.43, 45.34, 45.54, 143.44, 145.78, 146.11, 147.59, 173.37, 173.74; MS (ESI): *m/z* (%) 622.19 (100); $C_{34}H_{54}O_2S_4$ (623.06); Calcd.: C, 65.54; H, 8.73; S, 20.59; Found: C, 65.89; H, 8.22; S, 19.94.

2,3,5,6-Tetracyclohexylthio-1,4-benzoquinone (7):[12] Yield: 0.2 g, 9.1% (lit.[12] 0.2 g,12%); Black oil; R_f (CCl_4): 0.36 (lit.[12] (EtAc-CCl_4(1:1)): 0.58); IR (film, cm^{-1}): ν 2950 (C-H), 1650 (C = O), 1580 cm^{-1} (C = C) (lit.[12] 2980 (C-H), 1650 (C = O), 1540 cm^{-1} (C = C)); UV/vis ($CHCl_3$): λ_{max} 252, 405 nm; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.86-1.91 (m, 40H, CH_2), 3.60-4.35 (m, 4H, *CH*) (lit.[12] 1.00-2.30 (m, 40H, CH_2), 3.90-4.50 (m, 4H, *CH*)); ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.51, 25.02, 33.11, 45.51, 145.98, 173.59; MS (ESI): *m/z* (%) 565.12 (100) (lit.[12] 566.2 (100)); $C_{30}H_{44}O_2S_4$ (564.94 g); Calcd.: C, 63.78; H, 7.85; S, 22.70. Found: C, 64.14; H, 7.70; S, 20.88.

Synthesis of 2,3,5,6-tetrapropylthio-1,4-benzoquinone (4a), 2-methoxy-3,5,6-tripropylthio-1,4-benzoquinone (8a). Compounds **4a** and **8a** were synthesized by the reaction of 1 g (4.1 mmol) *p*-chloranil (**1**) with 0.9 g (12.2 mmol) *n*-propanethiol (**2a**) according to the standard procedure II.

2,3,5,6-Tetrapropylthio-1,4-benzoquinone (4a): Yield: 0.5 g, 31%; Dark brown oil; R_f (CCl_4): 0.24; IR (film, cm^{-1}): ν 2980 (C-H), 1660 (C = O), 1540 cm^{-1} (C = C); UV/vis ($CHCl_3$): λ_{max} 236, 403 nm; $C_{18}H_{28}O_2S_4$ (404.68). This compound was characterized by the R_f, IR and UV data like the other compound (**4a**) was above.

2-Methoxy-3,5,6-tripropylthio-1,4-benzoquinone (8a): Yield: 0.2 g, 13.2%; Dark brown oil; R_f [petroleum ether/$CHCl_3$ (2:1)]: 0.20; IR (film, cm^{-1}): ν 2960 (C-H), 1660 (C = O), 1590 cm^{-1} (C = C); UV/vis ($CHCl_3$): λ_{max} 247, 400 nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.90-0.96 (m, 9H, CH_3), 1.48-1.59 (m, 6H, CH_2), 2.91-3.08 (m, 6H, SCH_2), 3.97 (s, 3H, CH_3O-); ^{13}C NMR (125 MHz, $CDCl_3$): δ 12.26, 12.27, 12.29, 22.54, 22.86, 22.89, 33.98, 35.47, 35.79, 60.00 (CH_3-O-), 130.01, 141.45, 146.03, 156.13, 173.83, 177.66; MS (APCI): *m/z* (%) 360.98 (100); $C_{16}H_{24}O_3S_3$ (360.56); Calcd.: C, 53.31; H, 6.71; S, 26.68. Found: C, 53.06; H: 6.63; S, 24.70.

Synthesis of 2,3,5,6-tetrapentylthio-1,4-benzoquinone (4b), 2-methoxy-3,5,6-tripentylthio-1,4-benzoquinone (8b). Compounds **4b** and **8b** were synthesized by the reaction of 1 g (4.1 mmol) *p*-chloranil (**1**) with 1.3 g (12.2 mmol) *n*-pentanethiol (**2b**) according to the standard procedure II.

2,3,5,6-Tetrapentylthio-1,4-benzoquinone (4b): Yield: 0.5 g, 23.15; Dark brown oil; R_f (CCl_4): 0.40; IR (film, cm^{-1}): ν 2980 (C-H), 1660 (C = O), 1510 cm^{-1} (C = C); UV/vis ($CHCl_3$): λ_{max} 234, 406 nm; $C_{26}H_{44}O_2S_4$ (516.89). This compound was characterized by the R_f, IR and UV data like the other compound (**4b**)

was above.

2-Methoxy-3,5,6-tripentylthio-1,4-benzoquinone (8b): Yield: 0.2 g, 8.2%; Dark brown oil; R_f [petroleum ether/$CHCl_3$ (2:1)]: 0.37; IR (film, cm^{-1}): ν 2980 (C-H), 1650 (C = O), 1580 cm^{-1} (C = C); UV/vis ($CHCl_3$): λ_{max} 248, 399 nm; ^1H NMR (500 MHz, $CDCl_3$): δ 0.82 (t, ^3J = 7.32 Hz, 9H, CH_3), 1.23-1.55 (m, 18H, CH_2), 2.93-3.09 (m, 6H, SCH_2), 3.97 (s, 3H, CH_3O-); ^{13}C NMR (125 MHz, $CDCl_3$): δ 12.89, 21.21, 21.22, 28.83, 29.15, 29.16, 29.83, 29.85, 32.03, 33.51, 33.86, 59.99 (CH_3-O-), 130.13, 141.39, 146.04, 156.04, 173.83, 177.66; MS (ESI): *m/z* (%) 445.24 (100); $C_{22}H_{36}O_3S_3$ (444.72); Calcd.: C, 59.42; H, 8.16; S, 21.63. Found: C, 58.85; H, 8.51; S, 22.03.

Synthesis of 2,3,5,6-tetradecylthio-1,4-benzoquinone (4c), [10] ***2,3,5-tridecylthio-6-methoxy-1,4-benzoquinone (8c).*** Compounds **4c**[10] and **8c** were synthesized by the reaction of 1 g (4.1 mmol) *p*-chloranil (**1**) with 2.1 g (12.2 mmol) *n*-decanethiol (**2c**) according to the standard procedure II.

2,3,5,6-Tetradecylthio-1,4-benzoquinone (4c):[10] Yield: 1.1 g, 37.7%; Red crystal; R_f (CCl_4): 0.75; m.p. 43 ~ 44 °C (lit.[10] 45 °C); IR (KBr, cm^{-1}): ν 2920 (C-H), 1650 (C = O), 1510 cm^{-1} (C = C); UV/vis ($CHCl_3$): λ_{max} 243, 405 nm; $C_{46}H_{84}O_2S_4$ (797.34). This compound was characterized by the R_f, mp, IR and UV data like the other compound (**4c**) was above.

2,3,5-Tridecylthio-6-methoxy-1,4-benzoquinone (8c): Yield: 0.3 g, 11.1%; Dark brown oil; R_f [petroleum ether/$CHCl_3$(2:1)]: 0.81 ; IR (film, cm^{-1}): ν 2970 (C-H), 1650 (C = O), 1590 (C = C); UV/vis ($CHCl_3$): λ_{max} 249, 401 nm; ^1H NMR (500 MHz, $CDCl_3$): δ 0.82 (t, ^3J = 6.83 Hz, 9H, CH_3), 1.19-1.55 (m, 48 H, CH_2), 2.93-3.09 (m, 6H, SCH_2), 3.97 (s, 3H, CH_3O-); ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.07, 21.66, 27.69, 27.72, 27.73, 28.16, 28.17, 28.29, 28.30, 28.50, 28.51, 28.53, 28.55, 29.17, 29.48, 29.50, 30.88, 32.07, 33.55, 33.89, 59.99 (CH_3-O-), 130.13, 141.37, 146.06, 156.02, 173.82, 177.65; MS (APCI): *m/z* (%) 655.32 (100); $C_{37}H_{66}O_3S_3$ (655.13); Calcd.: C, 67.84; H, 10.15; S, 14.68. Found: C, 66.96; H, 10.35; S, 15.00.

Synthesis of 2,3,5,6-tetradodecylthio-1,4-benzoquinone (4d), [10] ***2,3,5-tridodecylthio-6-methoxy-1,4-benzoquinone (8d).*** Compounds **4d**[10] and **8d** were synthesized by the reaction of 1 g (4.1 mmol) *p*-chloranil (**1**) with 2.45 g (12.2 mmol) *n*-dodecanethiol (**2d**) according to the standard procedure II.

2,3,5,6-Tetradodecylthio-1,4-benzoquinone (4d):[10] Yield: 1.7 g, 46.5%; Orange crystal; R_f (CCl_4): 0.77; m.p. 47 ~ 48 °C (lit.[10] 48 ~ 49 °C); IR (KBr, cm^{-1}): ν 2920 (C-H), 1650 (C = O), 1540 cm^{-1} (C = C); UV/vis ($CHCl_3$): λ_{max} 248, 406 nm; $C_{54}H_{100}O_2S_4$ (909.64). This compound was characterized by the R_f, mp, IR and UV data like the other compound (**4d**) was above.

2,3,5-Tridodecylthio-6-methoxy-1,4-benzoquinone (8d): Yield: 0.4 g, 14.5%; Black crystal; R_f [petroleum ether/$CHCl_3$ (2:1)]: 0.76 ; m.p. 77 ~ 78 °C; IR (KBr, cm^{-1}): ν 2960 (C-H), 1650 (C = O), 1550 cm^{-1} (C = C); UV/vis ($CHCl_3$): λ_{max} 249, 402 nm; ^1H NMR (500 MHz, $CDCl_3$): δ 0.81 (t, ^3J = 7.32 Hz, 9H, CH_3), 1.18-1.55 (m, 60H, CH_2), 2.92-3.09 (m, 6H, SCH_2), 3.97 (s, 3H, CH_3O-); ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.08, 21.68, 27.70, 27.74, 28.17, 28.19, 28.34, 28.51, 28.53, 28.59, 28.61, 28.64, 28.65, 28.67, 29.19, 29.49, 29.51, 30.92, 32.07, 33.55, 33.90, 59.98 (CH_3-O-), 130.14, 141.37, 146.06, 156.01, 173.81, 177.64; MS (APCI): *m/z* (%) 739.45 (100); $C_{43}H_{78}O_3S_3$ (739.29); Calcd.: C, 69.86; H, 10.63; S, 13.01; Found: C, 69.90; H, 10.84; S, 14.17.

Synthesis of 2,3,5,6-tetra(2-methyl-2-propyl)thio-1,4-benzoquinone (4e), [10] ***2-methoxy-3,5,6-tri(2-methyl-2-propyl)thio-1,4-benzoquinone (8e).*** Compounds **4e**[10] and **8e** were synthesized by the reaction of 1 g (4.1 mmol) *p*-chloranil (**1**) with 1.1 g (12.2 mmol) 2-methyl-2-propane thiol (**2e**) according to the standard procedure II.

2,3,5,6-Tetra(2-methyl-2-propyl)thio-1,4-benzoquinone (4e):[10] Yield: 0.3 g, 15.5%; Red crystal; R_f (petroleum ether/$CHCl_3$(2:1)): 0.23 ; m.p. 141 ~ 142 °C (lit.[10] 141 ~ 143 °C); IR (KBr, cm^{-1}): ν 1370 (C-H), 1670 (C = O), 1540 cm^{-1} (C = C); UV/vis ($CHCl_3$): λ_{max} 263, 399 nm; $C_{22}H_{36}O_2S_4$ (460.79). This compound was characterized by the R_f, mp, IR and UV data like the other compound (**4e**) was above.

2-Methoxy-3,5,6-tri(2-methyl-2-propyl)thio-1,4-benzoquinone (8e): Yield: 0.1 g, 6.7%; Red oil; R_f [petroleum ether/$CHCl_3$(2:1)]: 0.15 ; IR (film, cm^{-1}): ν 1370 (C-H), 1670 (C = O), 1580 cm^{-1} (C = C); UV/vis ($CHCl_3$): λ_{max} = 246, 347 nm; ^1H NMR (500 MHz, $CDCl_3$): δ 1.19-1.48 (m, 27H, CH_3), 4.12 (s, 3H, CH_3O-); ^{13}C NMR (125 MHz, $CDCl_3$): δ 28.68, 30.92, 31.49, 31.55, 49.16, 50.85, 51.73, 60.43 (CH_3-O-), 145.43, 155.02, 163.13, 177.16, 179.89; MS (ESI): *m/z* (%) 402.32 (100); $C_{19}H_{30}O_3S_3$ (402.64); Calcd.: C, 56.68; H, 7.51; S, 23.89. Found: C, 57.26; H, 7.03; S, 19.49.

Acknowledgments. We gratefully thank the Research Fund of the University of Istanbul for financial support of this work.

References

1. McReynolds, M. D.; Doughtery, J. M.; Hanson, P. R. *Chem. Rev.* **2004**, *104*, 2239.
2. Zhu, J. *Synletters* **1997**, *2*, 133.
3. Becker, J. Y.; Bernstein, J.; Bittner, S.; Harlev, E.; Sarma, J. A. R. P.; Saik, S. S. *New J. Chem.* **1988**, *12*, 875.
4. Otsubo, T.; Nobuhara, Y.; Kanefuji, K.; Aso, Y.; Ogura, F. *J. Phys. Org. Chem.* **1988**, *1*, 275.
5. Vanelle, P.; Terme, T.; Crozet, M. P. *Tetrahedron Lett.* **2000**, *41*, 6383.
6. Mohanda, J.; Chennell, A. F.; Duggin, G. G.; Horvat, J. S.; Til Horvat Ier, D. J. *Carcinogenesis* **1986**, *7*, 353.
7. Bittner, S.; Lemperit, D. *Synthesis* **1994**, *9*, 917.
8. Smith, M. T. *J. Toxicol. Environ. Health* **1985**, *16*, 665.
9. Batra, M.; Kriplani, P.; Batra, C.; Ojha, K. G. *Bioorganic & Medicinal Chemistry* **2006**, *14*, 8519.
10. Tjepkema, J. J. *Rec. Trav. Chim.* **1952**, *71*, 853.
11. Takagi, K.; Mizuno, A.; Iwamoto, A.; Furusyo, M.; Matsuoka, M. *Dyes and Pigments* **1998**, *36*(1), 35.
12. Goksel, F. S.; Ibis, C.; Bayrak, N. A. *Phosphorus, Sulfur, and Silicon* **2005**, *180*, 1961.
13. Ibis, C.; Gunes Z. O. *Dyes and Pigments* **2008**, *77*(1), 39.
14. Romanyuk, A. L.; Litvin, B. L.; Ganushchak, N. I.; Vishnevskii, R. M. *Russain Journal of General Chemistry* **2006**, *76*(11), 1834.
15. Murata, T.; Morita, Y.; Fukui, K.; Sato, K.; Shiomi, D.; Takui, T.; Maesato, M.; Yamochi, H.; Saito, G.; Nakasuji, K. *Angew. Chem. Int. Ed.* **2004**, *43*, 6343.
16. Aslan, M.; Masnovi, J. *Spectrochimica Acta Part A* **2006**, *64*, 711.
17. Horiuchi, S.; Kumai, R.; Okimoto, Y.; Tokura, Y. *Synthetic Metals* **2003**, *133-134*, 615.
18. Takeya, T.; Kondo, H.; Otsuka, T.; Doi, H.; Okamoto, I.; Kotani, E. *Chem. Pharm. Bull.* **2005**, *53*(2), 199.
19. Gaber, M.; Al-Shihry, S. S. *Spectrochimica Acta Part A* **2005**, *62*, 526.

20. Sadeghi, S.; Karimi, E. *Chem. Pharm. Bull.* **2006**, *54*(8), 1107.
21. Marder, S. R. *Metal Containing Materials for Nonlinear Optics, Inorganic Materials*. 2nd ed.; Bruce D. W; Hare D. O`., Eds.; Chichester: Wiley, 1996; p 121.
22. Tjepkema, J. J. *Manufacture of Organomercapto-substituted Quinones*, U. S. 2,691,661; October 12, 1954.
23. Matsumoto, S.; Miura, H.; Mizuguchi, J. *Dyes Pigments* **2002**, *52*, 9.
24. Matsumoto, S.; Mizuguchi, J. *Acta Crystallographica Section B* **2001**, *57*, 82.
25. Sammis, J. L. *J. Am. Chem. Soc.* **1905**, *27*, 1120.
26. Yoshioka, T.; Kurumada, T.; Yamazaki, M. *2-Mercaptoquinone Derivate*, J. P. 57085366; May 28, 1982.
27. Raymond, C. S. *Tetra-T-Dodecylamarcapto-p-Benzoquinone*, U. S. 3764535; October 9, 1973.
28. Snell, J. M.; Weissberger, A. *J. Am. Chem. Soc.* **1938**, *61*, 450.
29. Bittner, S.; Meenakshi, C.; Temtsin, G. *Tetrahedron* **2001**, *57*, 7423.