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A reaction of 3,6-di(*tert*-butyl)-4-chloro-1,2-benzoquinone with potassium ethyl xanthate. New sulfur-containing *o*-quinones

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In a reaction of 3,6-di(*tert*-butyl)-4-chloro-1,2-benzoquinone with potassium ethyl xanthate, the halogen atom was replaced by the ethyl xanthate group. Acid hydrolysis of the product gave 4,7-di(*tert*-butyl)-5,6-dihydroxy-1,3-benzodithiol-2-one containing a pyrocatechol fragment, which was oxidized into the corresponding quinone. When irradiated in solution with visible light, this quinone quantitatively eliminated a CO molecule with contraction of the ring to a five-membered one. The quinones obtained were studied as ligands in coordination spheres of metals by ESR spectroscopy.

Key words: sterically hindered *o*-quinones and pyrocatechols, 1,3-dithiole, metal complexes with *o*-semiquinones.

In recent years, investigations of complexes of transition and Main Group elements with sterically hindered ligands genetically related to *o*-quinones have become a separate area of coordination chemistry. Such rapt attention is due to at least two reasons.

1. When entering the coordination sphere of a metal, these variable-valence ligands conform their valences to the redox potential of the metal in the rest of the ligand environment. Thus, the structure of a redox ligand allows one to control the valences in the complex.

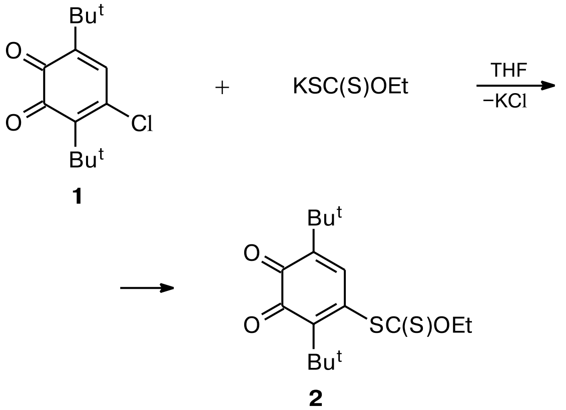
2. Bringing the valences of a metal and a redox ligand to thermodynamic agreement is usually accompanied by intramolecular electron transfer. With consideration that stable radical species are conveniently detected by the ESR method, this provides a powerful source of information on the structure and dynamics of the coordination sphere of the metal.

Extension of the range of the redox properties of ligands attracts attention to the problem of functionalization of *o*-quinones. The range of the latter can be substantially extended by using reactions of 3,6-di(*tert*-butyl)-1,2-benzoquinone with organometallic compounds and CH acids.[1,2] An alternative is nucleophilic displacement of the halogen from positions 4 and 5 of sterically hindered *o*-quinone. We employed this reaction for the synthesis of sulfur-containing *o*-quinones. 3,6-Di(*tert*-butyl)-4-chloro-1,2-benzoquinone (**1**) was used as a substrate and potassium ethyl xanthate was used as a nucleophilic reagent. In the present work, we studied new synthetic potentialities associated with subsequent hydrolysis of the substitution product.

Results and Discussion

When equimolar amounts of the reagents were mixed in THF at room temperature, the starting *o*-quinone (**1**) virtually completely converted into quinone **2** in 20 min (Scheme 1).

Scheme 1



Quinone **2** is a dark red crystalline solid with m.p. 83 °C, which is soluble in common organic solvents. Its acid hydrolysis occurs anomalously. It is known[3] that the hydrolysis of xanthates mainly yields thiols through cleavage of the C—S bond in the sulfide fragment. However, quinone **2** in the presence of dilute HCl underwent closure of the 1,3-dithiole ring to give pyrocatechol **3**.

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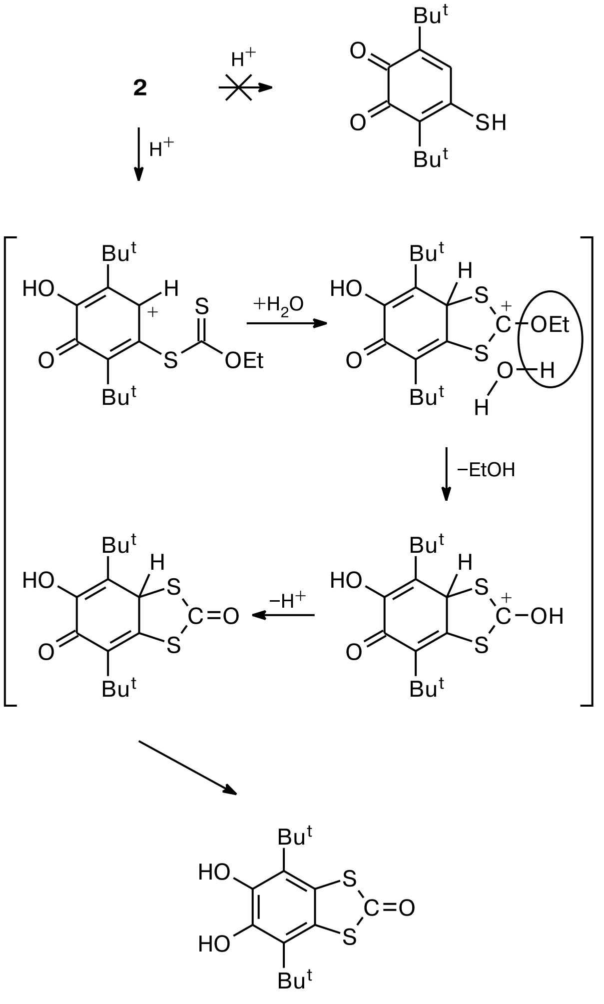
The suggested mechanism of the reaction is shown in Scheme 2.

Scheme 2



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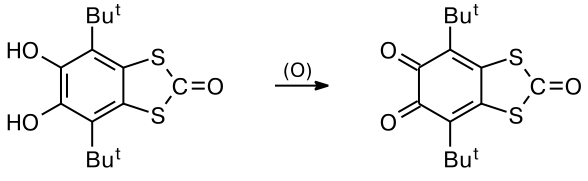
The overall equation of the process has the form

$$\mathbf{2} + H_2O \rightarrow \mathbf{3} + EtOH.$$

The formation of such 1,3-dithiole rings from dithiocarbamate derivatives of substituted pyridines has been reported earlier.[4]

Like most of the known analogs, pyrocatechol **3** is a colorless crystalline solid with m.p. 110 °C. Its IR spectrum shows characteristic bands of the C=O stretching vibrations in the dithiole ring (1630 cm^{-1}) and of the stretching vibrations of the sterically hindered OH groups of pyrocatechol (3420 and 3250 cm^{-1}). The compound is easily oxidized with alkali metal ferricyanide in ethereal solution into the corresponding *o*-quinone **4** (Scheme 3).

Scheme 3

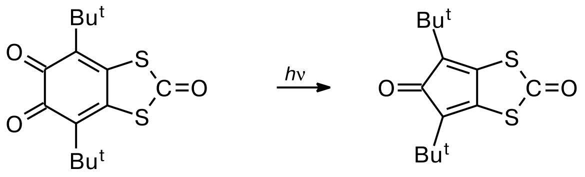


3 **4**

The structure of quinone **4** was confirmed by X-ray diffraction analysis. According to the crystallographic data, its molecule is virtually planar; the bond lengths in the quinone ring distinctly alternate, which is typical of the *o*-quinone structure (Fig. 1) (C(3)—C(2), 1.358(3) Å; C(3)—C(4), 1.479(3) Å; C(4)—C(4A), 1.535(5) Å; C(2)—C(2A), 1.508(4) Å). The bond lengths in the five-membered ring are typical of 1,3-dithiole rings.[5]

When a solution of compound **4** in toluene was irradiated with visible light (a KGM-24-150 halogen lamp), the *o*-quinone ring eliminated a CO molecule to give bright red dienone **5** (Scheme 4).

Scheme 4



4 **5**

The reaction proceeded almost quantitatively over several hours (TLC data). A similar process is known for 3,6-di(*tert*-butyl)-1,2-benzoquinone;[6] however, it requires more drastic conditions (UV irradiation) and is followed by the Diels—Alder dimerization of the resulting dienone.[7]

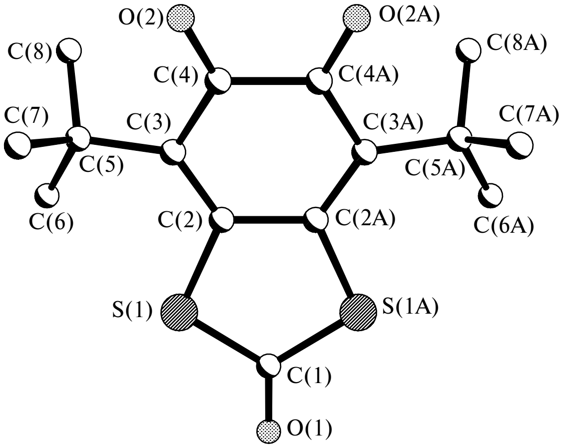


Fig. 1. General view of structure **4**.

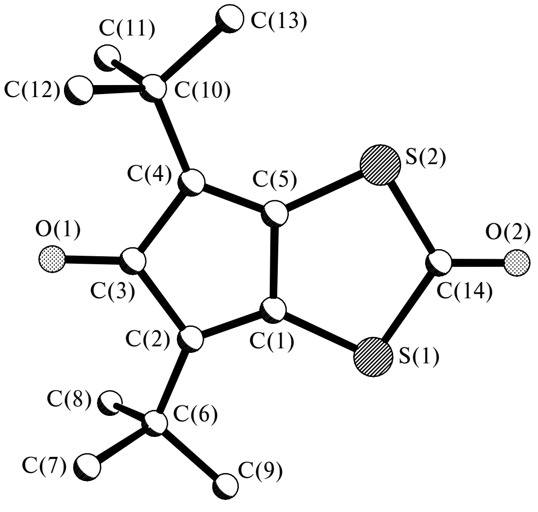


Fig. 2. General view of structure **5**.

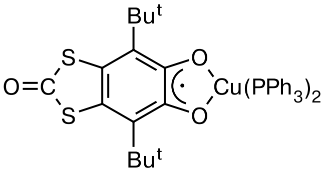
Table 1. Parameters of the isotropic ESR spectra of metal complexes with quinones **2** and **4** in THF at 290 K

Quinone	Metal-containing fragment	*g* Factor	$a_{\rm H}$	$a_{\rm M}$	$a_{\rm L}$
				mT	
2	K	2.0049	0.27	—	—
	Tl	2.0001	0.30	6.30	—
4	K	2.0046	—	—	—
	Tl	1.9995	—	6.11	—
	$Cu(PPh_3)_2$	2.0059	—	1.11	1.86
	Cu(bpy)	2.0999	—	8.74	0.88

The structure of compound **5** was unambiguously determined by IR and NMR spectroscopy and X-ray diffraction analysis (Fig. 2).

Like most of the sterically hindered *o*-quinones studied, compounds **2** and **4** in solution can be reversibly reduced successively in two one-electron steps with alkali metals and thallium amalgam to give radical anions of *o*-semiquinones and catecholate dianions. The parameters of the ESR spectra of complexes of compounds **2** and **4** in THF are given in Table 1. The character of these spectra is typical of *o*-semiquinones. Because derivatives **4** contain no ring protons or other magnetic nuclei (except ^{13}C and ^{33}S), the hyperfine structure is only due to splitting on the magnetic nuclei of metal cations. In addition, the lines in the ESR spectra of derivatives **4** are very narrow and thus the new quinone is of purely methodical interest for analysis of complex ESR multiplets when excessive lines of a radical ligand proper should be get rid of as far as possible. An example of such systems are semiquinone copper complexes with phosphine ligands (**6**).

Like a number of other *o*-quinones, compound **4** in THF in the presence of α,α´-bipyridyl dissolves metallic copper to give copper(II) catecholate complex **7**. In this complex, the unpaired electron is localized at the Cu atom (d^9 configuration), which is evident from the parameters of the ESR spectrum (see Table 1).



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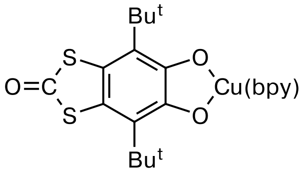

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Thus, we studied the reaction of 3,6-di(*tert*-butyl)-4-chloro-1,2-benzoquinone with potassium ethyl xanthate and obtained two novel *o*-quinones. These *o*-quinones can be used as ligands in the coordination spheres of metals.

Experimental

3,6-Di(*tert*-butyl)-1,2-benzoquinone was prepared as described earlier[8] and used for the synthesis of 3,6-di(*tert*-butyl)-4-chloro-1,2-benzoquinone (**1**) according to a known procedure.[9] Solvents were purified in standard ways.[10] High-purity potassium ethyl xanthate was used. A KGM-24-150 lamp with a focusing unit served as a light source. A radiation with $\lambda \geq 440$ nm was isolated by an appropriate light filter. ESR spectra were recorded on a Bruker ER 200D-SRC spectrometer. The *g* factor was determined with dinitrophenylpicrylhydrazyl (DPPH) as the standard. Samples of semiquinone and catecholate complexes for ESR studies were prepared according to known procedures.[11,12] IR spectra were recorded on a Specord M-80 spectrometer (Nujol). ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX-200 instrument (200 (^1H) and 50 MHz (^{13}C)) in $CDCl_3$. X-ray diffraction analysis was carried out on a Smart Apex diffractometer (Bruker AXS) at 100 K. All structures were solved by the direct method and refined by the least-squares method on F^2_{hkl} in the anisotropic approximation for all non-hydrogen atoms. The H atoms were located from an electron-density difference map and refined isotropically. All calculations were performed with the SHELXTL program package (v. 6.10). Atomic coordinates have been deposited with the Cambridge Crystallographic Data Center.

***S*-[2,5-Di(*tert*-butyl)-3,4-dioxocyclohexa-1,5-dien-1-yl] *O*-ethyl dithiocarbonate (2).** Compound **1** (5 g, 20 mmol) and potassium ethyl xanthate (3.1 g, 20 mmol) were dissolved in THF (20 mL) and the solution was stirred for 45 min. The degree of conversion of the starting quinone was checked by TLC. The mixture was filtered and the filtrate was concentrated. The product was recrystallized from hexane to form red-brown crystals. The yield was 9.03 g (85%), m.p. 83—84 °C. Found (%): C, 59.21; H, 6.97; S, 19.02. $C_{17}H_{24}O_3S_2$. Calculated (%): C, 59.97; H, 7.10; S, 18.83. IR, ν/cm^{-1}: 1680, 1660 (C=O). ^1H NMR, δ: 1.22, 1.39 (both s, 9 H each, Bu^t); 1.44 (t, 3 H, $OCH_2C\underline{H}_3$, *J* = 7.3 Hz); 4.72 (q, 2 H, $OC\underline{H}_2CH_3$, *J* = 7.3 Hz); 6.86 (s, 1 H, C=CH). ^{13}C NMR, δ: 14.0 ($OCH_2\underline{C}H_3$); 29.1, 31.0 ($C(5)C(\underline{C}H_3)_3$, $C(2)C(\underline{C}H_3)_3$); 35.2, 38.0 ($C(5)\underline{C}(CH_3)_3$, $C(2)\underline{C}(CH_3)_3$); 72.1 ($O\underline{C}H_2CH_3$); 144.1 (C(6)); 138.7, 147.0, 157.5 (C(1), C(2), C(5)); 184.9, 187.7 (C(3), C(4)); 208.8 ($\underline{C}$=S).

4,7-Di(*tert*-butyl)-5,6-dihydroxy-1,3-benzodithiol-2-one (3). Dilute HCl (20 mL) was added to a solution of compound **2** (6.8 g, 20 mmol) in THF (20 mL). The mixture was stirred with a magnetic stirring bar for 20 min and diluted with water (100 mL). The organic material was extracted with ether. The ethereal solution was washed with water to a neutral reaction. The solvent was removed and the colorless crystals that formed were recrystallized from methanol. The yield was 4.99 g (80%), m.p. 110—111 °C. Found (%): C, 57.80; H, 6.51; S, 20.67. $C_{15}H_{20}O_3S_2$. Calculated (%): C, 57.66; H, 6.45; S, 20.53. IR, ν/cm^{-1}: 3420, 3250 (OH); 1630 (C=O). ^{1}H NMR, δ: 1.59 (s, 18 H, Bu^t); 6.28 (s, 2 H, OH). ^{13}C NMR, δ: 31.3 ($C(\underline{C}H_3)_3$); 38.0 ($\underline{C}(CH_3)_3$); 124.0, 129.1, 143.7 (C arom.); 192.1 (C=O).

4,7-Di(*tert*-butyl)-5,6-dihydro-1,3-benzodithiole-2,5,6-trione (4). Compound **3** (6.2 g, 20 mmol) was dissolved in diethyl ether (50 mL). A solution of $K_3[Fe(CN)]_6$ (0.04 mol) and $NaHCO_3$ (0.08 mol) in water (100 mL) was added. The mixture was stirred with a magnetic stirring bar for 1 h. The ethereal layer was separated, washed with water, dried over $CaCl_2$, and concentrated. The residue (dark red tabular crystals) was recrystallized from hexane. The yield was 6.01 g (97%), m.p. 84—85 °C. Found (%): C, 57.95; H, 5.91; S, 20.59. $C_{15}H_{18}O_3S_2$. Calculated (%): C, 58.04; H, 5.84; S, 20.66. IR, ν/cm^{-1}: 1690, 1660, 1640 (C=O). ^{1}H NMR, δ: 1.55 (s, 18 H, Bu^t). ^{13}C NMR, δ: 31.24 ($C(\underline{C}H_3)_3$); 37.98 ($\underline{C}(CH_3)_3$); 124.01, 128.78 ($\underline{C}=\underline{C}$); 191.43 (S$\underline{C}$(O)S); 193.44 (C$\underline{C}(O)\underline{C}$(O)C).

The molecular formula: $C_{15}H_{18}O_3S_2$, M = 310.41, orthorhombic crystals, space group *Pnma*. At 100 K: a = 7.5066(19) Å, b = 20.914(5) Å, c = 9.411(2) Å, V = 1477.5(6) Å^3, Z = 4, R_1 = 0.0651 ($I > 2\sigma$), wR_2 = 0.1403 (for all reflections).

4,6-Di(*tert*-butyl)-5*H*-cyclopenta[*d*][1,3]dithiole-2,5-dione (5). A solution of compound **4** (3.12 g, 10 mmol) in toluene (100 mL) was exposed for 8 h to light emitted by a halogen lamp. The solvent was removed and the bright red needle-like crystals that formed were recrystallized from ether. The yield was 2.78 g (98%), m.p. 90—91 °C. Found (%): C, 59.47; H, 6.45; S, 22.20. $C_{14}H_{18}O_2S_2$. Calculated (%): C, 59.54; H, 6.42; S, 22.71. IR, ν/cm^{-1}: 1720, 1695 (C=O). ^{1}H NMR, δ: 1.24 (s, 18 H, Bu^t). ^{13}C NMR, δ: 29.55 ($C(\underline{C}H_3)_3$); 32.67 ($\underline{C}(CH_3)_3$); 130.19, 145.60 ($\underline{C}=\underline{C}$); 190.50 (SC(O)S); 193.60 (C$\underline{C}$(O)C).

The molecular formula: $C_{14}H_{18}O_2S_2$, M = 282.42, monoclinic crystals, space group $P2(1)/c$. At 100 K: a = 9.9560(8) Å, b = 10.4078(9) Å, c = 13.8278(12) Å, α = 90°, β = 92.470(2)°, γ = 90°, V = 1431.5(2) Å^3, Z = 4, R_1 = 0.0368 ($I > 2\sigma$), wR_2 = 0.0864 (for all reflections).

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