Functionalized derivatives of sterically hindered *o*-quinones and pyrocatechols. 3,6-Di-*tert*-butyl-4-dicyanometyl-1,2-benzoquinone and its isomers

G. A. Abakumov, V. I. Nevodchikov, N. V. Zaitova, N. O. Druzhkov, L. G. Abakumova, Yu. A. Kurskii, and V. K. Cherkasov*

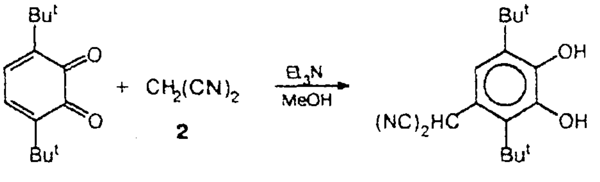
G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,
49 ul. Tropinina, 603600 Nizhnii Novgorod, Russian Federation.
Fax: 007 (831 2) 66 1497. E-mail: imoc@infotel.msk.su

Base-catalyzed interaction of 3,6-di-*tert*-butyl-1,2-benzoquinone with malononitrile mainly occurs as 1,4-addition to give 3,6-di-*tert*-butyl-4-dicyanomethylpyrocatechol. Its oxidation leads to 3,6-di-*tert*-butyl-4-dicyanomethyl-1,2-benzoquinone, which converts into 3,6-di-*tert*-butyl-2-hydroxy-α,α-dicyano-1,4-quinomethane in solution and in the solid state. The latter rearranges into isomeric 3,6-di-*tert*-butyl-5-dicyanomethylenecyclohex-3-ene-1,2-dione. Reverse conversion occurs under the action of amines. Semiquinone complexes of dicyanomethylquinone were studied in solutions by ESR.

Key words: *o*-quinones, pyrocatechol.

One of the new and promising trends in the chemistry of *o*-semiquinone metal complexes is the synthesis of coordination polymers on the basis of bifunctional *o*-semiquinone ligands.[1] Synthesis of the ligands themselves can be performed by introducing into the corresponding alkylated *o*-quinones and pyrocatechol groups which can, like the *o*-quinone fragment, coordinate with a metal, *e.g.*, amino and carboxy groups, β-diketones, cyano groups, *etc.* Interaction of 3,6-di-*tert*-butyl-1,2-benzoquinone (**1**) with malononitrile (**2**) was studied in the present work. Addition of CH-acids is a well-known reaction in the chemistry of *p*-quinones.[2] The direction of this addition — on the carbonyl group or to the ring carbon atoms — depends on the nature of a CH-acid, the presence of substituents in the quinone ring, and their steric properties. Interaction of malononitrile with alkylated *o*-quinones was not hitherto studied.

It was established that compound **1** reacted with an equimolar amount of **2** in MeOH in the presence of a catalytic amount of Et_3N to give 3,6-di-*tert*-butyl-4-dicyanomethylpyrocatechol (**3**) in high yield, which is essentially a product of 1,4-addition of a nucleophile to a carbonyl group conjugated with the double bond.



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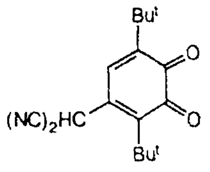
The structure of pyrocatechol **3** was confirmed by the data from elemental analysis and IR and ^{1}H NMR spectroscopy (see Experimental).

Oxidation of pyrocatechol **3** results in the formation of the corresponding 3,6-di-*tert*-butyl-4-dicyanomethyl-1,2-benzoquinone (**4**). *o*-Quinone **4** is an unstable compound and rearranges into isomeric 3,6-di-*tert*-butyl-2-hydroxy-α,α-dicyano-1,4-quinomethane (**5**) both in solution and in the solid state. According to IR spectroscopic data, the period of half-conversion in the solid state at ~20 °C is ~25—30 h. Dissolution of the solid product is accompanied by a rapid rearrangement into compound **5**, but when pyrocatechol **3** is oxidized with conc. HNO_3 (d = 1.5), *o*-quinone **4** is rather stable in non-polar solvents. According to UV spectroscopic data,



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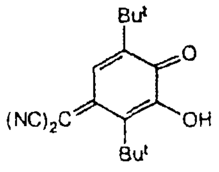

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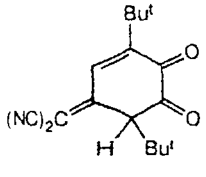

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Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 2, pp. 351—354, February, 1997.

the period of half-conversion at ~20 °C is 4—5 h, which allowed us to carry out the spectral (UV and ^{1}H NMR) studies of the solutions of *o*-quinone **4** and detect the formation of its semiquinone derivatives by ESR.

In solvating media in the presence of a catalytic amount of AcOH quinomethane **5** isomerizes quantitatively into 3,6-di-*tert*-butyl-5-dicyanomethylenecyclohex-3-ene-1,2-dione (**6**). The reverse transformation of diketone **6** into quinomethane **5** occurs in nonpolar solvents in the presence of diethylamine.

The visible region of the electronic spectrum of compound **4** has an absorption band with λ = 590 nm typical of alkylated *o*-quinones.[3] Along with absorption bands in the carbonyl region (1680 and 1660 cm^{-1}), which are characteristic of *o*-quinones,[3] the IR spectrum of *o*-quinone **4** also contains a low-intense absorption band with ν 2260 cm^{-1} corresponding to the stretching vibrations of the CN groups of the substituent. The low absorption is probably due to the strong electron-acceptor properties of the quinone fragment.

The value of ν(CO) 1655 cm^{-1} in the IR spectrum of compound **5** corresponds to the literature data for hydroxy-*p*-quinones and quinomethanes.[3] Two absorption bands (1680 and 1730 cm^{-1}) are observed in the IR spectrum of compound **6** in the region of the stretching vibrations of carbonyl groups. The displacement of one of them to the high-frequency region with respect to the values of ν(CO) characteristic of alkylated *o*-quinones is in agreement with the α-diketone structure of **6** (one of the carbonyl groups is not conjugated with the double bond and must have a higher value of ν(CO) than *o*-quinones).

In addition to the singlet signals of the protons of the *tert*-butyl groups, two doublets (δ 4.02 and 7.73) corresponding to the protons at C(6) and C(4), respectively, are observed in the ^{1}H NMR spectrum of diketone **6**. The spin-spin coupling constant observed (^4J = 1.1 Hz) shows that all five atoms are located in one plane, *i.e.*, *W*-conformation is realized. The ^{13}C NMR spectrum confirms the structure of compound **6**. Thus, the carbon atoms C(6) and $\underline{\text{C}}$(CN)$_2$ resonate at δ 66.9 and 87.9 (*cf.* Ref. 4a). The carbon atoms of the CN groups are not equivalent (δ 110.6 and 111.9) (*cf.* Ref. 4b).

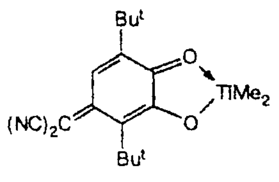
Two bands are observed in the UV spectrum of quinomethane **5**. One of them λ = 350 nm (ε 15000) refers to the $\pi \to \pi^*$-transition. The position of this absorption maximum correlates with the literature data for α,α-dicyanoquinomethanes.[5] A band with λ = 460 nm (ε 2300) corresponds to the $n \to \pi^*$-transition.

The shape of the electronic spectra of the solutions of diketone **6** depends on the solvent used. In toluene, the spectrum contains two absorption bands with λ = 310 nm (ε 15000) and λ = 490 nm (ε 150). The $\pi \to \pi^*$-transition in methanol is also characterized by intense absorption (λ = 300 nm, ε 25000) and an inflection in the visible region of the spectrum (λ = 470 nm).

o-Semiquinone complexes, derivatives of quinone **4**, can be obtained from both *o*-quinone itself and pyrocatechol **3**. Interaction of **4** with Mn$_2$(CO)$_{10}$ and Ph$_3$SnSnPh$_3$ results in the formation of paramagnetic products with the following parameters of ESR spectra: $a_i(^{55}\text{Mn})$ = 0.86 mT, a_i(H) = 0.27 mT, a_i(H') = 0.10 mT and $a_i(^{119}\text{Sn})$ = 0.48 mT, $a_i(^{117}\text{Sn})$ = 0.42 mT, a_i(H) = 0.37 mT, and a_i(H') = 0.10 mT. An *o*-semiquinone derivative of dimethylthallium, stable in solution, with the following parameters of the ESR spectrum: a_i(Tl) = 3.45 mT, a_i(H) = 0.30 mT, a_i(H') = 0.11 mT, and g = 2.0035, was obtained according to a reaction described earlier.[6] The HFS constant a_i(H) ~ 0.3 mT is due to HFI of the unpaired electron with the proton of the aromatic ring, and a_i(H') ~ 0.1 mT is caused by HFI with the proton of the dicyanomethyl moiety.

The values of a_i(H') obtained make it possible to determine the conformation of the dicyanomethyl substituent in the semiquinone derivatives of **4**. 3,6-Di-*tert*-butyl-4-methyl-1,2-benzosemiquinone[7] was chosen as a model for determination of the dihedral angle between the plane of the aromatic ring and the C—H bond of the substituent. This was made because, first, the HFI constant with the methyl protons gives a reference point for calculations, and, second, by comparing the a_i(H) constants of the ring protons, one can see that the distribution of spin density of the unpaired electron on C(4) and C(5) in semiquinones under consideration is almost the same. The dihedral angle calculated[8] is ~20°.

The presence of electron-acceptor CN substituents in quinomethane **5** leads to an increase in acidity of the proton of the hydroxy group. Owing to this the quinomethane is sensitive to the action of basic reagents (TlOH, NaOH, Et$_3$N), which is accompanied by the change in color of a methanolic solution from red, characteristic of quinomethane **5**, to intense blue (λ = 620 nm). Dimethylthallium 3,6-di-*tert*-butyl-α,α-dicyano-1,4-quinomethan-2-olate (**7**), a product of the reaction of compound **5** with Me$_2$TlOH, was isolated in the individual state.



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Compound **7** was characterized by the data from elemental analysis and IR and ^{1}H NMR spectroscopy. Intense absorption in the range of 1630—1440 cm^{-1} of the IR spectrum suggests the presence of a conjugated intramolecular chelate metal cycle in compound **7**.

Along with the signals of two Bu^t groups and that of the ring proton, a signal caused by the presence of two equivalent Me groups of the Me$_2$Tl fragment is observed in the ^{1}H NMR spectrum. This signal is a doublet (δ 1.0, J = 410 Hz) with broadened components. The splitting is due to an interaction with the magnetic nuclei ^{203}Tl and ^{205}Tl.

Hydroxyquinomethane derivatives (analogous to **7**) with different metal fragments can serve as synthons for the synthesis of bimetallic paramagnetic derivatives.

Experimental

The IR spectra were recorded on a Specord M80 spectrometer; the UV spectra were recorded on a Specord M40 spectrometer. The ^{1}H NMR spectra were recorded on a Tesla BS-567A spectrometer (100 MHz) with HMDS as the internal standard. The ESR spectra were obtained with a Bruker ER 200D-SRC with the double resonator ER 4105 DR at an operating frequency of 9.5 GHz. DPPH was used as the standard for determination of *g*-factor.

3,6-Di-*tert*-butyl-1,2-benzoquinone[9] and malononitrile[10] were synthesized according to the known procedures.

3,6-Di-*tert*-butyl-4-dicyanomethylpyrocatechol (3). 2—3 drops of Et_3N were added to a solution of 3,6-di-*tert*-butyl-1,2-benzoquinone (2.2 g) and malononitrile (0.66 g) in 100 mL of MeOH, and the reaction mixture turned dark blue. The course of the reaction was monitored by TLC (Silufol UV 254, the eluent was heptane—ethyl acetate, 200 : 1). After the initial quinone reacted completely, the reaction mixture was neutralized with AcOH, and the products were extracted with Et_2O. The ethereal layer was washed with water to neutral pH and dried with $MgSO_4$. After removal of the solvent, the product was crystallized from a heptane—toluene mixture. White crystals were obtained, yield 78%, m.p. 148—150 °C. Found (%): C, 71.30; H, 7.92. $C_{17}H_{22}N_2O_2$. Calculated (%): C, 71.33; H, 7.69. IR, ν/cm^{-1}: 2270 (CN); 3440, 3480, 3520 (OH). ^{1}H NMR ($CDCl_3$), δ: 1.42 (s, 9 H, 6-Bu^t); 1.58 (s, 9 H, 3-Bu^t); 5.66 (s, 1 H, OH); 5.74 (s, 1 H, $CH(CN)_2$); 5.97 (s, 1 H, OH); 7.12 (s, 1 H, H(5)).

3,6-Di-*tert*-butyl-4-dicyanomethyl-1,2-benzoquinone (4). Pyrocatechol **3** (0.14 g) was dissolved in 20 mL of toluene, and HNO_3 (0.08 mL, d = 1.5) was added dropwise; the reaction mixture turned thereby red-green. Heptane (15 mL) was then added, and the mixture obtained was cooled to −5 °C. The reddish-brown crystals that formed were filtered off, washed with heptane, and dried *in vacuo*. Yield 80%, m.p. (decomp.) 120 °C. Found (%): C, 70.20; H, 6.94. $C_{17}H_{20}N_2O_2$. Calculated (%): C, 71.83; H, 7.04. IR, ν/cm^{-1}: 1660, 1680 (C=O); 2260 (CN). ^{1}H NMR ($CDCl_3$), δ: 0.79 (s, 9 H, 6-Bu^t); 0.96 (s, 9 H, 3-Bu^t); 4.52 (s, 1 H, $CH(CN)_2$); 6.75 (s, 1 H, H(5)).

3,6-Di-*tert*-butyl-2-hydroxy-α,α-dicyano-1,4-quinomethane (5). ***A.*** Pyrocatechol **3** (0.3 g) was dissolved in MeOH, and 63% HNO_3 (0.1 mL) was added dropwise. The resulting solution was diluted with 2—3 vol. of water, and the product was extracted with Et_2O. The red-orange ethereal layer was washed with water to neutral pH and dried with $MgSO_4$. Following removal of the solvent, the residue was crystallized from heptane. Red plates were obtained, yield 91%, m.p. 131 °C. Found (%): C, 71.86; H, 7.25. $C_{17}H_{20}N_2O_2$. Calculated (%): C, 71.83; H, 7.04. IR, ν/cm^{-1}: 1655 (C=O); 2240 (CN); 3350 (OH). ^{1}H NMR ($CDCl_3$), δ: 1.29 (s, 9 H, 6-Bu^t); 1.53 (s, 9 H, 3-Bu^t); 7.54 (s, 1 H, H(5)); 7.96 (s, 1 H, OH). UV (toluene), λ_{max}/nm (ε): 350 (15000); 460 (2300).

B. Diketone **6** (0.3 g) was dissolved in toluene, and Et_2NH (2 mL) was added. The reaction mixture turned dark blue. AcOH (3 mL) was added, the mixture was kept for 3—5 min, then washed with water to neutral pH, and dried with $MgSO_4$. The solvent was removed, and the product was crystallized from heptane (yield 92%).

3,6-Di-*tert*-butyl-5-dicyanomethylenecyclohex-3-ene-1,2-dione (6). Quinomethane **5** (0.3 g) was dissolved in a methanol—water mixture, and 3—4 drops of acetic acid were added. The mixture was left for 10—15 h and during this period turned from red-orange to light yellow. The product was extracted with Et_2O, washed with water to neutral pH, and dried with $MgSO_4$. The solvent was removed, and the residue was crystallized from toluene. Yellow needles were obtained, yield 93%, m.p. 151 °C. Found (%): C, 71.71; H, 7.03. $C_{17}H_{20}N_2O_2$. Calculated (%): C, 71.83; H, 7.04. IR, ν/cm^{-1}: 1680, 1730 (C=O); 2220 (CN). ^{1}H NMR ($CDCl_3$), δ: 1.07 (s, 9 H, 6-Bu^t); 1.33 (s, 9 H, 3-Bu^t); 4.02 (d, 1 H, H(6), J = 1.1 Hz); 7.72 (d, 1 H, H(4), J = 1.1 Hz). ^{13}C NMR ($CDCl_3$), δ: 28.4 (3-$C(\underline{C}H_3)_3$); 28.9 (6-$C(\underline{C}H_3)_3$); 36.7 (3-$\underline{C}Me_3$); 40.5 (6-$\underline{C}Me_3$); 66.9 (6-CH); 87.9 ($\underline{C}(CN)_2$); 110.6 (CN); 111.9 (CN); 136.1 (4-CH); 160.5 (C(3)); 163.9 (C(5)); 180.6 (2-CO); 189.9 (1-CO). UV (toluene), λ_{max}/nm (ε): 310 (15000), 490 (150).

Dimethylthallium 3,6-di-*tert*-butyl-α,α-dicyano-1,4-quinomethane-2-olate (7). ***A.*** A mixture of quinomethane **5** (0.3 g) and Me_2TlOH (0.3 g) was dissolved in 20 mL of MeOH in an evacuated ampule and left for 5—7 h. Then the solvent was removed, and the residue was crystallized from toluene. Dark blue crystals were obtained, yield 94%, m.p. 168 °C. Found (%): C 44.91; H, 5.00; Tl, 39.44. $C_{19}H_{25}O_2N'_2Tl$. Calculated (%): C, 44.10; H, 4.84; Tl, 39.46. IR, ν/cm^{-1}: 1440 ($C \doteq O$); 1540, 1630 (C=O + C=C); 2210 (CN). ^{1}H NMR ($CDCl_3$), δ: 1.00 (d, 6 H, Me_2Tl, J = 410 Hz); 1.25 (s, 9 H, 6-Bu^t); 1.44 (s, 9 H, 3-Bu^t); 7.37 (s, 1 H, H(5)).

B. Pyrocatechol **3** (0.3 g) was dissolved in 10 mL of MeOH, and 10 mL of 1 *M* aqueous Me_2TlOH was added. The reaction mixture was left for 6—7 h. The precipitate that formed was filtered off and crystallized from toluene (yield 92%).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 95-03-09455). The spectrometric studies were performed at the analytical center of the Institute of Organometallic Chemistry of Russian Academy of Sciences with financial support from the Russian Foundation for Basic Research (Project No. 95-03-10729d).

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Received June 27, 1996;
in revised form September 11, 1996