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Synthesis and characterization of 2,6-di-*tert*-butyl-1-thio-1,4-benzoquinone, the first isolable monothio-1,4-benzoquinone

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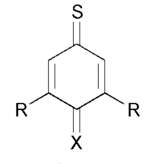
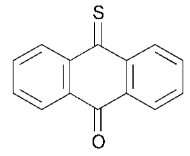
The title compound, a labile but isolable substance owing to appreciable steric protection, shows substantially higher electron affinity than the corresponding 1,4-benzoquinone and is reduced by water.

While *p*-benzoquinones have been extensively studied,[1] little has been known about the corresponding sulfur analogues. A major reason may be the general lability of thiocarbonyl compounds that makes their handling and isolation in pure form difficult.[2] Bock and co-workers have reported the pyrolytic generation and spectroscopic characterization of the parent dithio- and monothio-1,4-benzoquinones, **1** and **2**, in low temperature matrices.[3] Recently 2,6-dialkyl-4-thio-1,4-benzoquinones **3** have been generated and trapped by cycloaddition with 1,3-dienes.[4] The only isolable, related monothioquinone so far known is monothioanthraquinone **4**.[5] We have recently reported the synthesis and properties of thioquinone methides **5** in which *tert*-butyl groups give steric protection to a considerable extent.[6] Here we report the synthesis and characterization of 2,6-di-*tert*-butyl-1-thio-1,4-benzoquinone **6**, the first isolable, monothio-1,4-benzoquinone.



1: X = S; R = H
2: X = O; R = H
3: X = O; R = alkyl



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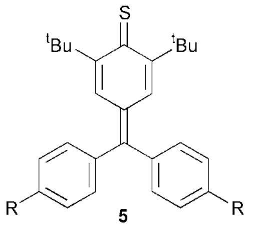

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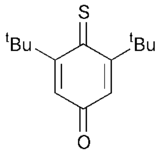

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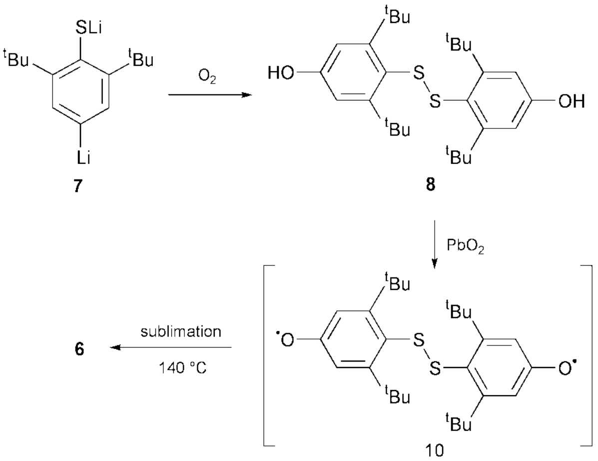
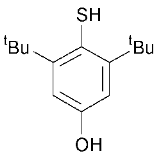
We have already described the generation of lithium 2,6-di-*tert*-butyl-4-lithiothiophenoxide **7** as the key synthon for **5**.[6] The exposure of a THF solution of **7** to O_2 at −70 °C followed by the usual work-up afforded bisphenol disulfide **8**† in 50% yield. A major byproduct was 2,6-di-*tert*-butylthiophenol, a reduction product. Obviously, the two *tert*-butyl groups at the *ortho*-positions are not bulky enough to hinder the coupling of the intermediate thiophenoxy radical as reported for the 2,6-di-*tert*-butylthiophenoxy radical itself.[7] The initially expected mercaptophenol **9**† was obtained by reduction of **8** with zinc powder in acetic acid (60%). The attempted oxidation of **9** to **6** with DDQ in benzene or acetone resulted, however, in the formation of **8**. We therefore expected that oxidation of **8** to its bis(phenoxy radical) **10** would cause cleavage of the rather weak disulfide bond, leading to the generation of **6**. In fact, NMR monitoring of a mixture of **8** and excess DDQ (3.5 equiv.) in deaerated benzene-d_6 in a sealed tube at room temperature gave rise to new proton signals as singlets at δ 1.14 and 6.48 and a ^{13}C signal at δ 233.45 (C=S) which are reasonable for the desired **6**. However, in spite of the use of excess DDQ, the reaction seemed to form a 2 : 1 equilibrium mixture of **6** and **8** probably by mediation of DDQ and its hydroquinone. Although the signals of **6** remained almost unchanged in the solution for at least two months, the attempted isolation of **6** from the mixture failed because of its lability. This failure suggests that the isolation of **6** from solutions should be difficult. In the end, the isolation of **6** in almost pure form was achieved in 70% yield by its sublimation to a water-cooled cold finger from a solid-state mixture of **8** and PbO_2 (1 : 30 w/w) heated at 140 °C under vacuum.





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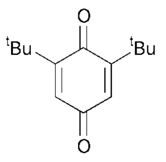

11

The monothiobenzoquinone **6**† thus obtained is a greenish yellow solid. Although relatively stable in the solid state as well as in neutral aprotic solvents such as benzene and acetone at room temperature, **6** is sensitive to moisture and other protic substances. The IR spectrum of **6** shows an intense carbonyl absorption at 1639 cm^{-1} and a less intense thiocarbonyl absorption (intense in the Raman spectrum) at 1141 cm^{-1}. This thiocarbonyl stretching frequency is considerably lower than that of **4** (1212 cm^{-1})[5] and even lower than the significantly dipolar 4*H*-pyran-4-thione (1168 cm^{-1}).[8] The electronic spectrum of **6** exhibits a weak absorption (ε = 32) at 758 nm, which is assignable to the n $\rightarrow$ π^* transition of the thiocarbonyl group, as well as a strong absorption at 321 nm. The visible absorption of **6** is at an appreciably longer wavelength than those of **2** (500 nm)[3] and **4** (697 nm).[5] The IR and visible absorption spectral

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results suggest a substantial polarization of the thiocarbonyl group of **6**. In this context, a semiempirical theoretical calculation (PM3) predicts that **6** should take the boat form, due to steric congestion, with bow and stern angles of 50° and 27°, respectively. This molecular deformation from planarity could be responsible for the enhanced polarization (elongation) of the thiocarbonyl bond.

Thiocarbonyl compounds are usually more easily reduced than the corresponding carbonyl compounds.[9] Upon cyclic voltammetry, **6** shows two irreversible reduction waves at -0.60 and -1.33 V (both peak potentials *vs*. Ag/Ag^+, in 0.1 M n-Bu_4NClO_4–CH_3CN, ferrocene/ferrocene$^+$ = 0.10 V). These reduction potentials are about 0.5 V lower than those of 2,6-di-*tert*-butyl-1,4-benzoquinone **11** (the corresponding peak potentials: 1.07 and 1.88 V) measured under the same conditions, indicating that **6** is a substantially strong electron acceptor. Surprisingly, **6** was found to be reduced rather than hydrolysed by water: when a small amount of D_2O was added into an acetone solution of **6** either in the dark or light at room temperature, the signals of **6** at δ 1.37 (s) and 6.46 (s) disappeared within 1 h with the concurrent appearance of new signals at δ 7.00 (s), 6.93 (br s), 6.73 (br s) and 6.52 (s) in the olefinic to aromatic region. The products were identified to be monothiohydroquinone **9**, disulfide **8** and benzoquinone **11**, formed in a 45 : 50 : 5 ratio (^{1}H NMR and TLC comparison with those of the authentic samples). The formation of **8** (probably also **9**) points to the intermediate formation of the corresponding thiophenoxy radical. In addition, the ferricyanide test as a preliminary qualitative test afforded a positive result, conforming the formation of hydrogen peroxide in the solution. Thus, hydrolysis of **6** to **11** is a very minor process, different from the usually easy hydrolysis of thioketones to ketones.

In conclusion, although the two *tert*-butyl groups at the *ortho* positions are not bulky enough for steric protection, 2,6-di-*tert*-butyl-1-thio-1,4-benzoquinone **6** was synthesized as a labile but isolable compound at around room temperature and was found to show a considerably high electron affinity and to undergo an unusual reaction with water. We are now investigating the detailed chemical properties of **6**.

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Notes and references

† *Selected physical and spectroscopic data*; **6**: mp 87–88 °C; MS (EI) *m/z* 238 ($M^+ + 2H$, 100%), 236 (M^+, 20), 221 ($M^+ - CH_3$, 27), 180 ($M^+ - C_4H_8$, 25), 165 ($M^+ - 71$, 69); IR: ν (KBr)/cm^{-1} 2963 (s), 1639 (s, C=O), 1556 (m), 1456 (m), 1366 (m), 1302 (m), 1261 (m), 1232 (m), 1200 (m), 1141 (m, C=S), 1096 (m), 1072 (m), 1022 (m), 910 (m), 801 (m); δ_H (400 MHz, C_6D_6) 1.13 (s, 18H), 6.49 (s, 2H); δ_C(100 MHz, C_6D_6) 30.98, 36.87, 121.94, 163.58, 189.94 (C=O), 233.45 (C=S); UV–Vis (cyclohexane) λ_{max}/nm (ε) 321 (14 300), 456 sh, 758 (32); **8**: mp 210–213 °C; MS (EI) *m/z* 474 (M^+, 12%), 238 ($M^+/2 + 1$, 100), 181 ($M^+/2 - C_4H_9$, 16); δ_H(270 MHz, CD_2Cl_2) 1.04 (s, 18H), 1.60 (s, 18H), 4.84 (br s, 2H, OH), 6.65 (s, 2H), 6.86 (s, 2H); The NMR spectra show restricted rotation of the S–S or C–S bond with an estimated energy barrier of $\Delta G^\ddagger = 16.5 \pm 0.2$ kcal mol^{-1} (T_c = 75 °C in benzene); see also ref. 10; **9**: mp 124–127 °C; MS (EI) *m/z* 238 (M^+, 100%), 181 ($M^+ - C_4H_9$, 17); δ_H(270 MHz, $CDCl_3$) 1.58 (s, 18H), 3.24 (s, 1H), 4.57 (s, 1H), 6.89 (s, 2H).

1 *The Chemistry of the Quinonoid Compounds*, ed. S. Patai and Z. Rappoport, Wiley, 2nd edn., 1988.

2 M. V. Lakshmikantham, M. Levinson, M. Menachery and M. P. Cava, *J. Org. Chem.*, 1986, **51**, 411; M. V. Lakshmikantham, M. S. Raasch, M. P. Cava, S. G. Bott and J. L. Atwood, *J. Org. Chem.*, 1987, **52**, 1874.

3 H. Bock, S. Mohmand, T. Hirabayashi, G. Maier and H. P. Reisenauer, *Chem. Ber.*, 1983, **116**, 273.

4 B. Cantini, G. Capozzi, S. Menichetti and C. Nativi, *Synthesis*, 1999, 1046.

5 M. S. Raasch, *J. Org. Chem.*, 1979, **44**, 632.

6 R. Suzuki, H. Kurata, T. Kawase and M. Oda, *Chem. Lett.*, 1999, 571.

7 W. Rundel, *Chem. Ber.*, 1968, **101**, 2956.

8 Á. Somogyi, G. Jalsovszky, C. Fülop, J. Stark and J. E. Boggs, *Spectrochim. Acta, Part A*, 1989, **45**, 679.

9 J. Simonet, in *The Chemistry of Sulfur-Containing Functional Groups*, ed. S. Patai and Z. Rappoport, Wiley, 1993, pp. 440–448.

10 H. Kessler and W. Rundel, *Chem. Ber.*, 1968, **101**, 3350; N. Ueyama, T. Okamura, Y. Yamada and A. Nakamura, *J. Org. Chem.*, 1995, **60**, 4893.