

The reactions of 3,6-di-*tert*-butyl-1,2-benzoquinone and 3,6-di-*tert*-butylcatechol with *tert*-butyl hydroperoxide

V. N. Glushakova,* N. A. Skorodumova, V. I. Nevodchikov, L. G. Abakumova,
N. P. Makarenko, V. K. Cherkasov, and N. O. Druzhkov

G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,
49 ul. Tropinina, 603600 Nizhnii Novgorod, Russian Federation.
Fax: +7 (831 2) 66 1497. E-mail: cherkasov@imoc.sinn.ru

Reaction of 3,6-di-*tert*-butyl-1,2-benzoquinone and 3,6-di-*tert*-butylcatechol with *tert*-butyl hydroperoxide in aprotic solvents leads to the generation of semiquinone (SQ·H), alkylperoxy (ROO·), and alkyloxy radicals. The reaction of SQ·H and ROO· produces 2,5-di-*tert*-butyl-6-hydroxy-1,4-benzoquinone, 3,6-di-*tert*-butyl-1-oxacyclohepta-3,5-diene-2,7-dione, and 2,5-di-*tert*-butyl-3,6-dihydroxy-1,4-benzoquinone. The radical generated from solvent attacks SQ·H at position 4 with C—C bond formation. 4-Benzyl-2,5-di-*tert*-butyl-6-hydroxycyclohexa-2,5-diene-1-dione produced in this way is transformed into 4-benzyl-3,6-di-*tert*-butyl-1,2-benzoquinone under the reaction conditions.

Key words: *tert*-butyl hydroperoxide, 3,6-di-*tert*-butyl-1,2-benzoquinone, 3,6-di-*tert*-butylcatechol, alkylperoxy radicals, alkyloxy radicals, semiquinone radicals.

The interest of researchers in the behavior of quinones and catechols in oxidative systems and their reactions with oxygen and organic peroxides is due to the fact that they are formed when oxidation of organic compounds is inhibited by phenols.^{1,2} In addition, the reaction of catechols with oxygen and organic hydroperoxides can serve as a model reaction for some stages of enzymatic oxidation of hydroxyl-containing aromatic compounds.^{3,4}

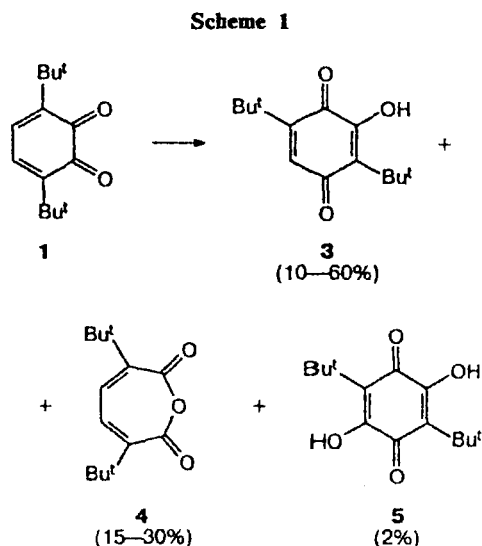
The oxidation of catechols with oxygen has been studied fairly comprehensively; however, their oxidation with peroxides is little studied. Oxygen oxidation of catechols gives *o*-benzoquinones as the major products. In the presence of transition metal compounds, products of extra- and intra-diol expansion of the six-membered ring are formed in addition to *o*-benzoquinones.^{5–7} The reaction of *o*-benzoquinones with hydrogen peroxide and inorganic and organic peroxy acids can be accompanied by ring opening,^{8,9} which is not observed when *tert*-butyl hydroperoxide (TBHP) is used as the oxidant.¹⁰ It has been reported that TBHP oxidizes 3,5-di-*tert*-butyl-1,2-benzoquinone to 3,5-di-*tert*-butyl-5,6-epoxycyclohex-3-ene-1,2-dione.¹¹

In the present work, we study the reactions of 3,6-di-*tert*-butyl-1,2-benzoquinone (1) and 3,6-di-*tert*-butylcatechol (2) with TBHP in aprotic solvents.

The composition of the reaction products and the degree of conversion of the initial compounds change as functions of the experimental conditions. It was shown by a special experiment that in the absence of compounds 1 and 2, TBHP does not decompose under the conditions used. The transformation of 1 mole of 1 or 2

requires 1.0–1.8 moles of TBHP, which is converted into *tert*-butyl alcohol (30–100%), di-*tert*-butyl peroxide (1–15%), and acetone (4–10%) (the yields are referred to 1 mole of consumed TBHP).

The main products formed when reaction is carried out in toluene are shown in Scheme 1.



Reagents and conditions: TBHP, toluene, 70–90 °C, vacuum.

Small amounts of products formed in the reaction of quinone 1 with the solvent, 4-benzyl-2,5-di-*tert*-butyl-6-hydroxycyclohexa-2,5-dien-1-one (6) (2–9%), 4-ben-

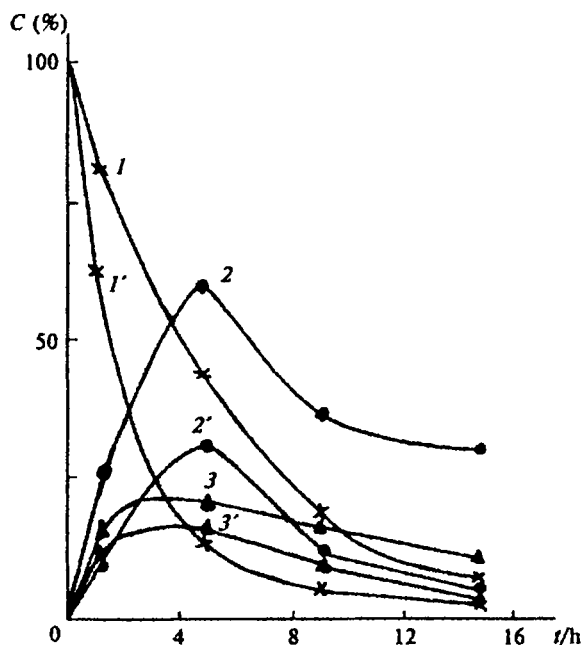
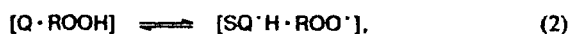


Fig. 1. Variation of the concentrations of compound 1 (*I*, *I'*) and products 3 (*2*, *2'*) and 4 (*3*, *3'*) (mol.% relative to reacted 1) during the reaction with TBHP at 70 °C (*I*–*3*) and 90 °C (*I'*–*3'*).

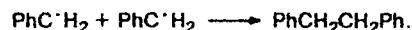
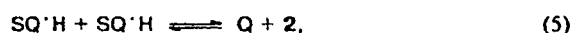
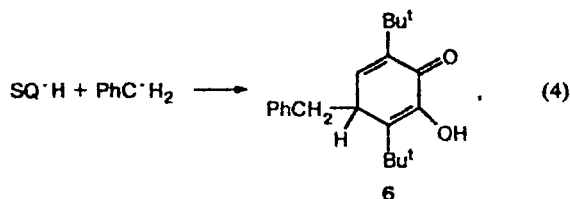
zyl-3,6-di-*tert*-butyl-1,2-benzoquinone (7) (1–9%), benzaldehyde (2%), and dibenzyl (2–6%), were also isolated (the yields are referred to 1 mole of consumed 1). More extensive oxidation of compound 1 gives 3-*tert*-butylfuran-2,5-dione (8) in addition to the above-listed products, as indicated by characteristic absorption bands at 1860 and 1765 cm^{-1} in the IR spectrum⁵ and by the formation of unidentified dimers and resinous substances. The composition of reaction products, unlike their yields, slightly depends on the temperature (Fig. 1). It can be seen from Fig. 1 that products 3 and 4 undergo subsequent transformations. In the case of catechol 2, quinone 1 (10–50%) is formed along with the above-listed compounds.

Based on the product composition, a scheme including both radical and molecular steps was proposed for this process. Quinone 1 (Q) and TBHP (ROOH) are bound into the [Q·ROOH] complex, due to hydrogen bonding. This is indicated by the IR absorption band corresponding to this associate at 3470 cm^{-1} ([TBHP] = $5 \cdot 10^{-3}$ mol L⁻¹, [I] = 0.02 to 0.10 mol L⁻¹); the intensity of this band increases with increase in the concentration of compound 1. It should be noted that the hydroperoxide is monomeric at the concentration used and the shift of the absorption band is close to those observed for complexes of TBHP with benzaldehyde and acetophenone.^{12,13} This step (reaction (1)) can be considered in terms of the concept of "activating complexation,"¹⁴ which is followed by the formation of semiquinone and peroxy radicals, which initiate the

traditional radical decomposition of the hydroperoxide (reactions (2) and (3)). In all probability, the radical intermediates arise upon the attack by the hydroperoxide on the Q·ROOH complex, in which the quinone acquires higher electron-withdrawing capacity due to the appearance of the positive charge:



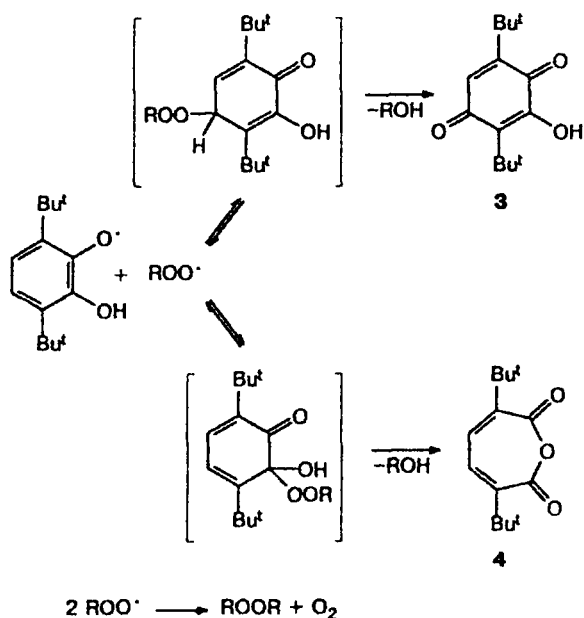
The intermediate formation of a semiquinone radical is indicated by the fact that the process is accelerated on exposure to light and on addition of compound 2. The radicals having emerged from the cage can react with the hydroperoxide or with the solvent, or disproportionate:



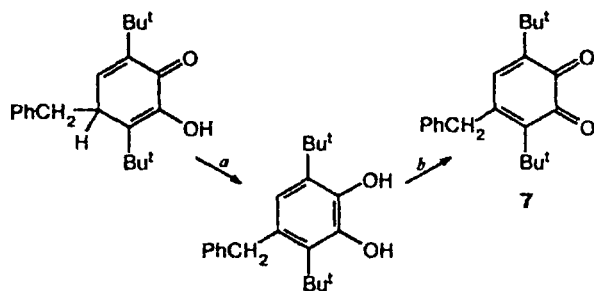
Reactions (2) and (3) are the rate-determining steps in this scheme. The high rates of reactions (4)–(6) preclude the possibility of detecting the ESR signal of the semiquinone radical. The formation of products 3 and 4 can be interpreted by assuming the interaction between the semiquinone and peroxy radicals (Scheme 2). However, a molecular mechanism of their formation, namely, nucleophilic 1,2- and 1,4-addition of hydroperoxide to the system of conjugated bonds including one carbonyl-bond of *o*-quinone, also cannot be ruled out. Product 3 can be oxidized under the reaction conditions to dihydroxybenzoquinone 5.

The formation of compound 6 as a product of recombination of benzyl and semiquinone radicals is of interest. The PhCH₂· radical adds to the SQ·H radical at position 4, which concentrates ~25% of the spin density of the unpaired electron (reaction (4)). Product 7 is formed upon oxidation of 4-benzyl-3,6-di-*tert*-butylcatechol, resulting from a rearrangement¹⁵ (Scheme 3).

Scheme 2



Scheme 3



Reagents and conditions: a. ROH, Δ ; b. ROOH, toluene.

The structures of products 6 and 7 were confirmed by their comparison with the corresponding compounds formed in the reaction of quinone 1 with dibenzylzinc.^{15,16}

The product of addition of the radical derived from the solvent at position 4 of the quinone was also detected when cyclohexane was used as the solvent. The reactions of compounds 1 and 2 with TBHP in acetonitrile, acetone, ethyl methyl ketone, cyclohexanone, and acetic acid give diketones 3 and 4 as the major products. No 4-substituted products were detected in this case; this is apparently due to the decrease in the steady-state concentration of the semiquinone radical upon the shift of the equilibrium in reaction (4) to the right occurring in polar solvents. The attempt to increase the yields of products 6 and 7 by initiating the radical decomposition of TBHP by adding azobis(isobutyronitrile) or cobalt stearate¹ was unsuccessful. In these cases, the degree of

conversion of TBHP increased, while the degrees of conversion of compounds 1 and 2 and the yields of products 6 and 7 remained unchanged. Apparently, this is due to the higher oxidizability of 3,4,6-substituted quinones, caused by the presence of an additional reaction site, a methylene or methine group able to be oxidized, at position 4. In this case, oxidative reactions resulting in the cleavage of the C—C bond to give quinone 1 become possible. It was shown in relation to compound 7 that under conditions similar to those used for the oxidation of quinone 1, the consumption of TBHP increases to 3 moles per mole of 7; in addition, a more complex product mixture is formed containing, among other compounds, compound 3 (12%), 4 (3%), 6 (3%), and diphenyl (traces), and the yield of benzaldehyde increases (9%).

Thus, the reaction of compounds 1 and 2 with TBHP involves oxygenation of the ring including that accompanied by ring expansion. The solvent radical adds into position 4 of the ring in 1 and 2; this can be regarded as a new channel of the decay of radicals R[·] in the reactions involving quinones and catechols, since only one route of their decay, *via* the formation of ethers, has been reported previously.^{17–19}

Experimental

Reaction products were analyzed by HPLC, GLC, TLC, and ¹H NMR and IR spectroscopy. HPLC analysis was carried out on a Milikhrom-1A microcolumn liquid chromatograph (variable-wavelength UV detector ($\lambda = 230 \text{ nm}$, $\lambda = 250 \text{ nm}$), a 2×64 mm steel column, Separon S6X as the adsorbent, hexane—THF (200 : 1) as the eluent, $\nu = 200 \text{ mL min}^{-1}$). Qualitative and quantitative analysis was performed using reference compounds. GLC analysis was carried out using a Tsvet-500 chromatograph (0.3×200 cm glass columns, 15% Reoplex-400 on Chromaton N-AW, heat conductivity detector, 70 °C, helium as the carrier gas). TLC was carried out on Silufol UV-254 plates in the heptane—THF system (9 : 1). Slightly colored spots on the chromatograms were visualized by treatment with iodine vapor. ¹H NMR spectra were recorded on a Tesla BS-567A spectrometer (100 MHz) in CDCl₃ using HMDS as the internal standard.

All solvents were purified by standard procedures.²⁰ Compounds 1 and 2 were prepared by known procedures.^{21,22} The reactions of TBHP with compounds 1 and 2 in solution were carried out at 1 : 1 and 5 : 1 ratios of the reactants; [TBHP] = 0.02–1.00 mol L⁻¹ at 70 and 90 °C in air or *in vacuo* for 3–24 h. After the experiment, the liquid products, unreacted TBHP, and the solvent were separated by condensation under reduced pressure, and the bottom residue and the condensate were analyzed separately, because compound 1 and some reaction products can also be determined by iodometric titration. The condensate was analyzed by iodometric titration for TBHP; the amounts of *tert*-butyl alcohol, acetone, and di-*tert*-butyl peroxide were determined by GLC. The bottom residue, thoroughly purified from the solvent, was dissolved in the eluent and analyzed by HPLC. The reference compounds were prepared by the procedures presented below.

2,5-Di-*tert*-butyl-6-hydroxy-1,4-benzoquinone (3) was synthesized by a procedure described previously,²³ m.p. 84 °C.

3,6-Di-*tert*-butyl-1-oxacyclohepta-3,5-diene-2,7-dione (4) was obtained by the reaction of quinone 1 with peracetic acid,⁸ m.p. 101 °C. Found (%): C, 71.10; H, 8.45. C₁₄H₂₀O₃. Calculated (%): C, 71.18; H, 8.47. IR, ν/cm^{-1} : 1740, 1780 (C=O). ¹H NMR, δ : 1.25 (s, 9 H, Bu^t); 6.39 (s, 2 H, H(4), H(5)).

2,5-Di-*tert*-butyl-3,6-dihydroxy-1,4-benzoquinone (5) was synthesized similarly to compound 3 from 3,6-di-*tert*-butyl-4,5-dimethoxy-1,2-benzoquinone. Found (%): C, 66.92; H, 8.11. C₁₄H₂₀O₄. Calculated (%): C, 66.67; H, 7.94. IR, ν/cm^{-1} : 1615, 1635 (C=O); 3260 (OH). ¹H NMR, δ : 1.36 (s, 9 H, Bu^t); 8.66 (s, 2 H, OH).

4-Benzyl-2,5-di-*tert*-butyl-6-hydroxycyclohexa-2,5-dien-1-one (6). A solution of dibenzylzinc (4.95 g, 0.02 mol) in 10 mL of THF was added dropwise to a solution of quinone 1 (4.4 g, 0.02 mol) in 50 mL of THF in an evacuated tube. The reaction mixture was hydrolyzed with AcOH; the products were extracted with hexane and dried with CaCl₂. Compound 6 was isolated from the resulting solution as colorless crystals (3.27 g, 52%), m.p. 89 °C. Found (%): C, 81.03; H, 8.82. C₂₁H₂₈O₂. Calculated (%): C, 80.77; H, 8.97. IR, ν/cm^{-1} : 1635 (C=O); 3370 (OH). ¹H NMR, δ : 1.12 (s, 9 H, Bu^t); 1.43 (s, 9 H, Bu^t); 2.20 (m, 1 H, H(4)); 3.43–3.64 (m, 2 H, CH₂); 6.64 (d, 1 H, H(5), *J* = 4.4 Hz); 7.10–7.40 (m, 5 H, Ph).

4-Benzyl-3,6-di-*tert*-butyl-1,2-benzoquinone (7). Several drops of HCl were added to a solution of compound 6 (1.6 g, 0.005 mol) in MeOH; after 30 min, the mixture was extracted with hexane, and the extract was washed with water to neutral reaction. An aqueous solution containing potassium ferricyanide (14 g) and KOH (1.6 g) was added to the hexane solution, and the mixture was stirred with a magnetic stirrer for 3 h. The organic layer was separated and washed with water to neutral reaction. Compound 7 was isolated from the hexane solution as dark-brown crystals (1.5 g, 95%), m.p. 97 °C. Found (%): C, 81.01; H, 8.20. C₂₁H₂₆O₂. Calculated (%): C, 81.29; H, 8.39. IR, ν/cm^{-1} : 1660, 1675 (C=O). ¹H NMR, δ : 1.11 (s, 9 H, Bu^t); 1.38 (s, 9 H, Bu^t); 4.00 (s, 2 H, CH₂); 6.43 (s, 1 H, H(5)); 7.10–7.40 (m, 5 H, Ph).

The spectroscopic measurements and chromatography were performed at the Analytical Center of the G. A. Razuvaev Institute of Organometallic Chemistry of the RAS and were financially supported by the Russian Foundation for Basic Research (Project No. 95-03-10729g).

References

1. E. T. Denisov, in *Itogi nauki i tekhniki. Kinetika i kataliz [Advances in Science and Engineering. Kinet. Catal.]*, VINITI, Moscow, 1984, 17, 3 (in Russian).
2. V. A. Roginskii, *Fenol'nye antioksidanty. Reaktivnaya sposobnost' i effektivnost'* [Phenolic Antioxidants. Reactivity and Efficiency], Nauka, Moscow, 1988, 140 pp. (in Russian).
3. L. Que and R. J. N. Ho, *Chem. Rev.*, 1996, 96, 2607.
4. V. A. Baraboi, V. E. Orel, and I. M. Karnaukh, *Perekisnoe okislenie i radiatsiya [Peroxide Oxidation and Radiation]*, Naukova Dumka, Kiev, 1991, 225 pp. (in Russian).
5. T. Funabiki, A. Mizoguchi, T. Sujimoto, S. Tada, M. Tsuji, H. Sakamoto, and S. Joshida, *J. Am. Chem. Soc.*, 1986, 108, 292.
6. P. Barbaro, C. Bianchini, P. Frediani, A. Meli, and F. Vizza, *Inorg. Chem.*, 1992, 31, 1523.
7. B. Galeffi, M. Postel, A. Grand, and P. Rey, *Inorg. Chim. Acta*, 1987, 129, 1.
8. C. Grundmann, in *Methoden der Organischen Chemie*, Houben-Weyl, Germany, 1977, VII/3b, 1.
9. J. Sawaki and C. S. Foote, *J. Am. Chem. Soc.*, 1983, 105, 5035.
10. J. Tsuji, T. Ohta, T. Ido, H. Minbu, and J. Watanabe, *J. Organomet. Chem.*, 1984, 270, 333.
11. K. Albert, H.-P. Schneider, D. Koch, and A. Ricker, *Z. Naturforsch., B*, 1978, 33, 100.
12. V. V. Voronenkov, G. B. Ushakov, O. P. Yablonskii, and G. S. Kazakova, *Zh. Fiz. Khim.*, 1984, 58, 1254 [*J. Phys. Chem. (USSR)*, 1984, 58 (Engl. Transl.)].
13. V. G. Makitra, V. Ya. Zhukovskii, Ya. N. Pirig, and B. I. Chernyak, *Zh. Prikl. Spektrosk.*, 1982, 36, 962 [*J. Appl. Spectr. (USSR)*, 1982, 36 (Engl. Transl.)].
14. G. A. Abakumov, in *Metalloorganicheskie soedineniya i radikaly [Organometallic Compounds and Radicals]*, Nauka, Moscow, 1985, 85 pp. (in Russian).
15. G. A. Abakumov, V. K. Cherkasov, L. G. Abakumova, N. O. Druzhkov, V. I. Nevodchikov, Yu. A. Kursky, and N. P. Makarenko, *Metalloorgan. Khim.*, 1991, 4, 925 [*Organomet. Chem. USSR*, 1991, 4 (Engl. Transl.)].
16. G. A. Abakumov, V. K. Cherkasov, L. G. Abakumova, V. I. Nevodchikov, N. O. Druzhkov, N. P. Makarenko, and Ju. A. Kursky, *J. Organomet. Chem.*, 1995, 491, 127.
17. M. A. Azatyay, G. V. Karpukhina, I. S. Belostotskaya, and N. L. Komissarova, *Neftekhimiya [Petrochemistry]*, 1973, 435 (in Russian).
18. E. S. Torsueva and Yu. A. Shlyapnikov, *Vysokomolek. soedineniya, B*, 1977, 19, 377 [*Polym. Sci. USSR, Ser. B*, 1977, 19 (Engl. Transl.)].
19. Yu. A. Shlyapnikov, V. A. Roginskii, and V. B. Miller, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 2487 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1978, 27, 2215 (Engl. Transl.)].
20. A. Weissberger, E. Proskauer, J. Riddick, and E. Toops, *Organic Solvents. Physical Properties and Methods of Purification*, Interscience Publ., New York—London, 1955.
21. N. S. Belostotskaya, N. L. Komissarova, E. V. Dzhuryan, and V. V. Ershov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1972, 1594 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1972, 21 (Engl. Transl.)].
22. N. S. Belostotskaya, N. L. Komissarova, E. V. Dzhuryan, and V. V. Ershov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, 1380 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1973, 22 (Engl. Transl.)].
23. N. Yu. Kabarova, V. K. Cherkasov, L. N. Zakharov, G. A. Abakumov, Yu. T. Struchkov, and L. G. Abakumova, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 2798 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, 41, 2224 (Engl. Transl.)].

Received April 13, 1998;
in revised form November 20, 1998