The formation and thermal decomposition of 4-hydroperoxy-2-hydroxy-3,4,6-triisopropylcyclohexa-2,5-dienone

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Auto-oxidation of 3,4,6-triisopropylcatechol affords crystalline 2-hydroxy-4-hydroperoxy-3,4,6-triisopropylcyclohexa-2,5-dienone. Thermal decomposition of the resulting hydroperoxide was carried out and the reaction products were determined. The decomposition mainly proceeds by a route without cleavage of the O—O bond, unusual for hydroperoxides, to give the starting 3,4,6-triisopropylcatechol and 3,4,6-triisopropylbenzo-1,2-quinone. The hydroperoxide decomposes in part according to the traditional pattern involving the O—O bond cleavage to give 3-hydroxy-2,5-diisopropylbenzo-1,4-quinone.

Key words: quinones, catechols, oxidation, hydroperoxide, hydroperoxycyclohexadienone, thermal decomposition, NMR, 2D NMR procedures.

Catechols and quinones readily undergo redox reactions. Compounds of this type are used as oxidation inhibitors and participate in many biological processes; therefore, oxidation of these compounds with both oxygen[1—4] and other oxidants,[5] including those giving rise to peroxides,[1,6] has been studied rather comprehensively.

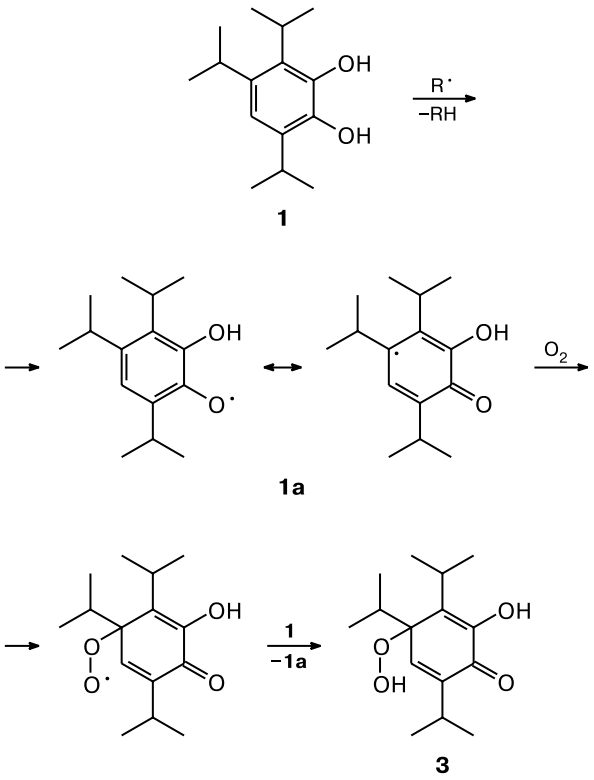
Spontaneous oxidation of 1,3,6,8-tetra-*tert*-butyl-4,5-dihydroxyphenanthrene with oxygen in the light to give 1,3,6,8-tetra-*tert*-butyl-1-hydroperoxy-5-hydroxy-4(1*H*)-phenanthrenone is documented.[1] Studies dealing with the synthesis of substituted alkylperoxycyclohexadienones have been reported.[6] Hydroperoxyhydroxycyclohexadienone has been suggested as an intermediate in the oxidation of 3,6-di-*tert*-butylbenzo-1,2-quinone and 3,6-di-*tert*-butylcatechol with *tert*-butylhydroperoxide.[5] When investigating the oxidation of quinones and catechols, some researchers[5,6] assumed the involvement of peroxycyclohexadienone radicals.

This study deals with the oxidation of 3,4,6-triisopropylcatechol (**1**). This compound was prepared by alkylation of unsubstituted catechol with propan-2-ol. Oxidation of catechol **1** gave 3,4,6-triisopropylbenzo-1,2-quinone (**2**).

Upon slow crystallization of compound **1** from hexane, colorless needle-like crystals were isolated. The ^{1}H NMR spectrum of the product exhibited signals for three isopropyl groups, two OH groups, and one ring proton, as was to be expected for **1**; however, all the methyl groups of the isopropyl fragments were nonequivalent. More detailed investigation using 1D (^{1}H, ^{13}C, DEPT [7]) and 2D (COSY, NOESY)[7] NMR techniques allowed identification of the isolated compound as 4-hydroperoxy-2-hydroxy-3,4,6-triisopropylcyclohexa-2,5-dienone (**3**). The presence of the HOO group was confirmed by

Scheme 1

Auto-oxidation of catechol **1** by atmospheric oxygen



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iodometric titration. It was further demonstrated that the addition of compound **3** to a solution of **1** or keeping of a solution of **1** in the light accelerates the formation of hydroperoxide **3**.

The transformation of catechol **1** into hydroperoxide **3** is apparently similar to auto-oxidation of some substituted dihydroxyphenanthrenes[1] (Scheme 1).

Crystalline hydroperoxide **3** is rather stable; it decomposes on heating above the melting point (107—109 °C).

The COSY spectrum of compound **3** (Fig. 1) shows spin-spin coupling of the methyl (δ 0.8—1.4) and methine (δ 2.9—3.1) protons of the isopropyl groups and coupling of the methine proton of one isopropyl group (δ 3.0) with the ring proton C(5)H (δ 6.76). The observed nonequivalence of the methyl groups in the isopropyl substituents is caused by the presence of a chiral center in the molecule of **3**; the largest difference between the chemical shifts of the CH_3 groups in the isopropyl substituent is observed for C(4)Pr^i (Δδ 0.39), a smaller difference is found for C(3)Pr^i (Δδ 0.09), and in the case of C(6)Pr^i, which is fairly remote from the chiral center, this difference is negligible (Δδ 0.02).

In the NOESY spectrum of compound **3**, the dipole-dipole couplings of the protons of the C(3)C$\underline{H}(CH_3)_2$ (δ 2.72) and C(4)C$\underline{H}(CH_3)_2$ (δ 2.12) fragments and one of the methyl groups of the C(4)(C$\underline{H}_3$)CHCH_3 fragment (δ 1.10) are observed together with the trivial coupling of the methine and methyl protons within each isopropyl group. The C(5)H proton (δ 6.76) is coupled with the protons of the two methyl groups in C(6)C$H(CH_3)_2$ (δ 1.12 and 1.14) and the methyl group in C(4)(CH_3)CHC$\underline{H}_3$ (δ 0.71). One can observe weak coupling of the proton of the C(2)OH hydroxy group (δ 6.65) with the methyl groups of C(3)C$H(C\underline{H}_3)_2$ (δ 1.29, 1.38) and peaks indicating the exchange between OH and OOH groups with each other and with water protons.

According to X-ray diffraction data (Fig. 2, selected bond lengths are given in the Experimental), the C—C and C—O bond lengths are close to the average lengths for such bonds in known compounds. In the crystal structure, the molecules are connected by hydrogen bonds (Fig. 3), two of these bonds being weak (the O(2A)...O(1C), 2.7537(19) Å, and O(4B)...O(2C), 2.881(2) Å, distances are close to twice the van der Waals radius of oxygen, 2.80 Å) and the third one being somewhat stronger (O(1A)...O(2C) 2.6298(19) Å).

The data from 2D NMR spectra are consistent with X-ray diffraction data and confirm the fact that the conformations of compound **3** in solution and in the crystalline state are similar.

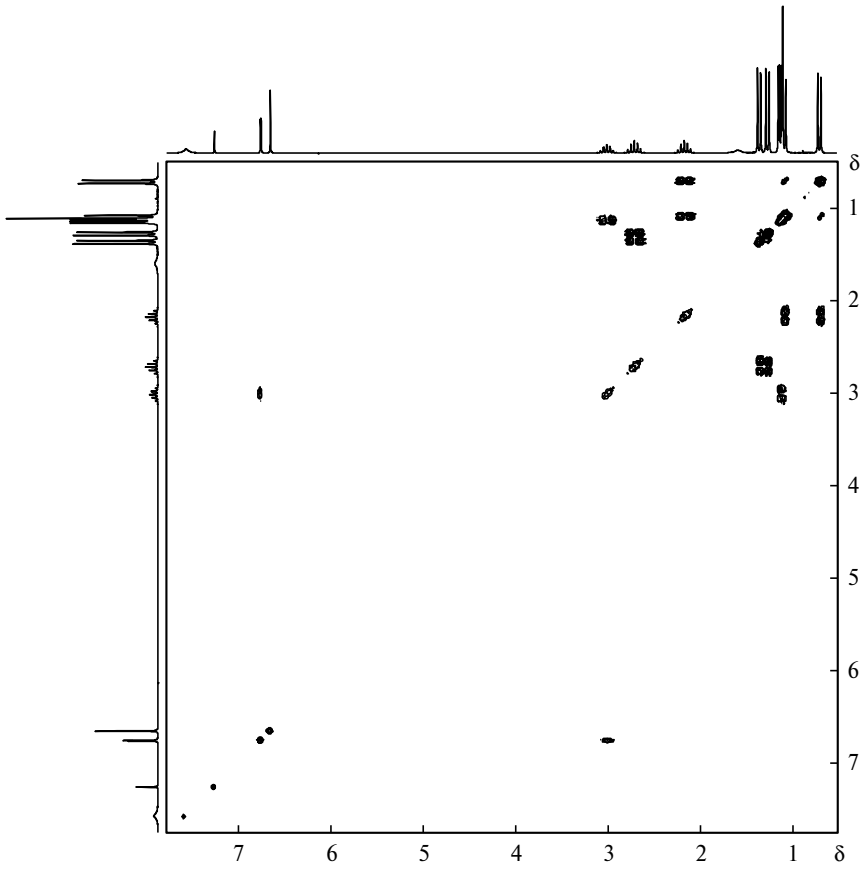


Fig. 1. Two-dimensional $^1H—^1H$ (COSY) correlation spectrum of compound **3**.

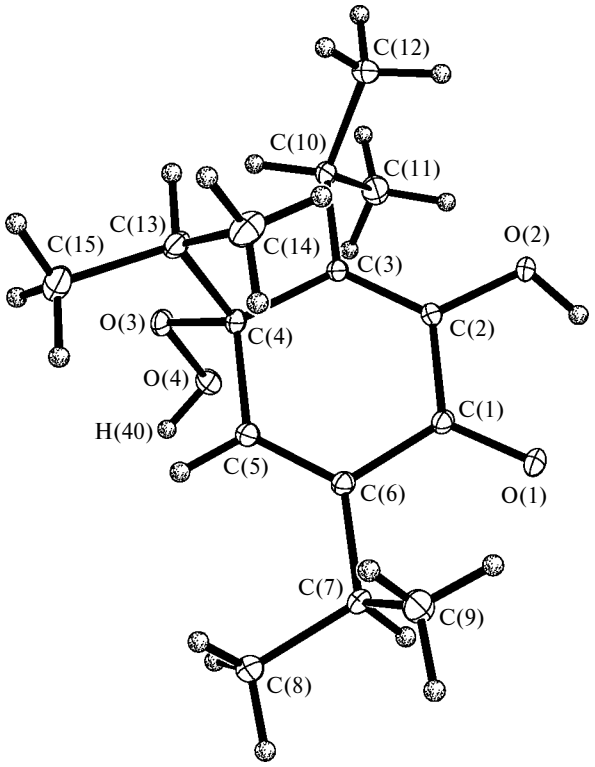


Fig. 2. Structure of hydroperoxide **3**.

The thermal decomposition of hydroperoxide **3** without a solvent (vacuum, 120 °C) is accompanied by gas evolution. According to NMR data, the volatile products isolated from the reaction mixture included water, propan-2-ol (major components), and a minor amount of acetone. The presence of H_2O_2 (~1—2%) in the volatile products was established by iodometric titration.

The major nonvolatile products formed in the decomposition of **3** include catechol **1** (~35%), quinone **2** (~20%), and 3-hydroxy-2,5-diisopropylbenzo-1,4-quinone (**4**) (~25%). Attractive features are unusually high yield of catechol **1** and the fact that the content of **1** in the products is substantially higher than that of quinone **2**. The relative molar contents of identified compounds were determined from the integral intensities of the ^{1}H NMR signals of the nonvolatile products formed upon decomposition of hydroperoxide **3**. The resulting values coincided, to within the experimental error, with the yields determined after chromatographic separation of the products.

Thermal decomposition of hydroperoxide **3** follows an unusual route with homolytic cleavage of the C—O bond of the hydroperoxide group (Scheme 2).

This decomposition route has been observed previously for related hydroperoxides with a cyclohexadiene structure and bulky substituents in the ring.[8] The radi-

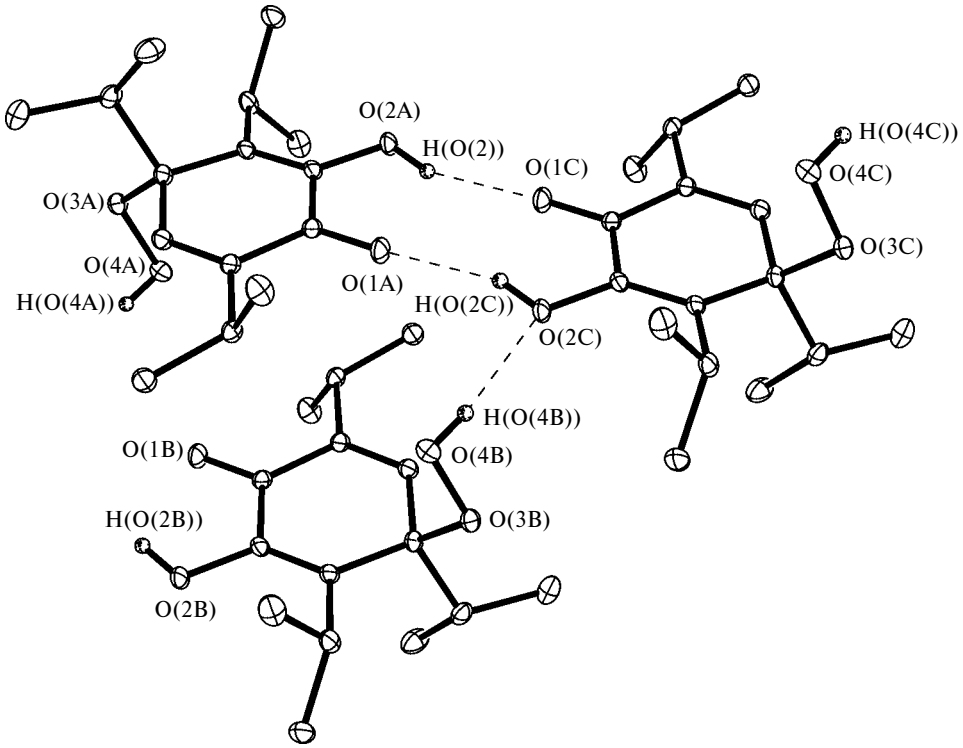
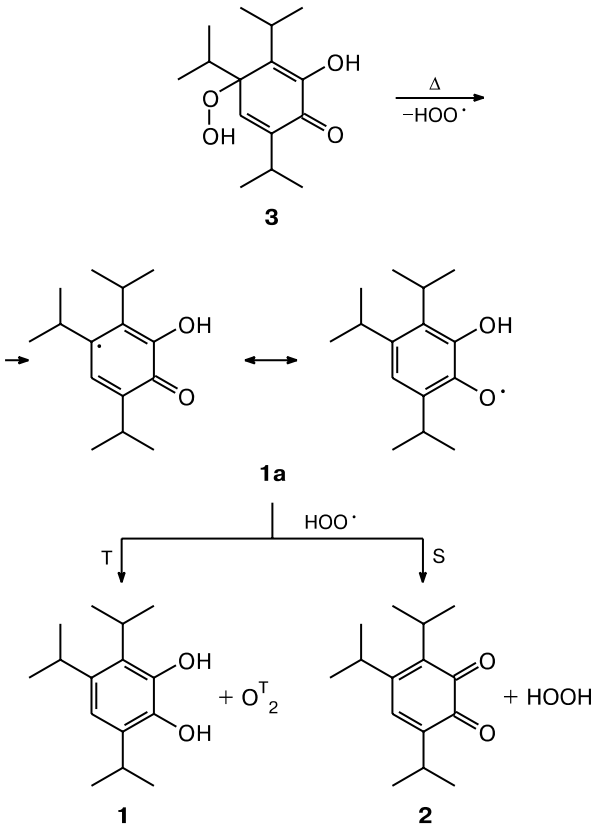


Fig. 3. Fragment of the crystal structure of **3** (only the hydrogen atoms at the OH groups are shown). Molecules B and C are identical and are enantiomers relative to molecule A.

Scheme 2

The major route of decomposition of hydroperoxide **3**



cal **1a** produced upon the homolytic cleavage can be transformed into the reaction products along two pathways, namely, (i) by reduction to give catechol **1** and oxygen and (ii) by disproportionation with the hydroperoxide radical (a radical pair in the singlet (S) state) yielding diamagnetic products, quinone **2** and H_2O_2. Despite the fact that only singlet radical pairs can recombine (disproportionate) to give diamagnetic products, the first disproportionation can also take place in the triplet (T) state of the radical pair because the ground state of oxygen is a triplet.

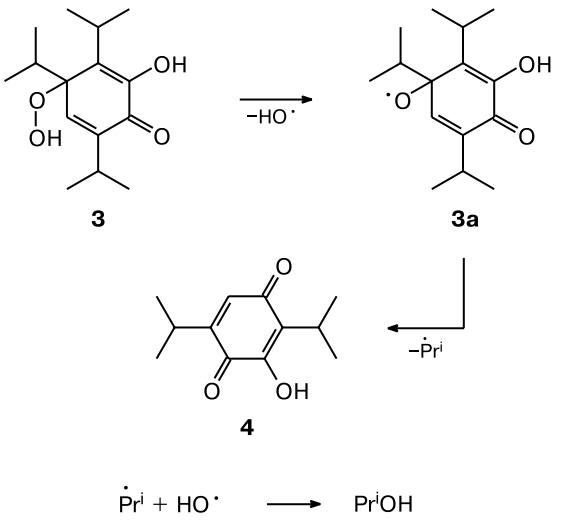
Typical decomposition of hydroperoxide **3** accompanied by homolytic cleavage of the O—O bond yields radical **3a**, which is further converted into quinone **4** upon fragmentation with elimination of an isopropyl radical (Scheme 3). The share of this route is less than one third.

The use of *C*-phenyl-*N*-*tert*-butylnitrone as a spin trap allowed detection of a stable radical resembling most closely in its parameters[9] (a_H = 2.55 mT, a_N = 14.75 mT, g = 2.0062, dH = 1.2 mT) the spin adduct with the isopropyl radical.

The two oxygen atoms in radical **1a** are involved in very fast proton exchange, similar to that in 3,6-di-*tert*-butyl-2-hydroxyphenoxyl radical[10] where the exchange

Scheme 3

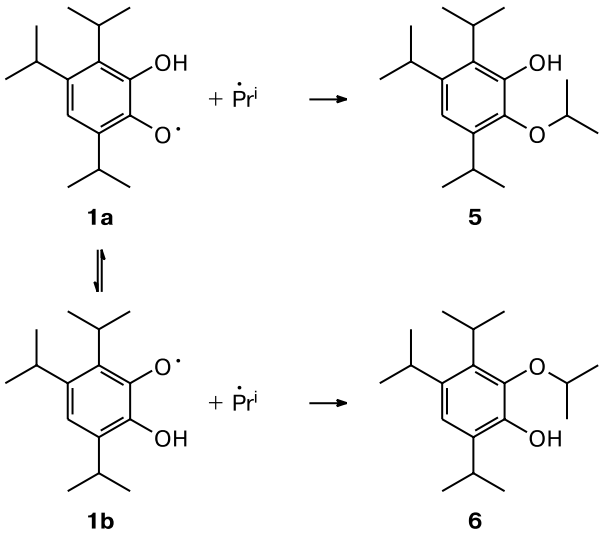
The minor route of decomposition of hydroperoxide **3**



frequency reaches 10^{10} s^{-1} at 120 °C. NMR analysis of the decomposition products of **3** showed the presence of isopropoxyphenols **5** and **6**, which resulted from the secondary recombination reaction of the isopropyl and phenoxyl radicals (**1a,b**) (Scheme 4).

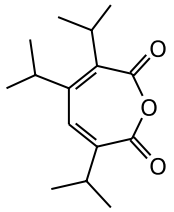
Scheme 4

Recombination of radicals to give isopropoxyphenols



The oxidation of quinones and catechols is known to give reaction products with ring expansion.[1,5] As shown by NMR spectroscopy, the decomposition products of **3** contained minor amounts of 3,4,6-triisopropyloxepine-

2,7-dione (**7**) (less than 10% of the total product yield) and 2-hydroxy-3,4,6-triisopropylbenzo-1,4-quinone (**8**) (~2—3%), which could be produced upon the secondary oxidation of catechol **1** and quinone **2** with oxidants present in the system.



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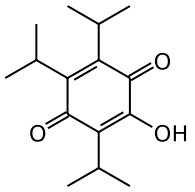

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When the thermal decomposition of hydroperoxide **3** is carried out in a toluene solution at 110 °C, *o*-quinone **2** (~40%) and *p*-quinone **4** (~40%) are formed as the major products, the fraction of catechol **1** being only 1—2% (the yields were determined from the ^{1}H NMR spectrum of the resulting mixture). Due to its stability, radical **1a** cannot abstract a hydrogen atom from the solvent (toluene) molecule. In our opinion, radical **1a** formed upon decomposition in a melt oxidizes predominantly the hydroperoxide radical (see Scheme 2), being thus reduced to catechol **1**. However, in solution, the hydroperoxide radical reacts with the solvent and is removed as H_2O_2. This accounts for the smaller amount of catechol **1** and, as a consequence, larger yields of quinones **2** and **4** as the reaction products.

The ease of formation and specific features of decomposition of hydroperoxide **3** are probably due to the stability of radical **1a** and its capability of being readily oxidized/reduced. At room temperature, radical **1a** is oxidized with oxygen to hydroperoxide **3**, whereas at 120 °C, **1a** itself mainly oxidizes the $^{\bullet}$OOH radical to produce oxygen, being thus reduced to catechol **1**.

Experimental

NMR spectra were recorded on a Bruker Avance DPX-200 instrument (200 MHz for ^{1}H and 50 MHz for ^{13}C). The following 2D NMR experiments were carried out: COSY (COSY45), *i.e.*, proton—proton correlation due to spin—spin coupling; NOESY, *i.e.*, proton—proton correlation due to dipole—dipole interaction; and XHCORR, *i.e.*, carbon—proton correlation due to the spin—spin coupling between neighboring nuclei. The XwinNMR 2.1 program was used for processing. In NOESY experiments, the mixing time was 250 ms. X-ray diffraction study was performed on a Bruker SMART 1000 CCD diffractometer (T = 193 K, Mo-Kα radiation). ESR spectra were run on a Bruker ER200D-SRC instrument operating at 9.5 GHz. IR spectra were measured on a Perkin—Elmer 577 spectrometer in Nujol.

3,4,6-Triisopropylcatechol (1). Concentrated H_2SO_4 (0.81 mol) was slowly added with vigorous stirring to a boiling mixture of catechol (0.2 mol), propan-2-ol (0.8 mol), and *n*-heptane (60 mL). The reaction mixture was stirred for 5 h. The organic layer was separated, washed with a dilute solution of NaOH and water, and dried with Na_2SO_4. After evaporation of the solvent, the residue was recrystallized from hexane to give 26 g (65%) of compound **1**, m.p. 75—77 °C. Found (%): C, 75.23; H, 10.23. $C_{15}H_{24}O_2$. Calculated (%): C, 75.46; H, 10.43. IR (hexane), ν/cm^{-1}: 3640, 3570 (OH free and intramolecular). IR (Nujol), ν/cm^{-1}: 3300 (OH intermolecular). ^{1}H NMR ($CDCl_3$), δ: 1.21, 1.26 (both d, each 6 H, Me, J = 6.9 Hz); 1.39 (d, 6 H, Me, J = 7.1 Hz); 3.05, 3.17 (both sept, each 1 H, C<u>H</u>Me$_2$, J = 6.9 Hz); 3.37 (br.sept, 1 H, C<u>H</u>Me$_2$, J = 7.1 Hz); 4.80, 5.37 (both br.s, each 1 H, OH); 6.65 (s, 1 H, C(5)H). ^{13}C NMR ($CDCl_3$), δ: 21.0, 22.7, 24.3 (Me); 26.8, 27.5, 29.2 (<u>C</u>HMe$_2$); 113.5 (C(5)H); 128.9, 131.4, 138.6, 143.0 (C(1), C(2), C(3), C(4), C(6)).

3,4,6-Triisopropylbenzo-1,2-quinone (2). A solution of 3,4,6-triisopropylcatechol (**1**) (10 mmol) in Et_2O (100 mL) was stirred for 2 h with an aqueous solution containing $K_3Fe(CN)_6$ (15.0 g), KOH (3 g), and Na_2CO_3 (5 g). The colorless solution turned dark-red. After separation of the organic layer and evaporation of the solvent, the residue was recrystallized from hexane to give 1.6 g (70%) of brown-red crystals of **2**, m.p. 45—47 °C. Found (%): C, 76.78; H, 9.58. $C_{15}H_{22}O_2$. Calculated (%): C, 76.88; H, 9.46. IR, ν/cm^{-1}: 1665, 1685 (C=O). ^{1}H NMR ($CDCl_3$), δ: 1.11, 1.18, 1.25 (all d, each 6 H, Me, J = 6.9 Hz); 2.93, 3.10, 3.22 (all sept, each 1 H, C<u>H</u>Me$_2$, J = 6.9 Hz); 6.73 (s, 1 H, C(5)H). ^{13}C NMR ($CDCl_3$), δ: 20.3, 21.1, 21.5 (Me); 26.9, 27.4, 29.3(<u>C</u>H(Me)$_2$); 133.6 (C(5)H); 140.3 (C(6)); 146.9 (C(3)); 153.4 (C(5)); 180.6, 181.4 (O=C(1), O=C(2)).

4-Hydroperoxy-2-hydroxy-3,4,6-triisopropylcyclohexa-2,5-dienone (3). A solution of 3,4,6-triisopropylcatechol (**1**) (10 mmol) in light petroleum (50 mL) was left in a loosely covered beaker at ~20 °C for 20 days. The precipitated large, colorless columnar crystals of the hydroperoxide were separated and recrystallized from heptane to give 1.1 g (43%) of compound **3**, m.p. 107—109 °C. Determination of active oxygen by iodometric titration gave an overestimated result because the quinone formed also entered into the reaction together with hydroperoxide **3**. Found (%): C, 66.73; H, 9.00. $C_{15}H_{24}O_4$. Calculated (%): C, 67.13; H, 9.01. IR, ν/cm^{-1}: 970 (=CH def. vibr.); 1145, 1170 (Pr^i); 3420, 3320 (stretch. vibr. of the alcohol and hydroperoxy groups in an associated form); 1645 (C=O); 1620 (C=C). ^{1}H NMR ($CDCl_3$), δ: 0.71 (d, 3 H, C(4)(CH$_3$)CHC<u>H</u>$_3$, J = 6.9 Hz); 1.10 (d, 3 H, C(4)(C<u>H</u>$_3$)CHCH$_3$, J = 6.9 Hz); 1.12 (d, 3 H, C(6)(CH$_3$)CHC<u>H</u>$_3$, J = 6.9 Hz); 1.14 (d, 3 H, C(6)(C<u>H</u>$_3$)CHCH$_3$, J = 6.9 Hz); 1.29 (d, 3 H, C(3)(C<u>H</u>$_3$)CHCH$_3$, J = 7.0 Hz); 1.38 (d, 3 H, C(3)(CH$_3$)CHC<u>H</u>$_3$, J = 7.0 Hz); 2.12 (sept, 1 H, C(4)(CH$_3$)C<u>H</u>CH$_3$, J = 6.9 Hz); 2.72 (sept, 1 H, C(3)(CH$_3$)C<u>H</u>CH$_3$, J = 7.0 Hz); 3.01 (sept, 1 H, C(6)(CH$_3$)C<u>H</u>CH$_3$, ^3J = 6.9 Hz, ^4J = 1.0 Hz); 6.65 (s, OH), 6.76 (d, 1 H, C(5)H, J = 1.0 Hz); 7.60 (br.s, 1 H, OOH). ^{13}C NMR ($CDCl_3$), δ: 17.5 (C(4)(CH$_3$)CH<u>C</u>H$_3$); 17.9 (C(4)(<u>C</u>H$_3$)CHCH$_3$); 18.9 (C(3)(<u>C</u>H$_3$)CHCH$_3$); 19.5 (C(3)(CH$_3$)CH<u>C</u>H$_3$); 21.4 (C(6)(<u>C</u>H$_3$)CHCH$_3$); 22.2 (C(6)(CH$_3$)CH<u>C</u>H$_3$); 26.4 (C(3)<u>C</u>HMe$_2$); 26.8 (C(6)<u>C</u>HMe$_2$); 33.1 (C(4)<u>C</u>HMe$_2$); 87.6 (C(4)); 134.6, 145.8, 145.9 (C(2), C(3), C(6)); 142.5 (C(5)H); 181.5 (C(1)). The ^{1}H and ^{13}C NMR signals were assigned using COSY, NOESY, DEPT, and XHCORR techniques.

X-Ray diffraction study of compound **3** gave 3426 independent reflections (R_{int} = 0.0239). Crystal data at T = 193 K: $C_{15}H_{24}O_4$, triclinic system, space group $P\bar{1}$, a = 7.0974(12) Å, b = 9.3995(16) Å, c = 11.944(2) Å, α = 80.288(4)°, β = 85.954(4)°, γ = 73.028(4)°, V = 751.0(2) Å^3, Z = 2, d_{calc} = 1.187 g cm^{-3}.

The absorption corrections were applied using the SADABS program package (T_{min} = 0.9710, T_{max} = 0.9916). The structure of **3** (see Fig. 2) was solved by the direct method followed by calculation of difference Fourier series and refined by the full-matrix least-squares method for the structural factors F^2. All the nonhydrogen atoms were refined with anisotropic thermal parameters. The H atoms were located from the difference Fourier synthesis and refined in the isotropic approximation. The final R-factors were ($I > 2\sigma(I)$): R_1 = 0.0436, wR_2 = 0.0989. All calculations were carried out using a SHELXTL [11] (5.10) program package.

Selected bond lengths and angles in the molecule of hydroperoxide **3** and the geometric parameters of hydrogen bonds in the crystal structure of hydroperoxide **3** (see Fig. 3) are listed in Tables 1—3.

Decomposition of hydroperoxide 3. Hydroperoxide **3** (0.54 g, 2.21 mmol) was heated for 0.5 h at 115—120 °C in an evacuated tube; this was accompanied by vigorous bubbling and the colorless melt acquired a dark-red color. After gas evolution ceased, heating was terminated, the reaction mixture was cooled, and the liquid and gaseous reaction products were separated. The glassy residue (0.50 g) was dissolved in hexane and chromatographed on a column with Silochrome. Elution with hexane gave three zones: a colorless (1), a light-yellow (2), and a dark-yellow (3). Each of the three zones was subjected to preliminary qualitative TLC analysis on Silufol UV-254 plates with a 50 : 1 heptane—acetyl acetate solvent mixture. The faintly colored spots formed on the plates were visualized by iodine vapor. Then each zone was chromatographed once again on a column with Silochrome (using a 50 : 1 hexane—ethyl acetate mixture as the eluent) in order to isolate reaction products in a pure state. The yields are given in molar percent.

Table 1. Selected bond lengths in the molecule of hydroperoxide **3**

Bond	d/Å	Bond	d/Å
O(1)—C(1)	1.233(2)	O(4)—H(O(4))	0.84(3)
O(2)—C(2)	1.371(2)	C(2)—C(3)	1.340(2)
O(2)—H(O(2))	0.88(3)	C(3)—C(4)	1.510(3)
O(3)—C(4)	1.443(2)	C(5)—C(6)	1.336(3)
O(3)—O(4)	1.4679(19)		

Table 2. Selected bond angles in the molecule of hydroperoxide **3**

Angle	ω/deg
C(4)—O(3)—O(4)	107.43(12)
O(3)—O(4)—H(O(4))	93(2)
O(1)—C(1)—C(2)	118.87(17)
O(1)—C(1)—C(6)	121.70(16)
C(3)—C(2)—O(2)	122.94(16)
O(2)—C(2)—C(1)	113.94(15)
O(3)—C(4)—C(5)	109.24(14)
O(3)—C(4)—C(3)	109.96(15)

Table 3. Geometric parameters of hydrogen bonds in the crystal structure of hydroperoxide **3** (see Fig. 3)

Parameter	Value
Distance	d/Å
O(2A)—H(O(2A))	0.88(3)
O(1C)...(H(O(2)))	1.95(3)
O(2A)...O(1C)	2.7537(19)
O(2C)—H(O(2C))	0.88(3)
O(1A)...H(O(2C))	2.15(3)
O(1A)...O(2C)	2.6298(19)
O(4B)—H(O(4B))	0.84(3)
O(2C)...H(O(4B))	2.04(3)
O(4B)...O(2C)	2.881(2)
Angle	ω/deg
O(2A)—H(O(2A))...O(1C)	151(2)
O(1A)...H(O(2C))—O(2C)	113(2)
O(4B)—H(O(4B))...O(2C)	172(3)

Compounds **5**, **6**, and **7** were isolated from zone 1.

2-Isopropoxy-3,5,6-triisopropylphenol (5), yield 0.02 g (4%), white crystals. ^{1}H NMR ($CDCl_3$), δ: 1.21 (d, 12 H, Me, J = 6.9 Hz); 1.28 (d, 6 H, Me, J = 6.9 Hz); 1.34 (d, 6 H, OCH$\underline{Me}_2$, J = 6.2 Hz); 3.18 (sept, 1 H, C(6)C$\underline{H}Me_2$, J = 6.9 Hz); 3.19, 3.26 (both sept, each 1 H, C$\underline{H}Me_2$, J = 6.9 Hz); 4.07 (sept, 1 H, OC$\underline{H}Me_2$, J = 6.2 Hz); 5.87 (s, 1 H, OH); 6.64 (s, 1 H, C(4)H). The ^{1}H NMR signals were assigned using the COSY and NOESY techniques.

2-Isopropoxy-3,4,6-triisopropylphenol (6), yield ~0.008 g (~1.5%). ^{1}H NMR ($CDCl_3$), δ: 1.21, 1.23 (both d, each 6 H, Me, J = 6.9 Hz); 1.33 (d, OCH$\underline{Me}_2$, J = 6.2 Hz); 1.34 (d, 6 H, Me, J = 7.3 Hz); 3.19, 3.30 (both sept, each 1 H, C$\underline{H}Me_2$, J = 6.9 Hz); 3.48 (sept, 1 H, C$\underline{H}Me_2$, J = 7.3 Hz); 4.03 (sept, 1 H, OC$\underline{H}Me_2$, J = 6.2 Hz); 5.67 (s, 1 H, OH); 6.84 (s, 1 H, C(4)H). The ^{1}H NMR signals were assigned using the COSY and NOESY techniques.

3,4,6-Triisopropyloxepine-2,7-dione (7), yield 0.04 g (7%). ^{1}H NMR ($CDCl_3$), δ: 1.08, 1.17, 1.22 (all d, each 6 H, Me, J = 6.9 Hz); 2.92 (sept, 1 H, C(6)C$\underline{H}Me_2$, ^3J = 6.9 Hz, ^4J = 1.2 Hz); 3.02, 3.04 (both sept, each 1 H, C$\underline{H}Me_2$, J = 6.9 Hz); 6.41 (d, 1 H, C(5)H, ^4J = 1.2 Hz). ^{13}C NMR ($CDCl_3$), δ: 21.4, 21.53, 21.53 (Me); 28.9, 29.1, 32.8 ($\underline{C}HMe_2$); 128.4 (C(5)H); 137.4, 142.6, 142.7 (C(3), C(4), C(6)); 162.1, 162.3 (O=C(2), O=C(7)). The structure of this product was additionally confirmed by an alternative synthesis according to a known procedure.[12] The NMR spectra of compound **7** isolated from the product mixture after decomposition of hydroperoxide **3** fully coincided with the spectra of this compound synthesized by the known procedure.

Compounds **4** and **8** were isolated from zone 2.

3-Hydroxy-2,5-diisopropylbenzo-1,4-quinone (4), yield 0.112 g (24%), bright yellow, m.p. 56—58 °C (from pentane). Found (%): C, 69.32; H, 7.70. $C_{12}H_{16}O_3$. Calculated (%): C, 69.20; H, 7.74. IR (mineral oil), ν/cm^{-1}: 1610 (=C—); 1640, 1660 (C=O); 3380, 3280 (OH). ^{1}H NMR ($CDCl_3$), δ: 1.15 (d, 6 H, C(5)CH$\underline{Me}_2$, J = 6.8 Hz); 1.23 (d, 6 H, C(2)CH$\underline{Me}_2$, J = 7.1 Hz); 3.00 (sept, 1 H, C(5)C$\underline{H}Me_2$, ^3J = 6.8 Hz, ^4J = 1.1 Hz);

3.19 (sept, 1 H, C(2)C<u>H</u>Me_2, J = 7.1 Hz); 6.41 (d, 1 H, C(6)H, ^4J = 1.1 Hz); 7.06 (s, 1 H, OH). ^{13}C NMR ($CDCl_3$), δ: 19.9 (C(2)CH(<u>C</u>H_3)$_2$); 21.3 (C(5)CH(<u>C</u>H_3)$_2$); 24.2 (C(2)<u>C</u>HMe_2); 26.7 (C(5)<u>C</u>HMe_2); 125.1 (C(2)); 133.1 (C(6)H); 149.9 (C(5)); 151.0 (C(3)OH); 184.0 (O=C(4)); 187.9 (O=C(1)). The ^{1}H and ^{13}C NMR signals were assigned using COSY and XHCORR techniques.

2-Hydroxy-3,4,6-triisopropylbenzo-1,4-quinone (8), yield 0.008 g (1.5%). ^{1}H NMR ($CDCl_3$), δ: 1.23, 1.27, 1.28 (all d, each 6 H, Me, J = 7.0 Hz); 3.19, 3.26, 3.26 (all sept, each 1 H, C<u>H</u>Me_2, J = 7.0 Hz); 7.10 (s, OH).

Zone 3 was separated to give 3,4,6-triisopropylcatechol (**1**), yield 0.18 g (38%), and 3,4,6-triisopropylbenzo-1,2-quinone (**2**), yield 0.10 g (21%).

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