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Low-Temperature Oxidation of 3,6-Di-*tert*-butyl-*o*-benzoquinone and 3,6-Di-*tert*-butylpyrocatechol with *tert*-Butyl Hydroperoxide in the Presence of Aluminum, Titanium, and Zirconium *tert*-Butylates

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Abstract—Systems consisting of metal (Al, Ti, Zr) *tert*-butylate and *tert*-butyl hydroperoxide oxidize 3,6-di-*tert*-butyl-*o*-benzoquinone under mild conditions (room temperature, benzene). With $(t\text{-BuO})_3Al$ and $(t\text{-BuO})_4Zr$, the major reaction products are 5-hydroxy-3,6-di-*tert*-butyl-2,3-epoxy-*p*-benzoquinone, and with $(t\text{-BuO})_4Ti$, 2-hydroxy-3,6-di-*tert*-butyl-*p*-benzoquinone. Under the conditions of this reaction, 3,6-di-*tert*-butylpyrocatechol initially transforms into 3,6-di-*tert*-butyl-*o*-benzoquinone. The reactions involve metal-containing peroxides.

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The reactions of sterically hindered *o*-benzoquinones and the corresponding pyrocatechols with peroxy derivatives (H_2O_2, peroxy acids, hydroperoxides) yield various products depending on the nature of the oxidant and reaction conditions. 3,5-Di-*tert*-butylpyrocatechol and 4-*tert*-butylpyrocatechol are quantitatively oxidized with *tert*-butyl hydroperoxide **I** in the presence of catalytic amounts of $RuCl_2(PPh_3)_2$ [1] to the corresponding *o*-benzoquinones (20°C). 3,5-Di-*tert*-butyl-*o*-benzoquinone is oxidized with an alkaline solution of H_2O_2 in methanol to form products of intradiol cleavage and ring opening [2]. The reaction of this quinone with **I** in the presence of Triton B catalyst gives 3,5-di-*tert*-butyl-5,6-epoxycyclohexene-1,2-dione in 42% yield [3]. It should be noted that epoxy quinones are of particular interest because of their biological activity. They are widely used in biology, pharmacology, and as key intermediates in the synthesis of various organic compounds [4].

Glushakova et al. [5] reported that 3,6-di-*tert*-butyl-*o*-benzoquinone **II** and 3,6-di-*tert*-butylpyrocatechol **III** react with **I** at 70 and 90°C. They isolated a number of products; the major products were 3,6-di-*tert*-butyl-1-oxacyclohepta-3,5-diene-2,7-dione (15–30%) and 2-hydroxy-3,6-di-*tert*-butyl-*p*-benzoquinone (10–60%). Glushakova et al. believe that oxidation of **II** and **III** with **I** involves predominantly radical steps resulting in the intermediate formation of *o*-semiquinone and *tert*-butylperoxy radical; their further reaction yields the above products.

In this study we examined the reactions of quinone **II** and pyrocatechol **III** with the oxidizing systems *t*-BuOOH–metal *tert*-butylate (metal: Al, **IV**; Ti, **V**; Zr, **VI**). We showed previously that the reactions of the components of the oxidizing systems consisting of metal alcoholate **IV** [6], **V** [7], or **VI** [8] and *t*-BuOOH (1 : 2, C_6H_6, 20°C) involve the formation of metal-containing peroxides $(t\text{-BuO})_{n-1}MOOBu\text{-}t$ and trioxides $(t\text{-BuO})_{n-1}MOOOBu\text{-}t$. Decomposition of the latter species is accompanied by the release of oxygen and by homolysis with the generation of alkoxy and peroxy radicals identified by ESR [6–8]. Systems consisting of **I** and **IV**–**VI** are effective oxidants of various classes of organic compounds (alkanes, alkylarenes, alkenes, alcohols, saturated and unsaturated ethers and esters) [6–13]. Depending on the structure of the substrate, the oxidizing species can be oxygen generated by the systems, peroxides $(t\text{-BuO})_{n-1}MOOBu\text{-}t$, or trioxides.

The reactions of **II** and **III** with systems consisting of **I** and **IV**–**VI** were performed in benzene at 20°C and component ratio of 1 : 2 : 1. Under these condi-

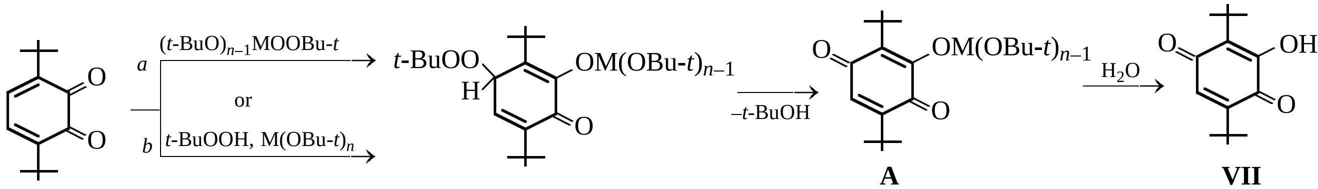
Table 1. Products of the reaction of 3,6-di-*tert*-butyl-*o*-benzoquinone with the system M(OBu-*t*)$_n$–*t*-BuOOH, 1 : 1 : 2 (M = Al, *n* = 3; M = Ti, Zr, *n* = 4) in C_6H_6 at 20°C (moles per mole of the starting quinone)

Reaction products[a]	Ti(OBu-*t*)$_4$		Al(OBu-*t*)$_3$	Zr(OBu-*t*)$_4$
	0°C	20°C	20°C	20°C
Volatile reaction products				
t-BuOH	3.59	3.43	3.45	3.93
Products of hydrolysis of nonvolatile residue[b]				
t-BuOH	2.27	2.44	1.59	2.10
2-Hydroxy-3,6-di-*tert*-butyl-*p*-benzoquinone	0.65	0.74	0.05	0.15
5-Hydroxy-3,6-di-*tert*-butyl-2,3-epoxy-*p*-benzoquinone	Traces	Traces	0.95	0.63
Unchanged 3,6-di-*tert*-butyl-*p*-benzoquinone	Not determined	0.20	–	0.13

[a] Averaged results. [b] Metal amount ~1 mol in all cases.

tions, compounds **II** and **III** react neither with peroxide **I** nor with metal alcoholates **IV**–**VI**, taken separately. Quinone **II** reacts with the oxidizing system consisting of **I** and **IV**–**VI** to form 2-hydroxy-3,6-di-*tert*-butyl-*p*-benzoquinone **VII** and 5-hydroxy-3,6-di-*tert*-butyl-2,3-epoxy-*p*-benzoquinone **VIII** (Table 1). The yield of hydroxy quinone **VII** is maximal with titanium alcoholate **V**, and epoxy quinone **VIII** is the major product of the reactions involving zirconium and especially aluminum alcoholates.

We believe that the first step of the reactions of quinone **II** with the oxidizing systems consisting of **I** and **IV**–**VI** is the nucleophilic 1,4-addition of a metal-containing peroxide or *tert*-butyl hydroperoxide to the conjugated system involving one of the carbonyl groups, followed by the reaction of the hydroxy group with the metal alcoholate [scheme (1)].



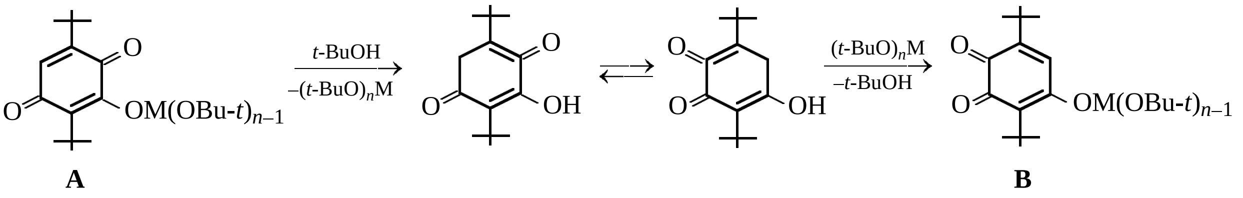
(1)

M = Al, *n* = 3; M = Ti, Zr, *n* = 4.

Scheme (1) fully describeds the oxidation of **II** with the system **I**–**V**. However, with aluminum and zirconium *tert*-butylates, alkoxy compounds **A** undergo further oxidation, yielding previously unknown 5-hydroxy-3,6-di-*tert*-butyl-2,3-epoxy-*p*-benzoquinone **VIII**. A single crystal X-ray diffraction study of **VIII** (see figure) showed that the *t*-Bu groups are arranged in the eclipsed conformation relative to each other. The carbon ring C^{1-6} has a *boat* conformation. The C^3 and C^6 atoms deviate from the $C^1C^2C^4C^5$ plane by 0.172 and 0.355 Å, respecively. The dihedral angle between the $C^1C^2O^1$ and $C^1C^2C^4C^5$ planes is 89.2° (Table 2). The known related compounds have a similar conformation [14]. The C–O and C–C distances in **VIII** are typical for compounds of this kind.

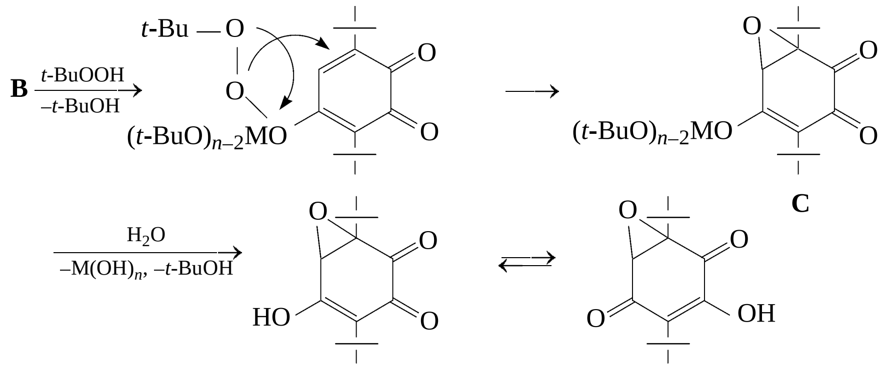
It is known that allyl-type alcohols are readily epoxidized with hydroperoxides in the presence of aluminum and titanium alcoholates; this reaction is a route to epoxy alcohols [15–17]. The process occurs by the intramolecular mechanism via formation of metal-containing peroxides. Zirconium complexes containing the methyl and allyloxy ligands take up oxygen with its insertion into the Zr–CH_3 bond and formation of the peroxymethyl group, also capable of intramolecular epoxidation [18].

It is well known that hydroxy-*p*-quinones and some of their derivatives exist in solutions in a thermodynamic equilibrium with the corresponding isomers of *o*-quinones [19–21]. Similar transformations can be suggested for compounds of type **A**. One of isomerization pathways is shown in scheme (2).



(2)

The subsequent reaction of compounds **B** with **I** yields metal-containing peroxides whose decomposition is accompanied by epoxidation of the allylic double bond [scheme (3)].



VIII

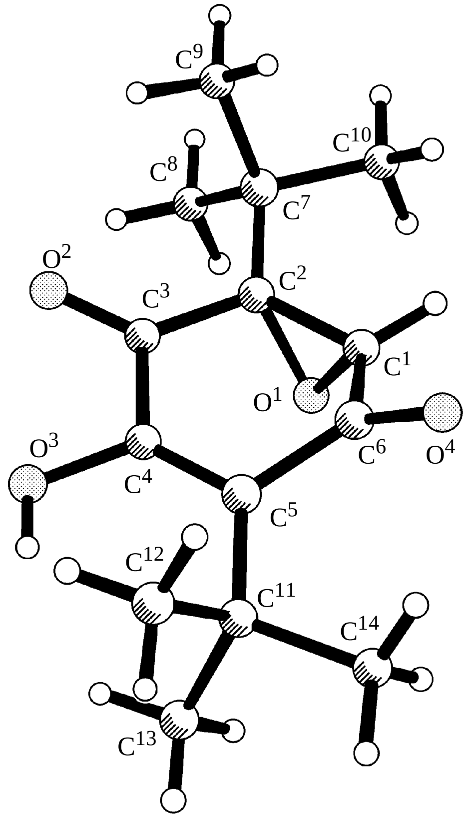
M = Al, $n = 3$; M = Zr, $n = 4$.

(3)

The presence of quinones **VII** and **VIII** in the reaction mixture in the form of alcoholates is confirmed by the pH-chromism [20]. The red-brown color of the solutions changes to yellow as a result of hydrolysis with a 10% solution of sulfuric acid.

Transformations described by schemes (2) and (3) were actually observed in the reaction of **VII** with the system **I**–**IV** (1 : 1 : 1, C_6H_6, 20°C): epoxy quinone **VIII** was isolated in a yield of 0.90 – 0.95 mol per mole of **VII**. However, with titanium alcoholate **V** this transformation was not observed. We assumed that titanium derivative **A** does not isomerize [scheme (2)]. Indeed, the reaction of **VII** with $Ti(OBu\text{-}t)_4$ yields compound **A** with the release of 1 mol of *t*-BuOH. However, the subsequent treatment of **A** (M = Ti) with 1 mol of peroxide **I** resulted in the recovery of 0.85 mol of **VII**, and only 0.07 mol of **VIII** was obtained.

To prove the participation of metal-containing peroxides in the formation of compounds **VII** and **VIII** [schemes (1), (3)], we performed model reactions of an aluminum-containing peroxide $(t\text{-BuO})_2AlOOBu\text{-}t$ [22, 23] with quinones **I** and **VII** at an equimolar ratio of the reactants (benzene, 20°C). The reaction of $(t\text{-BuO})_2AlOOBu\text{-}t$ with **I** yielded 0.26 mol of **VIII** and 0.60 mol of **VII**, which confirms the initial forma-



Molecular structure of **VIII**.

Table 2. Selected geometric parameters of **VIII**: bond lengths (*d*, Å) and bond angles (ω, deg)

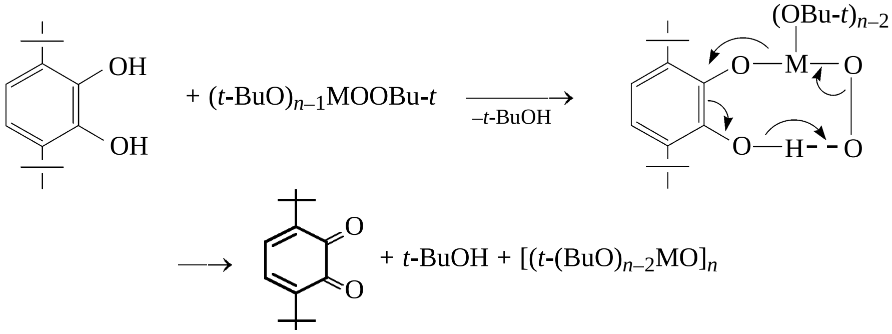
Bond	*d*	Bond	*d*
$O^1–C^1$	1.424(7)	$O^3–C^4$	1.355(6)
$O^1–C^2$	1.440(6)	$C^3–C^4$	1.472(8)
$C^1–C^6$	1.479(8)	$O^4–C^6$	1.228(6)
$C^1–C^2$	1.480(8)	$C^4–C^5$	1.356(7)
$O^2–C^3$	1.216(6)	$C^5–C^6$	1.472(8)
$C^2–C^3$	1.524(8)		
Angle	**ω**	**Angle**	**ω**
$C^1O^1C^2$	62.2(4)	$O^1C^2C^1$	58.4(3)
$O^1C^1C^2$	59.4(4)		

tion of compound **VII**. Hydroxy quinone **VII** is epoxidized with di-*tert*-butoxy-*tert*-butylperoxyaluminum. The yield of **VIII** reaches 0.90 mol.

Thus, the first step of the reaction of quinone **II** with the systems consisting of **I** and **IV**–**VI** is predominantly the nucleophilic 1,4-addition of the metal-containing peroxide to the conjugated system. With the aluminum- and zirconium-containing peroxides, this is followed by the epoxidation with the formation of the hydroxy(epoxy) quinone.

Oxidation of pyrocatechol **III** was studied with the systems **I**–**IV** and **I**–**V** as examples (C_6H_6, 20°C). The ratio pyrocatechol : metal alcoholate : hydroperoxide was 1 : 1 : 2. In both cases quinone **II** was detected, but its yield did not exceed 0.20 mol (here and hereinafter, per mole of **III**). The major fraction of **II** undergoes further oxidation [schemes (1)–(3)]; from the reactions, we isolated 0.76 mol of quinone **VII** with $Ti(OBu\text{-}t)_4$ and 0.55 mol of **VII** + 0.20 mol of epoxy quinone **VIII** with $Al(OBu\text{-}t)_3$.

Since the reactions of components of oxidizing systems are accompanied by the generation of alkoxy and peroxy radicals [6, 8], the homolytic pathway of formation of **II** seems also possible. However, we believe that the direct reaction of the metal-containing peroxides with pyrocatechol **III**, yielding quinone **II** [scheme (4)], is more probable.



(4)

Indeed, as major product of the reaction of **III** with $(t\text{-}BuO)_2AlOOBu\text{-}t$ (1 : 1, 20°C) we isolated quinone **II** (0.74 mol). Also we detected quinone **VII** (0.07 mol). The scheme involving a metal monoalkoxy compound was suggested previously for the oxidation of pyrocatechols to quinones with hydroperoxide **I** in the presence of ruthenium salts [1].

EXPERIMENTAL

The reaction products were analyzed by GLC, TLC, ^1H and ^{13}C NMR, and IR spectroscopy. The IR spectra were recorded on Specord-1000 and Bruker FS IR-120 devices (liquid films between KBr windows). The NMR spectra were measured in $CDCl_3$ on a Bruker Avance DPX-200 spectrometer.

The GLC analysis of reaction products in the liquid phase was performed with a Tsvet-2-65 chromatograph equipped with a flame-ionization detector; the carrier gas was argon. Low-boiling components (*tert*-butyl alcohol, *tert*-butyl hydroperoxide) were analyzed on a 1200 × 3-mm column, stationary phase 15% dinonyl phthalate on Chromaton N-AW-DMCS. The column temperature was varied within 60–120°C. The chromatographic analysis of 2-hydroxy-3,6-di-*tert*-butyl-*p*-benzoquinone and 5-hydroxy-3,6-di-*tert*-butyl-2,3-epoxy-*p*-benzoquinone was performed on a 1200 × 3-mm column, stationary phase 10% Reoplex-400 on Inerton AW-HMDC, column temperature 130–150°C.

The chromatograms were treated using authentic samples as external references. All manipulations with metal-containing compounds were performed under dry oxygen-free argon.

The qualitative identification of the quinones and their derivatives was performed by thin-layer chromatography on Silufol UVC-254 plates in the system petroleum ether–ethyl acetate (22 : 1) or THF–ethyl acetate (5 : 1).

In aqueous acid solutions from the hydrolysis, we determined the content of *t*-BuOH [24] and of the metal (precipitation of hydroxide followed by calcination to oxide).

Aluminum tri-*tert*-butylate was prepared by the reaction of Al with 2-methyl-2-propanol [25] and was sublimed at 160–170°C (1 mm Hg). Found Al, %: 11.08. $C_{12}H_{27}AlO_3$. Calculated Al, %: 10.98. Titanium tetra-*tert*-butylate was prepared by treatment of $TiCl_4$ with *tert*-butyl alcohol in the presence of NH_3 [26], bp 82–83°C (2 mm Hg), n_D^{20} 1.4420 [27]. Zirconium tetra-*tert*-butylate was synthesized by the Sinor company (Nizhni Novgorod); main substance content 99.9% {bp 70°C (2 mm Hg) [28]}.

Di-*tert*-butoxy-*tert*-butylperoxyaluminum was prepared from di-*tert*-butoxyaluminum chloride and *t*-BuOOH in the presence of diethylamine [22, 23]. The activity of the peroxide was no less than 96%. The concentration of *tert*-butyl hydroperoxide used in this study was no less than 99.6–99.8%.

2-Hydroxy-3,6-di-*tert*-butyl-*p*-benzoquinone was prepared by treatment of 3,6-di-*tert*-butyl-4-methoxy-*o*-benzoquinone with a 40% solution of HBr [29]; mp 84°C [5]. Compounds **II** and **III** were prepared by the previously described procedures; their melting points agree with published data [30, 31].

X-ray diffraction study of VIII. Single crystals of $C_{14}H_{20}O_4$ were prepared by crystallization from isooctane; the solvent was evaporated over a period of several weeks. The experimental sets of intensities were obtained with a Smart-APEX automatic diffractometer (graphite monochromator, MoK_α radiation, φ–ω scanning). Crystal data for **VIII** ($C_{14}H_{20}O_4$) at 20°C: monoclinic system, a 9.655(6), b 7.134(5), c 20.497(13) Å; β 100.725(11)°, V 1387.2(15) Å^3, space group $P2_1/c$, Z 4, $F(000)$ 544, $2.02° \le \theta \le 19.99°$, d_{calc} 1.208 g cm^{-3}, μ 0.088 mm^{-1}. A total of 6057 unique reflections were measured, of which 1292 (R_{int} 0.12) were observed; the final divergence factors were as follows: R_1 0.0829 [$I > 2\sigma(I)$], R_{W2} 0.1562 (whole data set).

The structure was solved by the direct method using the SHELXTL program package [32] and refined by the least-squares method with respect to F^2_{hkl} in the anisotropic approximation for all nonhydrogen atoms. The hydrogen atoms were placed in idealized positions and refined in the rider model. The corrections for absorption were made using the SADABS program [33].

The structure was deposited at the Cambridge Crystallographic Database, no. 263223.

Oxidation of 3,6-di-*tert*-butyl-*o*-benzoquinone with the Al(OBu-*t*)$_3$–*t*-BuOOH system (1 : 1 : 2). To a dark green solution of 0.90 g of 3,6-di-*tert*-butyl-*o*-benzoquinone in 15 ml of benzene, we added in succession 1.02 g of (*t*-BuO)$_3$Al and 0.75 g of *t*-BuOOH. After mixing the components, the solution became claret-colored. The solvent and low-boiling components were condensed in a trap cooled with liquid nitrogen. This fraction contained 1.05 g of *tert*-butyl alcohol. The residue was a dark cherry-red mobile mass; it was dissolved in diethyl ether and treated with 10% H_2SO_4. The ether extract, according to the chromatographic analysis, contained 0.48 g of *tert*-butyl alcohol, 0.97 g of 5-hydroxy-3,6-di-*tert*-butyl-2,3-epoxy-*p*-benzoquinone, and 0.05 g of 2-hydroxy-3,6-di-*tert*-butyl-*p*-benzoquinone. The presence of epoxy compound **VIII** was confirmed by qualitative reactions for oxirane ring: formation of a silver iodate precipitate [34] and a color reaction with pyridine on heating [35].

To isolate compound **VIII**, the ether extract was evaporated. The dry residue was dissolved in 3 ml of ethanol, and the solution was diluted with 150 ml of water. Within 5–6 h, lustrous pale yellow crystals precipitated from the solution; mp 81°C. IR spectrum (perfluorinated oil), ν, cm^{-1}: 3370, 3295, 3015, 2991, 2962, 2868, 1690, 1660, 1607, 1474, 1459, 1397, 1365, 1327, 1261, 1189, 1071, 1055, 946, 917, 799, 780, 728, 639, 617. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.15, 1.32 s [9H, $C(CH_3)_3$], 3.79 s (1H, CH), 7.26 s (1H, OH). ^{13}C NMR spectrum, DEPT ($CDCl_3$), δ_C, ppm: 25.8, 29.2 [$C(CH_3)_3$], 32.0, 34.7 [$C(CH_3)_3$], 57.1 (C^2H), 65.3 (C^3), 128.5 (C^6), 151.0 (C^5), 190.4, 193.2 (C=O). Found, %: C 66.71; H 7.96. $C_{14}H_{20}O_4$. Calculated, %: C 66.64; H 7.99.

Reaction of 3,6-di-*tert*-butyl-*o*-benzoquinone with the Zr(OBu-*t*)$_4$–*t*-BuOOH system, 1 : 1 : 2. A mixture of 0.17 g of 3,6-di-*tert*-butyl-*o*-benzoquinone and 0.30 g of Zr(OBu-*t*)$_4$ in 15 ml of benzene was treated with 0.14 g of *t*-BuOOH. The reaction is exothermic. The reaction solution was red-brown. The condensate of low-boiling products contained 0.22 g of *t*-BuOH. The residue, a dark cherry-red viscous mass, was hydrolyzed in ether with 10% H_2SO_4 and extracted with ether. The ether extract was yellow. The presence of hydroxy quinones **VII** and **VIII** in the ether extract was confirmed by the pH-chromism [20]. On adding several drops of 0.5 N NaOH to an aliquot of the ether solution, its color changed from yellow to crimson-red, and on acidification with 0.5 N H_2SO_4 it became yellow again.

The ether extract, according to the GLC analysis, contained 0.03 g of 2-hydroxy-3,5-di-*tert*-butyl-*p*-benzoquinone, 0.12 g of 5-hydroxy-3,6-di-*tert*-butyl-2,3-epoxy-*p*-benzoquinone, and 0.10 g of *t*-BuOH. Quinones **II**, **VII**, and **VIII** were separated by column chromatography (adsorbent Silicagel 60, 0.060–0.020 mm, eluent petroleum ether–diethyl ether, 22 : 1). The reaction progress was monitored by TLC. The initial quinone was washed out from the adsorbent successively with benzene and ethyl acetate; 0.022 g of 3,6-di-*tert*-butyl-*o*-benzoquinone was recovered. The samples of the isolated products, when mixed with the authentic samples, show no depression of the melting point. The ^{1}H NMR spectrum of **VII** is identical to that given in [29].

The aqueous acid phase contained 0.02 g of *t*-BuO groups, as determined by the Denigés method.

The reaction of **II** with the system **I**–**V** and the analysis of the reaction products were performed similarly.

Reaction of 3,6-di-*tert*-butyl-*o*-benzoquinone with (t-BuO)$_2$AlOOBu-*t*, 1 : 1. To 1.21 g of di-*tert*-butyl-*tert*-butylperoxyaluminum in 17 ml of benzene, we added 0.91 g of 3.6-di-*tert*-butyl-*o*-benzoquinone. The solution instantaneously turned wine-red, with slight warming up. The low-boiling fraction contained 0.30 g of *tert*-butyl alcohol.

The residue was a dark brown solid. The ether extract after its hydrolysis contained 0.50 g of *tert*-butyl alcohol, 0.65 g of 2-hydroxy-3,6-di-*tert*-butyl-*o*-benzoquinone, and 0.30 g of 5-hydroxy-3,6-di-*tert*-butyl-2,3-epoxy-*o*-benzoquinone. By TLC we identified unchanged 3,6-di-*tert*-butyl-*o*-benzoquinone. The aqueous acid solution contained 0.20 g of *t*-BuOH (determined as described previously).

Oxidation of 2-hydroxy-3,6-di-*tert*-butyl-*p*-benzoquinone with the aluminum *tert*-butylate–*tert*-butyl hydroperoxide system (1 : 1 : 1) in benzene. To a claret-colored solution of 0.38 g of aluminum *tert*-butylate and 0.37 g of 2-hydroxy-3,6-di-*tert*-butyl-*o*-benzoquinone in 10 ml of benzene, we added 0.14 g of *tert*-butyl hydroperoxide. In 20 h, the reaction mixture became orange-red. The solvent was condensed in a trap; this fraction contained 0.20 g of *tert*-butyl alcohol. The residue after removing the low-boiling components was an orange solid; it was worked up as described above. Chromatographic analysis of the ether extract revealed the presence of 0.37 g of 5-hydroxy-3,6-di-*tert*-butyl-2,3-epoxy-*o*-benzoquinone and 0.01 g of unchanged hydroxy quinone **VII**. The aqueous acid solution contained 0.08 g of *t*-BuOH.

Reaction of 3,6-di-*tert*-butylpyrocatechol with the Ti(OBu-t)$_4$–*t*-BuOOH system, 1 : 1 : 2. To a mixture of 0.33 g of 3,6-di-*tert*-butylpyrocatechol and 0.51 g of Ti(OBu-t)$_4$ in 10 ml of benzene, we added 0.27 g of *t*-BuOOH. On adding **I**, the emerald-green solution became claret-colored. The reaction mixture was allowed to stand at room temperature for 5 h. The solvent and low-boiling substances were condensed in a trap cooled with liquid nitrogen. The condensate contained 0.50 g of *t*-BuOH.

The residue was a dry claret-brown mass; it was hydrolyzed as described above. Chromatographic analysis of the ether extract revealed the presence of 0.08 g of *t*-BuOH and 0.26 g of 2-hydroxy-3,6-di-*tert*-butyl-*o*-benzoquinone. By TLC we identified 3,6-di-*tert*-butyl-*o*-benzoquinone and unchanged pyrocatechol (THF–ethyl acetate, 9 : 1). To isolate pure **VII**, the ether extract was evaporated. The dry residue was dissolved in 3 ml of ethanol. On adding 100 ml of water, bright yellow crystals of the hydroxy quinone precipitated (0.20 g, 75%); mp 84°C [5]. No depression of the melting point was observed on mixing with an authentic sample.

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