nitrogen bath), and *n*-butyllithium (0.020 mol) was added at a rate such that the temperature of the mixture did not exceed −140 °C. A yellowish slurry resulted, indicating that elimination rather than efficient bromine–lithium exchange (which produces brightly colored dianion solutions) was taking place. The mixture was stirred for 5 min at −140 °C and 15 min at −100 °C, at which temperature the turbidity almost completely disappeared. Methanol (5 mL) was added to quench the mixture. The yellow color was discharged, and the mixture was poured into water and processed as described for reactions of **1**. NMR analysis of the crude acidic product (2.08 g of yellowish crystals) showed no cinnamic acid, only phenylpropynoic acid (**7**): NMR ($CDCl_3$) δ 7.3–8.0 (m, 5, ArH), 10.0 (s, 1, CO_2H). Recrystallization from ligroin afforded 1.48 g (100% yield) of yellowish needles of **7**: mp 106–124 °C (lit.[22] mp 136–137 °C); IR ($\nu_{C\equiv C}$, mineral oil) 2200 cm^{-1}. In a separate experiment, white needles of **7** of mp 134–136 °C were obtained by recrystallization from water.

Acknowledgments. The support of this work by the U.S. Army Research Office through Grants DAHCO74-GD-128 and DAAG29-77-G-0170 is appreciated. The generous assistance of Professor C. K. Bradsher has made it possible for this part of the late Professor W. E. Parham's research to be continued.

Registry No.—**1**, 4541-91-7; **2**, 68344-90-1; **3a**, 606-84-8; **3b**, 17684-12-7; **3c**, 68344-86-5; **3d**, 68344-87-6; **3e**, 68344-88-7; **3f**, 68344-89-8; **3f** acid chloride, 68345-01-7; **4**, 10443-65-9; **5**, 471-25-0; **6**, 15813-24-8; **7**, 637-44-5; **13**, 68344-91-2; **14a**, 21690-34-6; **14b**, 68344-92-3; **14c**, 68344-93-4; **15**, 24186-31-0; **16**, 68344-94-5; **17**, 68344-95-6; **18a**, 13304-52-4; **18b**, 68344-96-7; **18c**, 68344-97-8; **18d**, 68344-98-9; **18e**, 68345-00-6; **21**, 60582-26-5; **22**, 23086-31-9; oxirane, 75-21-8; methyloxirane, 75-56-9; phenyloxirane, 96-09-3; 2-bromo-3-methyl-2-butenoic acid, 1578-14-9.

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Oxidation of Sterically Hindered Phenols by Periodic Acid

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Sterically hindered phenols react smoothly with periodic acid in methanol to give, dependent on the nature of the substituents, diphenoquinones, benzoquinones, or cyclohexadienones as major products. The formation of the various types of quinonoid compounds may be rationalized by a mechanism involving initial electrophilic substitution of the phenol by periodic acid.

The oxidation of methyl-, methoxy-, and hydroxymethyl-substituted phenols by periodic acid or its sodium salt has been the subject of detailed investigations.[1-8] The overall reaction, corresponding to a two-electron oxidation of the phenol, involves either intermolecular or intramolecular participation of nucleophiles to give 2,4-cyclohexadienones as main products (cf. reactions 1–3). Characteristic features of these reactions are the following: (a) intramolecular nucleophilic reaction is favored over intermolecular participation of nucleophiles, (b) cross-conjugated cyclohexadienones are formed as minor products only, and (c) oxidative coupling reactions typical of one-electron transfer are negligible.

The mechanism proposed for the oxidation of phenols by periodate involves the aryl periodate **1** and its heterolytic decomposition into iodate and phenoxonium ions (reaction 4).[9] Consequently, bulky R substituents conceivably might impair the formation of **1**. In order to study the potential effect of steric hindrance on the course of the reaction, we investi-

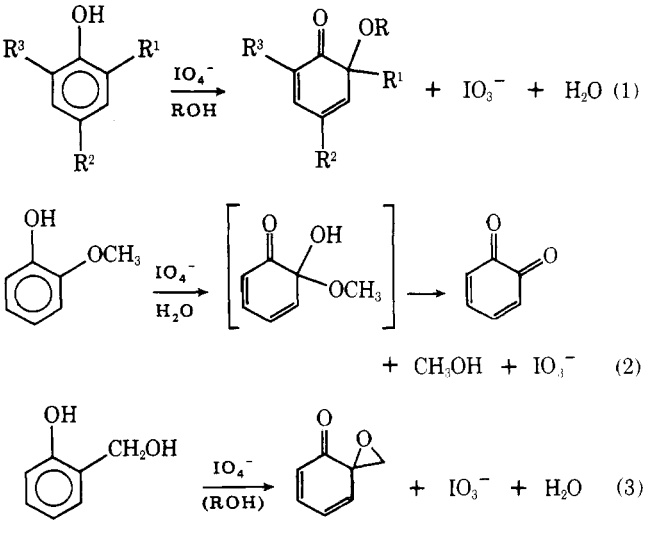

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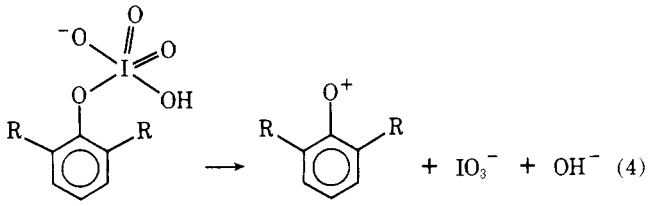
Table I. Oxidation of Phenols 2 by Periodic Acid in Methanol: Yields of Products 3–7

phenol 2	substituent R	registry no.	dimeric products 6	dimeric products 7	monomeric products 3	monomeric products 4	monomeric products 5
a	H	128-39-2		61[b]	7[c]		
b	Br	1139-52-2		24	33		
c	Cl	4096-72-4	48[a]		39		
d	OCH_3	489-01-0			60		
e	CH_3	128-37-0				83[d]	
f	t-C_4H_9	732-26-3				62[e]	
g	CPh_3	30748-85-7					92[f]

[a] Registry no., 27574-97-4. [b] Registry no., 2455-14-3. [c] Registry no., 719-22-2. [d] Registry no., 2411-18-9. [e] Registry no., 15910-49-3. [f] Registry no., 68297-76-7.



1

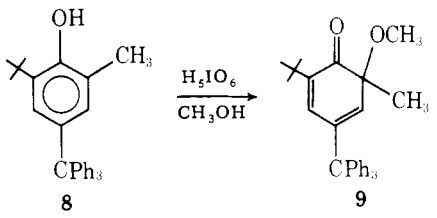
gated the oxidation of a series of 2-*tert*-butyl substituted phenols by periodic acid in methanol.

Results and Discussion

Periodic acid reacts smoothly with 2,6-di-*tert*-butyl-4-R-substituted phenols **2a–g** in methanol solution at room temperature to give quinonoid compounds **3–7** in fair to good yields (cf. Scheme I and Table I). Thus, mixtures of 2,6-di-*tert*-butyl-1,4-benzoquinone (**3**) and 3,3′,5,5′-tetra-*tert*-butyl-4,4′-diphenoquinone (**7**)[10] were obtained in the case of **2a** (R = H) and **2b** (R = Br), while the oxidation of **2c** (R = Cl) afforded a mixture of bis(cyclohexadienone) **6c** and 1,4-benzoquinone **3**. By contrast, 2,6-di-*tert*-butyl-4-R substituted phenols **2d** (R = OCH_3), **3e** (R = CH_3), **2f** (R = *tert*-butyl), and **2g** (R = trityl) gave one product each, namely, 1,4-benzoquinone **3**, 4-methoxy-2,5-cyclohexadienones **4e** and **4f**, and 3-*tert*-butyl-5-trityl-1,2-benzoquinone (**5g**), respectively.

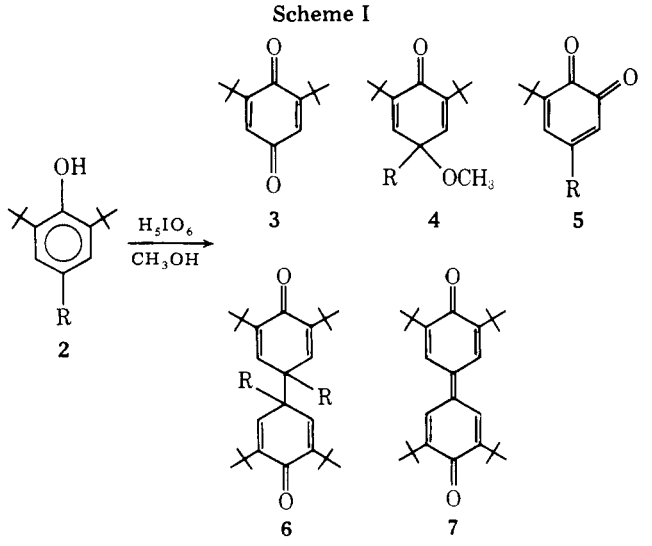
Comparison of these results with the oxidation of unhindered phenols by periodate reveals that sterically hindered phenols react differently with respect to the nature of the products. Thus, depending on the nature of the para substituent R, dimeric products typical of one-electron transfer reactions may be formed as major products. The formation of both **6** and **7** may be rationalized by phenoxy radical coupling reactions. Presumably, bis(cyclohexadienones) analogous to **6** are involved in the formation of diphenoquinone **7**.[11]

Cyclohexadienones formally resulting from nucleophilic participation of solvent are cross-conjugated, and we have found no evidence for the formation of 6-methoxy-2,4-cyclohexadienones from phenols **2e** and **2f**. As to whether 6-*tert*-butyl-6-methoxy-2,4-cyclohexadienones actually are stable under the reaction conditions appears uncertain in view of the high yield of 3-*tert*-butyl-5-trityl-*o*-benzoquinone (**5g**) from 2,6-di-*tert*-butyl-4-tritylphenol (**2g**). Apparently, steric hindrance by the trityl group makes nucleophilic substitution at the C-4 position impossible, and it is the least hindered of the electrophilic sites which undergoes attack by nucleophiles. Thus, oxidation of 2-*tert*-butyl-6-methyl-4-tritylphenol (**8**) by periodic acid in methanol proceeds smoothly to give the 2,4-cyclohexadienone **9** in 74% yield (reaction 5). The formation of 3-*tert*-butyl-5-trityl-*o*-benzoquinone (**5g**) may then be rationalized as shown in Scheme II.

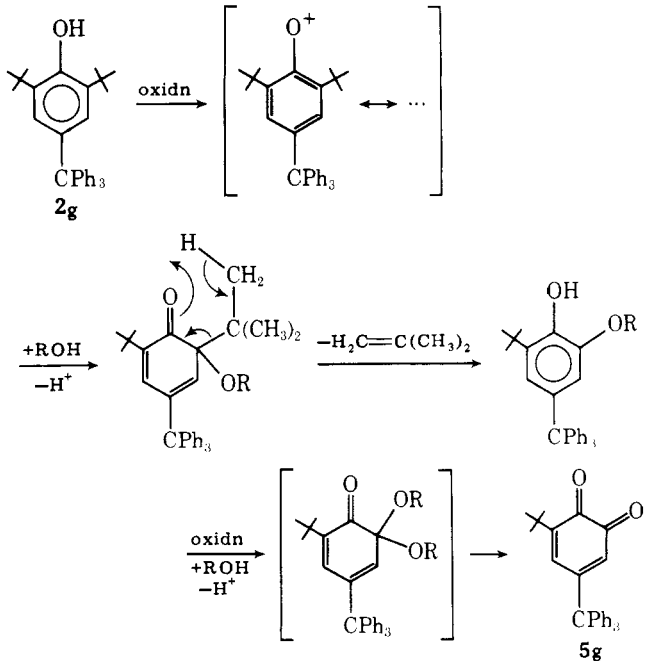


8 9 (5)

Scheme I

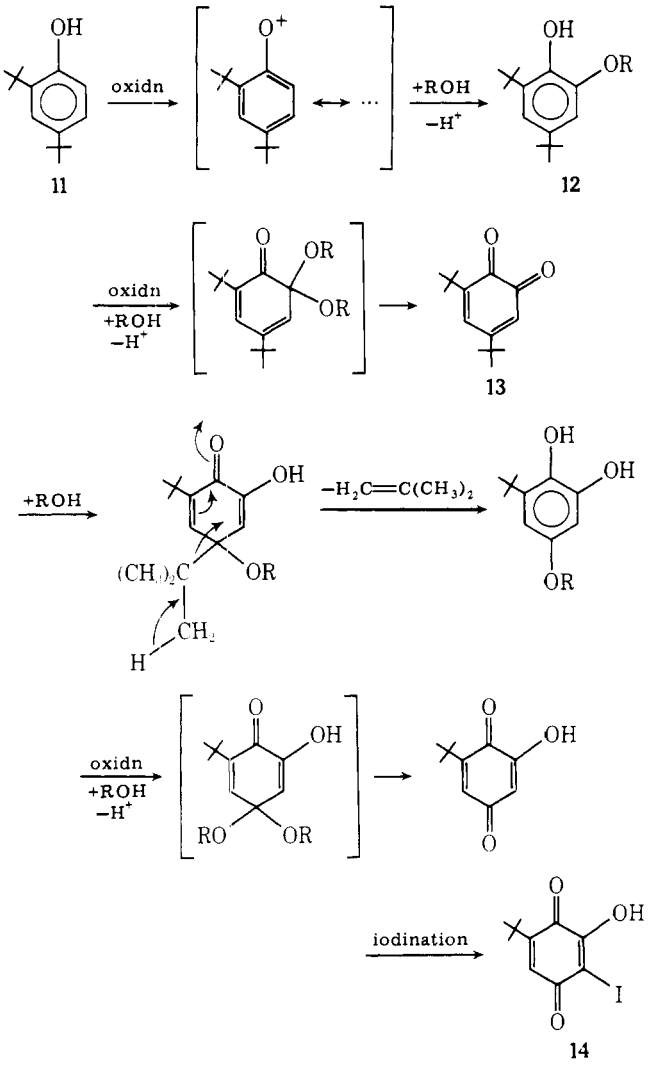


Scheme II



R = H or alkyl

Scheme III



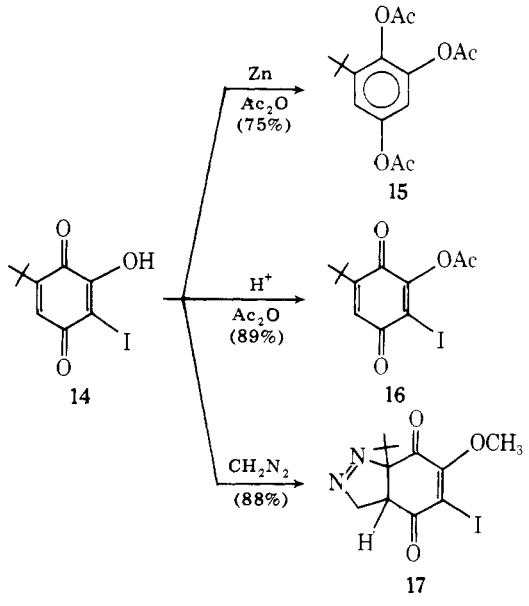
R = H or alkyl

Oxidation of 2-*tert*-butyl-4-tritylphenol (**10**) by periodic acid in methanol also afforded 1,2-benzoquinone **5g**. The decrease in yield to 79% may be indicative of possible oxidative dimerization occurring as a side reaction.[12] Dimeric oxidative coupling products (pentasubstituted dibenzofurans) not further investigated were found in the oxidation of 2,4-di-*tert*-butylphenol (cf. Experimental Section). In an apparently complicated sequence of reactions, the oxidation of 2,4-di-*tert*-butylphenol (**11**) by periodic acid in methanol containing perchloric acid ("liquid fire reaction"[13]) afforded 2-*tert*-butyl-6-hydroxy-5-iodo-1,4-benzoquinone (**14**) in 55% yield. Conceivable intermediates in the formation of **14** are 3,5-di-*tert*-butylcatechol (**12**, R = H) and 3,5-di-*tert*-butyl-*o*-benzoquinone (**13**) as both compounds are smoothly converted into the iodoquinone **14** by treatment with periodic acid–perchloric acid (see Scheme III).

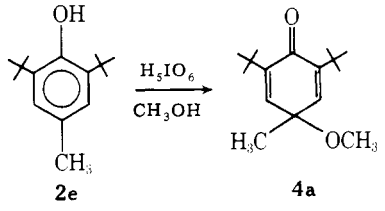
Spectroscopic data (UV–vis, IR, NMR, MS) of **14** and of its derivatives **15**, **16**, and **17** (see Scheme IV) are in agreement with the structural assignments (see Experimental Section).[14,15] In particular, ionization of **14** in ethanol solution [λ_{max} 435 nm (ϵ 1100)], brought about by either the pyridine or water, was easily recognizable by the appearance of an absorption maximum at 518 nm (ϵ 1350, isosbestic point at 454 nm).[17]

Mechanism of Oxidation. As shown in the Experimental Section, the decrease of the periodic acid/phenol ratio from 1:1 to 1:4 did not have any marked effect on the yield of oxidative methoxylation of 2,6-di-*tert*-butyl-4-methylphenol (**2e**)

Scheme IV



(reaction 6). Consequently, in contrast to the stoichiometrically proceeding oxidations of unhindered phenols according to reactions 1–3, oxidation states of iodine lower than seven



(6)

are involved in the oxidation of sterically hindered phenols by periodic acid.[19] A hypothetical sequence of reactions involving both periodic acid and iodic acid as oxidants, and the generation of iodine by disproportionation of iodous acid (HIO_2),[20] as outlined in Scheme V, would account for an oxidant/substrate ratio of 1:3.5.

As for the mode of attack of hindered phenols by periodic acid, in view of the types of oxidation products described above, it appears doubtful that the reaction involves an aryl periodate of structure **1**. In analogy to mechanistic interpretations given by Fatiadi on the oxidation of aromatic hydrocarbons,[21] electrophilic attack of periodic acid on sterically hindered phenols may give rise to a periodate of structure **18** whose different ways of reaction are outlined in Scheme VI.

We can neither exclude the heterolytic dissociation of **18** to give free phenoxonium ions, nor do we have any evidence for their involvement in the formation of typically ionic oxidation products. We do have evidence, however, for the generation of phenoxy radicals by oxidation of sterically hindered phenols with periodic acid. Thus, oxidation of 2,4,6-tri-*tert*-butylphenol (**2f**) in methanol under oxygen gave, besides 4-methoxy-2,4,6-tri-*tert*-butyl-2,5-cyclohexadienone (**4f**) in 54% yield, the peroxide **19** in 5% yield. The yield of peroxide **19** increased to 71% at the expense of **4f** (5%) when the oxidation

Scheme V

$$H_5IO_6 + ArOH + ROH \rightarrow QE + HIO_3 + 3H_2O$$

$$HIO_3 + ArOH + ROH \rightarrow QE + HIO_2 + H_2O$$

$$5HIO_2 \rightarrow 3HIO_3 + I_2 + H_2O$$

overall reaction:

$$2H_5IO_6 + 7ArOH + 7ROH \rightarrow 7QE + I_2 + 12H_2O$$

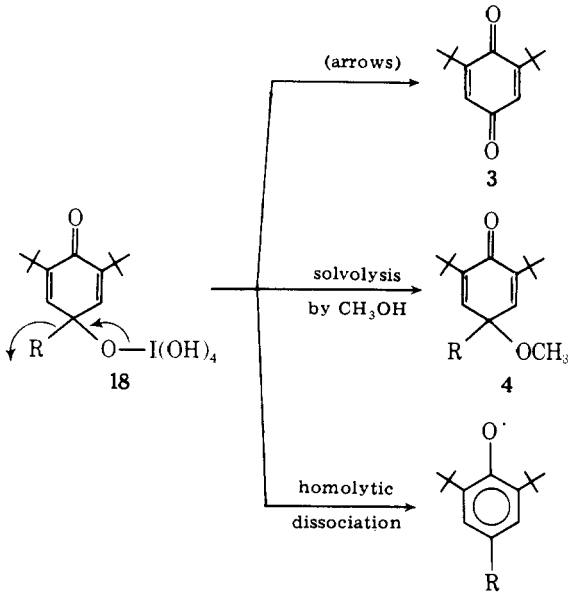
QE = quinol ether

Table II. Oxidation of Phenols 2a–d According to Standard Procedure

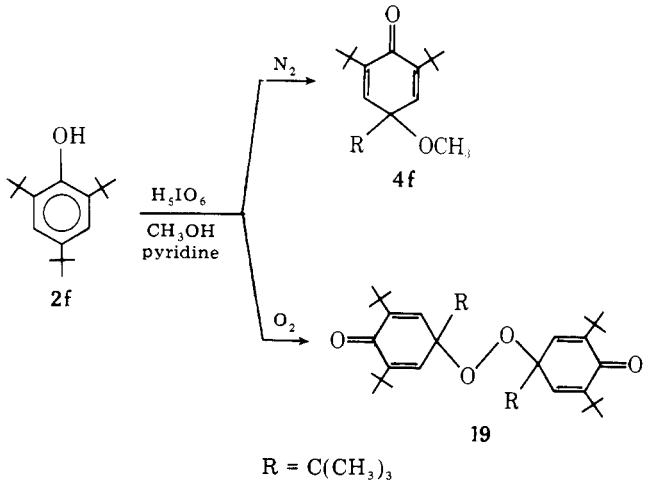
phenols **2a–d** (g, mmol)	product A yield, g (%)	product A mp, °C	product B yield, g (%)	product B mp, °C
2a (2.06, 10)	**7**: 1.25 (61)	242–245[a]	**3**: 0.16 (7)	62–65[c]
2b (1.43, 5)	**7**: 0.25 (24)	242–245[a]	**3**: 0.36 (33)	64–65[c]
2c (2.40, 10)	**6**: 1.14 (48)	148–151[b]	**3**: 0.85 (39)	62–65[c]
2d (0.472, 2)			**3**: 0.262 (60)	65–67[c]

[a] Lit.[22] mp 245–247 °C. [b] Lit.[11] mp 148.5–150 °C. [c] Lit.[23] mp 67–68 °C.

Scheme VI



was carried out in a methanol–pyridine mixture. Oxidation of 2,4,6-tri-*tert*-butylphenol in methanol–pyridine under nitrogen did give the 2,5-cyclohexadienone **4f** (43% yield) in a reaction which seems to be ionic but most likely proceeds by two consecutive one-electron steps.



R = $C(CH_3)_3$

Experimental Section

Melting points were determined on a hot-stage microscope and are uncorrected. Infrared and electronic absorption spectra were taken on Beckman IR9 and Beckman DK2 instruments, respectively. NMR spectra, in chloroform-*d* unless otherwise stated with chemical shifts reported in parts per million downfield from internal Me_4Si, were recorded on a Varian A-60 spectrometer. Mass spectra were obtained at 70 eV ionizing voltage on an AEI MS9 instrument. Elemental analyses were performed by NOVO Microanalytical Laboratory, Bagsvaerd, Denmark and by the Microanalytical Laboratory at the Department of Physical Chemistry, University of Vienna, Austria.

Table III. Oxidation of 2e with Periodic Acid in Methanol

2e, g (mmol)	periodic acid, g (mmol)	methanol, mL	yield of **4e**, %
2.20 (10)	2.28 (10)	25	83
2.20 (10)	1.14 (5)	25	79
2.20 (10)	0.57 (2.5)	25	68

Standard Procedure for the Oxidation of Phenols 2a–d. In a typical experiment, periodic acid (1 molar equiv) in methanol (10 mL) was added to a solution of the phenol (see Table II) in methanol (15 mL) under nitrogen. The reaction mixture was then left at room temperature for 24 h in the dark, and the precipitate thus obtained was filtered off, washed with methanol, and dried to give product A. Careful dilution of the filtrate with water gave a new precipitate (product B) which was removed by filtration and dried. Yields and melting points of isolated products are given in Table II.

Oxidation of 2,6-Di-*tert*-butyl-4-methylphenol (2e). The standard procedure with the amounts of periodic acid given in Table III gave **4e** as a precipitate after dilution of the reaction mixture with water. The yields of **4e** given in Table III refer to recrystallized material, mp 91–93 °C (lit.[24] mp 94 °C).

Oxidation of 2,4,6-Tri-*tert*-butylphenol (2f). A. Oxidation of 2f under Nitrogen. Careful addition of water to the reaction mixture obtained according to the standard procedure (10-mmol scale) afforded a precipitate which was recrystallized from aqueous methanol to give 1.81 g (62%) of 2,4,6-tri-*tert*-butyl-4-methoxy-2,5-cyclohexadienone (**4f**) as colorless crystals, mp 54–56 °C (lit.[25] mp 58–59 °C).

B. Oxidation of 2f in the Presence of Oxygen. Oxidation according to the standard procedure (10-mmol scale) with a stream of oxygen passing through the solution gave a precipitate which was recrystallized from methanol to give 0.15 g (5%) of bis(1,3,5-tri-*tert*-butyl-2,5-cyclohexadien-4-one) peroxide (**19**), mp 143–148 °C (lit.[26] mp 147–148 °C). Addition of water to the original filtrate precipitated **4f** which was recrystallized from aqueous methanol to give 1.58 g (54%) of colorless cyrstals, mp 54–55 °C.

C. Oxidation of 2f in Methanol–Pyridine under Nitrogen. The standard procedure (10-mmol scale) using methanol (200 mL) and pyridine (5 mL) as solvent gave, after dilution of the reaction mixture with water, compound **4f** as a precipitate. Recrystallization as above gave 1.28 g (43%) of colorless crystals, mp 52–55 °C.

D. Oxidation of 2f in Methanol–Pyridine under Oxygen. This was analogous to the previous experiment with a stream of oxygen passing through the solution. The precipitate thus obtained was recrystallized by dissolving in chloroform and adding methanol to give 1.98 g (71%) of peroxide **19** as yellow crystals, mp 143–148 °C. Dilution of the original filtrate with water gave **4f** (0.15 g, 5%) as pale yellow crystals, mp 53–56 °C.

Oxidation of 2,6-Di-*tert*-butyl-4-tritylphenol (2g). A solution of periodic acid (1.14 g, 5 mmol) in methanol (10 mL) was added to a stirred solution of 2,6-di-*tert*-butyl-4-tritylphenol[11] (2.24 g, 5 mmol) in chloroform (30 mL) under nitrogen. The reaction mixture was refluxed for 1 h. Vacuum evaporation of solvent gave a crystalline residue which was triturated with methanol and filtered off. Recrystallization from hot petroleum ether (bp 80–110 °C) gave 1.88 g (92%) of 3-*tert*-butyl-5-trityl-*o*-benzoquinone (**5g**) as brownish-red colored crystals: mp 232–234 °C (fast heating gave 245–247 °C); IR 1660 (s), 1625 (m) cm^{-1}; UV (CCl_4) λ ($\epsilon \times 10^{-3}$) 321 (4.5), 389 (2.0) nm; NMR 7.27 (s, 15 H), 6.55 (d, J = 2.5 Hz, 1 H), 6.40 (d, J = 2.5 Hz, 1 H), 1.02 (s, 9 H) ppm. Anal. Calcd for $C_{29}H_{26}O_2$ (406.53): C, 85.68; H, 6.45. Found: C, 85.68; H, 6.54.

2-*tert*-Butyl-6-methyl-4-tritylphenol (8). Concentrated sulfuric acid (10 mL) was added to a stirred solution of 2-*tert*-butyl-6-methylphenol (32.8 g, 0.2 mol) and triphenylcarbinol (52 g, 0.2 mol) in

glacial acetic acid (500 mL) at 45–50 °C. After stirring for 16 h at room temperature, the precipitate that formed was filtered off, washed with acetic acid and water, and then dried. Recrystallization from petroleum ether (bp 80–110 °C) gave 52.8 g (65%) of colorless crystals: mp 167–168 °C; IR 3570 cm^{-1}; NMR 7.20 (s, 15 H), 7.00 (d, J = 2.5 Hz, 1 H), 6.82 (d, J = 2.5 Hz, 1 H), 4.63 (s, 1 H), 2.11 (s, 3 H), 1.27 (s, 9 H) ppm. Anal. Calcd for $C_{30}H_{30}O$ (406.57): C, 88.63; H, 7.44. Found: C, 88.81; H, 7.47.

Oxidation of 2-*tert*-Butyl-6-methyl-4-tritylphenol (8). Periodic acid (2.28 g, 10 mmol) was added over a 5-min period to a stirred suspension of **8** (4.06 g, 10 mmol) in methanol (15 mL) under nitrogen, and the mixture was stirred for 24 h in the dark. The precipitate that formed was filtered off and recrystallized by dissolving in methylene chloride and adding methanol. The yield was 3.25 g (74%) of 2-*tert*-butyl-6-methoxy-6-methyl-4-trityl-2,4-cyclohexadienone (**9**) as greenish-yellow crystals: mp 215–216 °C; IR 1685 (s), 1650 (m) cm^{-1}; UV (chloroform) λ ($\epsilon \times 10^{-2}$) 270 sh (37.5), 277 (38.5), 310 (42.5), 370 (2.9) nm; NMR 7.27 (s, 15 H), 6.48 (d, J = 2.5 Hz, 1 H), 6.17 (d, J = 2.5 Hz, 1 H), 3.18 (s, 3 H), 1.28 (s, 3 H), 1.08 (s, 9 H) ppm. Anal. Calcd for $C_{31}H_{32}O_2$ (436.60): C, 85.28; H, 7.39. Found: C, 84.99; H, 7.36.

Oxidation of 2-*tert*-Butyl-4-tritylphenol (10). The oxidation was performed as described for **2g** using **10**[27] (1.97 g, 5 mmol) and periodic acid (1.14 g, 5 mmol). Recrystallization from petroleum ether (bp 80–110 °C) gave 1.60 g (79%) of **5g**, mp 232–234 °C.

Oxidation of 2,4-*tert*-butylphenol (11). A. In Methanol. In a typical experiment, periodic acid (2.28 g, 10 mmol) in methanol (10 mL) was added to a solution of 2,4-di-*tert*-butylphenol (2.06 g, 10 mmol) in methanol (15 mL) under nitrogen (exothermal reaction). The reaction mixture turned deep red within a few minutes. After 24 h, the precipitate that formed was filtered off and recrystallized by dissolving in chloroform and adding methanol to give 0.50 g (20%) of 4,6,8-tri-*tert*-butyl-*x*-iodo-2-methoxydibenzofuran as colorless crystals: mp 178–180 °C; UV (ethanol) λ ($\epsilon \times 10^{-3}$) 256 (10.9), 266 (13.0), 285 sh (14.3), 293 (22.5), 317 (8.1), 330 (7.1) nm; NMR 8.79 (d, J = 2 Hz, 1 H), 7.46 (d, J = 2 Hz, 1 H), 6.92 (s, 1 H), 3.95 (s, 3 H), 1.59 (s, 18 H), 1.45 (s, 9 H) ppm. Anal. Calcd for $C_{25}H_{33}IO_2$ (492.44): C, 60.98; H, 6.75. Found: C, 60.80; H, 6.64.

Acidification of the original methanol filtrate with hydrochloric acid (0.2 M) gave 2-*tert*-butyl-6-hydroxy-5-iodo-1,4-benzoquinone (**14**), which was recrystallized by dissolving in chloroform and adding *n*-pentane. The yield was 0.46 g (15%): mp 182–187 °C dec; IR 3230 (m), 1670 (m), 1635 (s), 1595 (m) cm^{-1}; UV (ethanol) λ_{max} (ϵ) 268 (10 500), 435 (1100) nm; NMR (acetone-d_6) 6.68 (s, 1 H), 5.08 (br s, 1 H), 1.32 (s, 9 H) ppm; mass spectrum, m/e 306 (100, M^+), 291 (8, M − 15), 278 (3, M − 28), 179 (13, M − 127). Anal. Calcd for $C_{10}H_{11}IO_3$ (306.10): C, 39.24; H, 3.62. Found: C, 39.58; H, 3.61.

B. In Methanol and Perchloric Acid ("Liquid Fire Reaction"). ***Caution!*** A solution of periodic acid (2.28 g, 10 mmol) in methanol (15 mL) and perchloric acid (10 mL) was added to a solution of 2,4-di-*tert*-butylphenol (2.06 g, mmol) in methanol (10 mL) to produce an immediate deep red-colored reaction mixture which gave a precipitate within a few minutes. The precipitate was filtered off, washed with water and aqueous methanol, and dried. Recrystallization from methylene chloride gave 1.68 g (55%) of **14**, mp 182–187 °C dec.

Oxidation of 3,5-Di-*tert*-butylcatechol (12). Oxidation was carried out as described for **11** in methanol and perchloric acid (method B). The yield was 1.69 g (55%) of **14**, mp 182–187 °C dec.

Preparation of 14 from 3,5-Di-*tert*-butyl-*o*-benzoquinone (13). 3,5-Di-*tert*-butyl-*o*-benzoquinone (**13**) was treated with periodic acid in methanol and perchloric acid as described for **11**. The yield was 1.45 g (47%) of **14**, mp 182–187 °C dec.

Reductive Acetylation of 2-*tert*-Butyl-5-iodo-6-hydroxy-*p*-benzoquinone. A suspension of **14** (1 g, 3.27 mmol), sodium acetate (0.2 g), and zinc powder (1 g) in acetic anhydride (10 mL) was refluxed for 5 min. Acetic acid (2 mL) was added, and the mixture was refluxed for another 5 min. Inorganic material was removed by filtration, and the residue was washed with warm acetic acid. Addition of ice and methanol afforded a precipitate which was filtered off. Recrystallization from hot petroleum ether (bp 60–70 °C) gave 0.76 g (75%) of 2,3,5-triacetoxy-*tert*-butylbenzene as colorless crystals: mp 105–107 °C (lit.[28] mp 105.5–106.5 °C); mixture melting point with an authentic sample gave 105–107 °C.

2-Acetoxy-6-*tert*-butyl-3-iodo-*p*-benzoquinone (16). A solution of **14** (3.06 g, 10 mmol) in acetic anhydride (50 mL) and concentrated sulfuric acid (1 mL) was stirred for 5 h at 5–10 °C, and the mixture was worked up in the usual way to give acetate **16** (3.10 g, 89%): mp 82–84 °C after recrystallization from aqueous methanol; IR 1760 (s), 1670 (s), 1660 (s), 1630 (s), 1595 (s) cm^{-1}; UV (ethanol) λ (ϵ) 248 (7300), 277 (7800), 378 (1300) nm; NMR 6.86 (s, 1 H), 2.40 (s, 3 H), 1.29 (s, 9 H) ppm. Anal. Calcd for $C_{12}H_{13}IO_4$ (348.13): C, 41.40; H, 3.76. Found: C, 41.32; H, 3.58.

7a-*tert*-Butyl-3a,7a-dihydro-5-iodo-6-methoxy-3*H*-indazolequinone 17. A solution of diazomethane in ether (50 mL) was added to a suspension of **14** (500 mg, 1.6 mmol) in methanol (10 mL) over a 20-min period. Evaporation of ether gave a crystalline precipitate which was filtered off and recrystallized by dissolving in methylene chloride and adding *n*-hexane. The yield was 510 mg (88%) of yellow-colored crystals: mp 138–142 °C dec; IR 1695 (s), 1660 (s), 1565 (s) cm^{-1}; NMR 5.07 (dd, J = 18.5 and 10 Hz, 1 H), 4.54 (dd, J = 18.5 and 7.5 Hz, 1 H), 4.20 (s, 3 H), 3.25 (dd, J = 10 and 7.5 Hz, 1 H), 1.13 (s, 9 H) ppm; mass spectrum, m/e 334 (58, M − 28), 319 (5, M − 28 − 15), 206 (4, M − 28 − 28), 252 (9, M − 28 − 82). Anal. Calcd for $C_{12}H_{15}IN_2O_3$ (362.16): C, 39.80; H, 4.17. Found: C, 39.72; H, 4.18.

Registry No.—**8**, 68297-77-8; **9**, 68297-78-9; **10**, 60043-12-1; **11**, 96-76-4; **12**, 1020-31-1; **13**, 3383-21-9; **14**, 68297-79-0; **15**, 4857-76-5; **16**, 68297-80-3; **17**, 68297-81-4; **19**, 1975-14-0; periodic acid, 13444-71-8; 2-*tert*-butyl-6-methylphenol, 2409-55-4; triphenylcarbinol, 76-84-6; 4,6,8-tri-*tert*-butyl-*x*-iodo-2-methoxydibenzofuran, 68297-97-2.

References and Notes

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