Base-Catalyzed Oxygenation of *tert*-Butylated Phenols. 2. Formation of 3-Aryl-2,5-di-*tert*-butyl-2,4-cyclopentadienones by Base-Catalyzed Oxygenation of 4-Aryl-2,6-di-*tert*-butylphenols: X-Ray Structure Determination of 2,5-Di-*tert*-butyl-3-(4-chlorophenyl)cyclopentadienone

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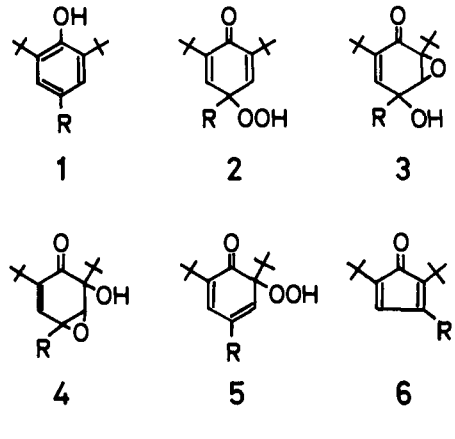
Abstract: The oxygenation of 4-aryl-2,6-di-*tert*-butylphenols catalyzed with *t*-BuOK in *t*-BuOH at 75 °C afforded 3-aryl-2,5-di-*tert*-butyl-2,4-cyclopentadienones in excellent yields. The formation of the cyclopentadienones from the phenols is affected by the substituent of the aryl group. When the oxygenation was carried out at room temperature the major products were 4-aryl-2,6-di-*tert*-butyl-4,5-epoxy-6-hydroxy-2-cyclohexenones (epoxy-*o*-quinols). The epoxy-*o*-quinols are confirmed to be intermediates in the formation of the cyclopentadienones. It has been found that the ring contraction step of the epoxy-*o*-quinol intermediate is subject to the substituent effect of the aryl group. The mechanism of the oxygenation of the phenols giving rise to the cyclopentadienones has been clarified with the aim of isolation of intermediates in the course of the reaction. This has revealed a new ring contraction process from the epoxy-*o*-quinols to the cyclopentadienones. Crystals of 2,5-di-*tert*-butyl-3-(4-chlorophenyl)cyclopentadienone are monoclinic, space group $P2_1$, with a = 18.218 (6), b = 7.990 (3), c = 5.981 (2) Å; β = 93.29 (2)°. The crystal structure has been refined to R = 0.060 based on 957 independent reflections.

In a preceding paper[2] we reported that the oxygenation of 4-alkyl-2,6-di-*tert*-butylphenols (**1**, R = alkyl) (Chart I)

Chart I



R	R	R
a; 4-MeOPh	d; 4-MePh	g; Ph
b; 3-MeOPh	e; 3-MePh	h; 4-ClPh
c; 2-MeOPh	f; 2-MePh	i; Mesityl

catalyzed with *t*-BuOK displays high regioselectivity depending on the medium: para oxygenation takes place in alcoholic (except tertiary alcohols) and aprotic polar solvents whereas ortho oxygenation is observed in tertiary alcohols.[3,4]

The present paper deals with the base-catalyzed oxygenation of 4-aryl-2,6-di-*tert*-butylphenols (**1**).[5] No reaction occurs in the solvents leading to the selective oxygenation at the para position but these phenols **1** are easily oxygenated in *t*-BuOH with *t*-BuOK at 75 °C to give 3-aryl-2,5-di-*tert*-butyl-2,4-cyclopentadienones (**6**) in good yields. This provides a novel route to synthesize 2,5-di-*tert*-butyl-2,4-cyclopentadienone derivatives.

Change in the reaction temperature reveals several intermediates in the course of the formation of **6a** from **1a**, making it possible to discuss the reaction mechanism of the present oxygenation.

Results

The Oxygenation of 4-Aryl-2,6-di-*tert*-butylphenols (1, R = Ar) in *t*-BuOH with *t*-BuOK at 75 °C. If solutions of **1** in *t*-BuOH containing *t*-BuOK are heated at 75 °C and oxygen is bubbled through these solutions, they turn orange-red owing to the formation of the 2,5-di-*tert*-butyl-2,4-cyclopentadienones (**6**). The starting phenols disappear normally within 1 h but the yields of **6** depend on the substituent of the 4-phenyl group and on the reaction time (Table I). An electron-releasing group at the 4 position of the aromatic ring seems to accelerate the reaction. Longer reaction times result in higher yields of **6**, although, if the reaction is carried out for too long a time, using insufficiently dried oxygen, further secondary reactions take place. Other major products are 4-aryl-2,6-di-*tert*-butyl-4,5-epoxy-6-hydroxy-2-cyclohexenones (epoxy-*o*-quinols, **4**) (Table I). As can be seen from Table I, the yields of **4** and **6** are complementary.

Structure of 3-Aryl-2,5-di-*tert*-butyl-2,4-cyclopentadienones (6). Spectral data of **6**[5] are all in good agreement with those observed for the known similar cyclopentadienone compounds.[6,7]

The structure of **6** was conclusively confirmed by the x-ray analysis of **6h**. The molecular parameters are listed in Table II and the atom numbering scheme is shown in the ORTEP[8] drawing of the molecule (Figure 1). The overall conformation

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Table I. Oxygenation of **1** in *t*-BuOH with *t*-BuOK at 75 °C for 1 and 6 h[a]

	Product yield,[b] %				Product **6**						
	1 h		6 h		M^+	IR,	^{1}H NMR ($CDCl_3$), δ (ppm)				UV-vis (cyclohexane),
1	**6**	**4**	**6**	**4**	(*m/e*)	cm^{-1}	*t*-Bu	Me	4-H	Ar H	λ_{max}, nm (ϵ)
a	97				298	1709	1.10, 1.17	3.83	6.30	6.8–7.4	417 (744)
b	20	78	44	53	298	1709	1.09, 1.17	3.82	6.29	6.7–7.5	413 (565)
c	29	40[c]	40	19[d]	298	1712	1.07, 1.17	3.84	6.27	6.7–7.5	410 (562)
d	53	[c]	71	[d]	282	1712	1.09, 1.16	2.37	6.27	7.14	414 (656)
e	27	69	48	45	282	1709	1.10, 1.17	2.40	6.34	6.9–7.5	413 (565)
f	9	88	20	75	282	1711	1.04, 1.17	2.30	6.23	7.0–7.4	410 (516)
g	22	73	50	40	268	1714	1.07, 1.16		6.29	7.2–7.4	414 (523)
h	27	71	35	39[e]	302	1713	1.08, 1.17		6.29	7.1–7.5	414 (586)
i	15	70	19	40[e]	310	1705	1.00, 1.16	2.21 2.29	6.11	6.85	412 (507)

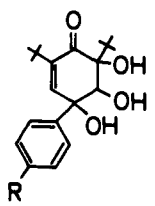
[a] No starting phenols (**1**) were detected after 1-h reaction. [b] Determined by isolation. [c] In addition, 26% **11c** from **1c** and 46% **11d** from **1d.** [d] In addition, 22% **11c** from **1c** and 15% **11d** from **1d.** [e] Another unidentified product was also obtained.

is dictated by the nonbonded contacts between substituents on the cyclopentadienone ring. Both *tert*-butyl groups are oriented to bring C(17) and C(13) into the plane of the ring minimizing the contacts between the other methyl groups and the oxygen atom. The phenyl ring is nearly perpendicular to the five-membered ring in order to reduce contacts with the C(13) methyl group. The angle between the planes of the two rings is 80° (Table III), and there is therefore no possibility of conjugation of the C(2)–C(3) double bond with the phenyl ring and the bond length of C(3)–C(6) is that of a single bond between two sp^2-hybridized carbon atoms. This can be also seen in the UV spectra (Table I), where practically no change in the long wavelength absorption is observed in passing over from **6a** to **6i.**

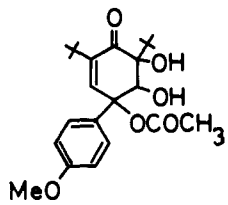
Although some delocalization might be expected in the cyclopentadienone ring the bond lengths are indicative of essentially localized single and double bonds.[9] This is an argument against any important contribution of a polar 4π-antiaromatic structure.[7,10] The phenyl ring has dimensions which are very similar to those observed in other chloro-substituted phenyl rings.[11]

The Oxygenation of 4-Aryl-2,6-di-*tert*-butylphenols (1) in *t*-BuOH with *t*-BuOK at 20 °C. The oxygenation of **1** in *t*-BuOH containing *t*-BuOK at room temperature results in the predominant formation of the epoxy-*o*-quinols (**4**). The oxygenation follows first kinetic order with respect to the phenols **1**[2] with rate constants of $\sim 2.1 \times 10^{-1}$ min^{-1} for **1a** and 9.9×10^{-2} min^{-1} for **1f** (at 20 °C). Since the reaction is completed within 1 h, the yields of **4a–4i** are practically the same (Table IV).

Structure of Epoxy-*o*-quinols (4). Elemental analyses of **4** show that molecular oxygen is incorporated in the compounds. The IR absorption near 1670 cm^{-1} and the chemical shift of the olefinic proton at about δ 7.0 ppm are attributed to the 2-cyclohexenone structure.[3,12] From the analogy to the product obtained in the oxygenation of 2,4,6-tri-*tert*-butylphenol,[2,3a] the structure **4** is easily deduced. The coupling constant (J = 1 Hz) of H-3 and H-5 is typical for the epoxy-*o*-quinol structure.[2,3] The epoxy-*p*-quinol **3a** (R = 4-MeOPh) separately



7a; R=OMe
7d; R=Me
7g; R=H



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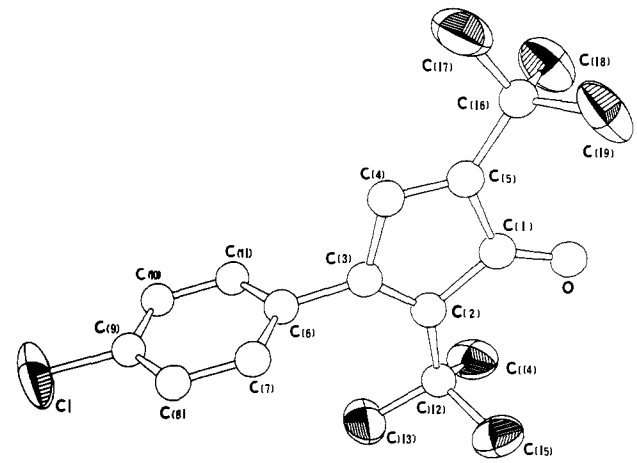


Figure 1. The molecular structure of **6h.**

synthesized and other analogous epoxy-*p*-quinols **3** (R = alkyl)[3a] display $J_{3,5}$ = 3 Hz. The existence of the epoxy group in **4** is confirmed by the reaction of **4** with aqueous acid to give the trihydroxy compound **7**[13] and with acetic acid to give the acetoxydihydroxy compound **8.** Structures of these compounds are further supported by ^{13}C NMR spectroscopy (Table V).

The signals are assigned by means of the off-resonance technique, by judgment of the intensity of the signals, and by taking into account the substituent effects on the chemical shift. The assignments of the carbon atoms of the substituted aryl ring R are not discussed in detail. It should be mentioned, however, that comparison with the corresponding 9-arylfluorenes[14] was of much help.

The ^{13}C signals of the cyclohexenone system inherent in **7** and **8** may be divided into three groups according to their chemical shift areas. The signal of C(1) is situated in the carbonyl region, C(2) and C(3) show typical olefinic resonances, of which the signal of C(3) is clearly distinguished by off-resonance spectroscopy. The signals of C(4), C(5), and C(6) are found close together between 71 and 81 ppm. The signal of C(5) is again easily characterized from the off-resonance spectrum. In the case of **7** the C(6) signal is shifted more downfield than that of C(4), because *tert*-butyl groups exhibit a larger α effect than phenyl rings.[15] Although the C(6) signals of **7a** and **8** (which resulted from the acetolysis of **4a**) show the same chemical shift (79.8 ppm), the C(4) signal (30.7 ppm) of **8** appears at lower fields than that (72.4 ppm) of **7a.** This is in good agreement with results reported,[16] where acetylation of *t*-OH groups leads to downfield shifts of the signals for the attached carbon atoms in the order up to 10 ppm. Thus, the ^{13}C spectrum confirms that the acetoxylic attack on **4a** occurs at C(4). The assignment of the *tert*-butyl resonances in Table V is discussed elsewhere.[17]

Table II. Intramolecular Distances and Angles

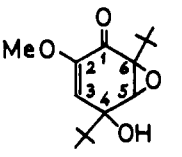
	A. Bonds, Å		
C(1)-O	1.23 (1)	C(10)-C(11)	1.40 (1)
C(1)-C(2)	1.50 (1)	C(6)-C(11)	1.37 (1)
C(2)-C(3)	1.34 (1)	C(9)-Cl	1.732 (9)
C(3)-C(4)	1.50 (1)	C(2)-C(12)	1.51 (1)
C(4)-C(5)	1.32 (1)	C(12)-C(13)	1.53 (1)
C(1)-C(5)	1.49 (1)	C(12)-C(14)	1.54 (1)
C(3)-C(6)	1.49 (1)	C(12)-C(15)	1.54 (1)
C(6)-C(7)	1.39 (1)	C(5)-C(16)	1.51 (1)
C(7)-C(8)	1.39 (1)	C(16)-C(17)	1.52 (1)
C(8)-C(9)	1.38 (1)	C(16)-C(18)	1.53 (1)
C(9)-(10)	1.36 (1)	C(16)-C(19)	1.53 (1)
	B. Angles, Degrees		
C(2)-C(1)-O	125.6 (8)	C(10)-C(9)-Cl	118.8 (7)
C(5)-C(1)-O	125.4 (7)	C(1)-C(2)-C(12)	123.1 (8)
C(1)-C(2)-C(3)	104.6 (7)	C(3)-C(2)-C(12)	132.3 (7)
C(2)-C(3)-C(4)	110.0 (6)	C(2)-C(12)-C(13)	113.1 (7)
C(3)-C(4)-C(5)	111.7 (7)	C(2)-C(12)-C(14)	109.7 (6)
C(4)-C(5)-C(1)	104.6 (7)	C(2)-C(12)-C(15)	109.3 (7)
C(5)-C(1)-C(2)	109.1 (7)	C(13)-C(12)-C(15)	108.4 (7)
C(6)-C(7)-C(8)	120.6 (7)	C(13)-C(12)-C(14)	108.4 (7)
C(7)-C(8)-C(9)	118.9 (8)	C(14)-C(12)-C(15)	107.8 (8)
C(8)-C(9)-C(10)	121.5 (8)	C(1)-C(5)-C(16)	124.8 (7)
C(9)-C(10)-C(11)	119.2 (8)	C(4)-C(5)-C(16)	130.5 (8)
C(10)-C(11)-C(6)	120.6 (7)	C(5)-C(16)-C(17)	108.8 (7)
C(11)-C(6)-C(7)	119.1 (7)	C(5)-C(16)-C(18)	111.0 (7)
C(3)-C(6)-C(11)	119.8 (6)	C(5)-C(16)-C(19)	110.5 (7)
C(3)-C(6)-C(7)	120.9 (6)	C(17)-C(16)-C(18)	108.5 (8)
C(2)-C(3)-C(6)	131.7 (7)	C(17)-C(16)-C(19)	109.1 (8)
C(4)-C(3)-C(6)	118.3 (7)	C(18)-C(16)-C(19)	108.9 (7)
C(8)-C(9)-Cl	119.7 (6)		
	C. Selected Torsion Angles, Degrees		
C(3)-C(2)-C(12)-C(13)	4	C(1)-C(2)-C(12)-C(14)	−53
C(4)-C(5)-C(16)-C(17)	123	C(1)-C(2)-C(12)-C(15)	65
C(1)-C(5)-C(16)-C(18)	61	C(2)-C(3)-C(6)-C(7)	84
C(1)-C(5)-C(16)-C(19)	−60	C(4)-C(3)-C(6)-C(11)	77

Table III. Deviations (Ångstroms) of Atoms from Various Mean Planes[a]

(*a*)	Phenyl ring: C(6), 0.011; C(7), −0.014; C(8), 0.006; C(9), 0.004; C(10), −0.006; C(11), −0.001; *Cl, 0.017; C(3), −0.072*
(*b*)	Cyclopentadienone ring: C(1), −0.005; C(2), 0.008; C(3), −0.008; C(4), 0.004; C(5), 0.001; *C(6), −0.012; O, −0.026; C(12), 0.070; C(16), 0.057*

[a] The angle between planes *a* and *b* is 80°. Atoms not included in the derivation of a plane are italicized.

The structure of compounds **4** is mainly confirmed by comparison of their ^{13}C NMR spectra with those of **7, 8,** epoxy-*p*-quinols **3a,** and **9.**[17] The structure of **9** was determined by x-ray analysis.[18] Since the signals of C(1), C(2), and C(3)



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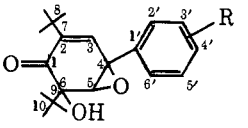
of **4** can be straightforwardly assigned as in **7** and **8,** only C(4), C(5), and C(6) will be considered here. The signal of C(5) is easily recognized by off-resonance spectroscopy; its shift value is almost constant for compounds **3, 4,** and **9.** This is quite reasonable because C(5) is a part of the oxirane system in all these compounds. It can be further seen that there is a resonance at 80–82 ppm present in the spectra of **4** as well as **7** and **8,** which is lacking in the spectra of **3a** and **9.** This resonance

Table IV. The Oxygenation of **1** in *t*-BuOH with *t*-BuOK at 20 °C. The Formation of **4**

Product yield, %[a]			IR (KBr) of **4**, cm^{-1}		NMR ($CDCl_3$), δ (ppm), of **4**				
1	**6**	**4**	ν_{OH}	ν_{CO}	*t*-Bu	Me	5-H[b]	OH[c]	3-H[b]
a	8	92	3489	1672	1.00, 1.26	3.85	3.66	4.10	7.09
b	6	94	3439	1668	1.00, 1.27	3.83	3.65	4.09	7.05
c	0	100	3488	1672	1.08, 1.23	3.82	3.71	4.10	6.85
d	8	92	3383	1673	1.00, 1.23	2.38	3.64	4.10	7.02
e	7	93	3429	1671	1.02, 1.28	2.39	3.64	4.09	7.05
f	5	95	3399	1670	1.14, 1.23	2.50	4.01	4.09	6.81
g	8	92	3500	1675	1.01, 1.28		3.63	4.09	7.02
h	5	93	3427	1668	0.96, 1.23		3.57	4.05	6.89
i	0	100	3444	1674	1.08, 1.20	2.24 2.38	3.83	3.65	6.54

[a] Yields were determined by NMR. [b] The signals show a doublet with J = 1.0 Hz. [c] Disappeared by addition of D_2O.

Table V. ^{13}C NMR Spectral Data, δ (Parts per Million) from Me_4Si ($CDCl_3$)



Compd	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(1')	C(2')	C(3')	C(4')	C(5')	C(6')	R
4a	199.9	150.8	141.5	58.0	63.6	81.2	35.4	29.5	37.7	25.9	130.3	126.6	114.3	159.8	114.3	126.6	55.3
4b	197.5	149.1	139.4	57.5	62.8	80.2	35.0	29.1	37.2	25.6	138.3	109.4[a]	158.3	112.4[a]	128.4	116.2	54.6
4c	200.4	147.8	143.2	58.0	62.2	81.6	35.0	29.6	37.7	25.8	126.6	157.2	110.6	127.6	120.9	129.8	54.9
4d	199.9	150.7	141.4	58.2	63.6	81.2	35.4	29.4	37.7	25.9	135.3	125.1	129.5	138.2	129.5	125.1	21.2
4e	199.9	150.8	141.4	58.2	63.5	81.2	35.4	29.5	37.8	25.9	138.3[a]	125.7	138.7[a]	129.2	128.8	122.4	21.5
4f	200.3	149.4	141.8	60.2	60.2	81.6	35.3	29.5	37.6	26.3	136.1[a]	137.6[a]	131.3	127.2	125.8	128.8	19.8
4g	199.9	150.9	141.2	58.2	63.6	81.2	35.4	29.5	37.7	26.0	138.3	125.2	128.9	128.4	128.9	125.2	
4h	199.6	151.3	140.3	57.9	63.7	81.2	35.5	29.4	37.7	25.9	135.4	126.6	129.1	136.9	129.1	126.6	
4i	200.7	149.8	141.8	59.6	61.8	82.6	35.3	29.7	37.4	26.3	134.2	138.3	128.8	132.5	130.2	139.6	*b*
3a	196.8	144.0	138.1	72.5	62.9	66.3	34.9	29.4	32.5	26.1	132.3	126.7	114.3	159.6	114.3	126.7	55.3
7a	203.4	153.1	143.2	72.4	71.3	79.8	35.3	30.1	39.5	25.4	137.6	126.5	114.1	159.2	114.1	126.5	55.3
8[c]	204.5	151.5	142.9	80.7	71.9	79.8	35.3	29.9	39.3	25.5	132.8	126.4	114.0	159.3	114.0	126.4	55.3

[a] The assignment is not confirmed and may be the other way. [b] Owing to restricted rotation of the mesityl group, three methyl signals are observed at δ 20.6, 20.9, and 22.1 ppm. [c] Acetyl signals appear at 168.8 (C=O) and 20.7 (CH_3) ppm.

Table VI. Conversion of **4** to **6** in *t*-BuOH with *t*-BuOK at 75 °C

4	Reaction time, h	Conversion, %	Yield,[a] %
a	0.5	100	100
b	1	50	100
	3	100	75
c	1	50	100
	3	100	80
d	0.5	35	100
	1	50	100
	3	100	95
e	0.5	25	100
	1	50	100
	3	100	90
f	1	35	100
	3	80	70[b]
	5	100	50[c]
g	1	50	100
	3	100	85
h	1	50	100
	3	100	50

[a] Yields were determined by NMR. [b] *o*-Benzoquinone, 20%. [c] *o*-Benzoquinone, 30%.

must be attributed to C(6); hence C(4) of **4** absorbs between 57 and 60 ppm.

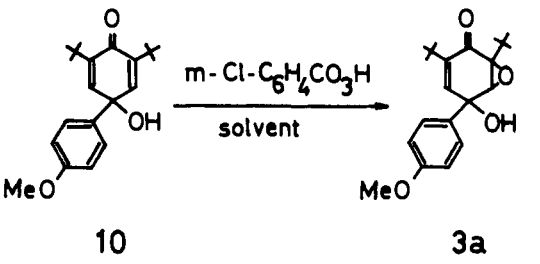
The most striking difference between ^{13}C NMR spectra of **4** and **7** is observed in the chemical shifts of C(4) (**4a**, 58.0 ppm; **7**, 72.4 ppm) and C(5) (**4a**, 63.6 ppm; **7**, 71.3 ppm). The resonances of C(3) and C(6), on the other hand, exhibit no prominent shift difference in going from **4** to **7**. From these observations, it is evident that ring closure of a glycol to the oxirane structure is accompanied by a characteristic high-field shift of the signals of carbon atoms involved.[19] The same conclusion can be derived from a comparison of the chemical shifts of the carbon atoms 5 and 6 in **7** and **3a**.

Formation of 6 by the Base-Catalyzed Reaction of 4. When the epoxy-*o*-quinols (**4**) were heated in *t*-BuOH in the presence of *t*-BuOK at 75 °C, the cyclopentadienone derivatives (**6**) were obtained, oxygen being not required. The reaction is affected by the substituent on the aromatic ring. As can be seen from Table VI, electron-releasing groups accelerate the reaction (e.g., **4a** > **4d** > **4e**, 0.5-h experiment). Sterically hindered substituents seem to retard it (e.g., **4d** > **4f**, 1-h experiment). No conversion occurs for the case of the highly hindered **4i**.

Detection of HCOOH on the Formation of 6. The oxygenation mixture of the phenol **1a** (50 °C, 1 h) contained potassium formate, which was detected by three qualitative tests. With sodium nitroprusside and sodium bisulfite in dilute sulfuric acid, the characteristic green color developed. With concentrated sulfuric acid, carbon monoxide evolved and reduced $PdCl_2$ to metallic palladium. With dilute sulfuric acid, formic acid was liberated, which was characterized by its mass spectrum. No *tert*-butyl formate could be detected by gas chromatography of the original oxygenation mixture. The direct production of CO or CO_2 in the oxygenation could also be ruled out by IR spectroscopy.

Synthesis of Epoxy-*p*-quinol 3a (R = 4-MeOPh). Since epoxy-*p*-quinols could not be prepared by direct oxygenation of 4-arylphenols **1**, compound **3a** necessary for spectroscopic comparison was synthesized by epoxidation of the corresponding *p*-quinol **10** with *m*-chloroperbenzoic acid or hydrogen peroxide-urea adduct (Scheme I).[20]

Scheme I



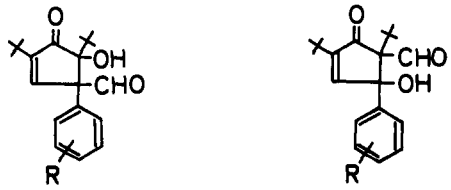
10 **3a**

Discussion

Mechanism of the Formation of 6. The results shown in Tables I and IV clearly indicate that the epoxy-*o*-quinol **4** is the intermediate in the formation of the cyclopentadienone derivative **6** from the phenol **1**. However, questions arise how the epoxy-*o*-quinol is produced on the oxygenation of **1** and how the cyclopentadienone **6** is obtained from **4** by the action of base. In order to clarify these questions, the oxygenation of **1a**, which gives **6a** in quantitative yield at 75 °C, was carried out at −25 °C (see Experimental Section). The hydroperoxide **5a** is formed in 85% yield. This hydroperoxide is transformed into the epoxy-*o*-quinol **4a** and cyclopentadienone **6a** in 92% and 8% yields, respectively, when treated with *t*-BuOK in *t*-BuOH under nitrogen at room temperature. If this hydroperoxide is heated with *t*-BuOK in *t*-BuOH at 75 °C for 30 min, the cyclopentadienone **6a** is obtained quantitatively. This indicates that the hydroperoxide is the intermediate in the

formation of **4** from **1**. The spectral and analytical data are all in good agreement with the structure **5a**. Acid treatment of **5a** gives 3-*tert*-butyl-5-(4-methoxyphenyl)-*o*-benzoquinone quantitatively.[21] Reduction of **5a** with dimethyl sulfide produced the corresponding *o*-quinol which finally affords 3-*tert*-butyl-5-(4-methoxyphenyl)catechol during the workup procedure. These results also confirm the structure **5a**. In summary, we may conclude that the reaction path **1** → **5** → **4** → **6** is followed.

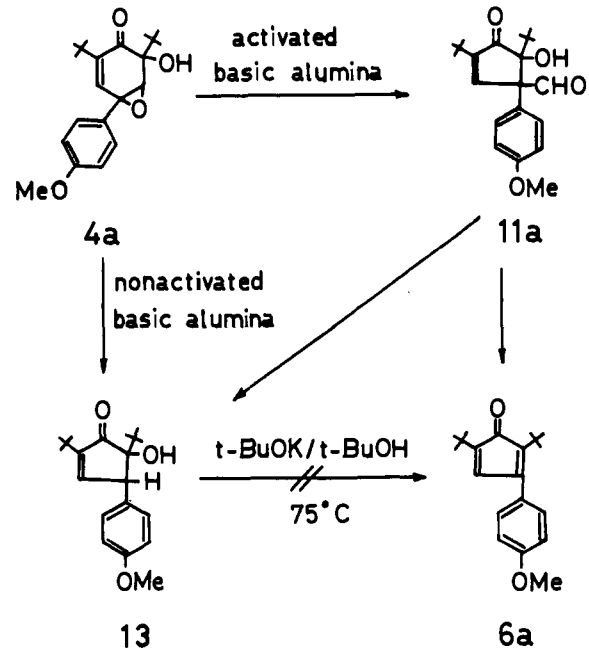
The formation of **6** from **4** involves ring contraction and the loss of one carbon unit. There are many reports dealing with the oxidation of polyhydroxybenzenes where such a ring contraction occurs.[22-31] It has also been reported that the one-electron oxidation of 2,4,6-tri-*tert*-butylresorcinol affords 2,3,5-tri-*tert*-butyl-2,4-cyclopentadienone accompanied by the generation of CO.[32] These reports suggest that the reaction **4** → **6** might involve a polyhydroxybenzene intermediate. The formation of **6** from any one of the compounds **1**, **4**, and **5**, however, is not accompanied by the generation of CO or CO_2, indicating that the formation of **6** does not involve a resorcinol derivative intermediate. Attempts to isolate any intermediate between **4** and **6** were successful only with **1c** and **1d** as far as the *t*-BuOH/*t*-BuOK system was used. Here, we succeeded in isolating isomeric ring contracted products, in which the existence of groups -COC (*t*-Bu)=CH-, -OH, and -CHO is confirmed (IR and NMR; see Experimental Section). The spectral data reveal the two structures **11** and **12** to be possible for the ring-contracted product. However, the aldehydes might have been produced from the corresponding epoxy-*o*-quinols (**4**) during workup by means of column chromatography. Indeed, upon adsorption of **4a** on activated basic alumina (activity I) in CH_2Cl_2 followed by elution with MeOH the ring-contracted product **11a**(**12a**) is also obtained. Finally, treatment of **4a** with silica gel in CH_2Cl_2 or with CF_3COOH produces this compound in good yield.



a; R = 4-OMe
c; R = 2-OMe
d; R = 4-Me
h; R = 4-Cl

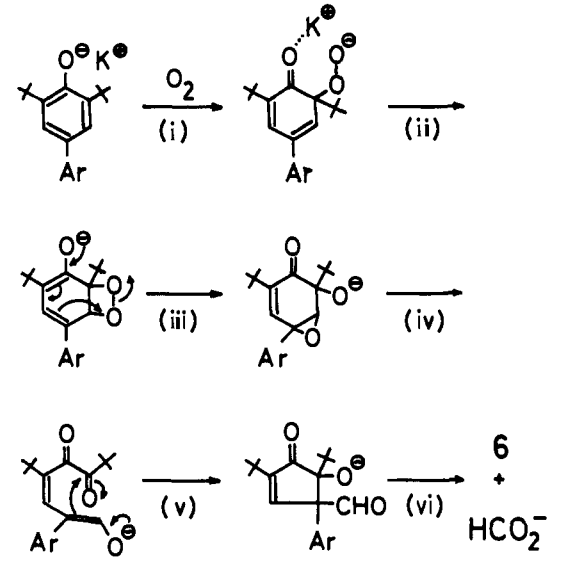
The findings by Hart et al.[33] suggest that the structure **11a** may be assigned to the ring contracted product from **4a**. Interestingly, when this ring contracted product was treated with nonactivated basic alumina in CH_2Cl_2 followed by elution with MeOH, a deformylated product **13** was obtained in 95% yield (Scheme II). The NMR spectrum of **13** (δ 4.08 (1 H, d, J = 2 Hz, =CCHAr) and 7.28 (1 H, d, J = 2 Hz, -COC=CH)) strongly supports the structure. This in turn clearly indicates that the structure **11a** was correctly assigned for the ring-contracted product. The compound **13** is also obtained upon adsorption of **4a** on nonactivated basic alumina in CH_2Cl_2 followed by elution with MeOH. The cyclopentadienone **6a** is quantitatively obtained upon heating **11a** with *t*-BuOK in *t*-BuOH at 75 °C, whereas no cyclopentadienone **6a** is formed from **13** by a similar treatment. The above scheme is therefore concluded to be characteristic for the formation of **6a** from **4a**.

Scheme II



Since neither **6a** nor **11a** is obtained upon heating **7a** or **8** with *t*-BuOK in *t*-BuOH at 75 °C, the key step for the ring contraction of **4a** is the cleavage of the epoxy ring accompanying the migration of the C(5)-C(6) bond. Presumably, the cleavage of the epoxy ring takes place at the C(4) position. This might be expected by analogy to the acid-catalyzed reactions of **4a** (e.g., **4a** → **8**) and since **11a** is produced in the reaction of **4a** with either *t*-BuOK or CF_3COOH. In the base-catalyzed ring opening of **4** an enolate anion would be formed (see step iv in Scheme III) showing an electron pair structure at C(4)

Scheme III



by resonance. This can lead to the aldehyde anion by nucleophilic attack on the ω-carbonyl group (step v). The substituent effect on the formation of **6** from **4** is rationalized by considering that the stability of the carbenate ion at the benzylic carbon (C(4)) is dependent on the substituent in the aryl ring, where electron-donating groups destabilize the negative carbon and hence accelerate the reaction. In the reaction mixture of the oxygenation of **1a** giving **6a** HCOOH was detected. On the other hand, no HCOO-*t*-Bu could be detected by GLC in the volatile part of the reaction mixture.

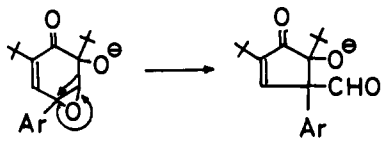
All these observations are compatible with the mechanism shown in Scheme III for the formation of **6** on the base-cata-

Table VII. Half-Wave Potentials of the Polarographic Oxidation of the Phenols **1**

1	4-R-2,6-Di-*tert*-butylphenol, R	$E_{1/2}$[a]
a	4-$MeOC_6H_4$	1120
b	3-$MeOC_6H_4$	1263
c	2-$MeOC_6H_4$	1282
d	4-MeC_6H_4	1200
e	3-MeC_6H_4	1320
f	2-MeC_6H_4	1441
g	C_6H_5	1210
h	4-ClC_6H_4	1287
i	Mesityl	1395

[a] In millivolts vs. SCE; Pt-disk electrodes; CH_3CN; NEt_4ClO_4, 10^{-1} M; concentration of depolarizator, 10^{-3} M.

lyzed oxygenation of **1**: The first step (i), the action of molecular oxygen on the phenolates of **1**, seems to be influenced not decisively by the substituent effect. This is reflected by the fact that there are no drastic differences in the polarographic half-wave potentials of the 4-aryl-2,6-di-*tert*-butylphenols **1** used in this study (Table VII). The formation of the epoxy-*o*-quinols from the *o*-hydroperoxides can be rationalized by assuming that the peroxy anion is subject to intramolecular Michael addition to the adjacent C=C double bond to give a transient dioxetane intermediate (step ii), which then undergoes the intramolecular asymmetric decomposition (step iii) as suggested for analogous reactions.[2] Another possible symmetric decomposition widely seen in many dioxetanes may be ruled out because no chemiluminescence was observed on the conversion of **4** to **6**. Step iv may be omitted to produce directly the ring-contracted product.



The last step (vi) may involve the intramolecular addition of oxide anion to the formyl group followed by the elimination of formate to give **6**.

Experimental Section

General. All melting points are uncorrected. Elemental analyses were performed by the Analytical Center of Kyoto University or the Analytical Laboratory of the Chemical Institutes of the University of Tübingen. Infrared spectra were recorded on a Jasco IRA-1 or Perkin-Elmer 221 spectrophotometer. Ultraviolet spectra were recorded on the Beckman spectrophotometer model 24. Proton magnetic resonance spectra were determined on a Varian T-60, A-60A, or EM 360 or on a Bruker HFX 90 spectrometer, with Me_4Si as internal standard. Carbon-13 magnetic resonance spectra were obtained under broad band decoupling conditions at 22.63 MHz on a Bruker HFX 90 spectrometer connected to a Bruker-Nicolet BNC 12 computer. Me_4Si was used as the internal reference. A radio-frequency pulse of 2.5 μs was applied up to 8000 times with a repetition time of 0.8 s over the spectrum width of 6000 Hz. Mass spectra were determined on a MS 9 instrument (AEI).

Single-Crystal X-Ray Data of 2,5-Di-*tert*-butyl-3-(4-chlorophenyl)cyclopentadienone (6h). $C_{19}H_{23}ClO$ (M 302.87): monoclinic, a = 18.218 (6), b = 7.990 (3), c = 5.981 (2) Å; β = 93.29 (2)°; Z = 2; U = 869.1 Å^3. d_c = 1.16 g cm^{-3}; F (000) = 364; Mo Kα radiation; μ (Mo Kα) = 2.2 cm^{-1}; space group $P2_1$ (No. 4) from systematic absences of $0k0$ for k odd.

The crystal used for data collection was a square plate of approximate size 0.3 × 0.3 × 0.1 mm with principal face {100} and mounted along c. Preliminary cell dimensions were derived from precession and Weissenberg films. The crystal was then transferred to a Hilger and Watts Y290 four-circle diffractometer and accurate cell dimensions obtained by least-squares treatment of the setting angles of 12 reflections. Intensity data for unique reflections with $\theta < 25°$ were measured using the $\omega/2\theta$ step scan technique with Mo Kα radiation (graphite crystal monochromator). The peak scan was carried out in 80 steps of 0.5 s each with 20-s background counts at either end of the scan. Three standard reflections were remeasured after every 100 reflections and showed no significant variation with time. The data were corrected for Lorentz and polarization effects but not for absorption. Reflections with $I < 3\sigma(I)$ were coded as unobserved leaving 957 independent observed reflections out of 1516 measured.

The complete data set was used to calculate normalized structure factors ($|E|$) and phases were derived by the multiple start tangent formula procedure[34] using the 152 reflections with $|E| > 1.5$. The starting set of 6 reflections was chosen by convergence mapping[35] and a total of 32 phase sets were derived. The four sets with the lowest Karle R values[36] were used to phase further reflections with $|E| > 1.0$, and a subsequent Fourier synthesis on one of these sets showed 12 of the nonhydrogen atoms. The remaining 9 atoms were located on a difference Fourier synthesis.

These atoms were refined isotropically by full-matrix least-squares using the 957 significant reflections with unit weights to a residual R = 0.16.[37] A difference Fourier map indicated considerable anisotropy of the methyl carbon atoms and the chlorine, and therefore these atoms were further refined anisotropically. A difference Fourier map then revealed the positions of the 23 hydrogen atoms which were included in the refinement at idealized positions[38] (d(C–H) 1.08 Å) and held fixed with B = 6.0. The data were assigned empirical weights (w) defined as $w = 1/\{1 + [(|F_o| - 5)/13]^2\}$ in order to give approximately constant average $w\Delta^2$ as a function of $|F_o|$. The reflection 201 which is very intense and has $|F_o| \ll |F_c|$ was assumed to be suffering from extinction and was removed from the least squares. Continued refinement converged at R = 0.060, R_w = 0.076. The maximum shift/error was 0.01 and the esd of an observation of unit weight was 1.8. A final difference Fourier map was everywhere less than ±0.2 eÅ^{-3}.

Scattering factors for neutral atoms were taken from ref 39 with no allowance for anomalous scattering. Initial data processing was done with local programs and the structure solution and refinement were carried out with the x-ray program system.[40] Final atom parameters are listed in Table VIII and a listing of final structure factors has been deposited as supplementary material at the editors' office.

Starting Phenols. 4-Aryl-2,6-di-*tert*-butylphenols **1** were synthesized according to the method previously published[41] and purified by repeated recrystallization from methanol.

Formation of 3-Aryl-2,5-di-*tert*-butyl-2,4-cyclopentadienones (6) from 1 by the Base-Catalyzed Oxygenation at 75 °C. Oxygen was bubbled through a solution of **1** (2 mmol) of *t*-BuOH (10 mL) containing *t*-BuOK (5 mmol) at 75 °C. The reaction mixture was poured into an excess of aqueous NH_4Cl solution and extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated. The residue was chromatographed on a silica gel column. Eluting with petroleum ether gave the cyclopentadienones **6**, which were recrystallized from methanol to give orange-red prisms. Further eluting with a mixture of petroleum ether and CH_2Cl_2 (9:1) gave epoxy-*o*-quinols (**4**), which were recrystallized from petroleum ether to give colorless prisms. Yields of the products were determined after 1- and 6-h oxygenations. The results and spectral data of **6** are presented in Table I. Melting points and analytical data are listed in Table IX.

In the case of **1a**, the reaction was completed within 30 min and **6a** was isolated in crystalline form directly from the solution after treatment of the reaction mixture with aqueous NH_4Cl solution, no further separation procedure being required.

From 4 by the Base-Catalyzed Reaction. A solution of **4** (1 mmol) in *t*-BuOH (5 mL) containing *t*-BuOK (2.5 mmol) was heated at 75 °C for appropriate reaction times. The reaction mixture was poured into ice-cooled aqueous NH_4Cl solution and extracted with ether. The extract was dried (Na_2SO_4) and evaporated. Yields of **6** were determined by the NMR analysis of the residue. The results are presented in Table VI.

Compound **6a** was also formed quantitatively from **11a** by the similar treatment with *t*-BuOK in *t*-BuOH at 75 °C.

Formation of 4-Aryl-2,6-di-*tert*-butyl-4,5-epoxy-6-hydroxy-2-cyclohexenones (Epoxy-*o*-quinols, 4). From 1 by the Base-Catalyzed Oxygenation at 20 °C. Oxygen was bubbled through a solution of **1** (1 mmol) and *t*-BuOK (2.5 mmol) in a mixture of *t*-BuOH (5 mL) and petroleum ether (1 mL) at 20 °C for 1 h. The reaction mixture was poured into ice-cooled aqueous NH_4Cl solution and extracted with ether. The extract was dried (Na_2SO_4) and evaporated to leave a pale

Table VIII. Final Atom Parameters

A. Positions ($\times 10^4$) and Isotropic Thermal Parameters ($\times 10^3$) with esds

	x	y	z	U_{iso}, Å^2
Cl	−0061 (2)	1410	9646 (6)	*
C(1)	3256 (4)	6320 (12)	3568 (11)	51 (2)
C(2)	2583 (4)	6402 (11)	4908 (11)	48 (2)
C(3)	2382 (4)	4808 (10)	5146 (12)	43 (2)
C(4)	2911 (4)	3677 (11)	4055 (12)	47 (2)
C(5)	3429 (4)	4528 (10)	3106 (12)	45 (2)
C(6)	1760 (3)	4032 (11)	6286 (11)	40 (2)
C(7)	1068 (4)	3894 (13)	5205 (13)	61 (2)
C(8)	0499 (5)	3106 (14)	6240 (15)	70 (2)
C(9)	0639 (4)	2412 (12)	8332 (14)	60 (2)
C(10)	1316 (4)	2493 (12)	9398 (14)	63 (2)
C(11)	1884 (4)	3318 (11)	8359 (14)	58 (2)
C(12)	2275 (4)	8023 (12)	5757 (13)	52 (2)
C(13)	1638 (5)	7763 (13)	7287 (17)	*
C(14)	2888 (5)	9008 (13)	7070 (15)	*
C(15)	2000 (5)	9100 (13)	3755 (15)	*
C(16)	4084 (4)	3934 (12)	1903 (12)	53 (2)
C(17)	4061 (5)	2029 (14)	1759 (18)	*
C(18)	4801 (4)	4450 (16)	3162 (14)	*
C(19)	4067 (5)	4661 (17)	−0468 (14)	*
O	3607 (3)	7535 (10)	2936 (11)	75 (2)

B. Anisotropic Thermal Parameters (Å$^2 \times 10^3$) in the Form
$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} . 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl	93 (2)	118 (2)	118 (2)	−47 (2)	57 (2)	0 (2)
C(13)	87 (6)	48 (5)	113 (8)	6 (5)	52 (6)	−9 (5)
C(14)	73 (5)	56 (5)	89 (6)	8 (5)	6 (5)	−19 (6)
C(15)	83 (6)	48 (5)	87 (6)	15 (5)	9 (5)	3 (5)
C(17)	68 (6)	87 (7)	106 (8)	9 (5)	36 (6)	−22 (6)
C(18)	48 (5)	122 (9)	68 (6)	−2 (5)	5 (4)	−9 (6)
C(19)	54 (5)	143 (10)	5 (5)	1 (6)	24 (4)	−1 (6)

Table IX. Analytical Data of 3-Aryl-2,5-di-*tert*-butyl-2,4-cyclopentadienones (**6**)

			Elemental analysis, %			
			Calcd		Found	
6	Mp, °C	Molecular formula	C	H	C	H
a	80–81	$C_{20}H_{26}O_2$	80.49	8.78	80.29	8.89
b	89–90	$C_{20}H_{26}O_2$	80.49	8.78	80.19	9.04
c	61–62	$C_{20}H_{26}O_2$	80.49	8.78	80.24	8.90
d	97–98	$C_{20}H_{26}O$	85.05	9.28	85.33	9.53
e	98–99	$C_{20}H_{26}O$	85.05	9.28	84.96	9.45
f	87–88	$C_{20}H_{26}O$	85.05	9.28	85.02	9.38
g	97–98	$C_{19}H_{24}O$	85.02	9.01	85.28	9.28
h	100–101	$C_{19}H_{23}ClO$[a]	75.36	7.66	75.91	7.59
i	113–114	$C_{22}H_{30}O$	85.11	9.73	85.24	9.88

[a] Calcd: Cl, 11.71. Found: Cl, 11.30.

yellow semicrystalline mass. This was crystallized and recrystallized from hexane to give **4**, colorless prisms. Yields of products in this reaction were determined by NMR analysis. The results and spectral data are summarized in Table IV. Melting points and analytical data are listed in Table X.

Compound 4a from 5a. A solution of **5a** (0.2 g, 0.64 mmol) and *t*-BuOK (0.3 g, 2.7 mmol) in a mixture of *t*-BuOH and petroleum ether (1:1, 10 mL) was allowed to react at 0 °C under nitrogen atmosphere for 1 h. The reaction mixture was poured into ice-cooled aqueous NH_4Cl solution and the petroleum ether layer was separated and dried (Na_2SO_4). Evaporation of the solvent gave **4a** (75%) and **6a** (25%), as determined by NMR. The product **4a** was isolated by crystallization from petroleum ether and identified with that obtained from the oxygenation of **1a** described above.

Formation of 2,6-Di-*tert*-butyl-6-hydroperoxy-4-(4-methoxyphenyl)-2,4-cyclohexadienone (5a). To a solution of *t*-BuOK (7.5 g, 70 mmol) in *t*-BuOH (50 mL) diluted with petroleum ether (50 mL) and cooled at −25 °C was added **1a** (4.7 g, 15 mmol) within 10 min under sufficient stirring and oxygen bubbling. After 5 h, the reaction mixture was diluted with excess of aqueous NH_4Cl solution at the same temperature. After adding petroleum ether (50 mL), the organic layer was separated, dried (Na_2SO_4), and evaporated to leave a crystalline residue. The residue was recrystallized from petroleum ether to give **5a:** yellow needles (4.4 g, 85% yield); mp 99–101 °C; IR (KBr) 3340 (OOH), 1665 (*o*-quinoid C=O) cm^{-1}; NMR ($CDCl_3$) δ 1.03 (9 H, s, *t*-Bu), 1.28 (9 H, s, *t*-Bu), 3.83 (3 H, s, OMe), 6.60 (1 H, d, vinyl H, J = 2.8 Hz), 7.06 (1 H, d, vinyl H, J = 2.8 Hz), 6.7–7.6 (4 H, m, Ar H), 9.00 (1 H, s, OOH exchangeable with D_2O). Anal. Calcd for $C_{21}H_{28}O_4$: C, 73.22; H, 8.19. Found: C, 73.05; H, 8.26.

Reduction of 5a with Dimethyl Sulfide. The hydroperoxide **5a** (0.2 g) was dissolved in dimethyl sulfide (2 mL) at 0 °C. The resulting solution was allowed to stand at room temperature for 15 min. Dimethyl sulfide was evaporated and the resulting residue was triturated with water and dried in a vacuum desiccator. During the drying the product underwent de-*tert*-butylation (foam!). Trituration of the resulting material with petroleum ether gave 3-*tert*-butyl-5-(4-methoxyphenyl)catechol as a colorless solid (0.155 g) which was recrystallized from a mixture of petroleum ether and chloroform to give

Table X. Analytical Data of 4-Aryl-2,6-di-*tert*-butyl-4,5-epoxy-6-hydroxy-2-cyclohexenones (**4**)

4	Mp, °C	Molecular formula	Elemental analysis, % Calcd C	Calcd H	Found C	Found H
a	95–97	$C_{21}H_{28}O_4$	73.22	8.19	73.00	8.38
b	95–96	$C_{21}H_{28}O_4$	73.22	8.19	73.40	8.41
c	Oil	$C_{21}H_{28}O_4$	73.22	8.19	72.99	8.36
d	88–90	$C_{21}H_{28}O_3$	76.79	8.59	76.54	8.64
e	87–88	$C_{21}H_{28}O_3$	76.79	8.59	77.04	8.76
f	95–97	$C_{21}H_{28}O_3$	76.79	8.59	77.06	8.78
g	Oil	$C_{20}H_{26}O_3$	76.40	8.33	76.23	8.21
h	137–138	$C_{20}H_{25}ClO_3$[a]	68.85	7.22	68.78	7.37
i	100–101	$C_{23}H_{32}O_3$	77.49	9.05	77.36	9.14

[a] Calcd: Cl, 10.16. Found: Cl, 10.30.

colorless needles: mp 137–138 °C; IR (KBr) 3540, 3420 cm^{-1}; NMR ($CDCl_3$) δ 1.44 (9 H, s, *t*-Bu), 3.85 (3 H, s, OMe), 5.76 (2 H, br s, 2OH), 6.88 (1 H, d, Ar H, J = 2 Hz), 7.01 (1 H, d, Ar H, J = 2 Hz), 7.17 (4 H, m, Ar H). Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 74.89; H, 7.56.

2,6-Di-*tert*-butyl-5,6-epoxy-4-hydroxy-4-(4-methoxyphenyl)-2-cyclohexenone (3a). 2,6-Di-*tert*-butyl-4-hydroxy-4-(4-methoxyphenyl)-2,5-cyclohexadienone (**10**,[42] 1.0 g, 3.05 mmol) was dissolved in dioxane (50 mL). A solution of 0.7 g (4.05 mmol) of 3-chloroperbenzoic acid (75% active peracid) in dioxane (50 mL) was added dropwise at 75 °C over a period of 3 h. The same procedure was repeated after 8 and 16 h. After 52 the starting material was no longer present (TLC). The solution was carefully concentrated in vacuo, quenched with 10% aqueous NaOH (400 mL), and extracted with ether. The organic layer after washing to neutrality and drying over Na_2SO_4 was again concentrated. After addition of a small amount of petroleum ether (bp 60–90 °C) and cooling, 740 mg (71%) of colorless crystals were obtained: mp 162–163 °C (after recrystallization from petroleum ether); IR (KBr) 3441 (OH), 2927 (*t*-Bu), 1676 (CO) cm^{-1}; NMR ($CDCl_3$) δ 1.01 (9 H, s, *t*-Bu), 1.21 (9 H, s, *t*-Bu), 3.81 (3 H, s, OMe), 3.60 (1 H, d, aliphatic H, J = 3.0 Hz), 3.04 (1 H. s, OH), 6.09 (1 H, d, vinyl H, J = 3.0 Hz), 6.8–7.5 (4 H, m, Ar H). Anal. Calcd for $C_{21}H_{28}O_4$: C, 73.23; H, 8.19. Found: C, 73.36; H, 8.37.

4-Aryl-2,6-di-*tert*-butyl-4,5,6-trihydroxy-2-cyclohexenones (7). When the oxygenated mixtures from **1a**, **1d**, and **1g** were acidified with aqueous HCl solution, the trihydroxy compounds **7** were obtained; the acidified mixtures were extracted with ether and the extracts were dried (Na_2SO_4), evaporated, and chromatographed on a silica gel column eluting with $CHCl_3$ to give **7a** (26%), **7d** (64%), and **7g** (20%), respectively. The following data were obtained.

7a: colorless needles (from petroleum ether); mp 141–143 °C; IR (KBr) 3450, 3380 (OH), 1685 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 1.00 (9 H, s, *t*-Bu), 1.27 (9 H, s, *t*-Bu), 3.84 (3 H, s, OMe), 3.3–3.4 (4 H, m, OH and CHO–), 6.65 (1 H, s, vinyl H), 6.9–7.5 (4 H, m, Ar H). Anal. Calcd for $C_{21}H_{30}O_5$: C, 69.61; H, 8.30. Found: C, 69.86; H, 8.32.

7d: colorless needles (from petroleum ether); mp 165–166 °C; IR (Nujol) 3400, 3600 (OH), 1685 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 0.99 (9 H, s, *t*-Bu), 1.27 (9 H, s *t*-Bu), 2.37 (3 H, s, Me), 3.1–4.3 (4 H, m, OH and CHO–), 6.64 (1 H, s, vinyl H), 7.27 (4 H, s, Ar H). Anal. Calcd for $C_{21}H_{30}O_4$: C, 72.80; H, 8.73. Found: C, 72.96; H, 8.81.

7g: colorless needles (from petroleum ether); mp 123–124 °C; IR (Nujol) 3560, 3510, 3420 (OH), 1685 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 0.97 (9 H, s, *t*-Bu), 1.26 (9 H, s, *t*-Bu), 3.5–4.2 (4 H, m, OH and CHO–), 6.63 (1 H, s, vinyl H), 7.35 (4 H, s, Ar H).

Anal. Calcd for $C_{20}H_{28}O_4$: C, 72.26; H, 8.49. Found: C, 72.28; H, 8.65.

7a from 4a. To ice-cooled CF_3COOH (2 mL) was added **4a** (0.2 g). The solution turned red-brown immediately. After a few minutes, the reaction mixture was poured into ice-cooled water and extracted with petroleum ether. The extract was washed with aqueous $NaHCO_3$ solution, dried (Na_2SO_4), and evaporated to give **7a** (80% yield) together with a small amount of 2,5-di-*tert*-butyl-4-formyl-5-hydroxy-4-(4-methoxyphenyl)-2-cyclopentenone (**11a**, 10% yield) (the yields were determined by NMR).

4-Acetoxy-2,5-di-*tert*-butyl-4,5-dihydroxy-4-(4-methoxyphenyl)-2-cyclohexenone (8). A solution of **4a** (0.2 g) in acetic acid (3 mL) was allowed to stand at room temperature for a few seconds. The reaction mixture was poured into ice-cooled water to give colorless precipitates, which were collected by suction and dried. Crystallization and recrystallization of the product from petroleum ether gave **8** (77% yield): colorless prisms: mp 114–115 °C; IR (KBr) 3440 (OH, br), 1735 (OAc), 1675 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 0.94 (9 H, s, *t*-Bu), 1.26 (9 H, s, *t*-Bu), 1.95 (3 H, s, OAc), 3.80 (3 H, s, OMe), 3.4–4.0 (3 H, m, 2OH and CHO–), 6.8–7.3 (5 H, m, vinyl H and Ar H). Anal. Calcd for $C_{23}H_{32}O_6$: C, 68.31; H, 7.92. Found: C, 68.45; H, 7.89.

2,5-Di-*tert*-butyl-4-formyl-5-hydroxy-4-(4-methoxyphenyl)-2-cyclopentenone (11a). To a solution of **4a** (0.2 g) in CH_2Cl_2 activated basic alumina (activity 1, 4 g) was added under stirring at room temperature. The mixture was stirred until the starting epoxide was no longer detected by TLC. The reaction mixture was eluted with MeOH through a column. The eluent was evaporated and the residue was triturated with petroleum ether to give a crystalline mass, which was recrystallized from a mixture of CH_2Cl_2 and petroleum ether to give **11a** in 50% yield: colorless needles; mp 158–160 °C; IR (KBr) 3460 (OH), 1730 (CHO), 1710 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 0.63 (9 H, s, *t*-Bu), 1.33 (9 H, s, *t*-Bu), 3.40 (1 H, s, OH), 3.84 (3 H, s, OMe), 7.25 (1 H, s, vinyl H), 6.9–7.4 (4 H, m, ArH), 9.17 (1 H, s, CHO); *m/e* 344. Anal. Calcd for $C_{21}H_{28}O_4$: C, 73.22; H, 8.19. Found: C, 73.41; H, 8.32.

From the petroleum ether solution after the trituration, the cyclopentadienone **6a** (25% yield) was isolated. The compound **11a** was also obtained by chromatography of **4a** on a silica gel column together with the trihydroxy compound **7a.**

Formation of 2,5-Di-*tert*-butyl-4-(4-chlorophenyl)-4-formyl-5-hydroxy-2-cyclopentenone (11h). Epoxy-*o*-quinol **4h** (300 mg) was dissolved in trifluoroacetic acid (2 mL) at 0 °C and kept for 1 h at this temperature. The solution was then poured into ice-cooled water. The crystalline precipitate was filtered by suction, dried, and recrystallized from petroleum ether to give 123 mg (41%) of **11h:** mp 169–170 °C dec; IR (KBr) 3447 (OH), 2939 (*t*-Bu), 1694 (CO), 1718 (CO) cm^{-1}; NMR ($CDCl_3$) δ 0.64 (9 H, s, *t*-Bu), 1.34 (9 H, s, *t*-Bu), 3.36 (1 H, s, OH), 7.23 (1 H, s, vinyl H), 7.43 (4 H, s, Ar H), 9.19 (1 H, s, CHO). Anal. Calcd for $C_{20}H_{25}ClO_3$: C, 68.86; H, 7.22; Cl, 10.16. Found: C, 69.09; H, 7.34; Cl, 9.87.

2,5-Di-*tert*-butyl-5-hydroxy-4-(4-methoxyphenyl)-2-cyclopentenone (13). A solution of **11a** (0.2 g) in CH_2Cl_2 was put on a nonactivated basic alumina column (10 g) and eluted with MeOH. The eluent was evaporated and the residue was distilled to give **13** in 95% yield: bp 140–145 °C (1 mm); IR (film) 3540 (OH), 1700 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 0.67 (9 H, s, *t*-Bu), 1.25 (9 H, s, *t*-Bu), 3.76 (3 H, s, OMe), 2.95 (1 H, s, OH), 4.08 (1 H, d, J = 2.0 Hz), 7.28 (1 H, d, J = 2.0 Hz), 6.7–7.3 (4 H, m, Ar H). Anal. Calcd for $C_{20}H_{28}O_3$: C, 75.91, H, 8.92. Found: C, 75.76; H, 8.66.

Qualitative Tests for Formate in the Oxygenation Mixture. Phenol **1a** was oxygenated at 50 °C as described above. After 1 h the temperature was raised to 100 °C and the mixture was evaporated to dryness. The residue was extracted with benzene several times in order to remove organic material and dried in vacuo. It was directly used for the formate tests by the use of sodium nitroprusside, palladium chloride, and mass spectrometry. The prusside test was carried out according to Comanducci[43] (green color). For the palladium chloride test, the dried inorganic residue was treated with concentrated sulfuric acid and the resulting gas was bubbled through a weak acidic (HCl) aqueous $PdCl_2$ solution. In the presence of formate the gas contains CO, which reduces Pd^{2+} to black metallic Pd. For the mass spectroscopic test, a small amount of the dried residue was dissolved in dilute

(4 N) sulfuric acid and extracted with a small amount of ether. The extract was evaporated at normal pressure until most of the ether had been removed and the residue was introduced into the mass spectrometer by means of a gas inlet system. The mass spectrum revealed the characteristic pattern of formic acid. Each of the above mentioned procedures was accompanied by several blank tests.

Acknowledgment. Supports of this work by the Fonds der Chemischen Industrie and by the Japan Association for the Promotion of Science are greatly acknowledged.

Supplementary Material Available: Hydrogen atom positions and structure factor listing (8 pages). Ordering information is given on any current masthead page.

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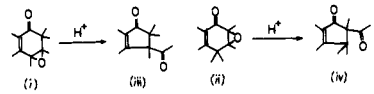

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