(21) The program maintains a table, called the "reaction dictionary," in which the reactions available to the program are listed. A description of the information stored in this table is given in the section entitled "The Reaction Dictionary".

(22) We shall henceforth call this the "product pattern".

(23) E. J. Corey and L. Hegedus, *J. Am. Chem. Soc.*, **91**, 4926 (1969).

(24) Sublisting is used in reactant patterns to indicate both distinct precursor substructures and branching. The first level of sublisting indicates distinct precursors; any deeper level (i.e., any sublist occurring within the first level) indicates branching.

(25) It may happen that the two routes are incompatible in that there is no ordering of the steps in the two routes such that each PFG is stable to the reaction taking place at the other PFG.

(26) The conditions for any reaction are embedded in the appropriate feasibility function.

(27) D. Lednicer, *Adv. Org. Chem.*, **8**, 179 (1972).

(28) One instance where latent functionality is not permitted is when the functional group which must be protected is one of those for which a functional group interconversion has been generated as a goal. In that case, the form in which this functional group must occur in the precursor is fixed by the goal.

(29) The symbol = 3 represents a triple bond.

Chemistry of Superoxide Ion. I. Oxidation of 3,5-Di-*tert*-butylcatechol with KO_2

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Abstract: The reaction between 3,5-di-*tert*-butylcatechol and KO_2 has been studied. Two main products, 3,5-di-*tert*-butyl-5-(carboxymethyl)-2-furanone (**6**) and 3,5-di-*tert*-butyl-5-(carboxyhydroxymethyl)-2-furanone (**7**), were obtained, resulting from oxidative cleavage at the 1,2- and 1,6-positions of the catechol ring. The two oxidative cleavages observed correspond to the enzymatic oxidations of catechol by pyrocatechase and metapyrocatechase, respectively.

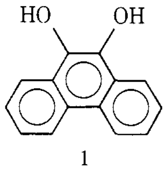
In recent years, special attention has been directed to superoxide ion, $O_2\cdot^-$, as a possible active species for certain biological oxidations.[1-15] It has been demonstrated by various methods, especially by using superoxide dismutase[1-9] that superoxide ion is formed in several biochemical reactions involving molecular oxygen. A number of oxidations are clearly inhibited in the presence of this enzyme. In some cases, the effect of superoxide ion has been examined by adding it directly into the biochemical systems[1-4] and, in other cases, its presence has been confirmed using ESR.[11-15]

In spite of its biochemical importance, very few studies have been done on the organic chemistry of superoxide ion.[16-22] Superoxide ion sometimes acts as oxidant[7] but more frequently as reductant[7,21] with organic substances; this behavior seems to be very important to its role as active species in biological systems. Thus further study of the interaction of superoxide ion with organic substances, especially with metabolic intermediates, should aid in understanding the mechanisms of biological oxidations involving molecular oxygen.

Oxidative cleavage of catechol is one of the most important reactions catalyzed by dioxygenases.[23-26] Catechol is oxidized to *cis,cis*-muconic acid by pyrocatechase[25] and to *o*-hydroxymuconic semialdehyde by metapyrocatechase.[26] Recently, Tsuji et al. reported an oxidative cleavage of catechol to *cis,cis*-muconic acid with molecular oxygen activated by cuprous chloride.[27] In the present work, a preliminary study of the reaction of potassium superoxide with some catechols is reported. While some reactions were carried out with catechol itself, and some muconic acid is formed, this line of inquiry was abandoned because of extensive polymerization accompanying oxidation. 9,10-Dihydroxyphenanthrene was used as a model substrate because of the simplicity of its reaction. The use of 3,5-di-*tert*-butylcatechol instead of catechol in oxidations has been often reported, because most of the reactive ring sites are blocked by bulky groups.[28,29] This paper will show the similarity of products obtained in the potassium superoxide oxidation of this substrate with those of enzymatic oxidations and present a proposal for the oxidation mechanism.

Results

9,10-Dihydroxyphenanthrene. 9,10-Dihydroxyphenanthrene (**1**) was oxidized by potassium superoxide suspended in THF in two different ways: in one case, under 1 atm of oxygen pressure in a closed reactor and, in the other, under a nitrogen stream in an open reactor. The results are summarized in Table I. Diphenic acid (**3**) with a minor amount of 9,10-phenanthrenequinone (**2**) was obtained in every run. The reaction was quantitative, and no other products except **2** and **3** were detected. After recrystallization, the properties of the recovered products were in good agreement with those of authentic samples.



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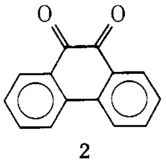

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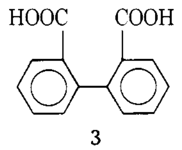


3

The oxidation of the quinone **2** by KO_2 to produce **3** has been reported by Le Berre and Berguer,[17] and the reaction was repeated and confirmed. Oxidations of both **1** and **2** by KO_2 were accompanied by the evolution of oxygen; the observed amounts were smaller than expected from eq 1 and 2. In addition, the amount of unreacted KO_2 was larger than stoichiometric after the reactions, especially under oxygen. Thus, it is clear that molecular oxygen as well as superoxide ion took part in the oxidations.

$$\mathbf{1} + 4KO_2 \rightarrow C_{12}H_8(COOK)_2 + 2KOH + 2O_2 \qquad (1)$$

$$\mathbf{2} + 2KO_2 \rightarrow C_{12}H_8(COOK)_2 + O_2 \qquad (2)$$

Reaction of **2** with KO_2 proceeded more slowly in CH_3CN than in THF. A higher yield of **2** was obtained in the oxidation of **1** in CH_3CN by stopping the reaction in a

Table I. Oxidation of 9,10-Dihydroxyphenanthrene (1) and 9,10-Phenanthrenequinone (2) by KO_2

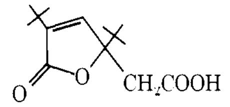
Run[a]	Reactant	Initial KO_2, mmol	Unreacted KO_2,[b] mmol	Absorbed O_2, mmol	Yield of product (mol %)[c]	
					2	3
1	1	8	3.5		16.8	84.3
2	1	8	4.5	1.06	9.0	90.6
3	1	8	*d*		38.0	55.1
4	2	4	1.5		15.6	83.3
5	2	4	1.9	0.42	9.2	90.8
6	2	4	2.3		38.9	60.6

[a] Reactant (2 mmol) and 25 ml of solvent were used in each run. Reaction temperature, 22°C. Solvent: THF for runs 1, 2, 4, and 5; CH_3CN for runs 3 and 6. Atmosphere: Nitrogen for runs 1, 3, 4, and 6; oxygen for runs 2 and 5. Reaction time was 2 hr except for run 3 (10 min). [b] As measured by O_2 evolution on addition of water after reaction. [c] As measured by weight of crude product before purification. [d] Not measured.

shorter time. It thus seems very likely that **2** is intermediate or can be produced by an intermediate in the reaction of **1** to **3** with potassium superoxide.

3,5-Di-*tert*-butylcatechol. Oxygenation of 3,5-di-*tert*-butylcatechol (**4**) was carried out using KO_2 suspended in CH_3CN and in THF. CH_3CN and shorter reaction times (1 hr) were chosen in order to isolate primary oxidation products. The combination of THF solvent and longer reaction time (3 hr) led to products of more extensive oxidation. Vigorous evolution of oxygen was observed in every run after mixing the catechol solution with KO_2 suspension, and the mixture was tinged with blue within several minutes. This color was due to the formation of 3,5-di-*tert*-butyl-*o*-benzosemiquinone[30] and did not disappear during the reaction except in the case of run 14. Various products were formed under the different conditions, and the yield of each is summarized in Table II.

3,5-Di-*tert*-butyl-*o*-quinone (**5**) was produced mainly in CH_3CN solvent. The yield of **5** depended on the reaction time, solvent, the ratio of KO_2 to **4**, and the oxygen pressure. The more extensive the oxidation, the smaller the yield of **5**. The main products in addition to **5** were two colorless crystalline carboxylic acids having γ-lactone rings. One was 3,5-di-*tert*-butyl-5-(carboxymethyl)-2-furanone (**6**) which was first reported from the photosensitized oxygenation of **4**.[28] It was found that oxidation of **4** by 13% peracetic acid in acetic acid solution also gave **6** as the sole product. After purification, the properties and spectral data of the product were in good agreement with those reported.[28] Another main product had physical and chemical properties in accord with structure **7**, 3,5-di-*tert*-butyl-5-(carboxyhydroxymethyl)-2-furanone.[29] The infrared, uv, and NMR spectra of the purified product and its methyl ester support the structure. A higher yield of **7** was obtained in CH_3CN, whereas the yield of **6** was higher in THF. An increase of the ratio of KO_2 to **4** also gave more **6**.



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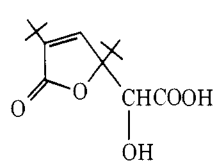

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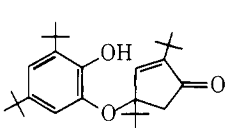
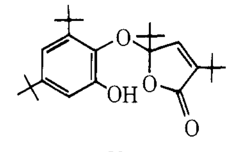
A neutral product **8**, colorless crystals, mp 141–143°C, was obtained only in the runs under nitrogen. The exact mass spectrum and elemental analysis indicated the formula $C_{26}H_{40}O_4$. Infrared, uv, and NMR spectra suggested the presence of one OH group, one aromatic ring, and one α,β-unsaturated γ-lactone ring in the molecule. Two structures, **8a** and **8b**, are possible for the product; however, **8a** seems more probable considering the neighboring bulky groups in structure **8b**.



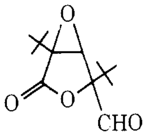
8a



8b

Three other products lost one or two carbon atoms compared with the starting material **4**. One of them, colorless sublimable crystals, was assigned the structure 3,5-di-*tert*-butyl-3,4-epoxy-5-formyl-2-furanone (**9**) by its spectral data. Dicarboxylic acid **10** was assigned as 2,4-di-*tert*-butyl-2-pentene-1,5-dioic acid and was only found in the runs in THF using a KO_2/**4** ratio of 4:1.

3,5-Di-*tert*-butyl-5-hydroxy-2-furanone (**11**) was found in every run; higher yields were obtained on more extensive oxidation in THF. An increased yield of **11** correlated with a decreased yield of acidic products **6**, **7**, and **10**, especially **7**.



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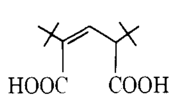

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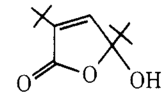


11

Oxidation of 3,5-Di-*tert*-butyl-*o*-quinone. Reaction of 3,5-di-*tert*-butyl-*o*-quinone (**5**) with KO_2 was examined, because it seemed likely that **5** was an early product in the oxidation of **4**. The reaction was carried out in a manner

Table II. Oxidation of 3,5-Di-*tert*-butylcatechol by KO_2

Run[a]	Initial KO_2, mmol	Unreacted KO_2,[b] mmol	Absorbed O_2, mmol	Yield of product (mol %)						
				5[c]	6	7	8	9	10	11
7	3.0			40.7	9.3	22.7	6.4	2.9		1.6
8	6.0	0.85		15.0	8.2	30.8	20.8	4.2		2.4
9	12.0	6.32		10.0	6.0	42.8	17.0	4.2		4.6
10	0.6		1.82	67.3	9.6	9.8				Tr
11	3.0		1.62	15.5	25.6	30.5	Tr	2.2		3.5
12	6.0	0.43		32.8	12.0	5.7	7.2	Tr		30.1
13	12.0	4.58			31.7	10.8	Tr	5.7	23.1	11.3
14	12.0	2.75			52.5	Tr			23.0	16.5
15	6.0	0.16	1.22		25.7	12.8				47.1

[a] 3,5-Di-*tert*-butylcatechol (667 mg, 3 mmol) and 25 ml of dry solvent were used in each run. All runs except 14 (35°C) were at 22°C. Solvent: CH_3CN for runs 7–11, THF for runs 12–15. Atmosphere: Nitrogen for runs 7, 8, 9, 12, 13, and 14; oxygen for runs 10, 11, and 15. Reaction time: 1 hr for runs 7–11; 3 hr for runs 12, 13, and 15; 4 hr for run 14. [b] Determined by O_2 evolution on addition of water after reaction. [c] Polymerization of 5 was observed in several runs.

Table III. Oxidation of 3,5-Di-*tert*-butyl-*o*-quinone by KO_2

Run[a]	Initial KO_2, mmol	Unreacted[b] KO_2, mmol	Yield of product,[c] mol %						
			5[d]	6	7	8	9	10	11
16	4	1.52	22.7	7.3	10.9	1.9	0.8		12.7
17[e]	4	0.54		24.9	7.1		Tr		53.0
18	7	3.49	3.4	21.1	26.6		8.7	6.9	9.4
19	4	1.42	21.3	7.2	11.9	2.4	2.1		4.5

[a] 3,5-Di-*tert*-butyl-*o*-quinone (440.6 mg, 2 mmol) and 25 ml of dry solvent were used in each run. Reaction time: 3 hr. Reaction temp: 25°C. Solvent: THF for runs 16–18, CH_3CN for run 19. Atmosphere: Nitrogen for runs 16, 18, and 19; oxygen for run 17. [b] Based on O_2 evolution on addition of water after reaction. [c] Based on starting material. [d] Unreacted 5. [e] Oxygen (0.34 mmol) was evolved.

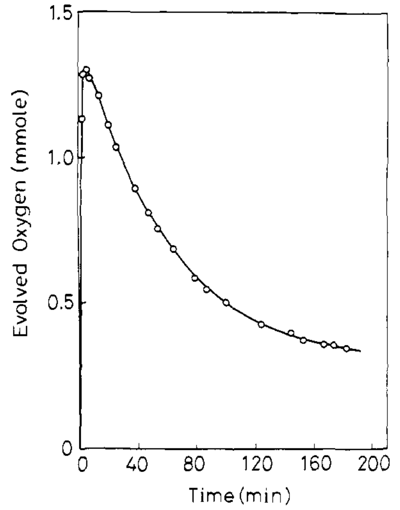
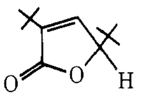


Figure 1. Evolution and uptake of oxygen with time during the oxidation of 3,5-di-*tert*-butyl-*o*-quinone by KO_2. Reaction conditions are shown in Table III, run 17.

similar to that of **4**; the yield of each product is shown in Table III. Although the yield of each product was somewhat lower, the observed distributions of the products were very similar to those obtained in the corresponding 3,5-di-*tert*-butylcatechol oxidations. In every run, vigorous evolution of oxygen was observed for about 10 min after addition of *o*-quinone solution to the KO_2 suspension. If oxidation was carried out under oxygen pressure, gradual uptake of oxygen followed the initial evolution. The evolution and uptake of oxygen with time is shown in Figure 1.

Reaction of 6 and 7 with KO_2. Interaction with KO_2 of two main products (**6** and **7**) obtained in the 3,5-di-*tert*-butylcatechol oxidation was tested in order to see whether some of the minor products were formed via these compounds. A solution of **6** was added to KO_2, and the suspension was stirred under a stream of nitrogen. No reaction was observed, and 98% of the starting material was recovered.

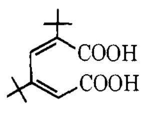
Interaction of hydroxylactone **7** with KO_2 was also examined in a similar manner. **7** (1 mmol) was mixed with 3 mmol of KO_2 in dry THF. The recovered materials after 3 hr reaction were unreacted **7** (47.9%), **11** (23.5%), and 3,5-di-*tert*-butyl-2-furanone (**12**, 23.5%) under a nitrogen stream, and unreacted **7** (47.3%), **11** (44.6%), and **12** (4.7%) under oxygen pressure. Compound **12** has been reported to be formed from **7** in alkaline solution without any oxidant.[29] A trace of **12** was detected in the oxidation of **4** described above. Thus, **11** is apparently a product formed in the secondary oxidation of **7** by KO_2.



12

Discussion

The results reported above show that the catechol ring is easily oxidized by potassium superoxide. One characteristic step is the oxidative cleavage of the carbon–carbon bond between the two hydroxyl groups to produce the corresponding dicarboxylic acid. This is the sole reaction observed in the oxidation of 9,10-dihydroxyphenanthrene, where all ring sites except those attached to hydroxyl groups are resistant to attack. Both 3,5-di-*tert*-butyl-5-(carboxymethyl)-2-furanone (**6**) and 3,5-di-*tert*-butyl-5-(carboxyhydroxymethyl)-2-furanone (**7**) were the principal products of the oxidation of 3,5-di-*tert*-butylcatechol (**4**) under all conditions. It is noteworthy that **6** and **7** are the γ-lactones of dicarboxylic acids **13** and **14**, respectively. Although neither **13** nor **14** were detected in any oxidation run, it has been reported that *cis,cis*-muconic acid and its derivatives are easily lactonized.[31] In addition, lactone **6** is the sole product from **4** on peracetic acid oxidation. It would be expected that two *tert*-butyl groups would promote the lactonization. Thus **6** and **7** are probably formed by lactonization following the oxidative cleavage at the 1,2-position and 1,6-position of **4**, respectively.



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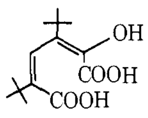
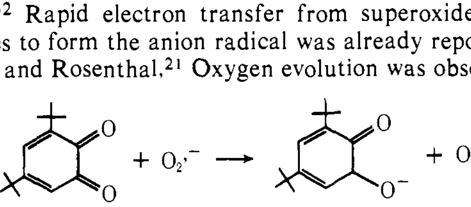


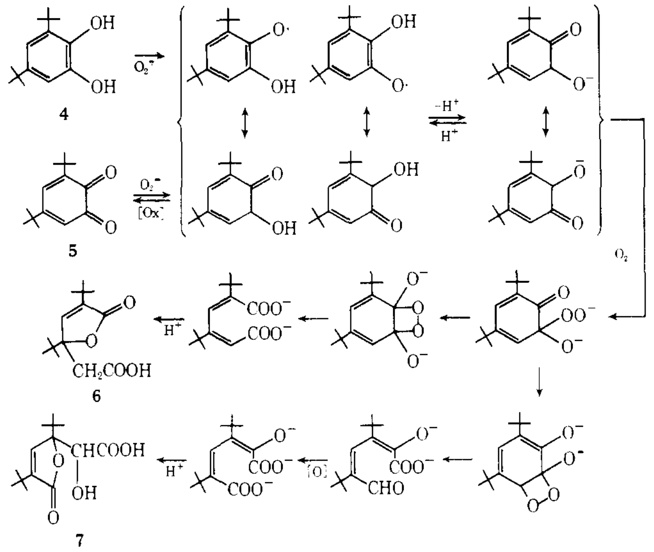
14

The main intermediate in the formation of **6** and **7** is *o*-semiquinone or its anion. When **4** or **5** was mixed with KO_2 suspension, an intense blue color assigned to the formation of 3,5-di-*tert*-butyl-*o*-benzosemiquinone[30] was observed. In addition, the product distributions observed in the oxidation of **5** (Table III) were quite similar to those obtained in the catechol oxidation under corresponding conditions (Table II). The superoxide ion may act as hydrogen abstracting agent in the initial stage of the reaction. Similar reactions of superoxide ion have been reported in the oxidations of epinephrine to adrenochrome[1] and tiron to its *o*-quinone.[9] Autoxidations initiated by the abstraction of hydrogen by superoxide ion have been also reported by several authors.[1,32] Rapid electron transfer from superoxide ion to quinones to form the anion radical was already reported by Poupko and Rosenthal.[21] Oxygen evolution was observed in every run during quinone oxidation, as exemplified in Figure 1. According to these observations, the oxidation of **4** by superoxide ion may be explained by Scheme I. Several steps undoubtedly involve not only superoxide ion but also molecular oxygen, because a considerable amount of gaseous oxygen was absorbed during the reaction under oxygen pressure. Some radical intermediates in Scheme I would react

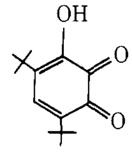


(3)

Scheme I



very rapidly with molecular oxygen. It has been suggested by Nishinaga et al. that **7** is produced via 3,5-di-*tert*-butyl-6-hydroxy-*o*-benzoquinone (**15**) in the base catalyzed oxy-



15

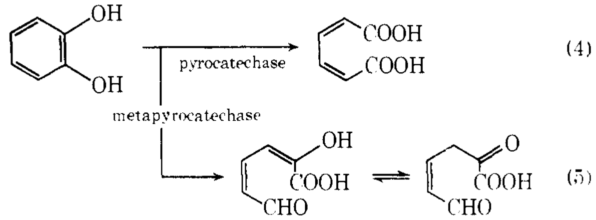
genation of **4**.[30] This route may also be possible for the formation of **7** involving molecular oxygen.

The mechanism by which minor products **9**, **10**, and **11** are formed is not clear. One or two carbon atoms in the starting material (**4**) are lost during the formation of three products. Products **10** and **11** were stable to KO_2 under the conditions used in this work and were the final products in the oxidation. They were probably formed by secondary reaction of the primary oxidation products of their precursors, especially via **7** or its precursor. Substantial amounts of **11** were formed by treatment of **7** with KO_2 under the reaction conditions. Compound **11** was also reported to be a secondary product in the photosensitized oxygenation of 4,6-di-*tert*-butylresorcinol[33] and *t*-BuOK catalyzed oxygenation of **4**.[30] The fact that the yield of **7** decreased and those of **10** and **11** increased in the more extensive oxidation runs supports the above considerations. The dimeric compound **8** is believed to result from the combination of the semiquinone radical or ion with the precursor for **11**.

The reaction system involving superoxide ion seems to be complicated by other active species resulting from its decomposition. It has been reported that the superoxide ion from KO_2 generates singlet molecular oxygen.[34] This suggests that some singlet oxygen might be involved in oxidation. However, the products reported in the dye sensitized photooxygenation of **4** in methanol were only **6** and its methyl ester.[28] No oxidation product cleaved at the 1,6-position was found in that reaction. Moreover, recent careful experiments showed that the fraction of singlet oxygen in the gaseous oxygen resulting from decomposition of superoxide ion is small, and that superoxide ion is a very poor source for singlet oxygen.[35-37] Thus, the role of singlet oxygen is probably insignificant in the present oxidation.

Hydrogen peroxide is another active species which may be involved in the oxidation. Abstraction of a proton or hydrogen atom from **4** by the superoxide ion produces hydroperoxy radical or ion, both of which can easily be converted to hydrogen peroxide. The reaction of 3,5-di-*tert*-butyl-*o*-quinone **5** with hydrogen peroxide in alkaline aqueous methanol has been reported to give oxidative cleavage exclusively at the 1,6-position.[29] While the product distribution obtained in the present investigation seems to be somewhat different from that reported for the hydrogen peroxide oxidation of **5**, there is no doubt that the oxidation by superoxide ion cannot be free from the effects of the hydrogen peroxide formed during the reaction. The precise role of hydrogen peroxide must await further investigation.

The present result is consistent with a possible role of superoxide ion or a metal-bound form in the enzymatic oxidation of catechol by pyrocatechase and metapyrocatechase. Pyrocatechase cleaves catechol at the 1,2-position to form *cis,cis*-muconic acid (eq 4),[22-25] and metapyrocatechase cleaves it at the 2,3-position (equivalent to the 1,6-position in **4**) to give α-hydroxy muconic semialdehyde (eq 5).[26]



That superoxide ion acts as reactive species in the enzymatic system has been proposed by Hayaishi.[23,24] Ferrous ion is at the active center in both enzymes. It was suggested that the enzyme, catechol, and molecular oxygen form a ternary complex, where electron transfer occurs from catechol to oxygen via ferrous ion to form a superoxide species. Allowing for secondary oxidation and lactonization in the present system, oxidized products are very similar in both oxidations. It has been also shown that enzymatic oxidation of tiron to its semiquinone was inhibited in the presence of superoxide dismutase in a recent paper.[9] Further studies on the precise mechanism of the reaction and other interactions of superoxide ion with organic substances analogous to biochemical oxidations will be reported in subsequent papers.

Experimental Section

Materials. Potassium superoxide was obtained from Ventron Alfa Products. Its purity was determined to be ≥97% by the following titration. A weighed sample of KO_2 was decomposed in excess sodium arsenite solution, the concentration of which was determined by the iodometric method. 9,10-Phenanthrenequinone, 3,5-di-*tert*-butylcatechol, and 3,5-di-*tert*-butyl-*o*-quinone were obtained from Aldrich Chemical Co. 9,10-Dihydroxyphenanthrene was prepared by the reduction of 9,10-phenanthrenequinone with zinc dust in hot acetic acid solution. Tetrahydrofuran was first distilled from sodium and then from $LiAlH_4$ under dry high purity nitrogen. Acetonitrile was refluxed over P_2O_5 for 5 hr and distilled under dry high-purity nitrogen.

Procedure. Reaction with KO_2 was carried out in a closed reactor under 1 atm of oxygen pressure or in an open reactor under a stream of dry high-purity nitrogen. Finely powdered potassium superoxide was suspended in 15 ml of dry solvent. The substance to be oxidized was dissolved in 10 ml of solvent and added dropwise within a few minutes to the KO_2 suspension. The mixture was stirred vigorously by a magnetic stirrer during the reaction. After the prescribed time, the mixture was diluted with 20 ml of water to destroy the unreacted KO_2. The amount of unreacted KO_2 was determined from the volume of the evolved oxygen. The neutral products were extracted with two portions of ether from the alkaline reaction mixture. The extracts were first washed with 10% $NaHCO_3$ and then with saturated NaCl. Excess HCl was added to the remaining aqueous solution combined with the 10% $NaHCO_3$ washings, and the acidic products were extracted with ether. The ether and organic solvent were removed under vacuum, and each component was separated by dry column chromatography. Alumina developed with 50% benzene-50% petroleum ether was used for the neutral products. Silica gel/chloroform was used for acidic ones. Each material separated was weighed after drying in vacuo and its structure confirmed by spectroscopic measurements.

3,5-Di-*tert*-butyl-5-(carboxymethyl)-2-furanone (6). The sample was recrystallized from benzene and petroleum ether twice after the purification by dry column chromatography and dried in vacuo at 80°C to give colorless crystals: mp 133–134°; the 60-MHz proton NMR spectrum in $CDCl_3$ showed δ 0.97 (s, 9 H), 1.22 (s, 9 H), 2.73 (d, J = 14 Hz, 1 H), 2.95 (d, 1 H), 6.90 (s, 1 H), 8.97 (s, 1 H, -COOH); uv λ_{max} (CH_3OH) 208.5 nm (ϵ 11600 M^{-1} cm^{-1}); ir ν_{max} (KBr) 3300–2700, 1740, 1715, 1638 cm^{-1}. These properties were in good agreement with those of another sample obtained by the peracetic acid oxidation of **4** and those reported previously.[28] The peracetic acid oxidation of **4** was carried out according to the same procedure used to form *cis,cis*-muconic acid from phenol.[31] **4** was dissolved in freshly prepared 13% peracetic acid and was allowed to stand for 24 hr. Removal of solvent and excess peracetic acid in vacuo gave crude **6** as sole product.

3,5-Di-*tert*-butyl-5-(carboxyhydroxymethyl)-2-furanone (7). Recrystallization from benzene and petroleum ether gave colorless crystals: mp 139–140° (reported[29] 140–142°); NMR (acetone-d_6) δ 1.07 (s, 9 H), 1.21 (s, 9 H), 4.65 (s, 1 H), 6.67 (s, 2 H, broad, hydroxyl and carboxylic protons), 7.24 (s, 1 H); uv: λ_{max} (CH_3OH) 208 nm (ϵ 11900 M^{-1} cm^{-1}); ir ν_{max} (KBr) 3550–3350, 3300–2700, 1720, 1705, 1630 cm^{-1}. Anal. Calcd for $C_{14}H_{22}O_5$: C, 62.20; H, 8.20. Found: C, 62.20; H, 8.29.

Methylation of **7** by diazomethane gave a colorless crystalline compound: mp 103–105° (reported[29] 103–106°C); NMR δ 1.07 (s, 9 H), 1.23 (s, 9 H), 3.28 (d, J = 7 Hz, 1 H), 3.70 (s, 3 H), 4.70 (d, J = 7 Hz, hydroxyl proton), 7.05 (s, 1 H). Anal. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51. Found: C, 63.10; H, 8.77.

3,5-Di-*tert*-butyl-5-(3,5-di-*tert*-butyl-2-hydroxyphenoxy)-2-furanone (8). An analytical sample was recrystallized from petroleum ether several times, to give colorless crystals with: mp 141–143°C; the molecular formula by exact mass spectrum was $C_{26}H_{40}O_4$; NMR ($CDCl_3$) δ 0.91 (s, 9 H), 1.19 (s, 9 H), 1.21 (s, 9 H), 1.34 (s, 9 H), 5.61 (s, 1 H, hydroxyl proton), 6.62 (s, 1 H), 6.81 (d, J = 2 Hz, 1 H), 6.99 (d, J = 2 Hz, 1 H); (the coupling constant for the peaks at δ 6.81 and 6.99 was identical with that for the corresponding peaks in 3,5-di-*tert*-butylcatechol); uv λ_{max} (CH_3OH) 275 nm (ϵ 1890 M^{-1} cm^{-1}), 205 (23600 M^{-1} cm^{-1}); ir ν_{max} (KBr) 3548, 3513, 1759 cm^{-1}. Anal. Calcd for $C_{26}H_{40}O_4$: C, 74.82; H, 9.80. Found: C, 74.96; H, 9.68.

3,5-Di-*tert*-butyl-3,4-epoxy-5-formyl-2-furanone (9). The analytical sample was prepared by two recrystallizations from petroleum ether, colorless crystals: mp 108–109°; NMR ($CDCl_3$) δ 1.08 (s, 9 H), 1.13 (s, 9 H), 4.07 (s, 1 H), 9.55 (s, 1 H); uv λ_{max} (CH_3OH) 199 nm (ϵ 994 M^{-1} cm^{-1}), 300 (24 M^{-1} cm^{-1}). The absence of any strong uv absorption near 210 nm suggested this compound was not an α,β-unsaturated γ-lactone, but a saturated lactone. This suggestion is confirmed by the position of the carbonyl absorption: ir ν_{max} (KBr) 2870, 2737, 1783, 1737 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 65.17; H, 8.27.

2,4-Di-*tert*-butyl-2-pentene-1,5-dioic acid (10). Two recrystallizations from chloroform gave colorless crystals: mp 197–197°; NMR (acetone-d_6) δ 1.01 (s, 9 H), 1.20 (s, 9 H), 3.13 (d, J = 11 Hz, 1 H), 5.80 (d, J = 11 Hz, 1 H), 9.45 (s, broad, -COOH); uv λ_{max} (CH_3OH) 205.5 nm (ϵ 6630 M^{-1} cm^{-1}); ir ν_{max} (KBr) 3300–2700, 1720, 1620 cm^{-1}. Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15. Found: C, 63.77; H, 8.81. Treatment with diazomethane gave a methyl ester of **10**, colorless liquid: bp 55–60° (0.02 Torr); NMR ($CDCl_3$) δ 0.94 (s, 9 H), 1.14 (s, 9 H), 2.87 (d, J = 11 Hz, 1 H), 3.63 (s, 3 H), 3.72 (s, 3 H), 5.70 (d, J = 11 Hz, 1 H). Anal. Calcd for $C_{15}H_{26}O_4$: C, 66.64; H, 9.69. Found: C, 65.78; H, 9.38.

3,5-Di-*tert*-butyl-5-hydroxy-2-furanone (11): colorless crystals, mp 97.5°; NMR ($CDCl_3$) δ 1.03 (s, 9 H), 1.25 (s, 9 H), 3.10 (s, 1 H, broad, hydroxyl proton), 6.73 (s, 1 H); uv λ_{max} (CH_3OH) 206 nm (ϵ 12500 M^{-1} cm^{-1}); ir ν_{max} (KBr) 3448, 1729, 1637 cm^{-1}. Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.86; H, 9.31.

3,5-Di-*tert*-butyl-2-furanone (12). Treatment of **7** with concentrated aqueous NaOH gave **12** as reported:[29] colorless crystals, mp 95°; NMR ($CDCl_3$) δ 0.96 (s, 9 H), 1.26 (s, 9 H), 4.48 (d, J = 3.5 Hz, 1 H), 6.92 (d, J = 3.5 Hz, 1 H); uv λ_{max} (CH_3OH) 211 nm (ϵ 12960 M^{-1} cm^{-1}); ir ν_{max} (KBr) 1730, 1680 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.18; H, 10.41.

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