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PHOTOINDUCED REACTIONS—LVII

PHOTOSENSITIZED OXYGENATION OF CATECHOL AND HYDROQUINONE DERIVATIVES: NONENZYMIC MODELS FOR THE ENZYMATIC CLEAVAGE OF PHENOLIC RINGS[1,2]

T. MATSUURA, H. MATSUSHIMA, S. KATO and I. SAITO

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan

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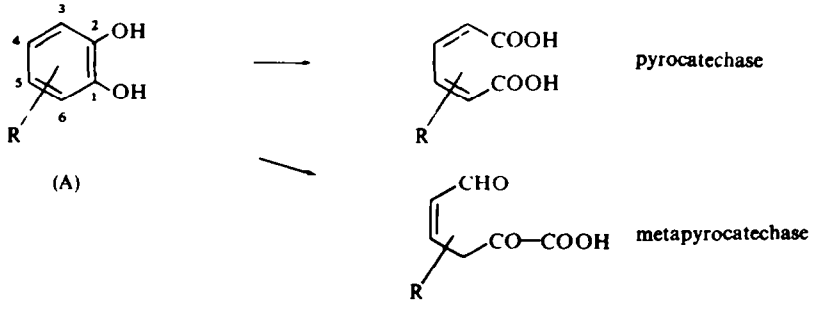
Abstract—Dye-sensitized and nonsensitized photooxygenation of 3,5-di-t-butylpyrocatechol (**1**), 2,5-di-t-butylhydroquinone (**14**), their monomethyl ethers **4** and **20**, and dimethyl ethers **5** and **21** has been investigated. In methanol, **1** and **4** undergo oxidative ring cleavage to give a lactonic acid **2** and/or its methyl ester **3**. This represents a model for the enzymatic cleavage of phenolic rings. Under similar conditions **14** and **20** give 2,5-di-t-butylbenzoquinone **15** and further transformation products. Mechanisms involving initial formation of a corresponding phenoxy radical are proposed. The dimethyl ethers **5** and **20** do not react under these conditions. Other related reactions are described.

THE ACTIVATION of molecular oxygen catalyzed by dioxygenases, by which an oxygen molecule is incorporated into a substrate, has received much attention in biological and chemical studies.[3] Several oxidative cleavage reactions, using oxygen as oxidizing agent, have been reported as nonenzymic models for the enzymatic cleavage of aromatic and heterocyclic compounds by dioxygenases.[4–9] Some of these dioxygenase reactions[6–9] resemble, at least formally, photosensitized oxygenation which usually involves singlet oxygen as the reacting species.[10,11]

Thus, we applied photosensitized oxygenation to catechol derivatives, which are known to be cleaved by dioxygenases in two ways: Pyrocatechase cleaves the 1,2-bond and metapyrocatechase the 2,3-bond.[3]



Protocatechuic acid (A: R = *p*-COOH), which is cleaved by protocatechuate-3,4-dioxygenase[12] at the 3,4-bond, and its methyl ester (A: R = *p*-COOMe) were found

to be resistant to photosensitized oxygenation (methylene blue or rose bengal/methanol). 3,4-Di-hydroxyhydrocinnamic acid (A; R = *p*-CH_2CH_2COOH) was susceptible to photosensitized oxygenation (rose begal/methanol) giving a complex mixture, from which no pure product could be isolated. The results suggest that the introduction of electron-withdrawing group decreases the reactivity of catechol to photooxygenation. Thus, 3,5-di-t-butylcatechol (**1**) was selected as a substrate.

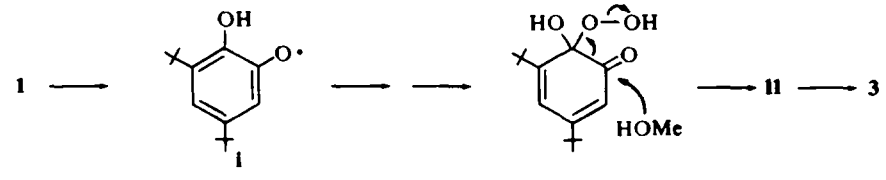
Photooxygenation of 3,5-*di*-t-*butylpyrocatechol* (**1**) *and its methyl ethers*

Photooxygenation of **1** was carried out under various conditions. (Table 1). A combination of sensitizer, oxygen and visible light or of oxygen and UV light (> 280 nm) is necessary for photooxidative degradation of **1**. Under these conditions, acid ($C_{14}H_{22}O_4$) and its methyl ester (**3**) were obtained in MeOH but only **2** in pyridine. This shows that the methyl ester (**3**) resulted from participation of solvent (MeOH). The structures of **2** and **3** were assigned from spectral data: **2**; log ε (210 nm) 4·08; ν_{max}^{KBr} 3400–2600, 1750, 1725, 1705, 1640 cm^{-1}; τ ($CDCl_3$) 0·65 s (1H), 3·33 s (1H), 7·10 d (1H, *J* 13·5 Hz), 7·37 d (1H, *J* 13·5 Hz), 8·84 s (9H), 9·06 s (9H), and **3**; ν_{max}^{KBr} 1748, 1733, 1634 cm^{-1}; τ ($CDCl_3$) 3·25 s (1H), 6·53 s (3H), 7·08 d (1H, *J* 13·5 Hz), 7·35 d (1H, *J* 13·5 Hz), 8·80 s (9H), 9·05 s (9H).

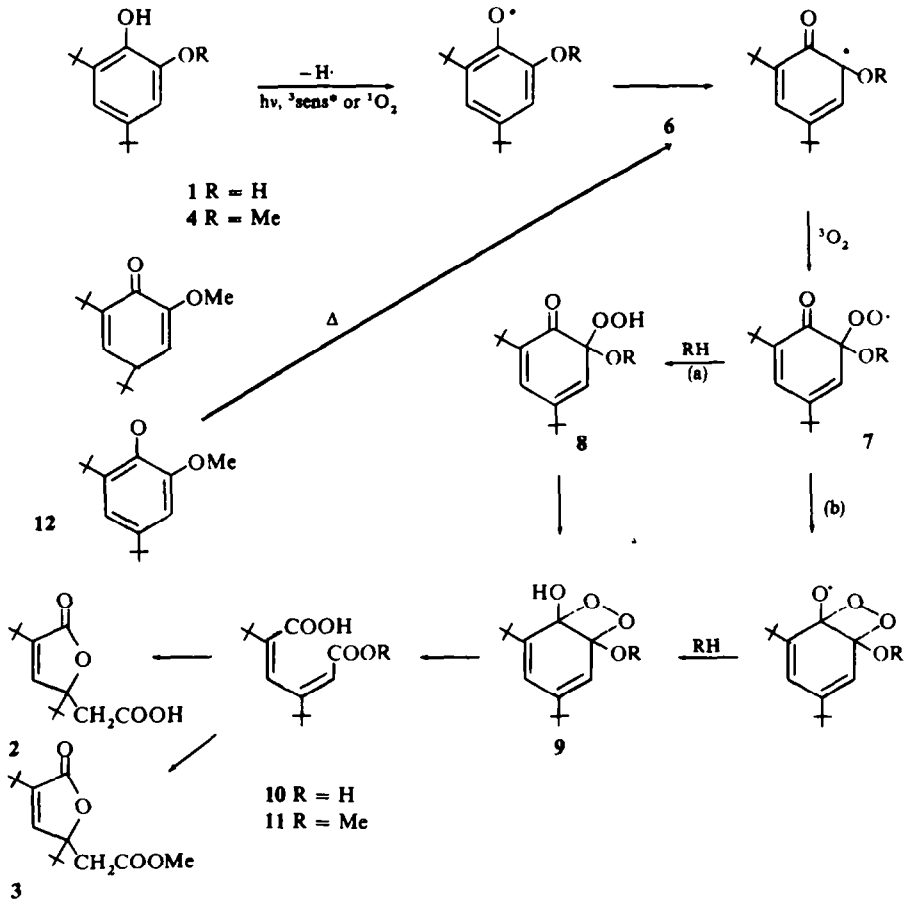
4,6-Di-t-butylguaiacol (**4**), the monomethyl ether of **1**, was also susceptible to photosensitized oxygenation giving methyl ester **3** (Table 1, Exp. 12 and 13), whereas 3,5-di-t-butylveratrole (**5**), the dimethyl ether of **1**, was completely unreactive to photosensitized oxygenation (Table 1, Exp. 14). The results obtained with **1**, **4** and **5** indicate that the presence of a phenolic hydroxyl is prerequisite to the photooxidative ring-cleavage of these compounds.

Since phenolic compounds including catechols are known to form phenoxy radicals either by direct photolysis[13, 14] or by dye-sensitized photolysis,[1, 15] it is most probable that a phenoxy radical (**6**) is the initial product of the photooxygenation of **1** and **4**. It has been proposed that both the triplet excited sensitizer and singlet oxygen, which are produced in the photosensitized oxygenation system, participate in hydrogen abstraction from a phenol.[1] The phenoxy radical intermediate **6** can account for products **2** and **3** (Scheme 1). Radical **6** reacts with ground state triplet oxygen to give a peroxy radical (**7**) which is then converted to a cyclic peroxide (**9**) either *via* path (a) or path (b). Cleavage of **9** gives α,β'-di-t-butylmuconic acid (**10**) or its monomethyl ester **11** which in turn cyclizes to give **2** or **3**, respectively.* The mechanism involving the phenoxy radical **6** was strongly supported by the fact that oxygenation of **6** (R = Me) generated by thermolysis of its dimer **12**[17] in MeOH and benzene gave **3** in 29% and 14% yields, respectively, in addition to **4**. An alternative mechanism involving an *o*-quinone intermediate (**13**) may also be applicable (Scheme 2). The *o*-quinone **13**, which can form by disproportionation of the phenoxy radical **6** (R = H)

* The formation of the ester **3** from **1** can be rationalized by assuming another phenoxy radical intermediate **i** which is degraded according to the scheme below.[16]



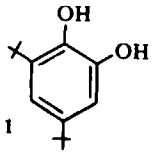
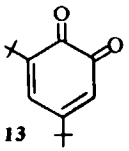
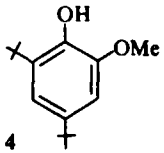
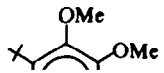
SCHEME 1.

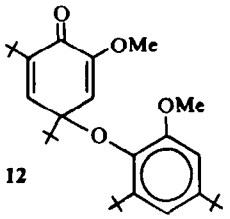
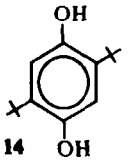
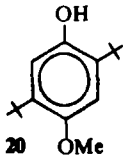
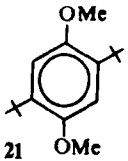


or by decomposition of the hydroperoxide **8** (R = H or Me), will be photooxidized to **10** and **11**, as reported by Gream[18] who demonstrated that cyclic 1,2-diketones including *o*-quinones are photooxidized in MeOH to give a corresponding dicarboxylic acid and/or its monomethyl ester *via* a cyclic acid anhydride. Therefore, photooxygenation of 3,5-di-t-butyl-*o*-benzoquinone (**13**) in MeOH under visible light was carried out. Although acid **2** was obtained in low yield but no **3** (Table 1, Exp. 11), the reaction was slower and more complex than for **1** and **4** and the VPC pattern of the product mixture was considerably different from that of **1**. Furthermore, an attempt to detect **13** from the photooxidized mixture of **1** was unsuccessful. These results led us to conclude that the pathway involving **13** may be a minor one even if it occurs.

The present reactions leading to the cleavage of an aromatic ring by molecular oxygen represent nonenzymic models for pyrocatechase and other dioxygenases which catalyze the cleavage of a phenolic ring.[3] Mechanisms for certain pyrocatechase- and metapyrocatechase-types of dioxygenases have been recently proposed.[19]

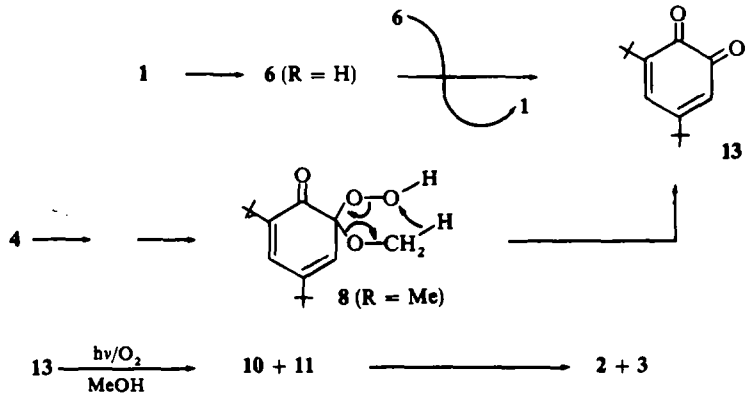
TABLE 1. PHOTOOXYGENATION AND OXYGENATION OF 3,5-DI-t-BUTYLPYROCATECHOL, 2,5-DI-t-BUTYLHYDROQUINONE, AND THEIR DERIVATIVES

Compound	Exp. No.	sensitizer	Atmosphere (O_2 absorbed mole/mole)	Irradiation[a]	solvent	recovered (%)	Yield of Products (%)[b]	
 1	1	R B[c]	O_2 (0·6)	VL	MeOH	—	2 (16)	3 (4)
	2	R B	O_2 (1·3)	UV	MeOH	—	2 (—)	3 (8)
	3	R B	O_2 (0)	dark	MeOH	100		
	4	none	O_2 (0)	VL	MeOH	100		
	5	none	O_2 (1·6)	UV	MeOH	—	2 (24)	3 (7)
	6	none	N_2	UV	MeOH	100		
	7	R B	O_2 (1·3)	UV	pyridine	21	2 (11)	
	8	none	O_2 (1·1)	UV	pyridine	41	2 (17)	
	9	none	O_2 (~0)	VL	pyridine	93		
	10	none	O_2 (~0)	dark	pyridine	100		
 13	11	none	O_2 (0·7)	VL	MeOH	15·5	2 (5·6)	
 4	12	R B	O_2 (1·1)	VL	MeOH	27	3 (22)	
	13	chlorophyllin oil	O_2 (2,4)	VL	C_6H_6	7	3 (22)	
	14	R B	O_2 (0)	VL	MeOH	100		

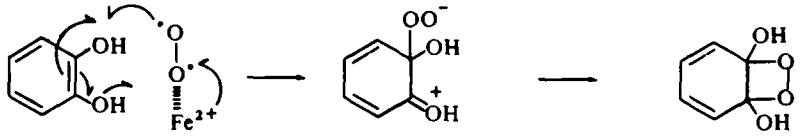
 12	15	none	O_2	dark	MeOH		3 (29)	4 (31)
	16	none	O_2	dark	C_6H_6		3 (14)	4 (11)
 14	17	R B	O_2 (1·1)	UV	MeOH	—	16 (16)	17 (11)
	18	R B	O_2 (1·0)	VL	MeOH	—	16 (10)	17 (13)
	19	none	O_2 (1·3)	UV	MeOH	—	16 (6.7)	17 (11)
	20	none	N_2	UV	MeOH	100		
	21	none	O_2 (~0)	dark	MeOH	90		
 20	22	R B	O_2	VL	MeOH	—	15 (75)	
 21	23	R B	O_2 (0)	VL	MeOH	100		

[a] VL: a tungsten-bromine lamp (window glass filter) or a tungsten lamp (window glass filter).
UV: a high-pressure mercury lamp (Pyrex filter).
[b] The yield was based on reacted starting material.

SCHEME 2.



These mechanisms can be formally written as shown below; a double electron transfer between a ferrous ion-oxygen complex and a catechol occurs to give a cyclic peroxide *via* a peroxy anion. These intermediates are analogous to **8** and **9** in Scheme 1.



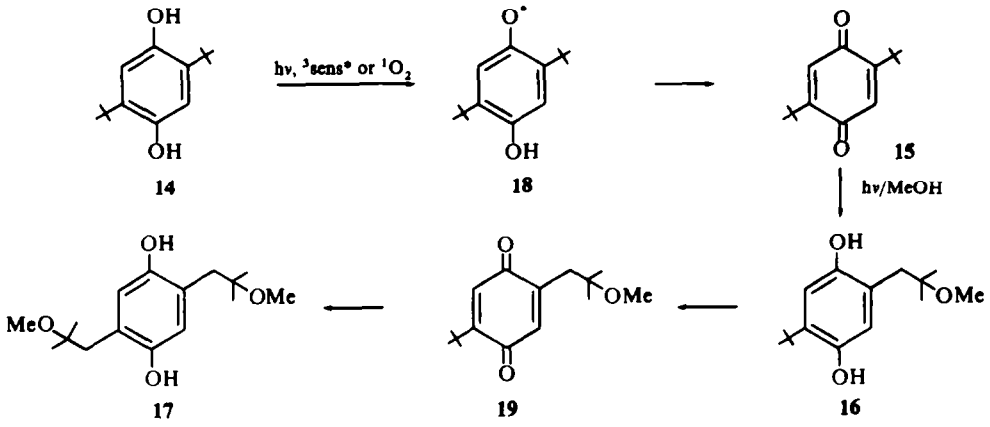
Photooxygenation of 2,5-*di-t-butylhydroquinone* (**14**) *and its methyl ethers*

Photooxygenation of **14** was examined under various conditions (Table 1, Exp. 17–21). Although **14** was very slowly oxidized by oxygen even in the dark to give 2,5-di-t-butyl-*p*-benzoquinone (**15**), dye-sensitized (visible light) or unsensitized (> 280 nm) photooxygenation in MeOH readily proceeded and after a long period of irradiation gave MeOH adducts, **16** and **17** in various ratios. The rose bengal-sensitized photooxygenation of **14** was followed as a function of time. The product distribution at different reaction times is shown in Fig. 1. The result clearly indicates the intermediary formation of quinone **15** which is then converted to **16**.

The structures of **16** and **17** were assigned from spectral properties (Experimental) and from the fact that various t-butylated *p*-benzoquinones, when irradiated in an alcoholic solvent are known to give 1:1 and 1:2 adducts analogous to **16** and **17** respectively.[20] We can now formulate a mechanism for the photooxygenation of **14** in Scheme 3 which is similar to Scheme 1. A phenoxy radical **18** could be formed by hydrogen abstraction from **14** by the triplet excited sensitizer and/or singlet oxygen, or by dissociation of the excited state of **14**. The *p*-benzoquinone **15**, derived from **18**, photochemically undergoes a solvent-addition reaction to give **16** which is further converted to **17** *via* a *p*-benzoquinone **19**.

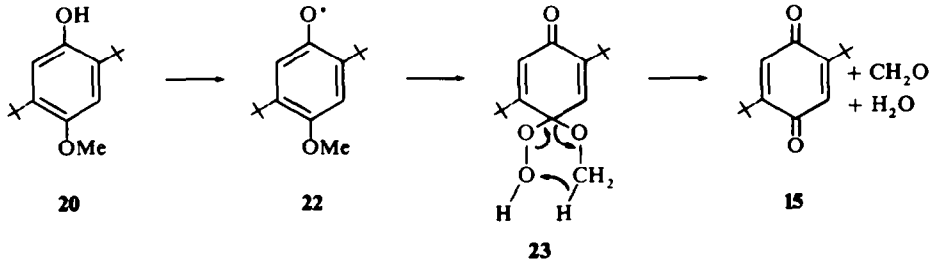
2,5-Di-t-butyl-4-methoxyphenol (**20**), the monomethyl ether of **14**, readily suffered photosensitized oxygenation to give the *p*-benzoquinone **15** in good yield, whereas

SCHEME 3.



the dimethyl ether (21) of **14** completely resisted photosensitized oxygenation. A possible mechanism involving a phenoxy radical (**22**) and a hydroperoxide (**23**) is shown in Scheme 4. Supporting this mechanism formaldehyde was detected in the mixture.

SCHEME 4.



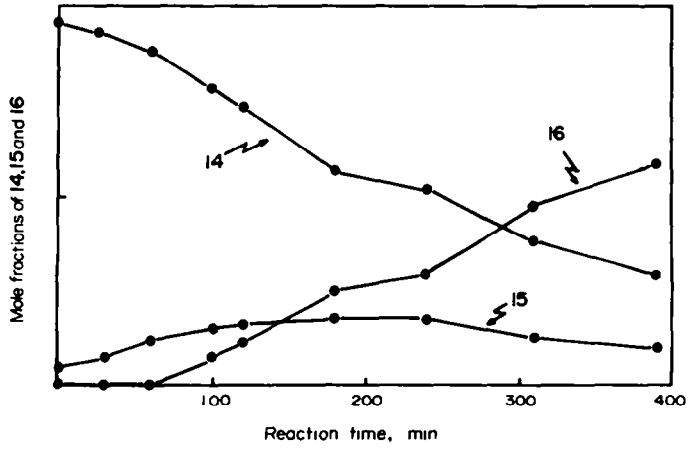
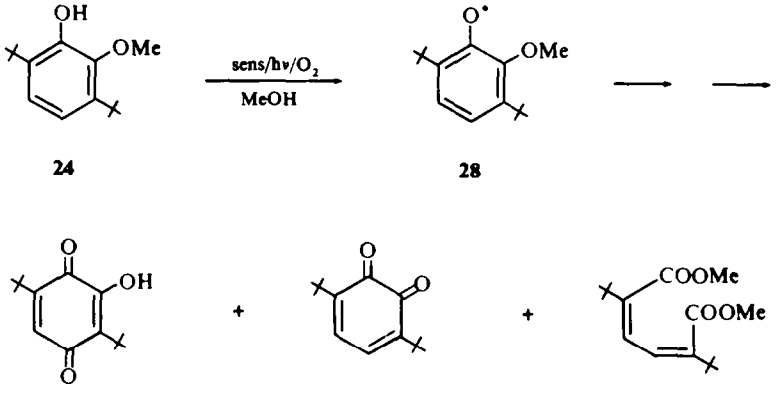


FIG 1. Product distributions in the photosensitized oxygenation of **14**

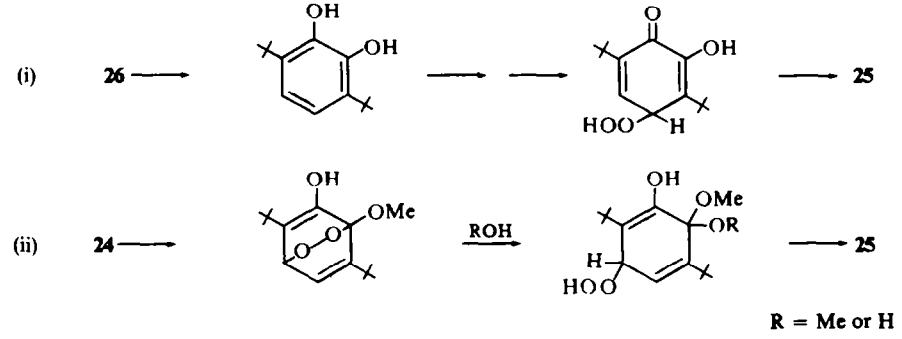
Photosensitized oxygenation of 3,6-*di-t-butylguaiacol* (**24**)

Rose bengal-sensitized photooxygenation of **24** in MeOH gave a mixture of products, from which three crystalline compounds were isolated. One was identified as 2,5-di-t-butyl-6-hydroxy-*p*-benzoquinone (**25**; 11%). For two other compounds the structures of 3,6-di-t-butyl-*o*-benzoquinone (**26**; 3%) and of dimethyl α,α′-di-t-butylmuconate (**27**; 20%) were assigned on the basis of their spectral data (Experimental). Although this reaction was not investigated in detail, it is reasonable to assume that these products were formed *via* a phenoxy radical intermediate (**28**) analogous to that of Scheme 1.*



In conclusion, the initial step of the photooxygenation of t-butylated catechol and hydroquinone derivatives seems to be the formation of a phenoxy radical intermediate which undergoes various modes of degradation in the presence of oxygen depending upon its structural features and environmental factors.

* Two mechanisms may be operative for the formation of **25**: (i) one involves further oxygenation of a catechol intermediate which could be formed by hydrogen transfer between **26** and **24**; and (ii) the other involves 1,4-cyclo-addition of singlet oxygen to **24** giving a 1,4-*endo*-peroxide intermediate, as seen in the case of 4,6-di-t-butylresorcinol derivatives.[2]



EXPERIMENTAL

3,5-Di-t-butylpyrocatechol (1). This compound was prepared by the following modified procedure of the known method.[5] To a soln of commercial 4-t-butylpyrocatechol (25 g) in dried t-BuOH (40 ml) and AcOH (40 ml) was added conc. H_2SO_4 (8 ml). The mixture was heated at 60° under N_2 for 12 hr, then room temp for 24 hr. After diluting with water, the mixture was ether extracted, The ethereal layer was dried and evaporated to give a residue which was recrystallized from cyclohexane to give colorless crystals (19 g), m.p. 97–99° (lit.[5] m.p. 96–97°); NMR ($CDCl_3$) τ 8·77 (s, 9H), 8·63 (s, 9H), 5·30 (broad. 1H), 4·70 (s, 1H), 3·44 (d, 1H, *J* 2 Hz) and 3·30 (d, 1H, *J* 2 Hz).

Photooxygenation of 3,5-*di-t-butylpyroatechol* (1). (*Exp.* 1–10). A solution containing 2·2 g of **1** and 50 mg of rose bengal in 400 ml of MeOH was irradiated under oxygen-bubbling using a 650 W tungsten-bromine lamp (visible light) with a water-cooling jacket. After 123 ml of oxygen had been consumed (5 hr, the mixture was evaporated *in vacuo* and the residue chromatographed on silica gel (45 g). Elution with CH_2Cl_2 (500 ml) gave a mixture of products, which was further chromatographed on silica gel (50 g). Elution with 3% acetone-CH_2Cl_2 (300 ml) gave 109 mg of **3**, which was recrystallized from cychohexane; m.p. 70–72°. (Found: C, 67·31; H, 9·13. Calc. for $C_{15}H_{24}O_4$; C, 67·13; H, 9·02%).

Elution with 5% acetone-CH_2Cl_2 (200 ml) gave 370 mg of **2** which recrystallized from light petroleum; m.p. 133–136°. (Found: C, 66·08; H, 8·97. Calc. for $C_{14}H_{22}O_4$; C, 66·11; H, 8·72%). The yield of the products was obtained by VPC: **2**. 16% and **3**, 4·1%. (Exp. 1). Treatment of **2** in MeOH with ethereal CH_2N_2 followed by product recrystallization gave **3**, m.p. 67–69°, identified by IR. Other photooxygenation experiments (Exp. 2–10) were carried out with **1** under various conditions (Table 1).

Photosensitized oxygenation of 3,5-*di-t-butyl-o-benzoquinone* (**13**). (*Exp.* 11). A solution containing 2·2 g of **13**[17, 21] in MeOH (400 ml) was photooxygenated as above. After 160 ml of oxygen had been consumed (9·5 hr), the mixture was evaporated and the residue was chromatographed on silica gel (50 g). Successive elution with CH_2Cl_2-benzene (1:19) (200 ml), CH_2Cl_2-benzene (1:1) (100 ml) and CH_2Cl_2 (100 ml) gave 340 mg of **13**. Further elution with acetone-CH_2Cl_2 (1:9) (100 ml) gave 121 mg (5·6%) of **2**, which recrystallized from petroleum ether; m.p. 137–140°. ν_{max}^{nujol} 3300–2600 (broad), 1760, 1720 cm^{-1}.

Photosensitized oxygenation of 4,6-*di-t-butylguaiacol* (**4**). (*Exp.* 12, 13). A solution containing 2·5 g of **4**[17] and 50 mg of rose bengal in MeOH (300 ml) was photooxygenated as above. After 253 ml of oxygen had been consumed (1·5 hr), the mixture was evaporated *in vacuo*. Residue analysis (2·81 g) showed it to consist of 0·64 g of **4** and 0·45 g (22%) of **3**, determined by VPC (Silicon DC, 1·5 m, 170°, He, 2 kg/cm^2).

A similar experiment was carried out in the presence of chlorophyllin oil (50 mg) as sensitizer in benzene (250 ml). After 550 ml of oxygen had been consumed (29 hr), the mixture was worked up as above giving 0·16 g of **4** and 0·56 g (22%) of **3**, isolated by prep. VPC.

Photosentized oxygenation of 3,5-*di-t-butylveratrol* (**5**) (*Exp.* 14). A solution containing 2·2 g of **5**, which was prepared from **4** by the procedure of Cook,[22] and 55 mg of rose bengal in MeOH (300 ml) was photooxygenated under the same conditions. After 13·5 hr, the solution contained only starting materials, shown by TLC (Silica gel; benzene-*n*-hexane, 1:1).

Autoxidation of the dimer **12** (*Exp.* 15, 16). A green solution containing 0·1 g of **12**[17] in absolute MeOH (20 ml) was allowed to stand in the dark under oxygen-bubbling for 10 days. After solvent removal, the residue was analyzed by VPC (Silicon DC 550, 1·5 m, 170°, 2 kg/cm^2, He) and shown to consist of 31 mg (29%) of **3** and 31 mg (31%) of **4**. When autoxidation was carried out at reflux, the reaction was completed in 40 min but only **4** (58%) was produced. A similar experiment with 0·56 g of **12** in benzene gave 94 mg (14%) of **3** and 64 mg (11%) of **4**.

Photooxygenation of 2,5-*di-t-butylhydroquinone* (**14**) (*Exp.* 17–21). A solution containing 5 g of **14** and 60 mg of rose bengal in MeOH (400 ml) was photooxygenated using a 450 W high-pressure mercury lamp. After 534 ml of oxygen had been consumed, the mixture was evaporated *in vacuo*. VPC analysis (Silicon DC 550, 1·5 m, 210°, He, 2·0 kg/cm^2) of the residue showed it to consist of 0·9 g (16%) of **16** and 0·7 g (11%) of **17**. (Exp. 17). Other experiments (18–21; various conditions) are in Table 1.

Product isolation. A solution containing 10 g of **14** and 50 mg of rose bengal in MeOH (110 ml) was photooxygenated using a 100 W high-pressure mercury lamp with a Pyrex water-cooling jacket at room temp. After 1520 ml of oxygen had been consumed (24 hr), crystals deposited during irradiation were collected by filtration. Recrystallization from MeOH gave 5·6 g (45%) of **16**, m.p. 203–204°; ν_{max}^{Nujol} 3400 cm^{-1}; τ ($CDCl_3$) 1·65 (1H), 3·20 (1H), 3·72 (1H), 5·43 (1H), 6·78 (3H), 7·33 (2H), 8·62 (9H), 8·82 (6H) [all as singlets].

A solution containing 2 g of **14** in MeOH (110 ml) was photooxygenated under similar conditions. After 360 ml of oxygen had been consumed (7¼ hr), crystals deposited during irradiation were collected and

recrystallized from EtOAc to give 550 mg (21%) of **17** as colorless crystals, m.p. 221–222°; ν_{max}^{Nujol} 3260 cm^{-1}; τ ($CDCl_3$) 1·70 (2H), 3·42 (2H), 6·75 (6H), 7·26 (4H), 8·80 (12H) [all as singlets].

Product distribution. A solution of 10 g of **14** and 10 mg of rose bengal in MeOH (110 ml) was photooxygenated with a 100 W high-pressure mercury lamp as above. The reaction was followed as a function of time by VPC. (Silicon DC 550, 1·5 m, 210°, He, 2 kg/cm^2). An approximation that the total concentration of **14**, **15** and **16** is constant was used for the estimation of the product distribution. The results are shown in Fig. 1.

Photosensitized oxygenation of 2,5-*di-t-butyl*-4-*methoxyphenol* (**20**) (*Exp.* 22). A solution of 1 g of **20**[22] and 51 mg of rose bengal in MeOH (250 ml) was photooxygenated with a 650 W tungsten-bromine lamp. Into the oxygen-circulating system, a trap filled with Schiff reagent (a mixture of 1 l of 0·1% aqueous *p*-roseaniline solution, 20 ml of 20% aqueous sodium bisulphite solution and 10 ml of conc HCl was inserted. After 74 ml of oxygen (0·88 mole/mole of **20**) had been consumed (20 min), oxygen-circulation was continued for 10 hr without irradiation. The reagent solution showed a violet color which proved the formation of formaldehyde. The mixture was evaporated under reduced pressure and the residue was chromatographed on silica gel (50 g). Elution with 300 ml of light petroleum–benzene (9:1) gave 118 mg of the starting material **20**. Elution with 100 ml of light petroleum–benzene (8:2) gave 623 mg (75%) of **15** as crystals; m.p. 148–150°; ν_{max}^{Nujol} 1645, 1600 cm^{-1}.

Photosentized oxygenation of 1,4-*di-t-butyl*-2,5-*dimethoxybenzene* (**21**). (*Exp.* 23). A solution of 2·5 g of **21**[22] and 50 mg of rose bengal in MeOH (250 ml) was photooxygenated using a 100 W high-pressure mercury lamp (5 hr). No oxygen consumption was observed. The solution contained only the starting material, which was detected by TLC (silica gel, light petroleum).

Photosensitized oxygenation of 3,6-*di-t-butylguaiacol* (**24**). A solution containing 2·0 g of **24**[23] and 40 mg of rose bengal in MeOH (200 ml) was photooxygenated using a 650 W tungsten-bromine lamp. After 300 ml of oxygen had been consumed (130 min), the mixture was evaporated under reduced pressure. The residue was chromatographed on silica gel (50 g). Elution with $CHCl_3$ (40 ml) gave 214 mg (11%) of pale yellow crystals, which, on recrystallization from MeOH containing a small amount of water, gave pure **25** as yellow crystals; m.p. 80–83° (lit.[24] yellow gum); λ_{max}^{EtOH} 265 nm (ε 15,400) and 400 nm (ε 1,400); ν_{max}^{Nujol} 3500, 1660, 1640 cm^{-1}; τ ($CDCl_3$) 2·4 s (1H; disappeared by addition of D_2O), 3·6 s (1H), 8·6 s (9H), 8·7 s (9H). (Found: C, 70·96; H, 8·50. $C_{14}H_{20}O_3$ requires C, 71·16; H, 8·53%). Further elution with $CHCl_3$ (450 ml) gave 938 mg of pale yellow crystals which were further chromatographed on silica gel (23 g). Elution of 200 ml of light petroleum-benzene (8:2) gave 54 mg (3%) of **26** as dark red crystals which were recrystallized from light petroleum; m.p. 173–175°; λ_{max}^{EtOH} 410 nm (ε 38,000); ν_{max}^{Nujol} 1680, 1665 cm^{-1}; τ ($CDCl_3$) 3·3 s (2H), 8·8 s (18 H). Elution with 200 ml of light petroleum–benzene (1:1) and of benzene (400 ml) gave 466 mg (20%) of **27** as colorless crystals which were recrystallized from MeOH containing a small amount of water; m.p. 85–87°; λ_{max}^{EtOH} 250 nm (ε 20,000); ν_{max}^{Nujol} 1725, 1200 cm^{-1}; τ ($CDCl_3$) 3·8 s (2H), 6·2 s (6H), 8·85 s (18H). (Found: C, 67·72; H, 9·41. $C_{16}H_{26}O_4$ requires C, 68·05; H, 9·28%).

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REFERENCES

1. Part LVI: T. Matsuura, N. Yoshimura, A. Nishinaga and I. Saito, *Tetrahedron*, **28**, 4933 (1972)
2. T. Matsuura, A. Nishinaga, N. Yoshimura, T. Arai, K. Omura, H. Matsushima, S. Kato and I. Saito, *Tetrahedron Letters* 1673 (1969); I. Saito, S. Kato and T. Matsuura, *Ibid.* 239 (1970)
3. K. Block and O. Hayaishi, *Biological and Chemical Aspects of Oxygenases*, Maruzen Co. Ltd., Tokyo (1966)
4. J. Tabone, N. Mamounas and D. Robert, *Bull. Soc. Chim. Biol.* **33**, 1560 (1951)
5. R. Grinstead, *Biochemistry* **3**, 1308 (1964)
6. Z. Yoshida and M. Kato, *Nippon Kagaki Kaishi* (*J. Chem. Soc. Japan*) **75**, 106, 109, 112 (1954)
7. G. Jori, G. Galiazzo and E. Scoffone, *Biochemistry* **8**, 2868 (1969)
8. J. E. Baldwin, H. H. Basson and H. Krauss, Jr., *Chem. Comm.* 984 (1968)
9. T. Matsuura, H. Matsushima and H, Sakamoto, *J. Am. Chem. Soc.* **89**, 6370 (1967); T. Matsuura, H. Matsushima and R. Nakashima, *Tetrahedron* **26** 435 (1970)
10. C. S. Foote, *Accounts Chem. Res.* **1**, 104 (1968)

[11] D. R. Kearns, *J. Am. Chem. Soc.* **91**, 6554 (1969)
[12] M. Nozaki, Y. Kojima, T. Nakagawa, H. Fujisawa, K. Ono, S. Kotani, O. Hayaishi and T. Yamano, *Biological and Chemical Aspects of Oxygenases* p. 347
[13] H.-I. Joschek and S. I. Miller, *J. Am. Chem. Soc.* **88**, 3269, 3273 (1966)
[14] A. W. Johnson and S. W. Tamm. *Chem. & Ind.* 1425 (1964)
[15] L. I. Grossweiner and E. F. Zwicker, *J. Chem. Phys.* **31**, 1141 (1959); **34**, 1411 (1961)
[16] E. G. Bordwell and A. C. Knipe, *J. Am. Chem. Soc.* **93**, 3416 (1971)
[17] F. R. Hewgill and B. S. Middleton, *J. Chem. Soc.* (C) 2316 (1967)
[18] G. E. Gream, J. C. Paice and C. C. R. Ramsay, *Austr. J. Chem.* **22**, 1229 (1969)
[19] S. Senoh, H. Kita and M. Kamimoto, *Biological and Chemical Aspects of Oxygenases* p. 378
[20] C. M. Orland, Jr., H. Mark, A. K. Bose and M. S. Manhas, *J. Am. Chem. Soc.* **89**, 6527 (1967); *J. Org. Chem.* **33**, 2512 (1968)
[21] K. Ley and E. Müller, *Chem. Ber.* **89**, 1402 (1956)
[22] C. D. Cook, R. G. Inskeep, A. S. Rosenberg, E. C. Curtis, Jr., *J. Am. Chem. Soc.* **77**, 1672 (1955)
[23] T. Matsuura and K. Ogura, *J. Am. Chem. Soc.* **89**, 3446 (1967)
[24] F. R. Hewgill and S. L. Lee, *J. Chem. Soc.* (C) 1549 (1968)