

PHOTOINDUCED REACTIONS. XXX. HYDROGEN ABSTRACTION FROM A PHENOL BY SINGLET OXYGEN<sup>1</sup>

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In a previous paper of this series,<sup>2</sup> it has been shown that several hindered phenols undergo dye-sensitized photooxygenation to give various oxidation products. For example, 2,6-di-*t*-butylphenol (1) yielded 2,6-di-*t*-butyl-*p*-benzoquinone (2) and 3,5,3',5'-tetra-*t*-butyl-4,4'-diphenoquinone (3) besides some polymers. We suggested that, as shown in Scheme 1, these products may result from a phenoxy radical 4 which is formed by hydrogen abstraction from 1 by the excited sensitizer as proposed by Grossweiner and Zwicker.<sup>3</sup> Recently participation of singlet oxygen in the dye-sensitized photooxygenation of various organic compounds has been supported by many workers.<sup>4</sup> These results prompted us to investigate the reaction of 1 with chemically generated singlet oxygen. In this communication we report an example of hydrogen abstraction by singlet oxygen.

Reaction of 1 with singlet oxygen was carried out by two different methods which have been already reported.<sup>5,6</sup> The results are shown in Table 1. In the reaction of 1 with singlet oxygen generated from 9,10-diphenylanthracene 9,10-peroxide,<sup>5</sup> 3 was the only isolable product under bubbling nitrogen, whereas 2 was obtained in an appreciable amount in addition to 3 under bubbling oxygen. The formation of 3 is easily rationalized by hydrogen abstraction from 1 by singlet oxygen followed by coupling of the phenoxy radical 4 to give 5 which is further dehydrogenated to 3. 2,6-Di-*t*-butyl-*p*-benzoquinone (2) can be formed only at sufficiently high oxygen pressure. Namely, the phenoxy radical 4 reacts with the ground-state triplet oxygen to give a hydroperoxy radical 6 followed by its conversion into a hydroperoxide 7 which is, in turn, dehydrated to form 2.<sup>7</sup> Similar observation was reported by Cook who demonstrated that oxidation of 1 with alkaline ferricyanide under oxygen gave both 2 and 3 but gave only 3 under nitrogen.<sup>8</sup>

On the other hand, when triphenylphosphite-ozone adduct was used as the source of singlet oxygen,<sup>6</sup> both 2 and 3 were formed either under bubbling nitrogen or oxygen. The formation of 2 under nitrogen is obviously due to sufficiently high triplet oxygen pressure

Table 1. Reaction of  $\underline{1}$  with singlet oxygen.

Source of singlet oxygen <sup>a</sup>	Atmosphere	Solvent	Recovered $\underline{1}$ (%)	Yield of products <sup>b</sup> (%)	
				$\underline{2}$	$\underline{3}$
A (2.5 mole equiv.)	N <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	75	0	47
A (1.9 mole equiv.)	O <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	82	7.3	30
B (2.5 mole equiv.)	N <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	29	7.0	32
B (3.0 mole equiv.)	O <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	34	9.0	37

<sup>a</sup> A: 9,10-Diphenylanthracene 9,10-peroxide at 80°. <sup>5</sup>

B: Triphenylphosphite-ozone adduct above -30°. <sup>6</sup>

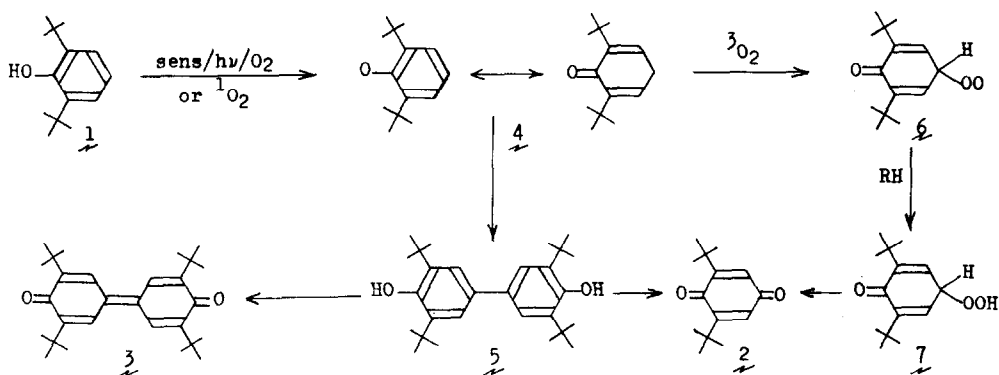
<sup>b</sup> Based on the reacted  $\underline{1}$ .

in the system. Since under the conditions employed triphenylphosphite-ozone adduct generates singlet oxygen much faster than 9,10-diphenylanthracene 9,10-peroxide, the concentration of the ground-state triplet oxygen, which is formed by deactivation of singlet oxygen, would be high enough to react with the phenoxy radical  $\underline{4}$  even under bubbling nitrogen.

In order to attempt a separation of the participation of singlet oxygen and the excited sensitizer in hydrogen abstraction during photooxygenation, competition reactions between  $\underline{1}$  and a singlet oxygen acceptor, linalool, were carried out. <sup>9</sup> At low conversion of  $\underline{1}$  (5-8%), the relative reactivity<sup>10</sup> of  $\underline{1}$  for linalool (1.0) was found to be 0.042 for singlet oxygen generated from triphenylphosphite-ozone adduct in methylene chloride and 0.073 for rose bengal-sensitized photooxygenation in methanol. The results indicate that the reactivity of  $\underline{1}$  for photooxygenation is higher than for singlet oxygen itself although different solvents were used. Consequently, it is reasonable to assume that not only the excited sensitizer but also singlet oxygen are responsible for hydrogen abstraction from  $\underline{1}$  in the dye-sensitized photooxygenation provided that the rate of deactivation of singlet oxygen to the ground-state triplet oxygen and also the reaction rate of singlet oxygen with the acceptors are nearly same in both methanol and methylene chloride. <sup>11</sup>

Kearns and coworkers have provided evidence that a hydrogen abstracting species, probably  $^1\Sigma_g^+$ -state singlet oxygen, is produced with sensitizers of sufficiently high triplet energy in dye-sensitized photooxygenation and that it can abstract hydrogen from cholesterol to give cholest-4-en-3-one. <sup>12</sup> At the present time there are insufficient data to determine whether  $^1\Sigma_g^+$ - or  $^1\Delta_g$ -singlet oxygen is involved in hydrogen abstraction from  $\underline{1}$ .

Scheme 1



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