PHOTOINDUCED REACTIONS. XL

ADDITION OF SINGLET OXYGEN TO MONOCYCLIC AROMATIC RING¹)

Isao Saito, Shigeyuki Kato, and Teruo Matsuura

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan. (Received in Japan 18 November 1969; received in UK for publication 18 December 1969)

In a previous communication²⁾ we reported the photooxidative ring cleavage of certain dihydric phenols as possible models for biological oxygenation. In an extension of this series of work we now wish to report the frist example of the addition of singlet oxygen to monocyclic aromatic compounds.³⁾

Photosensitized oxygenation⁴⁾ of the monomethyl ether 1 of 4,6-di-t-butylresorcinol(rose bengal/methanol) gave a hydroperoxide 2 (40% yield) which was identical with the authentic sample.⁵⁾ The dimethyl ether 7 suffered easily photosensitized oxygenation to give an epoxy-ketone 8 (70%); $c_{15}H_{24}O_4$; mp 183°; λ_{max}^{EtOH} 262nm(ε 9700); ν_{max}^{CHC1} 3 3400(intramolecular H-Bonding), 1665, 1625cm⁻¹; τ_{CDC1} 4.78(1H), 6.25(1H), 6.31(3H), 7.35(1H), 8.86(9H), 8.99(9H), all appears as singlet. Zinc-acetic acid reduction of 8 gave 1 in 70% yield. Hydrogenation (Pd-C) of 8 gave an enone 9 (35%); $c_{15}H_{26}O_3$; mp 137°; λ_{max}^{EtOH} 250nm(ε 15400); ν_{max}^{CHC1} 3 5500, 1665, 1620cm⁻¹; τ_{CDC1} 4.75(s, 1H), 6.35(s, 3H), 7.60(s, 1H), 7.40-8.30(m, 3H), 8.90(s, 9H), 8.93(s, 9H); which was also obtained by hydrogenation of 10.⁵) The above results led us to assign the structure 8 for the epoxyketone. In the absence of sensitizer, both 1 and 7 were recovered quantitatively upon photooxygenation.

We previously provided evidences that singlet oxygen, a reactive species in photosensitized oxygenation,⁷⁾ is capable of hydrogen abstraction from phenols.⁸⁾ Consequently it may be considered that the initial attack of singlet oxygen to 1 leads to the formation of a phenoxy radical 6. In order to ascertain this possibility, oxygenation of 6 generated by thermolysis of its dimer 5^{9} in methanol and in benzene was carried out. The major product was found to be 1 but the hydroperoxide 2 could not be detected. The result indicates that The phenoxy radical 6 may not be involved in the photosensitized oxygenation of 1.

Next, we examined possibility of the participation of singlet oxygen in these ractions.

Reaction of 1 and 7 with singlet oxygen generated from hydrogen peroxide and hypochlorite⁷⁾ gave 2 (70%) and 8 (75%), respectively. Relative reactivities of 1 and 7 to tetramethylethylene for photosensitized and chemical oxygenation were determined by competitive reactions.¹⁰⁾ The results are summarized below:

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	Relative reactivities to photooxygenation	tetramethylethylene (1.0 chemical oxygenation
1	0.0070	0.0067
7	0.0023	0.0030

Reactivities of each of 1 and 7 for photosensitized and chemical oxygenations are virtually the same. It can be, therefore, concluded that the reactive species in the photosensitized oxygenation is singlet oxygen, possibly the A_g state.⁷⁾

We can now formulate possible reaction pathways for the formation of $\frac{2}{2}$ and $\frac{8}{2}$ as shown in Schemes 1 and 2, respectively. The first step may involve 1,4-cycloaddition of singlet oxygen to the aromatic rings of 1 and 7 giving endo-peroxides 3 and 11, respectively. The peroxideoxygen atom of 3 may abstract a hydrogen in the transition state 4 to give 2^{11} . In the case of 7, the endo-peroxide 11 may rearrange to a diepoxide 12^{3} which is then solvolyzed to give 8.

The behaviors of the mono- and dimethyl ethers of 3,5-di-t-butylpyrocatechol and 2,5-di-tbutylhydroquinone were different from those of 1 and 7. The dimethyl ethers 13 and 14 resisted to photosensitized oxygenation under similar conditions. However photooxygenation of the monomethyl ether 15 gave a lactonic ester 16 in 24% (rose bengal/methanol) and 22% yields (chlorophyll/benzene). A pathway (Scheme 3) involving a phenoxy radical 17 may account for the formation of 16. The intermediary formation of the radical 17 was supported by the fact that oxygenation of 17 generated by thermolysis of its dimer 18¹² in mthanol and in benzene gave 16 in 29% and 14% yields, respectively, besides considerable amounts of 15.

On the other hand, photooxygenation of the monomethyl ether 19 (rose bengal/methanol) gave 2,5-di-t-butyl-p-benzoquinone (20) in 75% yield and formaldehyde was detected from the reaction mixture. The reaction can be rationalized by a pathway (Scheme 4) involving a phenoxy radical 21. Singlet oxygen and partly the excited triplet sensitizer may be responsible for the hydrogen abstraction from 15 and 19, as previously reported.^{2,8)}

The distinct difference of reactivities between the dimethyl ethers 8 and 1, (or 14) indicates that the introduction of electron-donating groups, 1,j such as methoxyland t-butyl, to an aromatic ring is not necessarily the conditions requisite for the addition of singlet

No.3

oxygen. Problems concerning the reactivity of singlet oxygen to aromatic compounds are under investigation.

This work was partly supported by a Grant-in-aid for Scientific Research from Ministry of Education.

Scheme 1



Scheme 2



Scheme 3



Scheme 4



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