Tetrahedron Letters No. 46, pp 4001 - 4004, 1974. Pergamon Press. Printed in Great Britain.

DYE-SENSITIZED PHOTOOXYGENATION OF DIMETHYLAMINO-SUBSTITUTED BENZENES.[1] CYCLOADDITION OF SINGLET OXYGEN IN COMPETITION WITH TYPE I REACTION.

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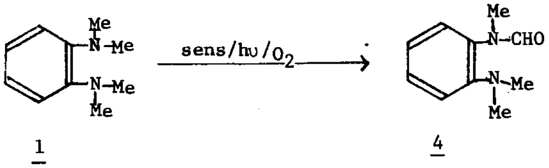
(Received in Japan 29 August 1974; received in UK for publication 8 October 1974)

Although it is well established that aliphatic amines may quench singlet oxygen,[2] it has recently been shown that certain amines did react with singlet oxygen to yield specific products.[2c,3] There have been several reports of photooxygenation of amines,[4] in which α-oxidation,[3c,5] β-oxidation,[6] dehydrogenation[5,6] and dealkylation[3b,6] have been observed. These reaction may take place either or both of two well recognized mechanisms, Type I and Type II (singlet oxygen) mechanism.[7] In Type I photooxygenations the excited sensitizer interacts with the substrate to give a substrate radical which reacts with oxygen to give products.[7] In a extension of our previous studies on the cycloaddition of singlet oxygen to electron-rich aromatic systems,[8] we investigated the dye-sensitized photooxygenation of dimethylamino-substituted benzenes and found that suitably substituted aromatic amines did react with singlet oxygen, in contrast to the quenching by *p*-substituted N,N-dimethylanilines.[2d]

We have tested five aromatic amines for the photooxygenation in methanol containing rose bengal as a sensitizer. Among them, N,N-dimethylaniline and N,N,N',N'-tetramethyl-*p*-phenylenediamine were found to be unreactive, whereas N,N,N',N'-tetramethyl-*o*-phenylenediamine (1), 4,5-bis(N,N-dimethylamino)-*o*-xylene (2) and 2,4-dimethoxy-N,N-dimethylaniline (3) consumed oxygen at an appreciable rate. Photooxygenation of 1 gave mainly polimeric tars accompanied with the formation of small amounts of a formamide 4[9] (2 %); υ^{nujol}_{max} 1680 cm^{-1}; τ (CDCl$_3$) 1.83 (s,1H), 2.98 (s, 4H), 6.83 (s, 3H) and 7.26 (s, 6H). However, when 2 (0.026M) was photooxygenated until 1.1 mole of oxygen was consumed, a formamide 5 and an epoxy-enone 6 were isolated in 33 and 17 % yield, respectively.[10] 5[9] ; mp 58-60°; υ^{nujol}_{max} 1675 cm^{-1} ; τ (CDCl$_3$) 1.90 (s, 1H), 3.25 (s, 2H), 6.88 (s, 3H), 7.30 (s, 6H), 7.78 (s, 3H), and 7.82 (s, 3H). 6[9] ; mp 121-122°; λ^{EtOH}_{max} 287 nm (ε=14700); $\upsilon^{CCl_3}_{max}$ 1705, 1563 cm^{-1}; τ (CDCl$_3$) 6.72 (d, 1H, J=16Hz), 6.75 (s, 6H), 7.44 (s, 6H), 7.83 (s, 6H), 8.13 (d, 1H, J=16Hz) and 8.67 (s, 3H).

We also found that the product ratio (5:6) is highly sensitive to sensitizer type and solvent (Table 1). When methylene blue having lower triplet energy (E_T=34 Kcal) than that of rose bengal (E_T=39.5 Kcal) or rose bengal attached to Amberlite IRA-400[11] (heterogeneous photooxidation) was used as a sensitizer, the yield of 5 decreased considerably, whereas the yield of 6 is independent of the sensitizer type. Aprotic solvents such as acetonitrile and benzene completely inhibited the formation of 5 in the heterogeneous photooxidation. Moreover, the addition of well known singlet oxygen quencher, β-carotene[12] (0.5 equiv.), to the reaction system inhibited the formation of 6 but had no significant effect on the yield of 5. These results indicate that a large portion of 5 formed in the rose bengal-sensitized photooxidation results from a Type I reaction and that singlet oxygen is definitely involved in the formation of 6.



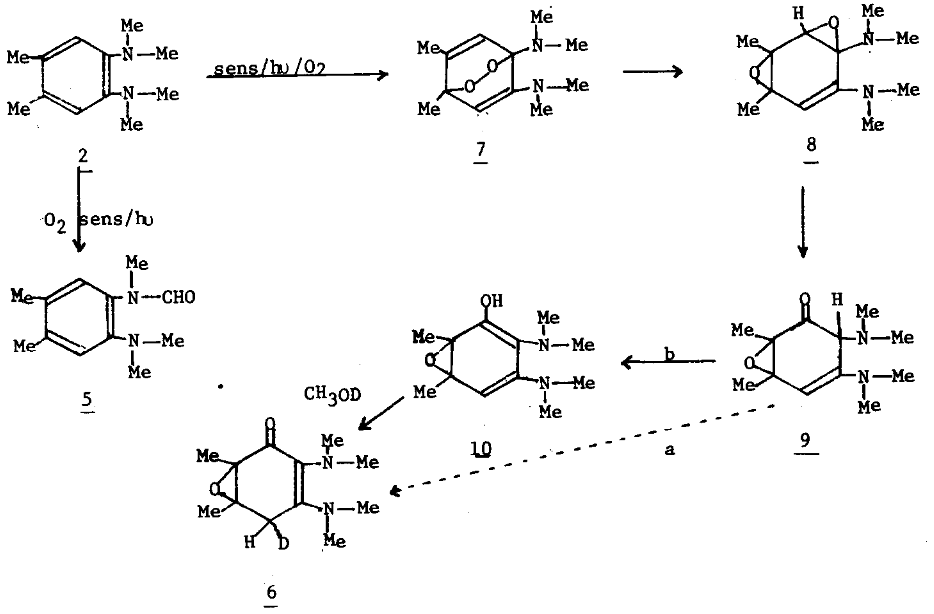


TABLE I

EFFECTS OF SENSITIZER AND SOLVENT ON THE PRODUCT RATIO (5:6) IN THE PHOTOOXYGENATION OF 2 (0.01M)

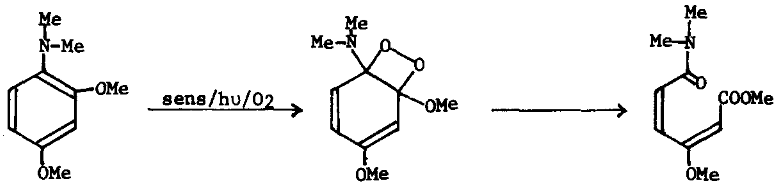
SOLVENT	SENSITIZER	QUENCHER	PRODUCT RATIO (5/6)*
Methanol	Rose bengal	---	0.39
Methanol	Methylene blue	---	0.16
Methanol	Rose bengal-Amberlite-IRA-400	---	0.11
Methanol	Rose bengal	β-carotene (0.005M)	0.83
Acetonitrile	Rose bengal-Amberlite-IRA-400	---	0
Benzene	Rose bengal-Amberlite-IRA-400	---	0

*The product ratio was obtained by g.l.c. analysis at low conversion (10-20 %).

The formation of 6 may be rationalized by a mechanism involving a 1,4-*endo*-peroxide 7 which is formed by 1,4-addition of singlet oxygen.[8] The arene-peroxide may rearrange to a bis-epoxide 8,[8,13,14] which would undergo 1,2-hydrogen shift to give 9. The epoxy-enone 6 may be formed either by 1,3-hydrogen shift from 9 (path a) or *via* the enol tautomer of 9, a benzene oxide 10 (path b). Evidence for the latter process (path b) was obtained by carrying out the photooxygenation in benzene-CH_3OD (4:1). In this case, the final product 6 was found to have incorporated 38 % deuterium in the methylene moiety from CH_3OD. This is to be expected for an intermediate corresponding to the benzene oxide 10.

Unlike 2 which gave the corresponding 1,4-*endo*-peroxide as a primary intermediate, rose bengal-sensitized photooxygenation of 3 in methanol yielded a 1,2-cleavage product 11 in 60 % yield. 11[9]; λ_{max}^{EtOH} 271 nm (ε=13700); ν_{max}^{nujol} 1715, 1640 and 1590 cm^{-1}; τ ($CDCl_3$) 2.66 (d, 1H, J=13Hz), 3.95 (d, 1H, J=13Hz), 4.95 (s, 1H), 6.34 (s, 3H), 6.36 (s, 3H) and 7.10 (s, 6H). The formation of 11 apparently indicates a 1,2-cycloaddition of singlet oxygen to give a benzene dioxetane 12 or its equivalents. To our knowledge, this is the first example of 1,2-addition of singlet oxygen to the benzene ring.

Further work on the structure and stability of the benzene oxide 12 is in progress.



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9. Satisfactory elemental analyses and mass spectra were obtained for all new compounds.

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