CHEMISTRY LETTERS, pp. 1213-1216, 1982.

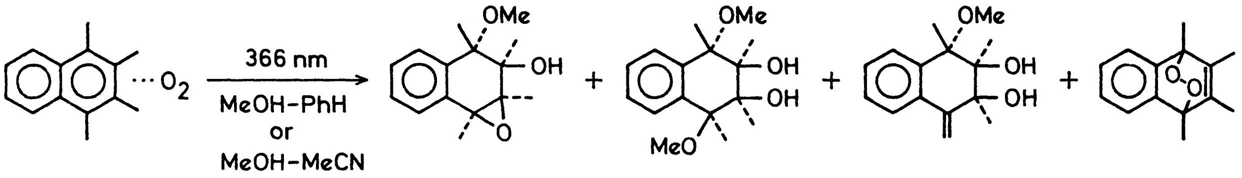
GENERATION OF SINGLET OXYGEN ON IRRADIATION OF CONTACT CHARGE-TRANSFER PAIRS OF 1,2,3,4-TETRAMETHYLNAPHTHALENE WITH OXYGEN

Hirochika SAKURAGI,* Gen-ichi FURUSAWA, Katsuhiko UENO,† and Katsumi TOKUMARU
Department of Chemistry, The University of Tsukuba, Sakura-mura, Ibaraki 305
† *Institute for Polymers and Textiles, Yatabe-Higashi, Tsukuba, Ibaraki 305*

Irradiation of 1,2,3,4-tetramethylnaphthalene (**1**) in methanol-benzene (1:1) or methanol-acetonitrile (1:1) under oxygen with 366-nm light resulted in the formation of an epoxyalcohol (**2**), a diol (**3**), an enediol (**4**), and an endoperoxide (**5**). Based on some features of the reaction, it is assumed that this photooxygenation is due to singlet oxygen generated on excitation of the contact charge-transfer pairs of **1** with oxygen.

Much current interest has been focused on photochemical reactions induced by exciplexes and excited electron-donor-acceptor complexes.1) Previously, we demonstrated that selective excitation of charge-transfer pairs of hexamethylbenzene2) and styrenes3) with molecular oxygen leads to the characteristic oxidation and dimerization, respectively. We now wish to report photochemical behavior of the contact charge-transfer pairs of 1,2,3,4-tetramethylnaphthalene with oxygen leading to oxygenation of the substrate probably with singlet oxygen generated on excitation of the charge-transfer pairs.

Irradiation of a solution (20 cm^3) of 1,2,3,4-tetramethylnaphthalene (**1**, 0.06 mol/dm^3) in methanol-benzene (1:1 by volume) under an oxygen atmosphere in a uranium glass tube with a 1-kW high pressure mercury lamp (effective at 366 nm) for 12 h at room temperature (conversion 50%) afforded an epoxyalcohol (**2**, yield 26%) and a diol (**3**, 13%).4) Prolonged irradiation of **1** (33.5 h, conversion 100%) produced an enediol (**4**, 13%) in addition to **3** (15%).4) On irradiation of **1** (0.03 mol/dm^3) in methanol-acetonitrile (1:1) under similar conditions (10 h), an endoperoxide (**5**, 30 %)5) was formed together with **2**, **3**, and **4** (14, 16, and 6%, respectively).4)



1 **2** **3** **4** **5**

The structure of **3** was established by single crystal X-ray method. This compound, mp 144-145°C, crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with the lattice constants a=9.072(2) Å, b=10.862(2) Å, c=15.196(3) Å, β=93.40(2)°, and

$Z=4$. A total of 2482 independent reflections in $2\theta_{\mathrm{Cu\ K}\alpha} \leq 158°$ was collected on a Nicolet automated diffractometer using θ-2θ scan mode with graphite monochromated Cu Kα radiation. The structural parameters have been refined by weighted full-matrix least-squares technique with anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms; the final R value was 0.057 and weighted R value was 0.059 for 2076 reflections with $|F_o| \geq 3\sigma(|F_o|)$. The structure is shown in Figure 1.

The structure of **2**, **4**, and **5** was determined by their spectral data and by reference to the structure of **3**. Elemental analyses are consistent with the structure.

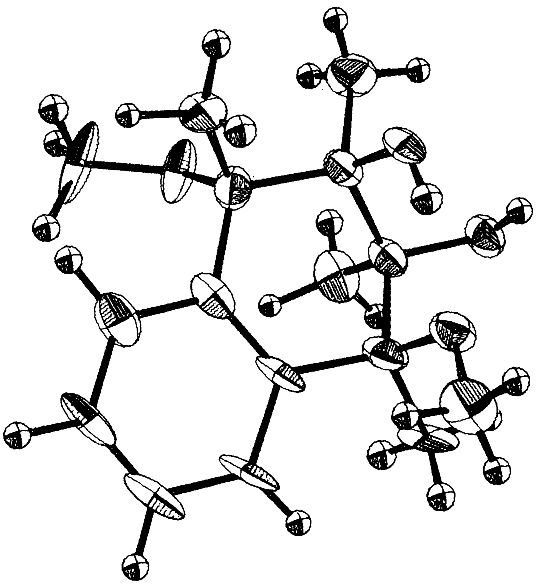
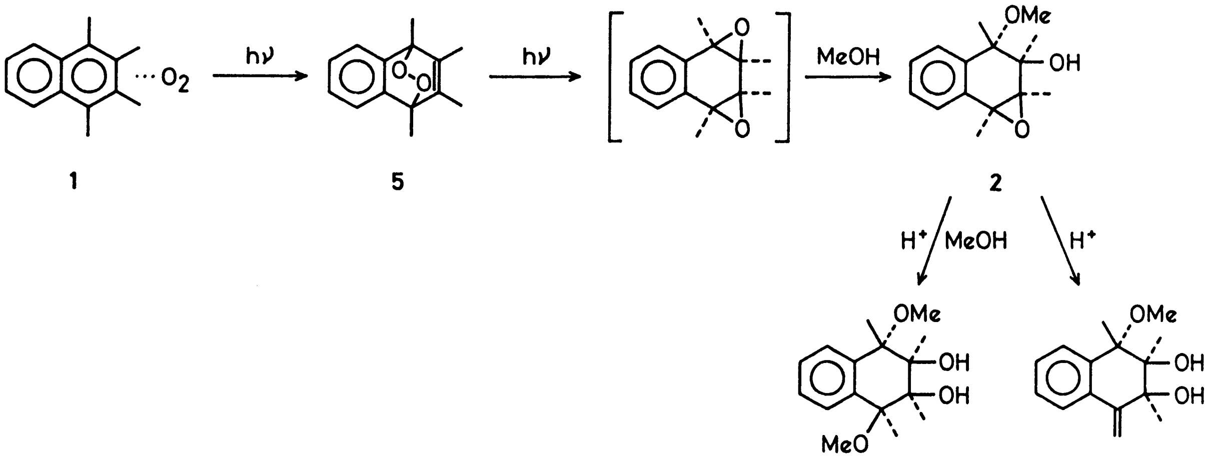


Figure 1. Structure of 1,2,3,4-tetrahydro-2,3-dihydroxy-1,4-dimethoxy-*r*-1,*t*-2,*t*-3,*t*-4-tetramethylnaphthalene

In control experiments, the endoperoxide, **5**, prepared from rose bengal-sensitized photooxygenation of **1** in methanol-benzene (1:1), was irradiated in the same solvent with 366-nm light under an argon and an oxygen atmosphere to afford **2** and **3**, respectively, as the main products. These results indicate the following processes for the formation of **2**, **3**, and **4**; the formation of **2** would be through a photochemical and a thermal process,[6] and that of **3** and **4** would be induced with acidic materials produced under oxidation conditions.



As to the formation of **5** from the excitation of the charge-transfer pairs of **1** and oxygen, there would be two possibilities. One is generation of singlet oxygen; excitation of the charge-transfer pairs would result in electron transfer from **1** to oxygen affording cation radicals of **1** ($\mathbf{1}^{+\cdot}$) and superoxide anion radicals. Back

Table 1. Solvent Effect on Photooxygenation of Tetramethylnaphthalene **1**

Solvent	ε a)	$\tau(^1\Delta)/\mu s$ b)	Conversion of **1** / %	Yield of **5** / % d)
Methanol	32.7	7	7.7	5.5 e)
Ethanol	24.6	12	8.9	6.7
Cyclohexane	2.0	17	9.2	2.7
Benzene	2.3	24	15	nd f)
Acetonitrile	37.5	30	24	20
Freon 113	2.4	1000 c)	84	62

a) J. A. Riddick and W. B. Bunger, ed., "Organic Solvents," 3rd ed., John Wiley, New York, N.Y. (1970). b) Reference 12. c) The lifetime in Freon 11. d) The yield based on **1** used. e) This value contains the secondary products from **5**. f) Not determined.

electron transfer from $O_2^{\overline{\cdot}}$ to $\mathbf{1}^{\dot{+}}$ in the solvent cage would generate singlet oxygen and the ground-state **1**.7) The other is the electron transfer followed by direct recombination of $O_2^{\overline{\cdot}}$ and $\mathbf{1}^{\dot{+}}$. The following observations, however, indicate that the excitation of the charge-transfer pairs generates singlet oxygen, which subsequently reacts with **1** to afford **5**.

First, the longest wavelength end of the absorption band of **1** lies at 350 nm in benzene, methanol, and acetonitrile. On saturation of the solvents with oxygen a new absorption band characteristic of the contact charge-transfer pairs of **1** with oxygen appeared in the range of 350-400 nm.8) Therefore, the use of 366-nm light excites only the charge-transfer pairs. Actually, light of longer wavelengths than 370 nm from a xenon lamp was also found to be effective for the oxygenation of **1**.9)

Second, the efficiency of the photooxygenation in various solvents is dependent on the lifetime of singlet oxygen in the solvents, but not on their polarity. Tetramethylnaphthalene **1** (0.03 mol/dm^3) was irradiated under oxygen in various solvents for 3 h with a 400-W high pressure mercury lamp equipped with an acetone filter (effective at 366 nm). The results are shown in Table 1 together with dielectric constants (ε) of the solvents and lifetimes of singlet oxygen [$\tau(^1\Delta)$] in the solvents.10) The conversion of **1** increases with increasing lifetimes of singlet oxygen in the solvent concerned. The yield of **5** also has a similar tendency.

Third, Dabco (1,4-diazabicyclo[2.2.2]octane, 1×10^{-6}-2.1×10^{-3} mol/dm^3) quenched the photooxygenation of **1** (0.025 mol/dm^3) in benzene and acetonitrile. The observed quenching constant [$k_q\tau(^1\Delta)$: 1.9×10^3 dm^3/mol] for the formation of **5** in benzene is in accord with the value (1.0×10^3 dm^3/mol) expected from the reported k_q and $\tau(^1\Delta)$ values.11,12)

Fourth, when **1** (0.02 mol/dm^3) was irradiated in the presence of 2,3-dimethyl-2-butene (**6**, 0.07 mol/dm^3), an efficient trap of singlet oxygen,13) in the same solvents as employed in Table 1 with 366-nm light from a 400-W high pressure mercury lamp through an acetone filter for 3 h at room temperature, 3-hydroperoxy-2,3-dimethyl-1-butene (**7**) was formed in all the solvents employed and its yield was much higher in Freon 113 (54% based on **6** used) than in the other solvetnts (26-32%).

Finally, in the competitive oxygenation of **1** and **6** in acetonitrile the relative efficiency for the formation of **5** from **1** and **7** from **6** was nearly the same as that of dye-sensitized photooxygenation of **1** with **6**. When a solution of **1** (0.02 mol/dm^3) and **6** (0.04 mol/dm^3) in acetonitrile was irradiated with 366-nm light under oxygen at room temperature, the ratio of the rate constants for the formation of **7** and **5** (k_7/k_5) was found to be 4.2 at conversions up to 50% of **6** as determined from their yields. The k_7/k_5 value for erythrosine-sensitized photooxygenation using light of wavelength longer than 520 nm was found to be 3.9 at similar conversion of **6**.

Based on the above observations, it is assumed that irradiation of the contact charge-transfer pair of **1** with oxygen generates singlet oxygen and this oxygen species reacts with the substrate, **1**, to give the endoperoxide, **5**, which is, in turn, photolyzed to afford the secondary products such as **2**, **3**, and **4** depending on the solvent employed.

Investigation concerning the detailed mechanism for the generation of singlet oxygen and the contribution of the contact charge-transfer pairs on photooxygenation of aromatic hydrocarbons is now in progress.

References

1) M. Gordon and W. R. Ware, ed., "The Exciplexes," Academic Press, New York, N.Y. (1975).

2) K. Onodera, H. Sakuragi, and K. Tokumaru, Tetrahedron Lett., **21**, 2831 (1980).

3) M. Kojima, H. Sakuragi, and K. Tokumaru, Tetrahedron Lett., **22**, 2889 (1981).

4) The products were isolated by column chromatography on silica gel eluting with dichloromethane.

5) H. H. Wasserman and D. L. Larsen, J. Chem. Soc., Chem. Commun., **1972**, 253.

6) C. Dufraisse, A. Etienne, and J.-J. Basselier, C. R. Seances Acad. Sci., **244**, 2209 (1957).

7) On the back electron transfer the formation of the triplet state of **1** and triplet (ground-state) oxygen would be also possible, but this process would be less exothermic than the singlet oxygen formation.

8) M. Tamres and R. L. Strong, "Molecular Association," Vol. 2, ed. by R. Foster, Academic Press, London (1979), p 397.

9) From preliminary results in methanol-acetonitrile, the use of 313-nm light for direct excitation of **1** under oxygen was less efficient than the 366-nm irradiation in the formation and decomposition of the endoperoxide.

10) In the absence of methanol **5** was the main product in these solvents. The yield of **5** and consumption of **1** were determined by HPLC.

11) C. S. Foote, E. P. Peterson, and K.-W. Lee, J. Am. Chem. Soc., **94**, 1032 (1972).

12) D. R. Kearns, "Singlet Oxygen," ed. by H. H. Wasserman and R. W. Murray, Academic Press, New York, N.Y. (1979), p 115.

13) K. Gollnick and H. J. Kuhn, "Singlet Oxygen," ed. by H. H. Wasserman and R. W. Murray, Academic Press, New York, N.Y. (1979), p 287.

(Received May 11, 1982)