

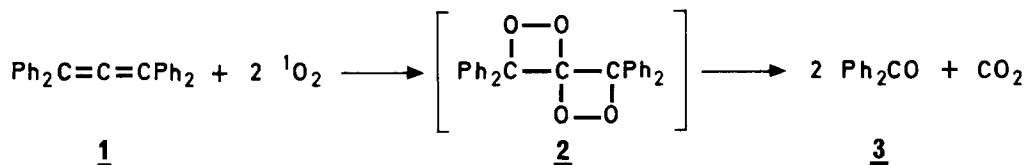
ELECTRON-TRANSFER PHOTOXYGENATION OF TETRAPHENYLALLENE
 FORMATION OF 1,3-DIHYDROPEROXY-1,1,3,3-TETRAPHENYL-
 2-PROPANONE AND ITS DECOMPOSITION UNDER CHEMILUMINESCENCE

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DCA-sensitized electron-transfer photooxygenation of tetraphenylallene (1) in acetonitrile yields benzophenone (3) and polymeric material. In acetone, the yield of 3 is better than twice the amount obtained in acetonitrile and very little of polymeric material is observed. If the acetone solution is worked-up immediately after the oxygen consumption ceased, 1,3-dihydroperoxy-1,1,3,3-tetraphenyl-2-propanone (8) is isolated. Its formation is proposed to occur via the peroxyallyl zwitterion 4 and the tetraphenylcyclopropanone (7) (Scheme 1). 8 decomposes slowly into 3, and CO + CO₂ (3:1) in neutral solution; in the presence of a base, decomposition is fast, resulting in the formation of two molecules of 3, one molecule of water, and one molecule of CO₂. Decomposition of 8 in the presence of various fluorescers and a base yields a bright fluorescence of the additives.

Some years ago, Greibrokk¹ reported that tetraphenylallene (1) yielded benzophenone (3) (about 50%), polymeric material and CO₂ if irradiated for some days in CS₂ in the presence of O₂ and eosin as a photosensitizer. The reaction was believed to occur via singlet oxygen cycloaddition to give the bis-dioxetane 2 which subsequently decomposed to CO₂ and two molecules of 3².



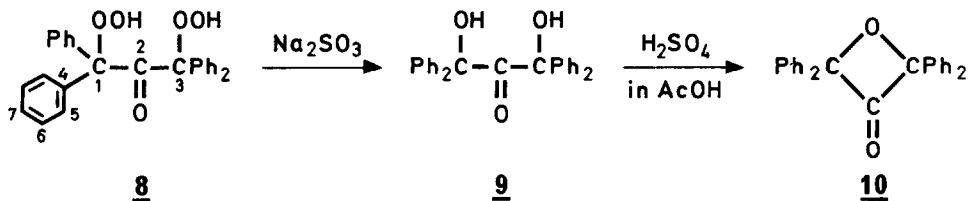
In our hands, 1 did not absorb O₂ if irradiated in acetonitrile (MeCN) or acetone (Me₂CO) in the presence of rose bengal (RB) for more than 8 hours indicating that the quantum yield of singlet oxygen oxygenation of 1 is well below 10⁻⁴ ^{3,4}.

However, if 1 was irradiated in MeCN in the presence of oxygen and 9,10-dicyanoanthracene (DCA), 1 consumed rapidly about 2 molecules of O₂. Less than 5% of 1 and about 40% of 3 (calculated by assuming that 1 yields 2 molecules of 3) were observed besides substantial amounts of resinous products.

If the DCA-sensitized photooxygenation was carried out in Me₂CO, and if, furthermore, the solutions were allowed to remain at room temperature for several hours before they were worked-up, about 80% of 3, less than 5% of 1, and only small amounts of polymeric material were obtained. On the other hand, if the solvent was removed at 15°C/15 Torr immediately

after the O_2 -consumption (about 2.5 moles of oxygen per mole of 1) ceased, the 1H NMR spectrum of the residue dissolved in $CDCl_3$ revealed that, in addition to about 40% of 3, a new product with signals at 7.18 and 8.33 ppm (singlets, 10:1) was formed. On standing at room temperature, these signals slowly disappeared, giving rise to 1H NMR signals due to 3.

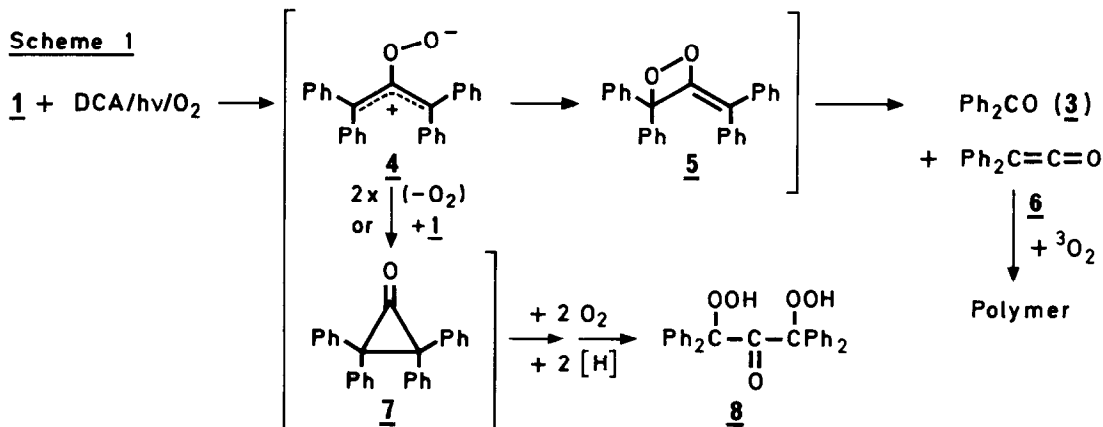
On adding n-pentane to the $CDCl_3$ -solution, the new product precipitated and could thus be separated from 3. According to its elemental analysis, molecular weight, spectral and chemical properties, this product represents the 1,3-dihydroperoxy-1,1,3,3-tetraphenyl-2-propanone (8)^{5,6}.



Reduction of 8 with aqueous sodium sulfite yielded 1,3-dihydroxy-1,1,3,3-tetraphenyl-2-propanone (9)⁹; dehydration of 9 afforded the well-known oxetanone derivative 10^{10,11}.

Since the DCA-sensitized photooxygenation of 1 does not proceed via singlet oxygen¹² (see above), an electron-transfer photooxygenation¹³ is the most likely oxygenation reaction to occur. Thus, singlet excited DCA should interact with 1 to give DCA^- and the radical cation of 1 ($1^{\cdot+}$) followed by electron transfer from DCA^- to oxygen to give $O_2^{\cdot-}$ and DCA. Addition of $O_2^{\cdot-}$ to $1^{\cdot+}$ may yield the peroxyallyl zwitterion 4 which may close the ring to dioxetane 5. Whereas ring-closure of 4 to 5 followed by cleavage of 5 to 3 and diphenylketene (6)¹⁴ seems to be the only reaction in MeCN, there is an additional reaction in Me_2CO , MeCN/ Me_2CO (2:1), and MeCN/cyclopentanone (2:1), in which 4 may be transformed into 8, probably via tetraphenylcyclopropanone (7) (Scheme 1)^{15,16}.

In Me_2CO , MeCN or methanol, the dihydroperoxy ketone 8 decomposes slowly into 3, $\text{CO} + \text{CO}_2$ (3:1, mass spectroscopically) and H_2O_2 and/or water. Addition of catalytic amounts of sulfuric acid does not appear to accelerate this process. However, heating or adding



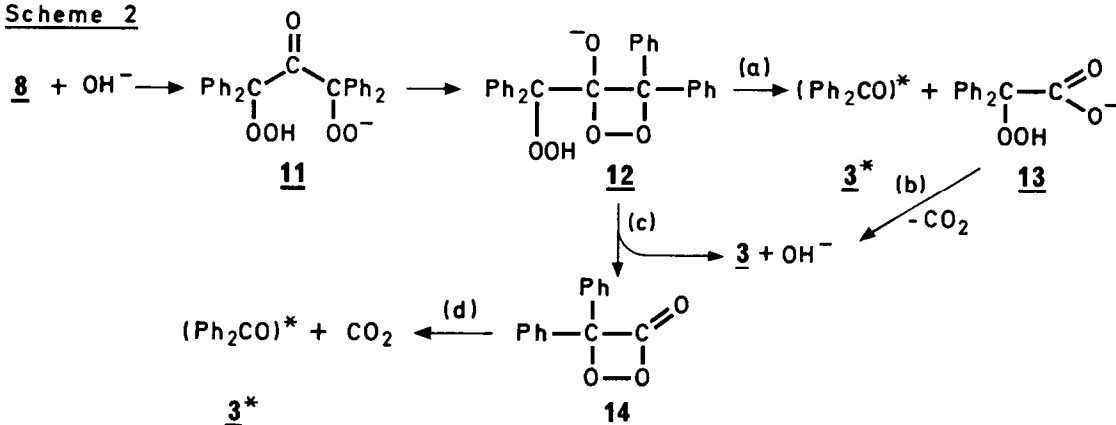
catalytic amounts of KOH results in a rapid decomposition. Adding 9,10-diphenylanthracene (DPA), tetracene (T), perylene (P), or dibromoperylene to a solution of 8 in CH_2Cl_2 or adding xanthene dyes such as fluorescein (Fl), eosin (E), and rhodamine B (RhB) to a solution of 8 in methanol gives rise to the occurrence of (indirect) chemiluminescence which is much enhanced in the presence of a base like potassium t-butoxide or KOH.

Several mechanisms are discussed for the base-catalyzed decomposition of α -hydroperoxy ketones¹⁷⁻¹⁹. Scheme 2 illustrates two possible pathways for the decomposition of 8 via energy-rich intermediates. According to paths (a) and (b), 12 cleaves into 3^* and the anion 13 which suffers a Grob-fragmentation into (unexcited) 3 + OH^- + CO_2 ; according to paths (c) and (d), 12 is transformed into 3 + OH^- + 14 followed by decomposition of the α -peroxy lactone 14 into 3^* and CO_2 ^{20,21}. Energy transfer from 3^* to the additive²² followed by fluorescence from the singlet excited additive may then terminate the reaction sequence.

Studies on photosensitized oxygenations of allenes are continued.

Acknowledgment: Support by Fonds der Chemischen Industrie, Frankfurt am Main, is gratefully acknowledged.

Scheme 2



References and Footnotes

1. T.Greibrokk, Tetrahedron Lett. 1973, 1663.
2. A more plausible mechanism was discussed by A.P.Schaap, K.A.Zaklika, in "Singlet Oxygen", H.H.Wasserman, R.W.Murray, Eds., Vol. 40, Organic Chemistry, Academic Press, New York, 1979, Ch. 6, p. 173.
3. For experimental conditions, see K.Gollnick, A.Schnatterer, Tetrahedron Lett. 25 (1984), 185. $2.5 \cdot 10^{-4} \text{M}$ of oxygen-acceptor (1 or 2,5-dimethylfuran (DMF)) and $2 \cdot 10^{-4} \text{M}$ of sensitizer (RB or DCA) in oxygen-saturated MeCN, Me_2CO , MeCN/ Me_2CO (2:1), or MeCN/cyclopentanone (2:1) at 13°C were applied.
4. In $\text{Me}_2\text{CO}/\text{RB}$, DMF absorbed 11.2 ml O_2 in 22 min.; 1 absorbed less than 0.032 ml O_2 in 500 min., since the smallest amount of oxygen that can be measured is 0.032 ml O_2 . Assuming that the limiting quantum yield of DMF-photooxygenation is unity, the quantum yield of singlet oxygen oxygenation of 1 should be less than $(0.032 \times 22) / (500 \times 11.2)$.
5. 8: m.p. 95-96°C (decomp.) (after recrystall. from CHCl_3/n -pentane); yield: 30%, with regard to 1 reacted. Elemental analysis: C 75.76%, H 5.29%; m.w. (osmometric in Me_2CO): 421; $\text{C}_{27}\text{H}_{22}\text{O}_5$ requires: C 76.04%, H 5.20%; m.w.: 426. - ^1H - and ^{13}C -NMR spectra, taken on a Bruker WP-80-CW spectrometer, using TMS as internal standard; ^1H NMR (CDCl_3 , 20°C): $\delta = 7.18$ (s, 20 H), 8.33 (s, 2 H); ^{13}C NMR (acetone- d_6 , -40°C): $\delta = 99.83$ (s, C-1, C-3) 127.88 and 130.18 (d, C-5 and C-6), 128.27 (d, C-7), 139.48 (s, C-4), 207.09 (s, C-2). Iodometric titration (after J.P.Wibaut, H.B.v.Leeuwen, B.v.d.Wal, Rec.Trav.Chim.Pays-Bas

- 73 (1954), 1033): 1.8 OOH per molecule of 1. - Solubility sequence: acetone = methanol > CHCl_3 > benzene = CCl_4 .
6. To the best of our knowledge, α, α' -dihydroperoxy ketones have not yet been made. Attempts to prepare and isolate the bis-hydroperoxide from diisopropyl ketone failed⁷, although titration of an autoxidized solution indicated the possible formation of a bis-hydroperoxide⁸.
 7. R.C.P.Cubbon, C.Hewlett, J. Chem. Soc. (C) 1968, 2978.
 8. H.R.Gersman, A.F.Bickel, J. Chem. Soc. (B) 1971, 2230.
 9. 9: m.p. 161-163°C (from ethanol); $\text{C}_{27}\text{H}_{22}\text{O}_3$: C 82.06, H 5.55 found; C 82.21, H 5.62 calc. ¹H-NMR: δ = 4.20 (s, 2 H), 7.21 (s, 20 H). - IR (KBr): 1723 (CO), 3510, 3420 cm^{-1} (OH, H-bonding).
 10. 10: m.p. 200-201°C (from ethanol); ref. 11: 199-201°C. - ¹H NMR: δ = 7.25 (m, 20 H). IR (KBr): 1814 cm^{-1} (CO).
 11. G.B.Hoey, D.O.Dean, C.T.Lester, J. Am. Chem. Soc. 77 (1955), 391.
 12. DCA is a rather potent singlet oxygen sensitizer: (a) A.Schnatterer, Diplomarbeit, University of München, 1982; (b) K.Gollnick, A.Schnatterer, manuscript in preparation; (c) L.E.Manring, C.S.Foote, J. Phys. Chem. 87 (1983), 40.
 13. J.Eriksen, C.S.Foote, T.L.Parker, J. Am. Chem. Soc. 99 (1977), 6455.
 14. Ketenes appear to react mainly with triplet oxygen to polymeric material even if irradiated in the presence of typical singlet oxygen sensitizers: N.J.Turro, Y.Ito, M.-F.Chow, W.Adam, O.Rodriguez, F.Yani, J. Am. Chem. Soc. 99 (1977), 5836. In our hands, diphenylketene yielded mainly polymeric material and some 3 when irradiated in MeCN or Me₂CO in the presence of DCA and oxygen. For the autoxidation of 6, see P.D.Bartlett, R.E.McCluney, J. Org. Chem. 48 (1983), 4165.
 15. The role of acetone and cyclopentanone is not clear. A Baeyer-Villiger-type reaction, however, does not seem to be involved since, if MeCN/cyclopentanone (2:1) was used, only 4% of δ -valerolactone was obtained (calculated by assuming that one molecule of lactone should be formed per molecule of 7). The small amount of lactone is probably due to some oxidation of cyclopentanone by 8. If added at the beginning, δ -valerolactone remains unchanged during the photooxygenation of 1 and may be recovered quantitatively.
 16. Turro postulated the intermediacy of a cyclic five-membered peroxide during the reaction of tetramethylcyclopropanone with triplet oxygen in benzene: N.J.Turro, P.A.Leermakers, H.R.Wilson, D.C.Neckers, G.W.Byers, G.F.Vesley, J. Am. Chem. Soc. 87 (1965), 2613. There is no indication that a 2,2,5,5-tetraphenyl-3,4-dioxa-cyclopentanone is formed in the DCA-sensitized photooxygenation of 1 in acetone.
 17. (a) W.v.E.Doering, R.M.Haines, J. Am. Chem. Soc. 76 (1954), 482; (b) W.H.Richardson, V.F.Hodge, D.L.Stiggall, M.B.Yelvington, F.C.Montgomery, J. Am. Chem. Soc. 96 (1974), 6652; (c) I.Kamiya, T.Sugimoto, Bull. Chem. Soc. Japan 54 (1981), 25.
 18. (a) F.G.Bordwell, A.C.Knipe, J. Am. Chem. Soc. 93 (1971), 3416; (b) Y.Sawaki, Y.Ogata, J. Am. Chem. Soc. 97 (1975), 6983.
 19. P.S.Bailey, Y.G.Chang, J. Org. Chem. 27 (1962), 1192.
 20. For chemiluminescence of α -peroxy lactones, see W.Adam, Pure Appl. Chem. 52 (1980), 2591.
 21. For "chemically initiated electron exchange luminescence" (CIEEL) of an α -peroxy lactone see S.P.Schmidt, G.B.Schuster, J. Am. Chem. Soc. 102 (1980), 306.
 22. 3* should be formed in its excited singlet state; intersystem crossing to its triplet state should be very effective. Transfer from triplet-3* ($E_T = 69$) to DPA, T, P, Fl, E and RhB ($E_S = 70, 60, 65, 55, 55, \text{ and } 49$ kcal/mol, respectively)²³ to give the singlet excited additives would be energetically allowed but spin-forbidden.
 23. H.G.O.Becker et al., Einführung in die Photochemie, VEB Deutscher Verlag der Wissenschaften, Berlin, 1976, Table 14.3, p. 451-455.

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