

PHOTOXYGENATION OF TETRAMETHYLLALLENE
 COMPETING (2+2) CYCLOADDITION AND ENE-REACTIONS
 WITH SINGLET OXYGEN

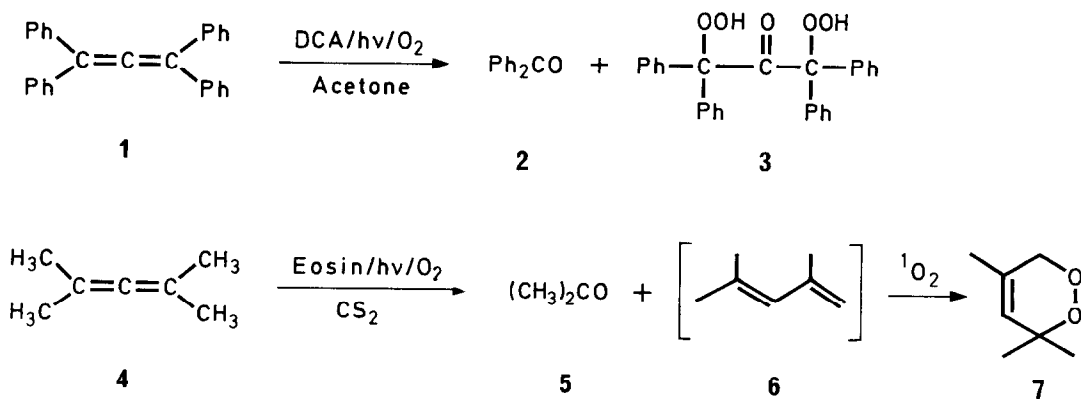
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TPP-sensitized photooxygenation of tetramethylallene (4) in carbon tetrachloride yields acetone (5), 2,4-dimethyl-4-hydroxy-1-penten-3-one (8) and 2,4-dimethyl-1,4-pentadien-3-one (9) in a ratio of 35:20:45, besides minor amounts of resinous products and carbon dioxide. Isomerization of 4 to 2,4-dimethyl-1,3-pentadiene (6) does not occur under the reaction conditions. DABCO quenches the photooxygenation, whereas 2,4,6-tri-*t*-butylphenol (10) enhances the oxygen consumption rate but leaves the ratio of 5:8:9 unchanged. These results indicate that 4 is oxygenated by singlet oxygen. A mechanism is proposed according to which acetone is generated via a (2+2) cycloaddition whereas 8 and 9 are formed via an ene-reaction between 4 and singlet oxygen.

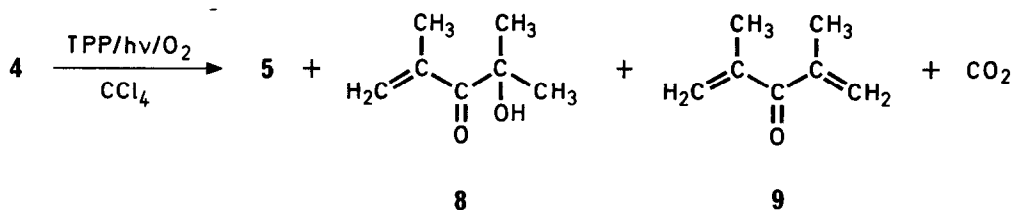
We have recently shown that tetraphenylallene (1) does not react with singlet oxygen (1O_2); it is, however, readily converted to benzophenone (2) and 1,3-dihydroperoxy-1,1,3,3-tetraphenyl-2-propanone (3) if submitted to the 9,10-dicyanoanthracene (DCA)-sensitized electron-transfer photooxygenation in acetone¹.

Tetramethylallene (2,4-dimethyl-2,3-pentadiene) (4) was reported by Crandall and Machleder² to be unreactive toward singlet oxygen generated from $H_2O_2/NaOCl$, whereas Greibrokk³ reported that 4 gave small amounts of acetone (5) and the cyclic product 7 as the main product on irradiation in CS_2 in the presence of oxygen and eosin. The latter product was believed to be formed by a photo-induced isomerization of 4 to 2,4-dimethyl-1,3-pentadiene (6) followed by a (4+2)-cycloaddition of singlet oxygen to 6³.



We now wish to report our results on the tetraphenylporphyrin (TPP)-sensitized photooxygenation of 4 in carbon tetrachloride.

Tetramethylallene (4; b.p. 86.5-87.5°C/760 Torr), prepared after Morton et al.⁴, was free of its isomer 6; it showed one peak in vpc and a singlet at 1.60 ppm in its ¹H NMR spectrum in CDCl₃. If 4 was irradiated in CCl₄ in the presence of oxygen and TPP, 4 consumed 1.3 molecules of O₂⁵. The ¹H NMR spectra taken immediately after the oxygen consumption ceased showed that the reaction mixture contained, besides less than 1% of 4 and about 5% of resinous products, only acetone (5), 2,4-dimethyl-4-hydroxy-1-penten-3-one (8) and 2,4-dimethyl-1,4-pentadien-3-one (9) in a ratio of 35:20:45⁷. In addition, the reaction mixture contained about 7% of CO₂⁹. Samples taken during the photooxygenation reaction did not show observable amounts of 6 or 7 thus excluding any isomerization of 4 to 6¹⁰.

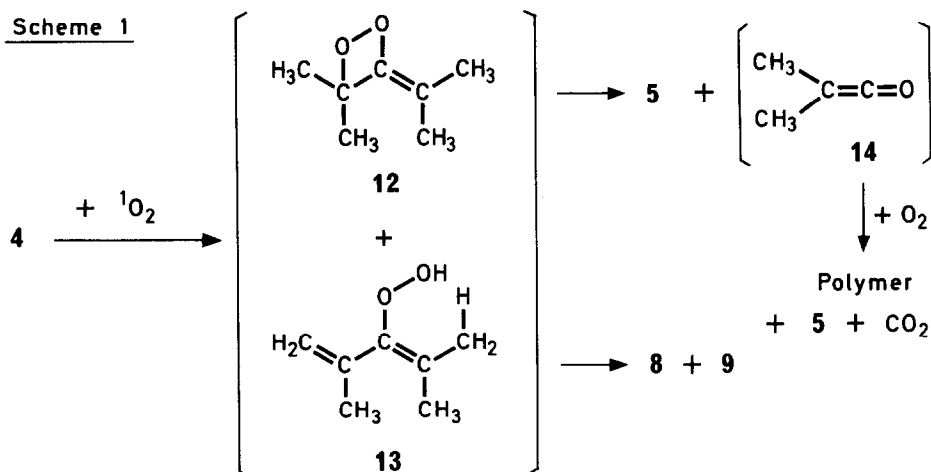


With TPP in CCl₄, photosensitization of an electron-transfer oxygenation is very unlikely to occur; even with DCA, a typical photosensitizer for such processes in polar solvents, only singlet oxygen reactions are observed in non-polar solvents such as CCl₄¹¹. On the other hand, TPP is a very efficient photosensitizer for the formation of ¹O₂. However, compared to the singlet oxygen reaction of our standard acceptor 2,5-dimethylfuran (DMF), the rate of oxygen consumption by 4 is rather slow, with a quantum yield of about 10⁻² at concentrations of 4 of 5·10⁻² M¹².

Thus, in order to distinguish between a singlet oxygen reaction and an autoxidation reaction via free radicals, the TPP-sensitized photooxygenation of 4 in CCl₄ was performed in the presence of 1,4-diazabicyclooctane (DABCO) as a singlet oxygen quencher¹⁴ on the one hand, and in the presence of 2,4,6-tri-*t*-butylphenol (10) as a free radical scavenger on the other. 0.05 M of DABCO quenched the oxygen uptake to practically nil¹⁵. If 0.10 M of 4 was submitted to the photooxygenation in the presence of 0.05 M of 10, the oxygen consumption rate was enhanced¹⁶. The total consumption of oxygen was raised from 0.13 M (without 10) to 0.18 M (with 10), indicating that 10 had taken up one molecule of oxygen¹⁷. According to the ¹H NMR spectra taken immediately after the O₂-consumption ceased, 2,4,6-tri-*t*-butyl-4-hydroperoxy-2,5-cyclohexadienone (11)¹⁸ was generated from 10 in addition to products 5, 8 and 9 from 4, the ratio of which remained unchanged.

All these results indicate that 5, 8 and 9 are generated by ¹O₂-reactions with 4. Since these reactions proceed with low quantum yields, the H₂O₂/NaOCl-method is rather inappropriate to generate singlet oxygen as was shown for α-pinene as another relatively unreactive substrate²⁰.

Scheme 1 rationalizes the formation of 5 as occurring via the (2+2) cycloaddition product 12 followed by cleavage into 5 and ketene 14²¹, that of 8 and 9 as occurring via the ene-product 13²⁴ which, as an unstable vinyl hydroperoxide, immediately rearranges to 8²⁵ or eliminates water to give 9²⁶. It thus appears that singlet oxygen is able to undergo (2+2) cycloaddition and ene-reactions with alkyl-substituted allenes, i.e. that ¹O₂ reacts in the same manner as it does with alkyl-substituted olefins and acyclic 1,3-dienes, though with rather reduced quantum yields.



Studies on photosensitized oxygenations of allenes are continued.

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

References and Footnotes

1. K.Gollnick, A.Schnatterer, *Tetrahedron Lett.* 26 (1985), 173.
2. J.K.Crandall, W.H.Machleder, *J. Am. Chem. Soc.* 90 (1968), 7292.
3. T.Greibrokk, *Tetrahedron Lett.* 1973, 1663.
4. D.M.Hilvert, M.D.Jacobs, T.H.Morton, *Org. Prep. Proc. Int.* 13 (1981), 197.
5. A 150 ml irradiation unit with automatic oxygen consumption registration was used for preparative oxygenations⁶. 0.2 M of **4** was irradiated in 150 ml of oxygen-saturated CCl₄ in the presence of 8·10⁻⁴ M of TPP; Tight source: Philips HPK 125 W.
6. K.Gollnick, G.O.Schenck, Ch. 10 in J.Hamer, ed., "1,4-Cycloaddition Reactions; the Diels-Alder Reactions in Heterocyclic Syntheses"; Academic Press, New York, 1967, p.255.
7. After removal of CCl₄ and **5** by distillation at normal pressure, **8** and **9** were isolated by fractional distillation of the residue at reduced pressure in the presence of tri-*t*-butylphenol in order to avoid polymerization of these products. **9** is rather volatile and thus co-distills partly with the solvent.
5: ¹H NMR (Bruker, WP-80-CW spectrometer; CCl₄, TMS as internal standard): δ = 2.06 (s,6H); 2,4-Dinitrophenylhydrazone: m.p. 125-126°C.
8: b.p. 58-60°C/11 Torr; ¹H NMR (CDCl₃, TMS): δ = 1.51 (s,6H); 1.95 (m,3H); 4.13 (s,1 OH); 5.85 (m,1H); 6.00 (m,1H). - All data identical with those obtained from **8** synthesized independently according to ref. 2.
9: b.p. 73-74°C/110 Torr; ¹H NMR (CDCl₃, TMS): δ = 1.94 (m,6H); 5.69 (m,4H). - 2,4-Dinitrophenylhydrazone m.p. 147-148°C. - All data identical to those obtained from **9** synthesized independently according to ref. 8.
8. A.Raphalen, G.Sturtz, *Bull. Soc. chim. France* 1971, 2962.

9. After the oxygen consumption of 4 ceased, the irradiation unit was connected to 2 flasks filled with Ba(OH)₂-solution. N₂ was blown through the unit until all CO₂ had precipitated as BaCO₃; the latter was dried and weighed. 4 gave thus rise to 7% of CO₂ calculated by assuming that one molecule of 4 yields one molecule of carbon dioxide.
10. If 6 is irradiated in CCl₄ in the presence of TPP and oxygen, the cyclic peroxide 7 is nearly quantitatively (97%) formed with a rather fast oxygen consumption rate: A.Griesbeck, Dissertation, University of München, 1984.
11. a. A.Schnatterer, Diplomarbeit, University of München, 1982; b. K.Gollnick, A.Schnatterer, manuscript in preparation.
12. A 20 ml irradiation unit with automatic oxygen consumption recording system was used: H.Paur, Dissertation, University of München, 1982. A Hg-high pressure lamp (Philips, HPK 125 W) was used as a light source; in order to cut off wavelengths shorter than 490 nm, filter glass GG 14 (Fa.Schott, Mainz) was applied. - 5·10⁻² M of 4 in oxygen-saturated CCl₄ in the presence of 8·10⁻⁴ M of TPP consumed 1.3 moles of O₂ per mole of 4. The rate of oxygen uptake at the initial concentration of 4 was 0.059 ml/min. Under the same conditions, DMF absorbed oxygen with a rate of 5.89 ml/min. Assuming that the latter reaction occurs with a quantum yield of unity¹³, the quantum yield of oxygen uptake at the initial concentration of 4 equals 10⁻².
13. K.Gollnick, A.Griesbeck, Tetrahedron 40 (1984), 3235.
14. C.Ouannes, T.Wilson, J. Am. Chem. Soc. 90 (1968), 6228.
15. In the presence of 0.025 M of DABCO, the rate of oxygen consumption is reduced from 0.059 ml/min (see ref. 12) to 0.0032 ml/min. I.e., the quantum yield decreases from 10⁻² to about 5·10⁻⁴.
16. Kinetic studies revealed that the interaction of ¹O₂ with 10 that results in product formation is about four times larger than that with 4 which produces 5 + 8 + 9 : A.Schnatterer, unpublished results.
17. For reactions of singlet oxygen with phenols, see C.S.Foote, Ch. 5 in H.H.Wasserman, R.W.Murray, eds., "Singlet Oxygen"; Academic Press, New York, 1979, p.139.
18. 11 was also synthesized by TPP-sensitized photooxygenation of 10 in CCl₄ in the absence of 4. - 11: ¹H NMR: δ = 0.94 (s,9H); 1.22 (s,18H); 6.55 (s,2H); 7.67 (s,1 OH); in accord with ref. 19.
19. M.J.Thomas, C.S.Foote, Photochem. Photobiol. 27 (1978), 683.
20. K.Gollnick, G.O.Schenck, Pure Appl. Chem. 9 (1964), 507.
21. Oligomerization of 14 as well as reactions of 14 with ¹O₂²² or ³O₂²³ should afford resinous products and additional amounts of 5 + CO₂, respectively.
22. W.Adam, H.C.Steinmetzer, Angew. Chem. Int.,Ed. Engl. 11 (1972), 540.
23. H.Staudinger, K.Dyckerhoff, H.W.Klever, L.Ruzicka, Ber. dtsch. chem. Ges. 58 (1925), 1079.
24. (2+2)-Cycloaddition reactions and ene-reactions of alkyl-substituted allenes with electron-deficient enophiles have been reported; e.g. C.B.Lee, R.J.J.Newman, D.R.Taylor, J. Chem. Soc. Perkin I, 1977, 1161.
25. To our knowledge, vinyl hydroperoxides have not yet been isolated; they have been postulated, however, quite frequently as intermediates in ozonolysis reactions which rearrange to α-hydroxy ketones: see, e.g., a. P.R.Story, J.R.Burgess, J. Am. Chem. Soc. 89 (1967), 5726; b. R.Criegee, Angew. Chem. 87 (1975), 765, and lit. cited.
26. 8 is not dehydrated under the reaction conditions applied; 9 should therefore be formed from 13 rather than from 8.

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