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FORMATION OF A 1,2-DIOXANE BY ELECTRON-TRANSFER PHOTOOXYGENATION OF 1,1-DI(p-ANISYL)ETHYLENE

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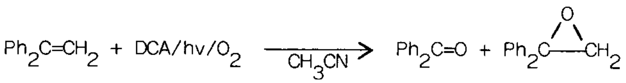
Summary: A new mode of electron-transfer photooxygenation is shown to occur with the title compound (4). With this electron-rich ethylene derivative, DCA-sensitization in acetonitrile gives rise to the quantitative formation of a cyclic peroxide (5) by cycloaddition of 2 molecules of 4 and 1 molecule of O_2. A mechanism is outlined for this reaction.

Electron-transfer photooxygenation has received much attention during the last six years[1]. Olefins, acetylenes, sulfides, and aryl-substituted saturated three-membered ring compounds are oxidized on irradiation in O_2-saturated polar solvents in the presence of cyano-aromatics as photosensitizers.

As with other phenyl-substituted ethylenes, Eriksen and Foote[2] showed that 9,10-dicyanoanthracene (DCA) photosensitized oxygenation of 1,1-diphenylethylene (1) yields the typical electron-transfer photooxygenation products, carbonyl compounds and oxiranes, in this case benzophenone (2) and 2,2-diphenyloxirane (3).

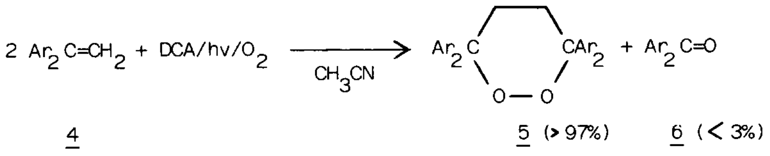


$$Ph_2C{=}CH_2 + DCA/h\nu/O_2 \xrightarrow[CH_3CN]{} Ph_2C{=}O + Ph_2\overset{O}{C{-}CH_2}$$

1 2 3

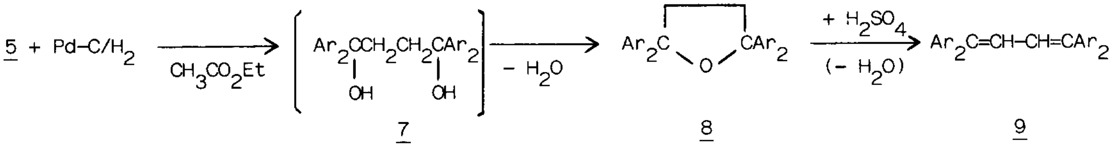
We now wish to report on the DCA-sensitized oxygenation of 1,1-di(p-anisyl)-ethylene (4) in oxygen-saturated acetonitrile[3] which exhibits a novel mode of electron-transfer photooxygenation.

4 absorbs exactly half a molecule of oxygen. If the reaction solution is left for some time in the dark, the cyclic peroxide 5 precipitates quantitatively from the solution[5a,b]. The solution itself contains less than 3% of p,p'-dimethoxybenzophenone (6) and less than 1% of the starting material (4)[5c,7].



Ar = p-CH$_3$O-C$_6$H$_4$-

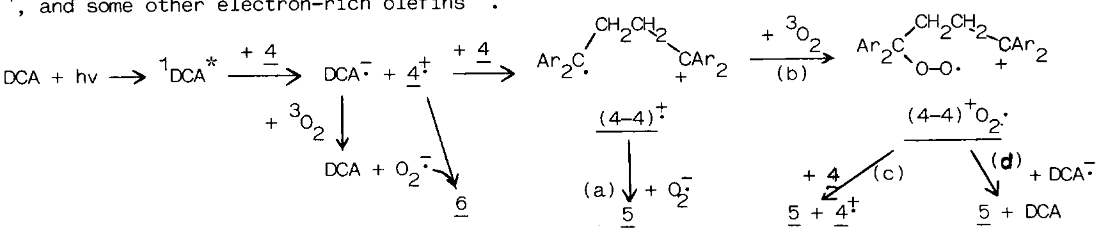
The structure of the cyclic peroxide 5 is unequivocally that of 3,3,6,6-tetra-(p-anisyl)-1,2-dioxane as revealed by elemental analysis, molecular weight and spectroscopic data as well as by catalytic hydrogenation and subsequent treatment with sulfuric acid:



Ar = p-CH$_3$O-C$_6$H$_4$-

Diol 7 expected as the hydrogenation product of 5 is not isolated under our reaction conditions; 7 eliminates one molecule of water to form the previously unknown tetrahydrofuran derivative $8^{9a,b}$. Heating of 8 in acetic acid in the presence of H$_2$SO$_4$ yields the 1,3-butadiene derivative 9^{9c}.

Singlet oxygen is not responsible for the production of 5 and 6 from 4[11]. Since 4 quenches the fluorescence of DCA considerably, it is safe to assume that interaction of ^{1}DCA* (the excited singlet state of DCA) with 4 leads to an electron transfer from 4 to ^{1}DCA* to form $4^{+\cdot}$ and DCA$^{-\cdot}$; phenyl-substituted ethylenes which are less electron-donating molecules than 4, were unequivocally shown to undergo such processes[2,12]. Interaction of DCA$^{-\cdot}$ with $^3O_2$ yields DCA and $O_2^{-\cdot}$, the superoxide anion radical; reaction of the latter with $1^{+\cdot}$ gives rise to products 2 and 3[2]. In the case of $4^{+\cdot}$, interaction with $O_2^{-\cdot}$ to give 6 is obviously much slower than with 4 and has only a chance after 4 has decreased to rather low concentrations. Interaction of $4^{+\cdot}$ with 4 should yield a more stable radical cation $(4\text{-}4)^{+\cdot}$. Such dimerizations have been observed in O$_2$-free solutions of p-methoxystyrene[13], 1[14], and some other electron-rich olefins[15].



We may consider several pathways for the production of 5 from $(4\text{-}4)^{+\cdot}$: first, interaction with $O_2^{-\cdot}$ should lead directly to 5 (path (a)); second, interaction with $^3O_2$ should lead to another radical cation, $(4\text{-}4)^{+}O_2^{\cdot}$ (path (b)), which on electron transfer from $DCA^{-\cdot}$ forms 5 and regenerates DCA (path (d)); third, $(4\text{-}4)^{+}O_2^{\cdot}$ is formed via path (b), but this time it reacts with another molecule of 4 to give 5 along with a new $4^{+\cdot}$ (path (c)). All pathways account for the fact that two molecules of 4 are consumed per one molecule of oxygen. Paths (a) and (b)/(d) should proceed with limiting quantum yields of 2 for the disappearance of 4. Path (b)/(c), however, represents a chain reaction the quantum yield of which may well exceed a value of 2. The radical chain reaction should be terminated by path (d).

The ratio of oxygen-uptake rates of 4 and *trans*-stilbene determined at same concentrations ($2\cdot10^{-2}$ M) equals about 12. The quantum yield of *trans*-stilbene disappearance at this concentration is estimated from Foote's paper[2] to be about 0.4. With this value, the quantum yield of O_2-consumption by 4 is about 5, and, consequently, the quantum yield of disappearance of 4 should be about 10. The production of 5 via a radical chain reaction is, therefore, suggested. The sensitivity of the production of 5 to impurities[7] is also compatible with this mechanism.

Investigation of 1,2-dioxane formation by electron-transfer photooxygenation of other electron-rich ethylenes is presently carried out at our laboratory.

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References and Footnotes

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3. 20 ml irradiation units[4a,b] and 150 ml irradiation units[4c,d] with automatic O_2-consumption recording systems were used. Irradiation was carried out with a Hg-high-pressure lamp (Philips HPK125W); to cut-off wavelengths shorter than 405 nm, a 1 cm path-length filter solution was used which was prepared from 2.7 g $CuSO_4\cdot5H_2O$, 3.0 g $NaNO_3$ and 5 ml of conc. NH_4OH diluted with water to 100 ml. 2.5 and $3.3\cdot10^{-2}$ M 4 + $2\cdot10^{-4}$ M DCA in oxygen-saturated acetonitrile at 13°C were applied.
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5. (a) Elemental analysis and spectroscopic data are in accord with the structures described; (b) 5: 90% yield of isolated colorless solid (from ethyl acetate); m.p. 211-212°C; m.w.: 513 (calc.), 517 (osmometric in benzene); ^{1}H-nmr ($CDCl_3$, 80 MHz): δ = 2.48 (s, broad, 4 H) 3.74 (s, 4 OCH_3), 6.84 (m, 8 arom. H), 7.22 (m, 8 arom. H).- (c) 6: colorless crystals (from ethanol); m.p. 142°C (144°C, ref.6).
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7. The purity of acetonitrile appears to be of critical importance; if it is not well enough purified[8], a decreasing oxygen-uptake rate is observed along with decreased amounts of 5 and increased amounts of 6. Similar results are obtained with acetone as a solvent.
8. Purification according to W.Bunge, Eigenschaften und Reinigung der wichtigsten organischen Lösungsmittel, in Houben-Weyl, Handbuch der organischen Chemie, 4th ed., Vol. I/2, Thieme Verlag, Stuttgart, 1959, p.828.
9. (a) Elemental analysis and spectroscopic data are in accord with the structures described; (b) 8: colorless crystals (from ethanol/ethyl acetate); m.p. 187-188°C; ^{1}H-nmr: δ = 2.55 (s, 4 H), 3.67 (s, 4 OCH_3), 6.69 (m, 8 arom. H), 7.24 (m, 8 arom. H).- (c) 9: yellowish-green crystals (from acetic acid); m.p. 202-203°C (203-204°C, ref.10).
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11.(a) If 4 is irradiated in acetonitrile in the presence of the singlet-oxygen sensitizer rose bengal[4d], a very slow oxygen-consumption is observed; the reaction product is mainly polymeric material which contains very little amounts of 6 but no traceable amounts of the cyclic peroxide 5. Irradiation of 4 in the presence of DCA in non-polar solvents such as CCl_4[11b] leads in a very slow O_2-consuming reaction to a complex product mixture which contains neither 6 nor the cyclic peroxide 5.

   (b) DCA is a rather potent singlet oxygen sensitizer in non-polar solvents:A.Schnatterer, Diplomarbeit, München 1982; L.E.Manring, C.L.Gu, C.S.Foote, J.Phys.Chem. 87 (1983), 40.
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