Tetrahedron Letters No.47, pp. 4105-4108, 1970. Pergamon Press. Printed in Great Britain.

PHOTO-OXIDATION OF 1,2,3,4-TETRACHLORO-9,10-DIHYDRO-9,10-DIMETHOXYETHENOANTHRACENE

J. Font, F. Serratosa and L. Vilarrasa

Instituto de Química. Centro de Investigación y Desarrollo de Barcelona.
Patronato "Juan de la Cierva". Zona Universitaria. Barcelona-17

(Received in UK 3 August 1970; accepted for publication 10 September 1970)

IN a recent communication[1] we have reported that adducts of type I (X = Cl or F), in the open atmosphere, are slowly transformed into diesters II (X = Cl or F) by some sort of a reverse acyloin condensation induced by molecular oxygen. However, since we have seen later on that adducts I are completely stable in the dark, even in the presence of pure oxygen, and the spontaneous oxidations were observed during the sunny summer days[2], we have investigated now for a photo-oxidation of the electron-rich olefinic double bond of I.

When oxygen was bubbled in the dark for 18 hrs into a 0.5% benzene solution of 1,2,3,4-tetrachloro-9,10-dihydro-9,10-dimethoxyethenoanthracene (I, X = Cl; m.p. 172º; λ_{max} (cyclohexane) 222, 276 and 309 nm (ε = 28,200; 2,730 and 2,090); ν_{max} (KBr) 1685 cm^{-1} (C=C st)), no oxidation at all was observed, even when the solution was heated up to reflux.

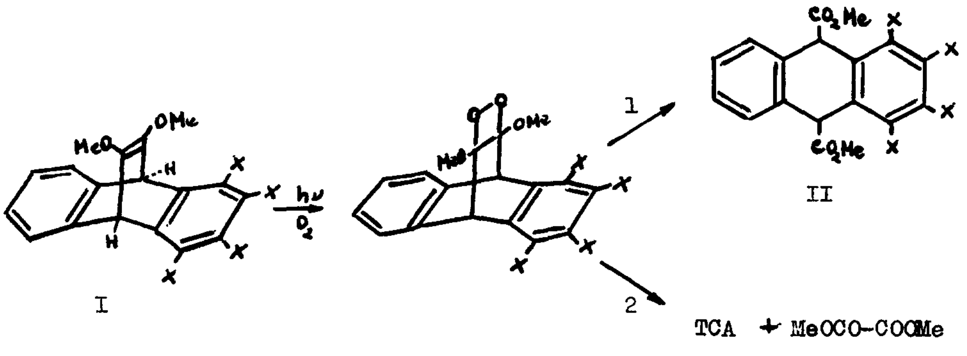
The same solution was irradiated with a 40 W commercial incandescent bulb in the presence of oxygen: after 2 hrs the i.r. spectrum showed the presence of the band at 1745 cm^{-1} (C=O st, ester). However, the photo-oxidation was very slow under these conditions. With a 500 W bulb, 110 hrs were necessary to achieve the total oxidation (fade of the C=C st band at 1685 cm^{-1}). No oxidation took place in methanol or acetone solution under these conditions.

Photo-oxidation of I (X = Cl) could be performed more rapidly when 1% benzene solutions were irradiated in a Rayonet photochemical reactor, model RPR-100. With RPR-3500 A lamps in pyrex vessel and in the presence of oxygen quantitative oxidations were achieved in 15 minutes (similar results in acetone solution, but only partial oxidation in hexane). With RPR-3000 A lamps in quartz vessel only partial oxidation took place after 15 minutes, but quantitative oxidation was achieved in 15 minutes if small amounts of 1,2,3,4-tetrachloroanthracene (TCA) were added to the solution.

In these photo-oxidations <u>cis</u>-1,2,3,4-tetrachloro-9,10-dihydro-9,10-dicarbomethoxyanthracene (II, X = Cl) was obtained together with a 8% yield of TCA, isolated by preparative t.l.c. Diester II (X = Cl) shows m.p. 270-271º; λ_{max} (cyclohexane) 215 nm (ε = 39,100); ν_{max} (KBr) 3020, 2990, 1745, 1500, 1280, 1200 and 1160 cm^{-1}; τ ($DCCl_3$) 2.40 (m, 4-H), 4.45 (s, 2-H) and 6.30 (s, 6-H); found 49.56 %C; 3.01 %H and 32.22 %Cl; requires 49.81 %C, 2.79 %H and 32.67 % Cl.

Although the best known sensitized photo-oxidation pathway of olefins is that leading to allylic peroxides[3], several examples of cleavage of double bonds by singlet oxygen have been reported, requiring however specially activated alkenes (amino or alkoxy groups as substituents) and the absence of active allylic hydrogen in the molecule[4]. Very recently isolation of dioxetanes as intermediates have been achieved in the photo-oxygenation of di- and tetraalkoxyethylenes at low temperatures[5]. Singlet oxygen is also probably involved in our oxidations since irradiation of 1% benzene solutions of I (X = Cl) in the presence of oxygen and tertiary amines (e.g. triethylamine), which are known to be good scavengers of singlet oxygen[6], give no traces of diester II (X = Cl), the adduct being recovered quantitatively.

The formation of TCA during the photo-oxidation and the fact that this compound acts as a good sensitizer for this reaction suggest a mechanism in which dimethoxyacetylene could be first photoextruded, and the TCA just formed would further sensitize competitively the photo-oxygenation. Nevertheless, irradiation of a benzene or an ether solution of pure adduct I (X = Cl), even with RPR-2537 A lamps, did not afford any TCA, and therefore the photolytic extrusion of dimethoxyacetylene must be excluded. Most probably TCA is formed through the dioxetane intermediate which can break down competitively either into diester II (X = Cl) (path 1) or into TCA and methyl oxalate (path 2)(some attempts to detect methyl oxalate in the photo-oxidation product have been unsuccesful, probably due to the small amounts of product we were dealing with.)



If this is the case, then the reaction is an autosensitized photo-oxidation of an electron-rich alkene through the formation of an 1,2-dioxetane, despite the presence of very active, doubly benzylic, allylic hydrogens in the molecule.

We have synthesized TCA in order to check its structure, and it is worth while to mention here that the white crystalline compound, m.p. 151-152º, described in the chemical literature[7] as the 1,2,3,4-tetrachloroanthracene is in fact its 9,10-dihydro derivative: found 52.55%C, 2.49%H and 44.56%Cl; requires 52.87%C, 2.55%H and 44.58%Cl; λ_{max} (cyclohexane) 217 nm (ε = 33,300); ν_{max} (KBr) 3060, 3030, 2890, 1500, 1410, 1390 and 740 cm^{-1}; τ (CS_2) 2.75 (s, 4-H) and 5.9 (s, 4-H). However, the true polyaromatic compound could be easily obtained by treatment of the 9,10-dihydro derivative with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone[8] in boiling benzene, as a yellow crystalline compound, m.p. 217-219º: found 53.18%C, 1.99%H and 44.62%Cl; requires 53.21%C, 1.90%H and 44.88%Cl; λ_{max} (cyclohexane) 225, 232, 258, 267, 323, 339, 355 and 374 nm (ε = 12,400; 13,800; 117,000; 220,000; 1,960; 3,920; 7, 310 and 10,600); ν_{max} (KBr) 3025, 1600, 1550, 1430, 880, 780 and 730 cm^{-1}; τ (CS_2) 1.15 (s, 2-H), 1.8-2.1 (m, 2-H) and 2.25-2.5 (m, 2-H).

REFERENCES

1. J. Font, F. Serratosa and L. Vilarrasa, Tetrahedron Letters, 1969, 4743.
2. In Barcelona, latitude 41º 23′N, we could expect a similar total number of quanta incident per second per square centimer of horizontal surface as in Cleveland (Ohio, latitude 41.5º N), *i.e.*, 2 x 10^{15} for λ 3500 A (data from J.G. Calvert and J.N. Pitts, "Photochemistry", John Wiley, New York, 1966, p. 722).
3. K. Gollnick and G.O. Schenck, in "Organic Photochemistry", IUPAC, Butterworths, London, 1965, p. 507; C.S. Foote, Accounts Chem. Research, 1968, 1, 104.
4. C.S. Foote and J. Wei-Ping Lin, Tetrahedron Letters, 1968, 3267; W. Fenical D.R. Kearns and P. Radlick, J. Am. Chem. Soc., 1969, 91, 3396; A. Miyake and M. Tomoeda, Chem. Comm., 1970, 240; R.S. Atkinson, Chem. Comm., 1970, 177; J. Font, S.C. Barton and O.P. Strausz, Chem. Comm., 1970, 499.
5. P.D. Bartlett and A.P. Schaap, J. Am. Chem. Soc., 1970, 92, 3223; S. Mazur and C.S. Foote, ibid., 3225.
6. C. Ouannés and T. Wilson, J. Am. Chem. Soc., 1968, 90, 6527.
7. G. Kircher, Ann. Chem., 1887, 238, 338.
8. E.A. Braude, A.G. Brook and R.P. Linstead, J. Chem. Soc., 1954, 3564.