Tetrahedron Letters, Vol.30, No.4, pp 485-488, 1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

SYNTHESIS OF 1,2-DIOXETANES VIA 9,10-DICYANOANTHRACENE-SENSITIZED CHAIN ELECTRON-TRANSFER PHOTOOXYGENATIONS

Luigi Lopez[a]*, *Luigino Troisi*[a] *S.M.Khaledur Rashid*[b] *and A. Paul Schaap*[b]*

a) CNR.Centro di Studio Sulle Metodologie Innovative di Sintesi Organiche.
Dipartimento di Chimica, Università di Bari, via Amendola 173, 70126 Bari Italy.
b) Department of Chemistry, Wayne State University, Detroit, MI 48202 USA.

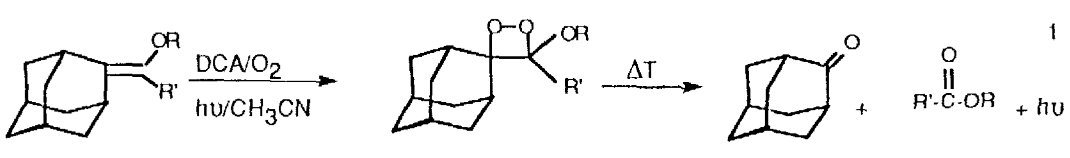
Abstract: Thermally stable 1,2-dioxetanes have been syntesized by 9,10-dicyano-anthracene (DCA)-sensitized photooxygenation of alkoxy (aryl)-methylidene adamantanes. The reactions most likely proceed via a chain electron-transfer process.

In the last two decades, a great number of papers have been devoted to the synthesis of 1,2-dioxetanes through chemical[1] and photochemical[2] procedures.These novel cyclic peroxides exhibit a wide range of thermal stabilities, strictly related to their structures and their competing chemilumescent fragmentation mechanism[3].

Among the few methods that are alternative to the Kopecky's and [2+2] -singlet oxygenation route, it is worthwhile to mention the electrochemical[4] and thermal oxidation of sterically hindered alkenes by means of one-electron oxidizing agents [5] and above all the sensitized photooxygenation of unsaturated organic substrates induced by fluorescent electron-deficient sensitizers[6].

We wish to report herein the results of our continuing studies [7] on (DCA) [E^{red}= -0.98 V vs SCE; E_S= 68 Kcal/mol] sensitized photooxygenation of several enol-ethers (**1,5**), also subsiding an easy functionalization *via* singlet oxygen[8] and with molecular oxygen *via* a chain induced cation radical process[5-9].

Typical experimental conditions for the synthesis of 4-alkoxy-(1-aryl) spiro [1,2-dioxetane-3,2' adamantanes] (**6,10**) are as follows: *oxygen-saturated dry acetonitrile solutions of (1,5) ($1x10^{-2}$M)* in the presence of (DCA) ($2x10^{-4}$M) are irradiated , at 0°C, with a 1000 Watt mercury lamp through a $CuSO_4$ filter solution so that only the acceptor absorbs light (eq.1).



(1,5) **(6,10)** **(11)** **(12,16)**

1. R=Me, R'=Ph; **2**. R=Me, R'=1-Np; **3**. R=Me, R'=2-Np; **4**. R=Bz, R'= Ph ; **5**. R=Me, R'=4,4'-Biph.

The progress of the reactions was monitored by tlc (hexane:ethylacetate 20:1 as eluant) and/or by ^{1}Hnmr spectroscopy by integration of their alkoxy peak absorptions until the total disappearance of the starting material (less than 1h). The dioxetanes (**6**,**10**) (90-95% yield), easily isolated by filtration of the reaction mixtures over a short silica gel colummn, were fully characterized by physical and spectral data[10], comparison with independently synthesized authentic samples [8,9] and chemiluminescent thermal fragmentation into 2-adamantanone (**11**) and the corresponding esters (**12**,**16**)[10].

The key step, in these (DCA)-sensitized photooxygenations of enol-ethers, involves a diffusion controlled rate electron-transfer fluorescence quenching of the singlet excited (DCA*) by the electron donors (**1**,**5**) with the generation of the radical ion pairs ($DCA^{\cdot -}$ $1,5^{+\cdot}$). In the table 1 are reported the CV measured oxidation potentials of the substrates and the free energy change (D G) calculated through the Weller equation [11].

Table 1. Oxidation Potentials and the ΔG of Electron-Transfer from the Enol-Ethers to DCA.

Substrate	$(E_D^{ox})^a$	ΔG(Kcal/mol)^b
1	1.29	-14.8
2	1.29	-14.8
3	1.28	-15.0
4	1.30	-14.5
5	1.27	-15.2

[a] All the oxidation potentials are reported in V vs Ag/AgCl in acetonitrile containing 0.1 M tetraethylammonium perchlorate with a scan rate of 500mV/sec.

[b] Oxidation potential of DCA has been reported to be -0.98 V vs SCE, a correction factor for Ag/AgCl to SCE was employed for the calculation of ΔG.

Seemingly, formation of the ultimate products (**6**,**10**) could be easily rationalized on the basis of the classical mechanism operating in the (DCA)-sensitized photooxygenation of appropriate electron-donor substrates, and involving a further electron-transfer process between the reduced sensitizer ($DCA^{\cdot -}$) and molecular oxygen with formation of superoxide ion $O_2^{\cdot -}$ which coupling with the cation radicals would afford the oxygenated products. [6-12]

However, the proneness of our substrates to the functionalization with singlet oxygen [8], and above all of the intermediate cation radicals, thermally generated, with molecular oxygen[5-9] induced us to investigate in this process.

First of all, the absence of any appreciable effect, observed in similar reactions carried out in the presence of p-benzoquinone (BQ), an efficient superoxide quencher[13], seems to leave out the exclusive involvement of superoxide anion, as the only oxygen active species involved in these (DCA)-sensitized photoinduced oxidation processes[14,15]. On the other hand, the inhibition, from total to partial, observed in three different reactions carried out on **4**, in the presence of progressively reduced amounts of 1,4-diazabicyclo [2,2,2]-octane (DABCO), indicates a different mechanism respect to that generally accepted[6]. In fact, (DABCO) is not only an efficient singlet oxygen quencher[16] , but at the same time it shows an oxidation potential (E^{ox}= 0.64 V vs SCE), lower than those of our substrates and so more easily oxidizable[7a,17] . This latter feature substantiates that the observed inhibition could be due to an easier electron-transfer process between the singlet excited sensitizer (DCA*) and (DABCO). Thus would inhibit or reduce, depending on (DABCO) concentration, the formation of the radical cations ($1,5^{\cdot+}$). Finally, the very high limiting quantum yield, calculated for the (DCA)-sensitized photooxygenation of (**4**) $\Phi=23.9$,[18] strongly supports a chain electron transfer mechanism in which the oxygen active species is the molecular oxygen, as depicted in the following scheme.

$$(\mathrm{DCA}) \xrightarrow{h\nu} (^{1}\mathrm{DCA}^{*})$$

$$(^{1}\mathrm{DCA}^{*}) + (\mathbf{1,5}) \longrightarrow (\mathrm{DCA}^{\cdot-}\quad 1,5^{\cdot+}) \longrightarrow (\mathrm{DCA}^{\cdot-}) + (1,5^{\cdot+})$$

$$(1,5^{\cdot+}) + O_2 \longrightarrow (1,5\ O_2^{\cdot+}) \longrightarrow (\mathbf{6,10}) + (1,5^{\cdot+}) \longrightarrow \quad \longrightarrow$$

In other words, the cation radicals ($1,5^{\cdot+}$), generated in the electron-transfer fluorescence quenching of the excited (DCA), easily escape out of the cage of the geminate pair, and the reaction of these cation radicals with molecular oxygen is fast enough, to favourably compete, either with the diffusion controlled recombination of the radical ions, either with the reduction process of molecular oxygen in the presence of the reduced sensitizer radical anion ($\mathrm{DCA}^{\cdot-}$).
Further detailed investigations in the area are warrented in the effort to rationalize, in relation to the physical properties of the cation radicals intermediate, the actual mechanism operanting in the (DCA)-sensitized photooxygenation processes.

Acknowledgements: This research has been supported by CNR (Rome) Progetti Strategici "Trasferimento Monoelettronico", A.P.S. also wishes to acknowledge support from the U.S. Army Office.

References and Footnotes.

1) Kopecky, R.K.; Mumford, C. Can. J. Chem. **1969**, 47, 709.
2) (a) Bartlett, P.D.; Schaap, A.P. J.Am.Chem.Soc. **1970**, 92, 3223; (b) Mazur, S.; Foote C.S. J.Am.Chem.Soc. **1970**, 92, 3225.
3) Adam, W.; Arias Ercanacion, L.A.; Zinner, K. Chem. Ber. **1983**, 116, 839 and refs therein.

4) Clennan,E.L.; Simmons, W.; Almgreen, C.W. *J.Am.Chem.Soc.* **1981**, 103, 2098.

5) Nelsen, S.F.; Akaba, R.J. *J.Am.Chem.Soc*. **1981**, 103, 2096.

6) (a) Eriksen, J.; Foote,C.S. *J.Am.Chem.Soc*. **1980**, 102, 6083; (b) Schaap, A.P.; Zaklika, K.A.; Bashir Kaskar, L.; M- Fung, L.W. *J.Am.Chem.Soc*. **1980**, 103, 389.

7) (a) Lopez, L. *Tetrahedron Lett.* **1985**, 4383; (b) Schaap, A.P.; Prasad, G; Gagnon, S.D. *Tetrahedron Lett.* **1983**, 3047 and refs. therein.

8) (a) Schaap, A.P.; Handley, R.S.; R.; Giri, B.P. *Tetrahedron Lett.* **1987**, 935.
(b) Schaap, A.P.; Chen, T.S.; Handley, R.S.; De Silva ,R.; Giri, B.P. *Tetrahedron Lett.* **1987**, 1115.

9) Curci, R; Lopez, L.; Troisi,L.; Rashid, S.M.K.; Schaap, A.P. *Tetrahedron Lett.* **1987**, 5319.

10) All the already known reaction products show consistent spectral and chemical data. The characterization of the dioxetanes (**6,10**) has also been performed by thermal chemiluminescent fragmentation, as reported in the refs **8**, and by gc/mass spectroscopy with the identification of their cleavage products *i.e.* 2-adamantanone (**11**) and the corresponding esters (**12, 16**). The new compounds **9,10** show the following physical and spectroscopic data:
4-benzyloxy-4-(phenyl) spiro[1,2-dioxetane-3,2'-adamantane] **9**. Yield 94%; m.p.105-106°C ^{1}Hnmr (CDCl$_3$) d 0.90-2.32 (m,13H), 3.18 (s, 1H), 4.26(d, 1H), 4.62 (d,1H) 7.28-7.75 (m, 10H); ^{13}Cnmr (CDCl$_3$) d 25.91, 26.08, 31.93, 32.30, 32.86, 33.95, 34.84, 36.44, 64.18,95.64, 112.02, 127.13, 127.36, 128.26, 128.29, 128.41, 129.47, 135.00, 138.05; ir (KBr) u 3040, 3015, 2959, 2856, 1230, 1174, 1100, 1066, 1042, 1029, 1008, 972, 955, 802 739 cm^{-1}.
4-Methoxy- 4-(biphenyl) spiro[1,2-dioxetane-3,2'-adamantané] **10**.
Yield 92%; m.p. 123°C; ^{1}Hnmr (CDCl$_3$) d 1.05-2.00 (m, 12H), 2.22 (s,1H), 3.07 (s, 1H), 3.25 (s, 3H), 7.34-7.70 (m, 12H); ^{13}Cnmr (CDCl$_3$) d 25.91, 26.04, 31.54, 31.70, 32.32, 32.93, 33.17 34.76, 36.40, 49.91, 95.45, 112.12, 126.80, 127.09, 127.69, 128.83, 129.14, 133.53,140.19, 142.07; ir (KBr) u 3040, 3905, 2850, 1600, 1440, 1390, 1268, 1188, 1092, 1070,999, 935, 893, 828, 750, 728, 690 cm^{-1}.

11) Knibbe, H.; Rehm, D.; Weller, A *Ber.Bunsenges Phys. Chem*. **1968**, 72, 257.

12) Mann,C.K.; Barnes, K.K. "Electrochemical Reactions in non Aqueous Systems", M. Dekker, New York **1970**.

13) Manring, L.E.; Kramer, M.K.; Foote, C.S. *Tetrahedron Lett.* **1984**, 2523.

14) Schaap, A.P.; Lopez, L. unpublished results.

15) Griffin, G.W. Kirschenheuter, G.P.; Vaz, C.; Umrigar, P.P.; Lankin, D.C.; Christiensen, S. *Tetrahedron* **1985**, 41, 2069.

16) Ouannes, C.; Wilson, T. *J.Am.Chem.Soc*. **1968**, 90, 6527.

17) (a) Mizuno, K.; Kamiyama, N.; Ichinose, N.; Otsui, Y. *Tetrahedron* **1985**, 41, 2207; (b) Gollnick, K.; Schnatterer, A. *Tetrahedron Lett.* **1984**, 25, 2735.

18) Heller, H.G.; Langan, J.R. *J.Chem.Soc. Perkin I* **1981**, 341.

(Received in UK 5 December 1988)