Tetrahedron Letters,Vol.25,No.26,pp 2735-2738,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

FORMATION OF 1,2-DIOXANES BY ELECTRON-TRANSFER PHOTOOXYGENATION OF 1,1-DISUBSTITUTED ETHYLENES

Klaus Gollnick* and Albert Schnatterer

Institut für Organische Chemie der Universität,
Karlstrasse 23, D-8000 München 2, Germany

Electron-rich 1,1-diarylethylenes (1a-e) afford 3,3,6,6-tetraaryl-1,2-dioxanes (3a-e) in high yields (>90%) when subjected to electron-transfer photooxygenation in the presence of DCA. Whereas 1,1-diphenylethylene (1f) and 1,1-di(p-chlorophenyl)ethylene (1h) yield the 1,2-dioxanes 3f and 3h at 30% and less than 10%, respectively, there is negligible (if any) 1,2-dioxane formation with 1,1-di(m-anisyl)ethylene (1i). 1,2-Dioxane formation proceeds in a chain reaction (Scheme 1). N-Vinylcarbazol (1g), however, yields the 1,2-dioxane 3g via the cyclobutane derivative 7 (Scheme 2).

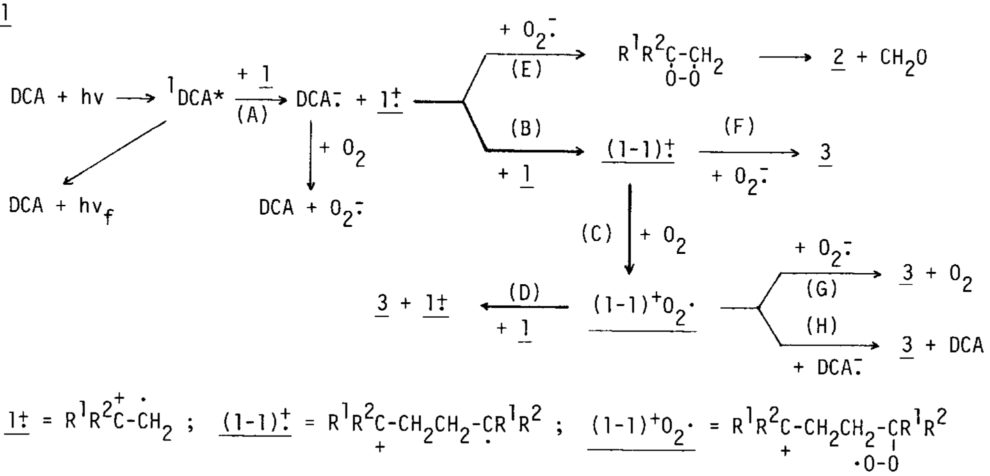
Phenyl-substituted ethylenes such as 1f are reported to yield carbonyl compounds and oxiranes by 9,10-dicyanoanthracene (DCA) sensitized electron-transfer photooxygenation in polar solvents[1].

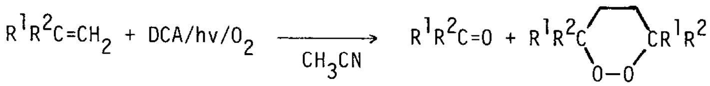
We have recently shown that, in a novel mode of DCA-sensitized electron-transfer-photooxygenation, 1,1-di(p-anisyl)ethylene (1b) yields nearly quantitatively the 1,2-dioxane derivative 3b[2]. Since the quantum yield of disappearance of 1b is well above 2, a chain reaction mechanism according to the sequence of steps A through D of Scheme 1 was proposed [2]. The dimeric radical cation $(1\text{-}1)^{+\cdot}$ should be more stable than the monomeric radical cation $1^{+\cdot}$, and since steps A and D should be favored by ethylenes carrying electron-donating substituents, a study of 1,1-disubstituted ethylenes such as 1a-i at relatively high initial concentrations (which favor step B over step E) seemed to be in order (Table 1).

Ethylenes 1a-e absorb half a molecule of oxygen[3]. 1,2-Dioxanes 3a-e[4] are formed in yields exceeding 90% and are generally isolated in high yields[6]. Ketone (2) formation is thus either negligible (with 1a and 1e) or occurs to small extents (3-10%) with ethylenes 1b-d. 1-(p-Anisyl)-1-phenylethylene (1a) and 1-(p-anisyl)-1-(p-chlorophenyl)ethylene (1d) give rise to 1,2-dioxanes 3a and 3d, respectively, which represent cis/trans-mixtures[4b,e,6]. Neither in the presence of oxygen nor under nitrogen were cyclobutanes or other dimerization products of 1a-e formed, even if under nitrogen the ethylenes were irradiated four times longer than under oxygen.

Quantum yields (Φ) of disappearance of 1 were determined at initial concentrations of 0.025 M by comparing the oxygen-uptake rates of 1 with that of trans-stilbene at 0.025 M. At this concentration, the quantum yield of disappearance of trans-stilbene is estimated from Foote's paper[1] to be about 0.4. For ethylenes 1a-e, Φ decreases from about 15 to 3 indicating chain reactions to occur.

Scheme 1



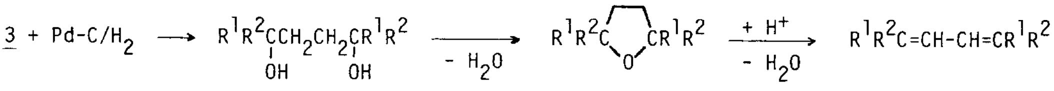


1 2 3

Table 1 : DCA-Photosensitized Oxygenation of Ethylenes in Acetonitrile

1	R^1	R^2	$O_2/1$ [a]	Φ [b]	2 (%)[c]	3 (%)[c]	3 (%)[d]	3-m.p.[e] (°C)
a	p-MeO-C_6H_4	C_6H_5	0.50	15.1	-	100	94	133-144[f]
b	p-MeO-C_6H_4	p-MeO-C_6H_4	0.50	8.3	3	97	90	211-212
c	o-MeO-C_6H_4	o-MeO-C_6H_4	0.50	3.3	5	95	85	216-217
d	p-MeO-C_6H_4	p-Cl-C_6H_4	0.55	3.3	10	90	77	175-187[f]
e	p-Me_2N-C_6H_4	p-Me_2N-C_6H_4	0.50	3.1	-	100	88	181-182
f	C_6H_5	C_6H_5	0.80	1.1	57[g]	30	20	247-248
g	Carbazol-9-yl	H	0.62	0.7[h]	-	100	51	168-170

a) O_2-consumption per molecule of 1 ; b) quantum yield of disappearance of 1 at the initial concentration of 1 = 0.025 M (see text) ; c) determined spectroscopically (^{1}H-NMR) ; d) isolated ; e) under decomposition ; f) cis/trans mixture (see text) ; g) + 13% of 1,1-diphenyloxirane ; h) quantum yield of disappearance of cyclobutane 7.



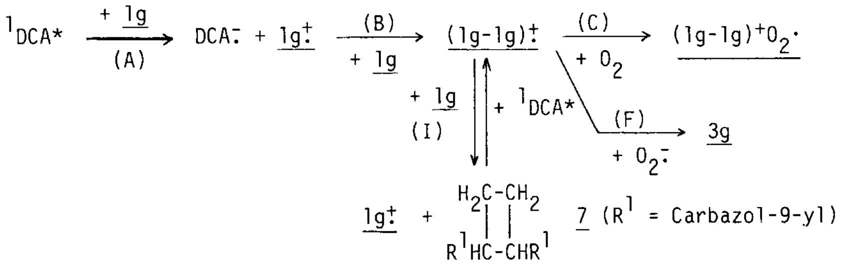
4 5 6

1,1-diphenylethylene (1f) absorbs about 0.8 molecules of oxygen per molecule of 1f. The main product is ketone 2f (57%) (+ 13% of 1,1-diphenyloxirane). However, 1,2-dioxane (3f) formation is still appreciable (30%)[8]. Under the experimental conditions applied, 1f can thus still compete with $O_2^{\dot{-}}$ for the monomeric radical cation $1f^{\dot{+}}$ as long as the concentration of 1f does not become too low.

Preliminary results, obtained with the comparatively electron-poor 1,1-di(p-chlorophenyl)ethylene (1h) and 1,1-di(m-anisyl)ethylene (1i) under similar reaction conditions, show that reaction step B can hardly compete with step E in case of 1h (yielding less than 10% of the corresponding 1,2-dioxane 3h according to ^{1}H-NMR analysis); in case of 1i, negligible (if any) 1,2-dioxane formation takes place[9].

N-Vinylcarbazole (1g) affords the 1,2-dioxane 3g[10]; there is no spectral evidence that 3g represents a cis/trans-mixture. There is also no evidence for the appearance of ketone 2g. However, some polymeric material is formed. Ledwith[11] observed that, with sensitizers such benzophenone, 1g cyclodimerized to cyclobutane 7 only when O_2 was present. Mizuno[12] reported that DCA-sensitized photooxygenation of 7 yielded 1,2-dioxane 3g. In our hands, DCA-sensitized (2+2)-cycloaddition of 1g occurs very rapidly and quantitatively in the presence of O_2 and - even faster - under N_2. Under the experimental conditions used for all the photooxygenation reactions[3], more than 60% of the starting 1g has reacted to 7 within one minute; after 90 seconds, when more than 95% of 1g is transformed into 7, O_2-uptake starts. After another 40 minutes, 7 is quantitatively transformed into 3g. Obviously, electron transfer from 1g to $(1g\text{-}1g)^{\dot{+}}$ (step I of Scheme 2) is much faster than addition of O_2 to the dimeric radical cation (step C). Only when there is practically no 1g present will the competing paths C and F become important. Since the quantum yield of cyclobutane disappearance is 0.7, reaction path F rather than C is likely to follow the production of $(1g\text{-}1g)^{\dot{+}}$ from 7.

Scheme 2



Further studies on 1,2-dioxane formation by electron-transfer photooxygenation are presently carried out at our laboratory[13].

Acknowledgment: This work was supported by Fonds der Chemischen Industrie, Frankfurt am Main.

References and Footnotes

1. J.Eriksen, C.S.Foote, J.Am.Chem.Soc. 102 (1980), 6083.
2. K.Gollnick, A.Schnatterer, Tetrahedron Lett. 25 (1984), 185.
3. For experimental conditions, see ref. 2.
4. (a) Elemental analyses and spectroscopic data are in accord with the structures described; (b) 3a: precipitates from acetonitrile; washed with methanol and dried: 94% yield of iso-

lated colorless crystals; m.p. 133-144°C; ^{1}H-NMR (CDCl$_3$, 80 MHz): δ = 2.51 (s, broad, 4H); 3.66 (s, OCH$_3$, 3H) and 3.69 (s,OCH$_3$, 3H); 6.59-7.58 (m, 18 arom. H); 1:1-cis/trans-mixt. Recryst. (2x) from ethyl acetate/ethanol: m.p. 156-161°C; m.w.: 453 (calc.), 458 (osmometric in benzene); isomer with OCH$_3$-signal at 3.69 enriched. - (c) 3b: see ref. 2; ref. 5: m.p. 217-220°C (from tetrahydrofuran). - (d) 3c: precipitates from acetonitrile; 85% yield of colorless crystals (from tetrahydrofuran): m.p. 216-217°C; ^{1}H-NMR: δ = 2.78 (s, broad, 4H); 3.40 (s, 4 OCH$_3$); 6.69-7.71 (m, 16 arom. H). - (e) 3d: precipitates from acetonitrile; washed with methanol and dried: 77% yield of isolated colorless crystals; m.p. 175-187°C; ^{1}H-NMR: δ = 2.51 (s, broad, 4H); 3.74 (s, OCH$_3$, 3H) and 3.76 (s, OCH$_3$, 3H); 6.64-7.56 (m, 16 arom. H); 1:1-cis/trans-mixt. Recryst. (2x) from ethyl acetate/ethanol: m.p. 193-196°C; m.w.: 522 (calc.), 510 (osmometric in benzene); isomer with OCH$_3$-signal at 3.74 enriched. - (f) 3e: precipitates from acetonitrile; 88% yield of colorless crystals (from tetrahydrofuran): m.p. 181-182°C; ^{1}H-NMR: δ = 2.48 (s, broad, 4H); 2.91 (s, 4 N(CH$_3$)$_2$, 24H); 6.59 (m, 8 arom. H); 6.69 (m, 8 arom. H). (3e is also formed with benzophenone as a sensitizer in acetonitrile, using a pyrex filter).

5. R.K.Haynes, M.K.S.Probert, I.D.Wilmot, Aust.J.Chem. 31 (1978), 1737.
6. Further proof of structures 3a and 3d: Catalytic hydrogenation yields cis/trans-mixtures of tetrahydrofuran derivatives 5a and 5d, respectively[7b,c]. As with 3b[2], the corresponding diols, 4a and 4d, were not isolated. Heating of 5a and 5d in acetic acid in the presence of H$_2$SO$_4$ yields mixtures of cis,cis-, trans,trans-, and cis,trans-substituted 1,3-butadienes 6a and 6d, respectively[7d,e].
7. (a) Elemental analyses and spectroscopic data are in accord with the structures described; (b) 5a: colorless crystals (from ethanol/ethyl acetate); ^{1}H-NMR: δ = 2.59 (s, 4H); 3.73 (s, 2 OCH$_3$); 6.69 (d, 4 arom. H); 7.04-7.41 (m, 14 arom. H). - (c) 5d: colorless crystals (from ethanol/ethyl acetate); ^{1}H-NMR: δ = 2.54 (s, 4H); 3.71 (s, 2 OCH$_3$); 6.66-7.38 (m, 16 arom.H). (d) 6a: colorless crystals (from acetic acid); ^{1}H-NMR: δ = 3.77 (s, OCH$_3$) and 3.86 (s, OCH$_3$) 6.65-7.42 (m, 2 olef. H + 18 arom. H). - (e) 6d: yellowish-green crystals (from acetic acid); ^{1}H-NMR: δ = 3.73 (s, OCH$_3$) and 3.81 (s, OCH$_3$); 6.55-7.45 (m, 2 olef. H + 16 arom. H).
8. (a) Elemental analysis and spectroscopic data are in accord with the structure described; (b) 3f: precipitates from acetonitrile; 30% yield of colorless crystals (from tetrahydrofuran): m.p. 247-248°C; ref. 5: m.p. 256-257.5°C; ^{1}H-NMR: δ = 2.57 (s, broad, 4H); 7.25 (m, 20 arom. H). Catalytic hydrogenation yields diol 4f: m.p. 204-206°C; ref. 5: m.p. 205-209°C.
9. G.Utschick, Diploma work, Univ. München.
10. 3g: 51% yield of colorless crystals (from ethanol/ethyl acetate): m.p. 168-170°C; ref. 12: m.p. 182-184°C; ^{1}H-NMR: 2.23 (d, broad, 2H); 3.22 (t, broad, 2 H); 6.66 (d, broad, 2H); 7.10-8.13 (m, 16 arom. H).
11. A.Ledwith, Acc.Chem.Res. 5 (1972), 133.
12. K.Mizuno, K.Murakami, N.Kamiyama, Y.Otsuji, J.Chem.Soc.,Chem.Comm. 1983, 462.
13. We were just informed that S.L.Mattes and S.Farid have reported their unpublished results on TCA-sensitized 1,2-dioxane (3b,e and f) formation in Vol.6 of Organic Photochemistry (A.Padwa, ed.), Marcel Dekker, New York, 1983, p.233, not yet available to us. We are very grateful to Dr.Farid for supplying us with a reprint of his review article.

(Received in Germany 3 March 1984)