

Photosensitized Oxidation of Furans. Part 15. Limitations to the Formation of Carbonyl Oxides from 2-Alkoxyfurans, and Direct Evidence for the First 3H-1,2-Dioxole

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Formation of the carbonyl oxides **3**, via the furan *endo*-peroxides **1**, can be accomplished only by dye-sensitized photo-oxygenation of 2-alkoxyfurans **2** unsubstituted at C-4, electron-withdrawing substituents at C-3 making the formation selective. Hydrogen or phenyl substituents at C-3 give rise either to carbonyl oxides **3** or to 3H-1,2-dioxoles **8**, the predominance of one over the other being dependent on the polarity of the solvent. For the first time, direct evidence for the formation of a 3H-1,2-dioxole, **8e**, has been obtained.

Recently we reported that some 1-methoxy-2,3,7-trioxabicyclo[2.2.1]hept-5-enes, e.g. compound **1a**, obtained by dye-sensitized photo-oxygenation, at -60°C of the parent 2-alkoxyfurans, e.g. the furan **2a**,¹ lead by thermal rearrangement to carbonyl oxides, e.g. the 1,3-dipole **3a**, which have been trapped by methanol,^{2,+} carbonyl compounds,^{1,2} or electron-rich and electron-poor alkenes.¹ We also reported that this behaviour is common to the 2-alkoxyfurans unsubstituted at C-4 and substituted at C-3 with electron-withdrawing groups.² Since the chemical behaviour of the 1,3-dipolar species leading, in this way, to carbonyl oxides represents a very convenient alternative method to the ozonolysis of alkenes³ or to other previously suggested routes,⁴ we have now examined the limitations of the new preparative method. In this connection account was taken of the fact that no carbonyl oxide was trapped by thermal rearrangement of the 1-methoxy-2,3,7-trioxabicycloheptenes substituted at C-5 or at both C-5 and C-6 with electron-withdrawing groups; e.g. compound **1b**. The latter, in methanol, behaves in the usual way,⁵ giving the 2-hydroperoxy-5,5-dimethoxy-2,5-dihydrofuran **5b**, and by thermal rearrangement in non-participating solvents gives, in addition to the epoxide **6b**, the keto ester **7b**, which was suggested to be formed via the 3H-1,2-dioxole **8b**,⁶ a member of a class of compounds hitherto unreported in the literature.

In order to examine the behaviour of a 1-methoxy-2,3,7-trioxabicyclo[2.2.1]hept-5-ene substituted at C-5 with an electron-donating group and at C-6 with an electron-withdrawing substituent, we have carried out the tetraphenylporphyrin-sensitized photo-oxygenation of methyl 2-methoxy-4-methyl-5-phenylfuran-3-carboxylate **2c** at -75°C in CDCl_3 - CFCl_3 . After 1 h the ^1H NMR spectrum of the reaction mixture, recorded at -80°C , showed the presence of only the *endo*-peroxide **1c**. By addition of methanol, precooled at -80°C , to the above solution of the peroxide **1c** kept at this temperature, only methyl 5-hydroperoxy-2,2-dimethoxy-4-methyl-5-phenyl-2,5-dihydrofuran-3-carboxylate **5c** was obtained. Also, when the sensitized photo-oxygenation was carried out in methanol under a variety of experimental conditions, compound **5c** was obtained quantitatively, the hemiperacetal **4c** never being detected. Furthermore, on working in ethyl vinyl ether or in acetone[‡] neither dioxolane nor trioxolane products, respectively, were detected.§ These results show that the carbonyl oxide **3c** is not an intermediate in these reactions. Therefore, also on the basis of the aforementioned behaviour of the trioxabicycloheptenes **1** substituted at C-5 and C-6 with electron-withdrawing groups,⁶ it is evident that the 1-methoxy-2,3,7-trioxabicyclo[2.2.1]hept-5-enes **1** collapse to

carbonyl oxides **3** only when a hydrogen atom is attached at C-5.

In order to investigate the role of the substituent at C-6 of compound **1** we then studied the behaviour of the *endo*-peroxides **1d** and **1e**,[¶] obtained quantitatively from dye-sensitized photo-oxygenation of the parent furans **2d** and **2e** at -70°C in non-participating solvents. The *endo*-peroxides **1d** and **1e**, which add methanol pre-cooled at -70°C to give the α -methoxy hydroperoxides **4d** and **4e**,^{||} lead by thermal rearrangement in non-participating solvents both to the carbonyl oxides **3d** and **3e** and to dioxoles **8d** and **8e**, the polarity of the solvent playing an important role in the product distribution. The temperature of rearrangement has practically no influence on product distribution; however, at temperatures higher than -20°C self-interactions of the carbonyl oxides **3d** and **3e** become predominant. Table 1 reports the percentage yields of the products obtained at -20°C ** in solvents of different polarity. Quantification was made on the basis of the ^1H NMR spectra of the reaction mixtures and was confirmed, compatible with product stability, by chromatography on silica gel which allowed the isolation of the products, except for **4d** and **4e**.^{††} In particular, the *endo*-peroxides **1d** and **1e** in the polar solvent nitromethane form mainly the carbonyl oxides **3d** and **3e** which interact with themselves to give ethylenes **9d** and **9e**, epoxides **6d** and **6e** and polymeric materials. In contrast, the dioxoles **8d**

† The hemiperacetal **4a** was obtained quantitatively.

‡ Dye-sensitized photo-oxygenation of compound **1a** in ethyl vinyl ether leads to a dioxolane in 84% yield,¹ and in acetone to a trioxolane in 30% yield.²

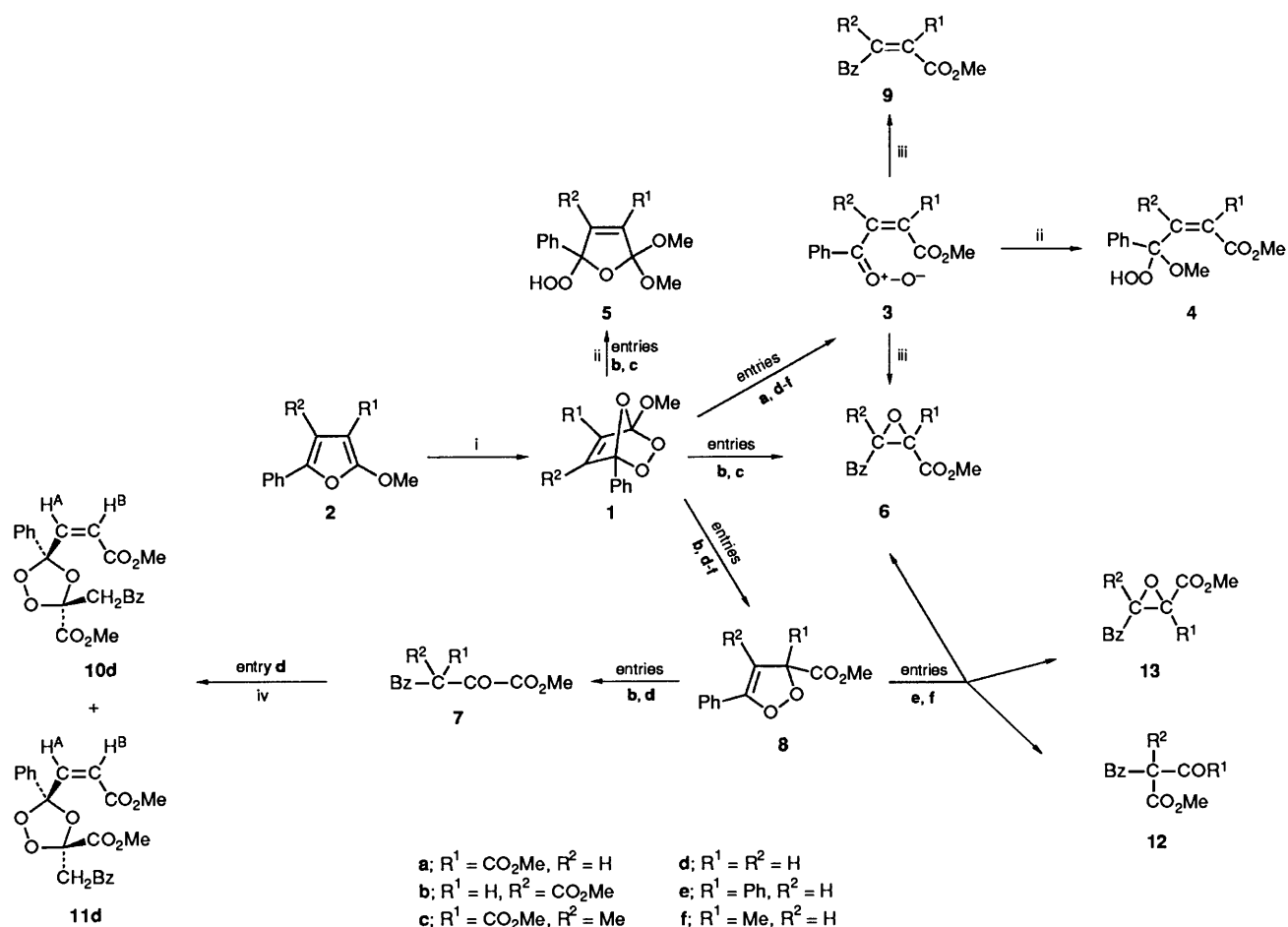
§ In the reaction mixture at room temperature the presence of only the epoxide **6c** along with polymeric materials was observed.

¶ Though on carrying out reaction of the furan **2d** in methanol at -40°C we obtained hemiperacetal **4d**, when the reaction was carried out in acetone no trioxolane derived from 1,3-cycloaddition of the carbonyl oxide **3d** on the dipolarophile was detected.²

|| Under these conditions the yield of compound **4e** is very low; however, it is improved by carrying out the sensitized photo-oxygenation in the polar solvent methanol (see Experimental section). In no case was the dihydrofuran **5e** detected.

** -20°C is the lowest temperature compatible with the freezing point of nitromethane and carbon tetrachloride.

†† Hemiperacetal **4e** decomposed on contact with the adsorbent, as observed for similar compounds.² It is noteworthy that in contrast with carbonyl oxides **3a** and **3d**, which add methanol almost quantitatively, the highest achieved yield for hemiperacetal **4e** was 45%. This experimental result can be interpreted by assuming that methanol addition to the 1,3-dipole **3** takes place by a five-centre transition state which, in the case of the carbonyl oxide **3e**, is difficult to form, the positive charge being delocalized on the chain.



Scheme 1 Reagents: i, $^1\text{O}_2$; ii, MeOH; iii, **3**; iv, **3d**. The letters A and B on structures **10d** and **11d** are used to clarify the description of the ^1H NMR data.

Table 1 Product distribution in the thermal conversion of the *endo*-peroxides **1d** and **1e** at -20°C

Substrate	Solvent ^a	Yield (%) ^b							Polymeric ^c materials
		4	6	7	9	10	12	13	
1d	MeNO_2^d		7	12	36	8			35
1d	CCl_4		5	5	10	50 ^e			10
1d	Me_2CO		7	40	7	13			30
1d	MeOH	93			5				trace
1e	MeNO_2		22		41		trace	12	16
1e	CCl_4		35		11		15	33	4
1e	Me_2CO		33		23		15	27	trace
1e	MeOH	15	15		42		trace	6	12

^a 2×10^{-2} mol dm^{-3} solution. ^b Deduced from the ^1H NMR spectrum and confirmed by silica gel chromatography (compatible with product stability). ^c Calculated from the molecular weight of the starting furan + $\text{O}_2/2$. ^d The percentage yields previously reported were a little different.² It is possible that under the reaction conditions used at that time the conversion of substrate **1d** was not complete. ^e Percentage yield includes that of a small amount of the stereoisomer trioxolane **11d**.

and **8e** are formed predominantly in the less polar solvents such as carbon tetrachloride and acetone. In carbon tetrachloride the dioxole **8d** collapses into the keto ester **7d**, which, by 1,3-cycloaddition of the higher electrophilic carbonyl group on the carbonyl oxide **3d**, yields the trioxolane **10d**, the main reaction product in this solvent. Trace amounts of its stereoisomer **11d** were also present in the reaction mixture. In acetone the main product is the keto ester **7d**;^{*} in addition there is a high yield of polymeric material derived from the carbonyl oxide **3d**. Under no conditions were we able to detect the dioxole **8d**. However, in

the case of the *endo*-peroxide **1e** intermediate formation of the dioxole **8e** was detected. The dioxole **8e** in $\text{CDCl}_3\text{-CFCl}_3$ is stable at -60°C and has been characterized on the basis of its spectral data recorded at this temperature (and reported in Table 2). It should be noted that the dioxole **8d** rearranges into

^{*} In this solvent the yield of the trioxolane **10d** is low, probably due to the negative influence of the solvent polarity on the [3 + 2] cycloaddition of the carbonyl oxide, which leads to the apolar species **10d**.⁷

Table 2 Physical, spectral, and analytical data for the products derived from dye-sensitized photo-oxygenation of the furans **2c-e**.

Product	M.p. (°C)	$\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$	$\delta_{\text{H}}(\text{CDCl}_3)$ (J -values in Hz)	$\delta_{\text{C}}(\text{CDCl}_3)$
1c			2.08 (3 H, s, Me), 3.90 and 3.91 (6 H, 2 × s, 2 × OMe) and 7.30–7.70 (5 H, m, Ph) ^a	
1d			3.82 (3 H, s, OMe), 6.96 (1 H, d, J 5.9, 5-H), 7.38 (1 H, d, J 5.9, 6-H) and 7.50–7.70 (5 H, m, Ph) ^b	
1e			3.99 (3 H, s, OMe), 6.97 (1 H, s, CH) and 7.30–7.60 (10 H, m, 2 × Ph) ^a	
4e			3.30 (3 H, s, OMe), 3.83 (3 H, s, CO ₂ Me), 6.13 (1 H, s, CH) and 8.60 (1 H, br s, OOH) ^c	50.3 and 52.0 (2 × q, 2 × OMe), 105.8 (s, C-4), 125.9 (d, C-3) and 169.8 (s, CO ₂) ^d
5c^e	oil	3528, 3267, 1724, 1680	2.08 (3 H, s, Me), 3.53 and 3.56 (6 H, 2 × s, 2 × OMe), 3.83 (3 H, s, CO ₂ Me), 7.25–7.63 (5 H, m, Ph) and 8.66 (1 H, br s, OOH)	12.1 (q, Me), 50.7 and 51.9 (2 × q, 3 × OMe), 113.3 (s, C-5), 122.5 (s, C-2), 126.2 (s, C-3), 126.5, 128.3 and 129.2 (3 × d, CH of Ph), 135.8 (s, C-1 of Ph), 155.3 (s, C-4) and 162.8 (s, CO ₂)
6c^f	oil	1757, 1687	1.70 (3 H, s, Me), 3.60 and 3.95 (6 H, 2 × s, 2 × OMe) and 7.30–8.20 (5 H, m, Ph)	17.9 (q, Me), 53.3 (q, 2 × OMe), 64.0 and 68.3 (2 × s, 2 × epoxidic C), 128.8, 129.0 and 134.0 (3 × d, CH of Ph), 133.5 (s, C-1 of Ph), 164.3 and 164.6 (2 × s, 2 × CO ₂) and 192.6 (s, CO)
6e^g	oil	1742, 1694	3.69 (3 H, s, OMe), 4.31 (1 H, s, CH) and 7.30–8.10 (10 H, m, 2 × Ph)	52.8 (q, OMe), 64.2 (d, epoxidic CH), 65.0 (s, epoxidic C), 126.1, 128.4, 128.7, 129.3 and 134.1 (5 × d, CH of two Ph), 133.3 and 135.4 (2 × s, C-1 of two Ph)
7d^{h,i}	60–61 (lit., ⁹ 60)	1738, 1625br	3.94 (3 H, s, OMe), 7.09 (1 H, s, CH), 7.40–8.10 (5 H, m, Ph) and 15.1 (1 H, br s, OH)	52.9 (q, OMe), 90.0 (d, CH), 127.9, 128.9 and 133.7 (3 × d, CH of Ph), 135.1 (s, C-1 of Ph), 162.7 and 169.9 (2 × s, C=COH and CO ₂) and 190.5 (s, CO)
8e			3.88 (3 H, s, OMe), 5.62 (1 H, s, CH) and 7.30–7.60 (10 H, m, 2 × Ph) ^a	53.4 (q, OMe), 93.0 (d, C-4), 94.5 (s, C-3), 124.3 (s, C-1 of 5-Ph), 126.7, 125.8, 128.7, 128.9, 129.8 and 130.3 (6 × d, CH of two Ph), 135.5 (C-1 of 3-Ph), 154.7 (s, C-5) and 170.8 (s, CO ₂) ^{a,j}
9e^k	oil	1729, 1663	3.96 (3 H, s, OMe), 7.39 (s, CH) and 7.30–8.10 (m, Ph) (together 11 H)	52.6 (q, OMe), 122.4 (d, CH), 127.1, 128.5, 128.7, 129.0, 130.5 and 133.3 (6 × d, CH of two Ph), 134.0 and 137.3 (2 × s, C-1 of two Ph), 147.4 (s, olefinic C), 168.9 (s, CO ₂) and 188.8 (s, CO)
10d^l	oil	1769, 1729, 1692	3.44 (3 H, s, 3-CO ₂ Me), 3.78 (s, OMe) and 3.85 (dd, J_{gem} 17.5, 3-CH ₂) (together 5 H), 6.08 (1 H, d, J_{cis} 12.1 H ^B), 6.41 (1 H, d, J_{cis} 12.1, H ^A) and 7.30–8.00 (10 H, m, 2 × Ph)	43.0 (t, CH ₂), 51.6 and 52.9 (2 × q, 2 × OMe), 105.0 and 109.8 (2 × s, C-3 and -5), 124.4 (d, CH ^B), 127.4, 128.2, 128.7, 130.1 and 133.7 (5 × d, CH of two Ph), 132.7 and 135.8 (2 × s, C-1 of two Ph), 139.4 (d, CH ^A), 166.4 and 167.3 (2 × s, 2 × CO ₂ Me) and 194.0 (s, CO)
11d^m			3.57 (s, 3-CO ₂ Me), 3.73 (dd, J_{gem} 17.5, 3-CH ₂), 3.86 (s, OMe), 6.05 (d, J_{cis} 12.1, H ^B) and 6.47 (d, J_{cis} 12.1, H ^A) ⁿ	
12e^o	109–110 (lit., ⁹ 109.5–110)	1748, 1696 ^p	3.82 (3 H, s, OMe), 6.24 (1 H, s, CH) and 7.30–8.10 (10 H, m, 2 × Ph) ^q	53.2 (q, OMe), 64.2 (d, CH), 128.6, 129.0 and 134.1 (3 × d, CH of two Ph), 135.5 (s, C-1 of two Ph), 166.1 (s, CO ₂) and 190.4 (s, 2 × CO)
13e^r	99–100 ^s	1743, 1698	3.86 (3 H, s, OMe), 4.79 (1 H, s, CH) and 7.10–7.90 (10 H, m, 2 × Ph)	53.4 (q, OMe), 63.1 (d, CH), 63.2 (s, epoxidic C), 127.6, 127.9, 128.2, 128.7, 128.9 and 133.9 (6 × d, CH of two Ph), 129.8 and 135.0 (2 × s, C-1 of two Ph), 168.3 (s, CO ₂) and 190.4 (s, CO)

^a Recorded in CDCl₃-CFCl₃ (3:1). ^b Recorded in deuterioacetone. ^c The phenyl hydrogens were not assigned since their signals and those of the products present in the mixture overlap. ^d The phenyl and olefinic carbons were not assigned since their signals and those of the products present in the mixture overlap. ^e Found: C, 58.0; H, 5.9; O active, 4.9. C₁₅H₁₈O₇ requires C, 58.06; H, 5.85; O active 5.2%. ^f Found: C, 60.3; H, 5.1. C₁₄H₁₄O₆ requires C, 60.43; H, 5.07%. ^g Found: C, 72.6; H, 4.9. C₁₇H₁₄O₄ requires C, 72.33; H, 5.00%. ^h Known product,⁸ but its spectral data are new. ⁱ The product is detectable only in enol form. ^j The ¹³C chemical-shift assignment was obtained by long-range C–H heteronuclear selective decoupling experiments. ^k Found: C, 76.8; H, 5.4. C₁₇H₁₄O₃ requires C, 76.67; H, 5.30%. ^l Found: C, 65.3; H, 4.9. C₂₂H₂₀O₈ requires C, 64.07; H, 4.89%. ^m In admixture with its isomer **10d**; Found: C, 65.1; H, 4.9. C₂₂H₂₀O₈ requires C, 64.07; H, 4.89%. ⁿ Recorded in admixture with its isomer **10d**: no integration nor assignment of the phenyl hydrogens was possible. ^o Known product,⁹ but its spectral data are new. ^p Recorded in CCl₄. ^q Two enol forms are present in very little amounts [δ 3.45 and 3.75 (2 × s, 2 × OMe), 13.05 and 16.12 (2 × br s, 2 × OH)]. ^r Found: C, 72.2; H, 4.8. C₁₇H₁₄O₄ requires C, 72.33; H, 5.00%. ^s Recrystallization solvent hexane.

the keto ester **7d** by hydrogen shift, as previously observed in similar cases.^{6,*} The dioxole **8e**, which at C-3 bears phenyl and methoxycarbonyl substituents, rearranges into the keto ester **12e** by methoxycarbonyl shift but leads mainly to the two

stereoisomeric epoxides **6e** and **13e**, probably by a concerted pathway.[†] It is evident that the shift of the hydrogen atom is the preferential route of rearrangement of dioxoles **8**. When substitution at C-3 cannot allow this conversion, methoxycarbonyl shift competes with the formation of the two epoxides.[‡]

* Only in the case of compound **8b** was a small methoxycarbonyl shift observed, the keto ester **7b** being by far the major product.⁶

† Table 1 shows that the yields of **6e** are always higher than those of **13e**, an amount of carbonyl oxide **3e**, which partly converts into **6e**, being formed in all cases.

‡ Preliminary experiments, on which we hope to report in the near future, show that the *endo*-peroxide **1f** at room temperature rearranges into the two stereoisomeric epoxides **6f** and **13f**, in addition to the keto ester **12f** and the ethylene **9f**. It is noteworthy that, compound **1f** adds methanol to give quantitatively the hemiperacetal **4f**.

Comparison of the behaviour of compounds **1a**,^{1,2} **1b**⁶ and **1d-f** allows us to determine that when there are no electron-withdrawing substituents at C-5, which would delocalize the C(5)-C(6) π -electrons to afford the corresponding dioxole **8**, the latter reaction may still occur if hydrogen or an electron-donating substituent is attached to C-6.

The previously known compounds were identified by straightforward comparison of their IR and ¹H NMR spectra with those of authentic samples. Spectral data of the keto ester **7d**,⁸ reported in Table 2, show only the presence of the enol form, evidently stabilized by hydrogen bonding. The structures of the new products were assigned on the basis of elemental analyses and/or spectral data (Table 2). In the dihydrofuran **5c** the location of the two methoxy ether groups was ascertained by comparison of the ¹H and ¹³C NMR data with those of similar compounds.^{2,6} The structure of the hemiperacetal **4e** was deduced from the ¹H and ¹³C NMR spectra of the mixture obtained by sensitized photo-oxygenation of the furan **2e** in methanol, the signals of the known products being subtracted. The *cis*-configuration was assigned to the hemiperacetal **4e**, the epoxide **6e**, and the ethylene **9e** on the basis of our previous results.² Confirmation of the stereochemistry of the epoxide **6e** comes from the upfield shift (δ 4.31), with respect to that observed for the *trans*-isomer **13e** (δ 4.79), of the signal of the epoxidic hydrogen which undergoes shielding by anisotropy of the aromatic ring linked to the adjacent carbon atom on the same side. The value (δ 4.79) for compound **13e** is in agreement with those reported for similar compounds where an epoxidic hydrogen is on the same side of a methoxycarbonyl group linked to the adjacent carbon atom.^{2,5a,10} The structure of the trioxolane **11d**, obtained in admixture with its isomer **10d** (see Experimental section), was deduced from analytical and ¹H NMR spectral data of the mixture, the signals of isomer **10d** being subtracted. The stereochemistry of the trioxolanes **10d** and **11d** was tentatively assigned by comparison, in the two isomers, of the chemical shifts of the signals of the methoxycarbonyl and methylene groups linked at C-3. In compound **10d** the signal of the methoxycarbonyl group (δ 3.44) undergoes an upfield shift with respect to that for isomer **11d** (δ 3.57) owing to the anisotropy of the aromatic ring linked at C-5. On the other hand it is the AB system of the methylene group in isomer **11d** (δ 3.73) which undergoes the upfield shift with respect to that for isomer **10d** (δ 3.85).

In conclusion, the formation of carbonyl oxides by dye-sensitized photo-oxygenation of 2-alkoxyfurans is governed by the structure of the starting material though the reaction conditions are of prominent importance. As regards the starting material, 2-alkoxyfurans unsubstituted at C-4 must be used, substitution at C-3 with an electron-withdrawing group making the formation of the 1,3-dipole *selective*. As regards the reaction conditions, it is necessary to work at temperatures not higher than -20 °C in order to lessen the risk of side-reactions. When the formation of the carbonyl oxide is not selective, it is convenient to work in a polar medium in order to minimize dioxole formation.

Experimental

IR spectra were recorded on a Perkin-Elmer 1760X-FT spectrophotometer with chloroform as solvent. ¹H and ¹³C NMR spectra were recorded with a Bruker AC-270 or AM-400 spectrometer using deuteriochloroform as solvent, unless otherwise stated, and tetramethylsilane as internal standard. The solvents used in the photo-oxygenation reactions were anhydrous. Silica gel [0.005-0.20 (Merck)] and light petroleum (boiling range 40-70 °C) were used for column chromatography. Tetraphenylporphyrin (TPP), Rose Bengal (RB), and Methylene Blue (MB) (Fluka) were used without purification.

Ethyl vinyl ether (Fluka, stabilized with diethylaniline) was freshly distilled.

Methyl 2-methoxy-4-methyl-5-phenylfuran-3-carboxylate **2c** was prepared according to a procedure previously reported for different furans,¹¹ starting from 5-methoxy-4-methyl-2-phenyl-oxazole and methyl butynoate. Silica gel chromatography of the reaction mixture [elution with light petroleum-diethyl ether (9:1 v/v)] gave ester **2c** (10%) as an oil (Found: C, 68.3; H, 5.6. C₁₄H₁₄O₄ requires C, 68.28; H, 5.73%; $\nu_{\max}/\text{cm}^{-1}$ 1715; δ_{H} 2.44 (3 H, s, Me), 3.82 and 4.14 (6 H, 2 \times s, 2 \times OMe) and 7.20-7.60 (5 H, m, Ph).

Dye-sensitized Photo-oxygenation of the Furan 2c.—A 5×10^{-2} mol dm⁻³ solution of the furan **2c** (1 mmol) in CDCl₃-CFCl₃ (3:1) was irradiated with a halogen-superphot lamp (Osram, 650 W) in the presence of TPP (3.6×10^{-4} mmol). During the irradiation, dry oxygen was bubbled through the solution which was kept at -75 °C. Periodically the solution was monitored (¹H NMR) for the disappearance of the furan **2c**. When the reaction was complete (1 h), the ¹H NMR spectrum, recorded at -80 °C, showed the presence of only the *endo*-peroxide **1c** (Table 2). The solution of compound **1c** was heated at room temperature. After 10 min the solvents were removed under reduced pressure and the residue was chromatographed on silica gel (10 g). Elution with light petroleum-diethyl ether (4:1, v/v) and then diethyl ether gave successively the epoxide **6c** (70%) and polymeric materials. The physical, spectral, and analytical data for the epoxide **6c** are reported in Table 2.

When the photo-oxygenation of **2c** was carried out according to the procedure reported above, but at -20 °C in acetone (sensitizer RB) or in ethyl vinyl ether (sensitizer TPP),* the reactions were complete after 1 h. The solutions were kept at -20 °C for 1 h and were then warmed to room temperature. After removal of the acetone or of the vinyl ether, respectively, under reduced pressure, the ¹H and ¹³C NMR spectra of the residues were recorded. No spectral evidence was obtained to support the presence of a trioxolane (acetone adduct on the carbonyl oxide **3c**) or of a dioxolane (vinyl ether adduct on the carbonyl oxide **3c**), respectively, the ¹H and ¹³C NMR spectra showing in both cases only the signals of the epoxide **6c**, in addition to the signals of the polymeric materials. The composition of the reaction mixtures, deduced by ¹H NMR spectroscopy, was confirmed by silica gel chromatography. Elution with light petroleum-diethyl ether (4:1, v/v) and then with diethyl ether gave, successively, the epoxide **6c** (40-50%) and polymeric materials.

A 2×10^{-2} mol dm⁻³ solution of the furan **2c** (1 mmol) in methanol was photo-oxygenated at -40 °C with MB as sensitizer according to the procedure reported above. When the reaction was complete (1 h), methanol was removed under reduced pressure. The ¹H and ¹³C NMR spectra of the residue showed only the presence of the dihydrofuran **5c**. No spectral evidence was obtained to support the presence of the hemiperacetal **4c**. Chromatography on a short column of silica gel (5 g), with light petroleum-diethyl ether (4:1, v/v) as eluent, led to the dihydrofuran **5c** (75%), whose physical, spectral, and analytical data are reported in Table 2. Similar results were obtained when the photo-oxygenation of the furan **2c** in methanol was carried out at concentrations of 2×10^{-2} and 5×10^{-3} mol dm⁻³ and at -70, -40 and -20 °C or when methanol pre-cooled to -75 °C was added to the CDCl₃-CFCl₃ solution of the *endo*-peroxide **1c** kept at this temperature.

Dye-sensitized Photo-oxygenation of the Furan 2d.—A

* These reaction conditions allowed the isolation of the adducts of the carbonyl oxide **3a** with acetone or ethyl vinyl ether in good yield.^{1,2}

2×10^{-2} mol dm⁻³ solution of the furan **2d**² (0.5 mmol) in deuterioacetone* was photo-oxygenated at -70°C with RB as sensitizer according to the procedure reported above for the furan **2c**. When the reaction was complete (90 min) a sample was transferred from the reaction apparatus into the spectrometer (probe temperature -70°C). The ¹H NMR spectrum showed the presence of only the *endo*-peroxide **1d** (Table 2). On raising of the probe temperature to -30°C the signals of the peroxide **1d** decreased while those of the keto ester **7d** appeared. After 90 min, in addition to compound **7d**,⁸ only trace amounts of the epoxide **6d**,² the ethylene **9d**² and the trioxolane **10d** were detectable. The latter was identified by comparison with an authentic sample obtained by sensitized photo-oxygenation of compound **2d** in carbon tetrachloride (see below).

To a second aliquot of the deuterioacetone solution of the *endo*-peroxide **1d** (1 cm³) kept at -70°C , dry methanol (1 cm³), pre-cooled to this temperature, was added and the mixture was warmed at -40°C . After 30 min, the solvents were removed under reduced pressure at room temperature. The ¹H NMR spectrum of the reaction mixture showed the presence of the hemiperacetal **4d**² as by far the major product, in addition to small amounts of the ethylene **9d**² and the epoxide **6d**.²

To a third sample of the *endo*-peroxide **1d** solution kept at -70°C was added a trace amount of 2 mol dm⁻³ hydrochloric acid. The ¹H NMR spectrum, recorded at -70°C , showed the presence of the ethylene **9d** as by far the major product.

The remainder of the deuterioacetone solution of the *endo*-peroxide **1d** was warmed to room temperature. After 30 min, removal of the solvent at reduced pressure and rapid filtration on a short column of silica gel (5 g) with light petroleum–diethyl ether (9:1, v/v) as eluent yielded keto ester **7d** (30%)[†] which was identified by comparison with an authentic sample.⁸ Elution with light petroleum–diethyl ether (1:1, v/v) and then with diethyl ether gave a fraction composed (¹H NMR) of the ethylene **9d**,² the epoxide **6d**,² and the trioxolane **10d** in *ca.* 1:1:1 molar proportions (together 30%), and polymeric materials.

Solutions of the furan **2d** (2×10^{-2} mol dm⁻³) were photo-oxygenated, according to the procedure reported above, with carbon tetrachloride (sensitizer TPP), acetone (sensitizer RB), nitromethane (sensitizer MB), or methanol (sensitizer MB) as solvent. The reactions were carried out at -20°C with 1 mmol of the furan, and when they were complete the solutions were kept at -20°C for 1 h. The solvent was removed under reduced pressure at room temperature and the residue was analysed by ¹H NMR spectroscopy. The composition of the mixtures, reported in Table 1, was deduced from the ¹H NMR spectra and was confirmed by silica gel chromatography, compatible with product stability. Chromatography of the mixtures [elution with light petroleum–diethyl ether (9:1, 4:1, 7:3, 1:1 v/v) and then with diethyl ether] gave, successively, the keto ester **7d**,^{8,†} the ethylene **9d**,² the epoxide **6d**,² the trioxolanes **10d** and **11d**, and polymeric materials. The physical, spectral and analytical data of the trioxolane **10d**, isolated in good yield from the mixture obtained with carbon tetrachloride, are reported in Table 2. In this Table the spectral data of the isomer **11d** are

also reported, which data were deduced from the ¹H NMR spectrum of a mixture composed of this trioxolane and of its isomer **10d**, the signals of the latter being subtracted. The analytical data of compound **11d**, reported in Table 2, were obtained by elemental analysis of this mixture.

Dye-sensitized Photo-oxygenation of the Furan 2e.—A 5×10^{-2} mol dm⁻³ solution of the furan **2e**¹³ (1 mmol) in CDCl₃–CFCl₃ (3:1) was photo-oxygenated at -75°C with TPP as sensitizer, according to the procedure reported above for the furan **2c**. When the reaction was complete (90 min), inspection of the ¹H NMR spectrum, recorded at -75°C , of a sample of the reaction mixture showed the presence of the *endo*-peroxide **1e** (Table 2) and small amount of the dioxole **8e**. On raising of the probe temperature to -60°C , the signals of the *endo*-peroxide **1e** readily diminished while those of the dioxole **8e** increased. When the signals of the *endo*-peroxide **1e** disappeared, the ¹H NMR spectrum showed the presence of the dioxole **8e** as well as small amounts of the epoxide **6e** and the ethylene **9e** (**8e**:**6e**:**9e** in *ca.* 8:1:1 molar proportions). Compounds **6e** and **9e** were identified by comparison with authentic samples (see below). The spectral data of the dioxole **8e** (Table 2) were deduced from those of this mixture, recorded at -60°C , the signals of the epoxide **6e** and the ethylene **9e** being subtracted. The dioxole **8e** slowly at -55°C , and rapidly, at higher temperatures, rearranged into the keto ester **12e** and into the *cis*- and *trans*-epoxide **6e** and **13e**. When the conversion of **8e** was complete the mixture was composed of compounds **6e**, **13e**, **12e**,⁹ and **9e** in *ca.* 4:3:2:1 molar proportions. The compounds were identified (¹H NMR) by comparison with authentic samples.

To a second aliquot of the solution of compound **1e** (4 cm³) kept at -75°C , was added dry methanol (4 cm³), pre-cooled to this temperature, and the mixture was warmed at -40°C . After 30 min, the solvents were removed under reduced pressure at room temperature. The ¹H NMR spectrum of the reaction mixture showed the presence of the ethylene **9e** as the main product, in addition to the epoxides **6e** and **13e** and trace amounts of the hemiperacetal **4e**. Compounds **9e**, **6e** and **13e** were identified by comparison with authentic samples, while the hemiperacetal **4e** was identified by comparison of the spectral data of this mixture with those of the mixture obtained by MB-sensitized photo-oxygenation of the furan **2e** in methanol at -70°C (see below).

The remainder of the solution of the *endo*-peroxide **1e** was warmed to room temperature. After 30 min the solvents were removed under reduced pressure and the residue was chromatographed on silica gel (10 g). Elution with light petroleum–diethyl ether (9:1, 4:1, 7:3, v/v) gave, successively, compounds **9e** (10%), **6e** (37%) and **13e** (26%). Elution with light petroleum–diethyl ether (1:1, v/v) and then with diethyl ether gave, successively, the keto ester **12e**⁹ (17%) and polymeric materials. The physical, spectral, and analytical data for compounds **9e**, **6e** and **13e** are reported in Table 2.

A 5×10^{-3} mol dm⁻³ solution of the furan **2e** (0.5 mmol) in methanol was photo-oxygenated at -70°C as above reported with MB as a sensitizer. When the reaction was complete (90 min), the solution was warmed to room temperature. After removal of the solvent, inspection of the ¹H NMR spectrum showed the presence of the hemiperacetal **4e**, the ethylene **9e**, and epoxide **6e** in *ca.* 5:3:1 molar proportions, in addition to trace amounts of the keto ester **12e**⁹ and the epoxide **13e**. No spectral evidence was obtained to support the presence of the dihydrofuran **5e**. Compounds **9e**, **6e** and **13e** were identified by comparison with authentic samples. All attempts to separate the hemiperacetal **4e** chromatographically failed since it decomposes on contact with the adsorbent. Its spectral data, reported in Table 2, were deduced by careful analysis of the ¹H and ¹³C

* In CDCl₃–CFCl₃ (3:1) at -70°C , the ¹H NMR spectrum of the reaction mixture, recorded at this temperature, showed the ethylene **9d** as by far the major product, no transient species being detected. These results must be due to the ready hydrolysis of the *endo*-peroxide **1d** catalysed by trace amount of hydrochloric acid which was present in the deuteriochloroform¹² [*cf.* below the results of the addition of trace amounts of 2 mol dm⁻³ hydrochloric acid to a deuterioacetone solution of the *endo*-peroxide **1d** at -70°C].

† The keto ester **7d** partly decomposes on contact with the adsorbent, therefore its yields are lower than those deduced from ¹H NMR spectrum of the reaction mixture.

NMR spectra of the reaction mixture, the signals of other products being subtracted.

Solutions of the furan **2e** (2×10^{-2} mol dm⁻³) were photo-oxygenated, according to the procedure reported above, with carbon tetrachloride (sensitizer TPP), acetone (sensitizer RB), nitromethane (sensitizer MB), or methanol (sensitizer MB) as solvent. The reactions were carried out at -20°C with 1 mmol of the furan and when they were complete the solutions were kept at -20°C for 1 h. The solvent was removed under reduced pressure at room temperature and the residue was analysed by ¹H NMR spectroscopy. The composition of the mixtures, reported in Table 1, was deduced on the basis of the ¹H NMR spectra and confirmed by silica gel chromatography, compatible with the product stability. Chromatography of the mixtures [elution with light petroleum–diethyl ether (9:1, 4:1, 7:3 and 1:1, v/v) and then with diethyl ether] gave, successively, compounds **9e**, **6e**, **13e**, **12e**,⁹ (which were identified by comparison with authentic samples) and polymeric materials. In methanol solution only the hemiperacetal **4e** was detected (¹H NMR) as its methanol-adduct; no spectral evidence supporting the presence of the dihydrofuran **5e** was obtained.

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