

## Photosensitized Oxidation of Furans. Part 14.<sup>1</sup> Nature of Intermediates in Thermal Rearrangement of Some *endo*-Peroxides of 2-Alkoxyfurans: New Rearrangement Pathway of Furan *endo*-Peroxides

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2-Methoxy-5-phenylfurans (**1a—c**) substituted at C-4 with electron-withdrawing groups, by dye-sensitized photo-oxygenation in non-participating solvents, give the *endo*-peroxides (**3a—c**) which by thermal rearrangement partly yield the 3*H*-1,2-dioxoles (**14a—c**). The latter, which are the first examples of this ring system, are thermally very unstable. Their formation can be deduced only from the products obtained by thermal rearrangement which are structurally related with the thermal rearrangement products of 3*H*-1,2,4-dioxazoles (**10**). The behaviour of the furans (**1a—c**) contrasts with that of the 2-methoxy-5-phenylfurans unsubstituted at C-4 which under the same conditions give carbonyl oxides.

Recently we reported incontrovertible evidence for carbonyl oxide intermediacy in dye-sensitized photo-oxygenation of 2-methoxyfurans unsubstituted at C-4.<sup>1</sup> We also reported that control experiments carried out in order to provide evidence of carbonyl oxide formation for 2-methoxyfurans substituted at C-4 with electron-withdrawing groups had been unsuccessful. In particular, by dye-sensitized photo-oxygenation in anhydrous methanol, the furans (**1a—c**) gave the 5-hydroperoxy-2,2-dimethoxy-2,5-dihydrofurans (**2a—c**), which are the methanol adducts of furan *endo*-peroxides.<sup>2,3†</sup> In order to confirm the intermediacy of the *endo*-peroxides (**3a—c**) and clarify the nature of the thermal rearrangement products of these peroxides, we have now carried out the dye-sensitized photo-oxygenation of the furans (**1a—c**) in non-participating solvents.

The presence of the transient dimethyl 1-methoxy-4-phenyl-2,3,7-trioxabicyclo[2.2.1]hept-5-ene-5,6-dicarboxylate (**3a**) (Scheme 1) in the photo-oxygenation of the furan (**1a**) in carbon tetrachloride at -20 °C was deduced by <sup>1</sup>H n.m.r. monitoring of the reaction mixture before complete conversion of (**1a**). In Table 1 the n.m.r. data are reported, the signals of the furan (**1a**) being subtracted. The *endo*-peroxide (**3a**) at room temperature rapidly decomposed into trimethyl benzoyl-1,2-epoxyethylenetricarboxylate (**4a**) and trimethyl benzoyloxalylmalonate (**5a**)≡(**6a**). A trace of trimethyl benzoylethylenetricarboxylate (**7a**) was also present in the reaction mixture. In Table 2 the percentage yields of the thermal conversion products of the *endo*-peroxide (**3a**) are reported. Quantification was made on the basis of the <sup>1</sup>H n.m.r. spectrum of the reaction mixture of the *endo*-peroxide (**3a**) after thermal conversion and confirmed by chromatography of the latter on silica gel. In this way, in addition to a trace of the ethylene (**7a**), the epoxide (**4a**) and the dimethyl benzoylmalonate (**8a**) were isolated. The latter was formed by hydrolysis of the keto ester (**5a**)≡(**6a**) on contact with the adsorbent. In fact, a control experiment showed that mild hydrolysis of the crude mixture obtained after thermal conversion gave in addition to the epoxide (**4a**) and a trace of the ethylene (**7a**), only the benzoylmalonate (**8a**) and the monomethyl oxalate (**9**).

No transient species were detected on carrying out dye-sensitized photo-oxygenation of the furans (**1b,c**) under the conditions employed for the furan (**1a**). However, it is evident

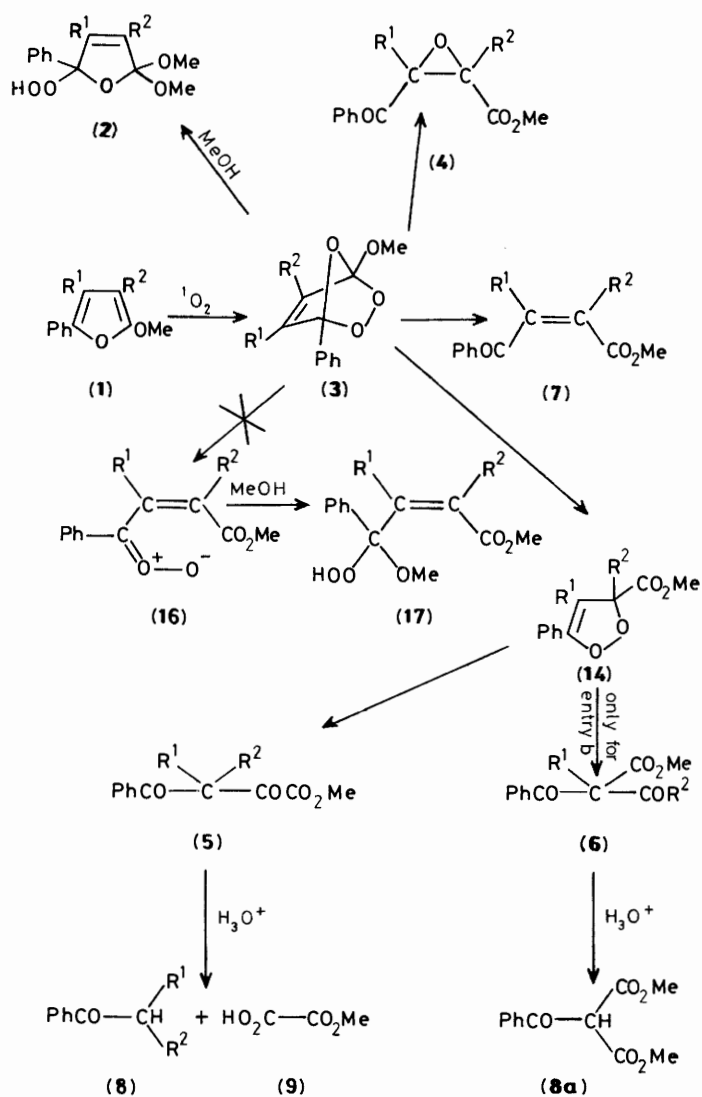
that the primary adducts obtained by reaction of singlet oxygen with the furans (**1b,c**) are the *endo*-peroxides (**3b,c**); in fact the obtained products are structurally related to those obtained when (**1a**) is the furan employed. Table 2 shows the percentage yields of the reaction products evaluated on the basis of the <sup>1</sup>H n.m.r. spectra of the reaction mixtures. Silica gel chromatography of the reaction mixture obtained from (**1b**) allowed the isolation, in addition to the epoxide (**4b**), and the benzoylacetate (**8b**), traces of the ethylene (**7b**), and the benzoylmalonate (**8a**). Silica gel chromatography of the reaction mixture of (**1c**) allowed isolation of the *cis*-epoxide (**4c**), the *cis*-ethylene (**7c**), and the benzoylacetone (**8c**). Compounds (**8a**), (**8b**), and (**8c**) were evidently formed by hydrolysis of the esters (**6b**), (**5b**), and (**5c**) respectively, on contact with the adsorbent. However, no chromatographic confirmation of the percentage yields of (**5b,c**) and (**6b**) were obtained since the hydrolysis is not quantitative, and the compounds showed a tendency to polymerize.‡

As aforementioned, Table 2 shows the results obtained using carbon tetrachloride as the solvent. However, control experiments showed that reactions carried out in chloroform or nitromethane at various concentrations gave substantially similar results.

The hitherto known compounds were identified by comparison with authentic samples. The structures of the new products (**4a—c**), (**7a**), and (**7c**) were assigned on the basis of elemental analyses and spectral data (see Table 1). The stereochemistry of (**4c**) and (**7c**) was assigned by a series of nuclear Overhauser effect (n.O.e.) difference experiments. In particular, in the <sup>1</sup>H n.m.r. spectrum of (**4c**) irradiation at δ 2.29 (COMe) caused enhancement of the signal at δ 3.94 (CH); in the <sup>1</sup>H n.m.r. spectrum of (**7c**) irradiation at δ 2.35 (COMe) caused enhancement of the signal at δ 6.86 (CH). Compounds (**5a,b**) and (**6b**), as reported above, are difficult to isolate owing to their ready hydrolysis. Therefore, structures (**5a,b**) and (**6b**) were deduced from the <sup>13</sup>C and/or <sup>1</sup>H n.m.r. spectra of the reaction mixtures, the signals of the known compounds being subtracted. Table 1 reports the spectral data so deduced. Compound (**5c**) was obtained in a purity of 90% (<sup>1</sup>H n.m.r.) by suitable treatment of the reaction mixture (see Experimental section) and its structure assigned on the basis of the spectral data reported in Table 1. Since the keto=enol equilibria for (**5b**) and (**5c**) in solution (carbon tetrachloride, deuteriochloroform,

† It is to be noted that 2-methoxyfurans unsubstituted at C-4 under the same conditions lead quantitatively to α-methoxy hydroperoxides.<sup>1</sup>

‡ Control experiments confirmed these data (see Experimental section).

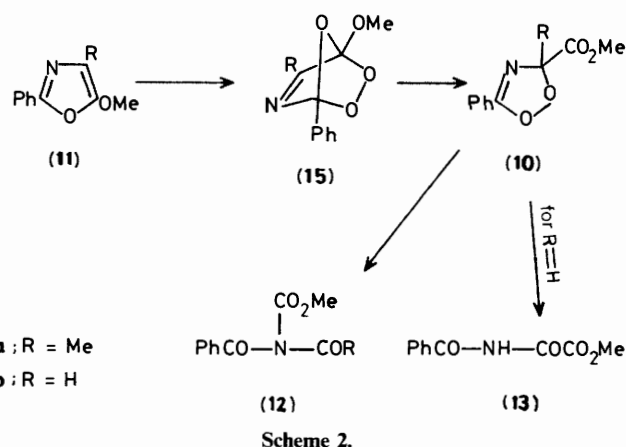


Scheme 1. a, R<sup>1</sup> = R<sup>2</sup> = CO<sub>2</sub>Me; b, R<sup>1</sup> = CO<sub>2</sub>Me, R<sup>2</sup> = H; c, R<sup>1</sup> = Ac, R<sup>2</sup> = H

deuteriomethanol) lie well over to the right, the spectral data reported in Table 1 refer to the enol forms.\*

Thermal rearrangement of 2,5-diarylfuran and 2-aryl-5-alkylfuran *endo*-peroxides into *cis* epoxides is well known<sup>2,4-6</sup> and it is also known that the behaviour of furan *endo*-peroxides depends on the nature of their 2,5-substituents.<sup>1,6-9</sup> However, in spite of the numerous paths by which thermal rearrangement may proceed, rearrangement products such as (5) and (6) are novel. The latter are structurally related to the thermal rearrangement products of the alkyl 3*H*-1,2,4-dioxazole-3-carboxylates such as (10)<sup>10</sup> which we earlier obtained by dye-sensitized photo-oxygenation in chloroform of 5-alkoxyoxazoles such as (11)<sup>10,11</sup> (Scheme 2). In particular, the fully substituted dioxazoles such as (10a) at 80 °C give, quantitatively, methyl *N,N*-diacylcarbamates such as (12a) by a [1,5] alkoxy-carbonyl shift,<sup>10</sup> while the C-3 monosubstituted

\* Compound (5b) differs from (5c) in deuteriochloroform and in carbon tetrachloride in that more than one enol form is detectable; the <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra are, therefore, reported in deuteriomethanol where only one enol form is detected. The study of the keto-enol equilibria for (5b) and (5c) in several solvents is in progress.



Scheme 2.

compound (10b), in addition to (12b), yields methyl *N*-benzoyloxamate (13) by a [1,5] hydrogen shift.<sup>12</sup> Therefore, it is quite conceivable that the *endo*-peroxides (3a–c) are partly converted into 3*H*-1,2-dioxoles (14a–c), and that these successively rearrange in the same way as the dioxazoles (10).† However, in no case were we able to detect the dioxoles (14a–c). It is to be noted that there are no reports in the literature of 3*H*-1,2-dioxoles such as (14).

As regards formation of the dioxole (14) from the *endo*-peroxides (3), the results previously obtained by dye-sensitized photo-oxygenation of the 2-alkoxyfurans unsubstituted at C-4<sup>1</sup> led us to examine the possibility that the carbonyl oxides (16) were the intermediates.‡ Therefore dye-sensitized photo-oxygenation of the furan (1a) in methanol was carried out under a variety of experimental conditions (–70, –40, –20, and 10 °C at concentrations of 2 × 10<sup>–2</sup> M and 5 × 10<sup>–3</sup> M) and the reaction mixtures were carefully analysed. If the carbonyl oxide (16a) was the intermediate, then the hemiperacetal (17a) should have been detected at least in small amounts. The <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra of the reaction mixtures, in addition to the signals for (2a), (4a), (5a)≡(6a), and (7a), showed only signals attributable to the 2-hydroperoxy-5-methoxydihydrofuran (18),§ an isomer of (2a). The hemiperacetal (17a) was never detected. Therefore, on the basis of these results and of those previously reported,<sup>1,¶</sup> it is concluded that the dioxole (14a), which is also formed in methanol as the presence of (5a)≡(6a)

† The alkoxyoxazole singlet oxygen primary adducts have never been isolated and in the absence of any evidence for their formation we suggested that the dioxazoles are formed by 1,2-addition of the singlet oxygen on the electron-rich heterocyclic system: this would give an unstable peroxirane intermediate which then should rearrange to a dioxazole.<sup>10</sup> The aforementioned results show a parallel behaviour for 5-alkoxyoxazoles and 2-alkoxyfurans substituted at C-4 with an electron-withdrawing group, the latter certainly giving *endo*-peroxides (3). The hypothesis recently put forward by Wasserman *et al.*<sup>13</sup> that dioxazoles such as (10) are formed *via* the oxazole *endo*-peroxides (15) is, therefore, supported.

‡ Similar cleavage of oxazole *endo*-peroxides into carbonyl oxides, followed by intramolecular addition of the peroxidic function to the imine carbon, has been suggested to explain dioxazole formation.<sup>13</sup>

§ All attempts to isolate (18) by chromatographic methods failed since the compound undergoes quantitative hydrolysis to the lactone (19) on contact with the adsorbent. Structure (18) was assigned on the basis of <sup>1</sup>H and <sup>13</sup>C n.m.r. spectral analyses of the reaction mixture, the signals of the known products being rejected (see Table 1). The stereochemistry of (18) has not been investigated; however on the basis of previous assignments<sup>3</sup> *trans* arrangement of the two OMe should be effective. The structure of the lactone (19) was assigned on the basis of the analytical and spectral data reported in Table 1.

¶ The carbonyl oxides previously obtained react with methanol to give hemiperacetals quantitatively.<sup>1</sup>

**Table 1.** Physical, spectral, and analytical data for the products derived from dye-sensitized photo-oxygenation of the furans (**1a–c**)

Product	M.p. (°C)	$\nu_{\max.}(\text{CHCl}_3)$ cm <sup>-1</sup>	$\delta_{\text{H}}(\text{CDCl}_3)$	$\delta_{\text{C}}(\text{CDCl}_3)/\text{p.p.m.}$	Formula	Found (%) (Required)	
						C	H
( <b>3a</b> )			3.65, 3.86, and 3.90 (3 × s, 3 × OMe), 7.30–7.60 (m, Ph) <sup>a-c</sup>				
( <b>4a</b> )	61–62 <sup>d</sup>	1 748 1 689	3.65, 3.79, and 3.92 (9 H, 3 × s, 3 × OMe), 7.40–8.01 (5 H, m, Ph)	53.5, 53.7, and 54.0 (3 × q, 3 × OMe), 63.8 and 66.0 (2 × s, C-1 and C-2), 128.9 and 129.0 (2 × d, C-2, C-3, C-5, and C-6 of Ph), 133.9 (s, C-1 of Ph), 134.6 (d, C-4 of Ph), 162.7, 163.0, and 164.0 (3 × s, 3 × CO <sub>2</sub> ), 186.9 (s, CO)	C <sub>15</sub> H <sub>14</sub> O <sub>8</sub> (322.26)	55.96 (55.90)	4.45 (4.38)
( <b>4b</b> )	Oil	1 751 1 690	3.67 and 3.81 (6 H, 2 × s, 2 × OMe), 4.11 (1 H, s, CH), 7.40–8.05 (5 H, m, Ph)		C <sub>13</sub> H <sub>12</sub> O <sub>6</sub> (264.23)	59.0 (59.09)	4.5 (4.58)
( <b>4c</b> )	114–116 <sup>e</sup>	1 758 1 722 1 688	2.29 (3 H, s, Me), 3.65 (3 H, s, OMe), 3.94 (1 H, s, CH), 7.40–8.05 (5 H, m, Ph)	25.2 (q, Me), 52.9 (q, OMe), 56.5 (d, C-2), 67.4 (s, C-1), 128.9 and 129.1 (2 × d, C-2, C-3, C-5, and C-6 of Ph), 134.3 (s, C-1 of Ph), 134.5 (d, C-4 of Ph), 165.5 (s, CO <sub>2</sub> ), 189.9 and 199.4 (2 × s, 2 × CO)	C <sub>13</sub> H <sub>12</sub> O <sub>5</sub> (248.23)	62.7 (62.90)	4.65 (4.87)
( <b>5a</b> )=( <b>6a</b> )			3.83 (6 H, s, 2 × OMe), 3.91 (3 H s, OMe) <sup>f</sup>	53.9 and 54.2 (2 × q, 3 × OMe), 78.6 (s, quaternary C), 160.6 and 163.8 (2 × s, 3 × CO <sub>2</sub> ), 183.1 and 190.3 (2 × s, 2 × CO) <sup>g,h</sup>			
( <b>5b</b> )			3.69 and 3.77 (6 H, 2 × s, 2 × OMe), 12.4 (1 H, br s, OH) <sup>f</sup>				
( <b>5c</b> )		1 735 1 670 1 598 <sup>a</sup>	2.23 (3 H, s, Me), 3.51 (3 H, s, OMe), 7.40–8.10 (5 H, m, Ph) <sup>b,i</sup>	25.1 (q, Me), 53.2 (q, OMe), 115.8 (s, C=C–OH), 130.1 (d, C-2, C-3, C-5, and C-6 of Ph), 134.5 (d, C-4 of Ph), 135.9 (s, C-1 of Ph), 139.2 (s, C=C–OH), 164.1 (s, CO <sub>2</sub> ), 194.9 and 196.5 (2 × s, 2 × CO) <sup>i</sup>			
( <b>6b</b> )			3.85 (6 H, s, 2 × OMe), 10.04 (1 H, s, CHO) <sup>f</sup>				
( <b>7a</b> )	66–68 <sup>d</sup>	1 730 1 670	3.62, 3.73, and 3.92 (9 H, 3 × s, 3 × OMe), 7.40–8.08 (5 H, m, Ph)	53.2, 53.3, and 53.5 (3 × q, 3 × OMe), 128.6 and 128.9 (2 × d, C-2, C-3, C-5, and C-6 of Ph), 134.1 (d, C-4 of Ph), 135.1 (s, C-1 of Ph), 142.4 and 151.7 (2 × s, C-1 and C-2), 161.9, 162.6, and 163.9 (3 × s, 3 × CO <sub>2</sub> ), 190.1 (s, CO)	C <sub>15</sub> H <sub>14</sub> O <sub>7</sub> (306.26)	58.6 (58.82)	4.5 (4.61)
( <b>7c</b> )	Oil	1 728 1 697 1 673	2.35 (3 H, s, Me), 3.62 (3 H, s, OMe), 6.86 (1 H, s, CH), 7.40–8.05 (5 H, m, Ph)	27.7 (q, Me), 52.5 (q, OMe), 127.9 (d, C-2), 128.6 and 128.9 (2 × d, C-2, C-3, C-5, and C-6 of Ph), 134.0 (d, C-4 of Ph), 135.7 (s, C-1 of Ph), 151.6 (s, C-1), 164.6 (s, CO <sub>2</sub> ), 192.8 and 194.9 (2 × s, 2 × CO)	C <sub>13</sub> H <sub>12</sub> O <sub>4</sub> (132.23)	67.0 (67.23)	4.9 (5.21)
( <b>18</b> )			3.19, 3.69, 3.75, and 3.87 (4 × s, 4 × OMe) <sup>f,j</sup>	105.7 and 122.5 (2 × s, C-2 and C-5), 146.5 and 151.0 (2 × s, C-3 and C-4), 162.4 and 165.2 (2 × s, 2 × CO <sub>2</sub> ) <sup>k</sup>			
( <b>19</b> )	Oil	1 798 1 730 1 685	3.67, 3.86, and 3.95 (9 H, 3 × s, 3 × OMe), 7.00–7.30 (5 H, m, Ph)	52.9, 53.3, and 53.5 (3 × q, 3 × OMe), 117.5 (s, C-5), 122.5, 125.9, and 129.5 (3 × d, C-2, C-3, C-4, C-5, and C-6 of Ph), 134.3 (s, C-1 of Ph), 150.0 and 151.0 (2 × s, C-3 and C-4), 159.2, 159.7, and 161.3 (3 × s, 3 × CO <sub>2</sub> )	C <sub>15</sub> H <sub>14</sub> O <sub>7</sub> (306.26)	58.6 (58.82)	4.4 (4.61)

<sup>a</sup> Recorded in carbon tetrachloride. <sup>b</sup> Recorded on a Varian EM-360 spectrometer. <sup>c</sup> It was not possible to integrate the signals owing to the high thermal instability of (**3a**). <sup>d</sup> Recrystallization solvent, light petroleum (b.p. 40–70 °C). <sup>e</sup> Recrystallization solvent, light petroleum (b.p. 60–80 °C).

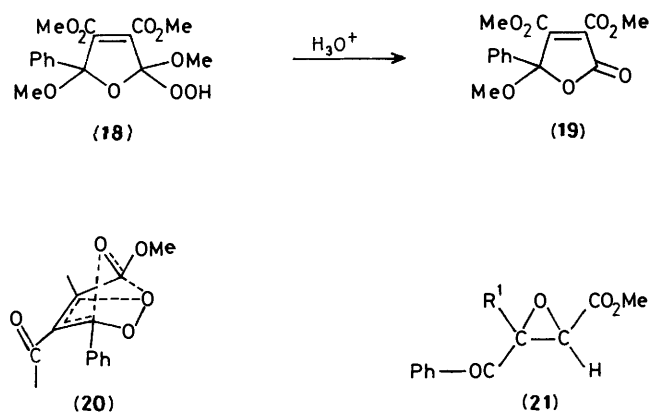
<sup>f</sup> The phenyl hydrogens were not assigned since their signals and those of the products present in the mixture overlap. <sup>g</sup> Recorded in deuterioacetone.

<sup>h</sup> The phenyl carbons were not assigned since their signals and those of the products present in the mixture overlap. <sup>i</sup> Recorded in deuteriomethanol.

<sup>j</sup> It was not possible to integrate the signals owing to the complexity of the spectrum. However, the intensities of the four singlets are in *ca.* 1:1:1:1 ratio. <sup>k</sup> The methoxy and phenyl carbons were not assigned since their signals and those of the products present in the mixture overlap.

shows, is not formed *via* the carbonyl oxide (**16a**) which could be trapped by methanol. On the other hand, as reported above, in non-participating solvents the yields of the keto esters (**5a–c**) and (**6b**) as well as those of the epoxides (**4a–c**) are both independent of the solvent polarity and invariant with the

concentration. Therefore, it seems justifiable to assume that both the dioxoles (**14a–c**) and the epoxides (**4a–c**) are formed from the *endo*-peroxides (**3a–c**) by two concerted rearrangements. The formation of the dioxoles (**14a–c**) from the 2,3,7-trioxabicyclo[2.2.1]hept-5-enes (**3a–c**) is certainly induced by



the presence of the 1-methoxy substituent which promotes an intramolecular rearrangement as shown in (20), by loosening both the peroxide oxygen-bridgehead carbon bond and the furan oxygen-benzyl carbon bond. Thus the epoxides (4a—c) are formed by a path similar to that which we suggested for the reaction of 2,5-diarylfuran *endo*-peroxides in aprotic solvents.<sup>4</sup> The alternative hypothesis that the dioxoles (14) are common intermediates which partly rearrange to the keto esters (6) and/or (5) and partly to the epoxides (4) must be excluded. In fact, if this was the case the isomeric epoxides (21b,c) should also be obtained.

The reasons for the difference in behaviour towards singlet oxygen of 2-alkoxyfurans unsubstituted at C-4 and those substituted with an electron-withdrawing group at this position have not been conclusively established. It can be assumed that both give *endo*-peroxides such as (3). Successively, the 2,3,7-trioxabicyclo[2.2.1]hept-5-enes (3a—c), the C(5)—C(6)  $\pi$  electrons of which are delocalized on the C-5 electron-withdrawing substituent, could undergo concerted rearrangement into the dioxoles (14a—c) as shown in (20).<sup>\*</sup> In contrast, those unsubstituted at C-5 have the possibility of collapsing to carbonyl oxides since the 1,3-dipoles formed in these cases show good resonance stabilization and hydrogen bond formation between the negative oxygen and the hydrogen at the unsaturated carbon, which should be acidic enough for the conjugation with two or at least one electron-withdrawing group, may take place.<sup>14</sup> Alternatively, only *endo*-peroxides (3a—c) should be formed in that, as we suggested previously,<sup>1</sup> the transition states for reactions of singlet oxygen with C-4 unsubstituted 2-alkoxyfurans should be regarded as weakly perturbed zwitterions formed by combination of the diene and dienophile. The latter should then collapse very readily to carbonyl oxides.

### Experimental

I.r. spectra were recorded on a Perkin-Elmer 399 spectrophotometer with chloroform as solvent, unless otherwise stated. <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra were recorded with a Bruker WH-270 spectrometer using deuteriochloroform as solvent, unless otherwise stated, and tetramethylsilane as internal standard. Carbon tetrachloride and methanol used in the oxygenation reactions were anhydrous. Silica gel [0.05—0.20 mm (Merck)] and light petroleum (b.p. 30—50 °C) were used for column chromatography.

\* The concerted rearrangement could also be operative in polar solvents, the substituent effect prevailing over the solvent effect.

Table 2. Product distribution in the dye-sensitized photo-oxygenation of the furans (1a—c) in carbon tetrachloride

Substrate	Reaction time (min) <sup>a</sup>	Yields (%) <sup>b</sup>				Polymeric material <sup>c</sup>
		(4)	(5)	(6)	(7)	
(1a)	120	52	45 <sup>d</sup>		Trace	
(1b)	60	55	20	6	3	5
(1c)	60	42	45		6	7

<sup>a</sup> Required for the completion of the reaction at -20 °C (<sup>1</sup>H n.m.r.).

<sup>b</sup> Deduced on the basis of the <sup>1</sup>H n.m.r. spectrum and confirmed by silica gel chromatography (compatible with product stability). <sup>c</sup> Calculated on the basis of the molecular weight of the starting furan + O<sub>2</sub>/2. <sup>d</sup> (5a)  $\equiv$  (6a).

*Dye-sensitized Photo-oxygenation of the 2-Methoxyfurans (1a—c) in Carbon Tetrachloride.*—A 2  $\times$  10<sup>-2</sup>M solution of the furans (1)<sup>1</sup> (1 mmol) in carbon tetrachloride was irradiated with a halogen-superphot lamp (Osram, 650 W) in the presence of tetraphenylporphyrin (3.6  $\times$  10<sup>-4</sup> mmol). During the irradiation, dry oxygen was bubbled through the solution which was kept at -20 °C. Periodically the solution was monitored (<sup>1</sup>H n.m.r.) for the furan (1) disappearance. When the reaction was complete, the solution was warmed at room temperature (18—22 °C). Removal of the solvent under reduced pressure gave a mixture which was analysed by <sup>1</sup>H n.m.r. spectroscopy. The reaction time and the composition of the mixture, deduced on the basis of the <sup>1</sup>H n.m.r. spectrum and confirmed by silica gel chromatography (compatible with the product stability) are shown in Table 2.

The spectral analysis (<sup>1</sup>H n.m.r.) of the furan (1a) oxygenation mixture, carried out before it was completely changed, showed the presence of the peroxide (3a) (Table 1) which rapidly rearranged into the epoxide (4a) and the keto ester (5a)  $\equiv$  (6a). No transient species were detected in the furan (1b,c) oxygenation mixtures.

An aliquot of the crude reaction mixture resulting from oxygenation of the furan (1a) was chromatographed on silica gel. Elution with light petroleum-diethyl ether (4:1, v/v) yielded, successively, the benzoyl malonate (8a) [45%, formed by hydrolysis of the keto ester (5a)  $\equiv$  (6a) on contact with the adsorbent], the ethylene (7a) (trace amount), and the epoxide (4a) (52%). The benzoylmalonate (8a) was identified by comparison with an authentic sample.<sup>15</sup> The ethylene (7a) was identified by comparison with a sample obtained by reduction with diethyl sulphide of the methoxyhydroperoxide (2a), according to the procedure previously reported.<sup>2</sup> Physical, spectral, and analytical data of the compounds (4a) and (7a) are reported in Table 1. The spectral data of (5a)  $\equiv$  (6a) (Table 1) were deduced from the <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra of the reaction mixture, the signal of (4a) and (7a) being subtracted. A second aliquot of the crude reaction mixture dissolved in water-saturated chloroform was kept at room temperature for 10 days. Inspection of the <sup>1</sup>H n.m.r. spectrum of the solution then showed, in addition to the signals of the epoxide (4a) and of the ethylene (7a), only the signals of benzoylmalonate (8a) and monomethyl oxalate (9). The oxalate (9) was identified by comparison (<sup>1</sup>H n.m.r.) with an authentic sample.<sup>16</sup> After removal of the solvent under reduced pressure, silica gel chromatography of the residue gave the results obtained when the reaction mixture was immediately chromatographed.

An aliquot of the crude mixture resulting from oxygenation of the furan (1b) was chromatographed on silica gel. Elution with light petroleum-diethyl ether (9:1, v/v) yielded methyl

benzoylacetate (**8b**) [16%, formed by hydrolysis of the keto ester (**5b**) on contact with the adsorbent]. Elution with light petroleum–diethyl ether (4:1, v/v) yielded the benzoylmalonate (**8a**) [4%, formed by hydrolysis of keto aldo ester (**6b**) on contact with the adsorbent], the ethylene (**7b**) (3%), and the epoxide (**4b**) (55%) successively. Elution with diethyl ether gave polymeric material (6%). The compounds (**8b**),<sup>17</sup> (**8a**),<sup>15</sup> and (**7b**)<sup>18</sup> were identified by comparison with authentic samples. Physical, spectral, and analytical data of the epoxide (**4b**) are reported in Table 1. The spectral data of the keto esters (**5b**) and (**6b**) (Table 1) were deduced from a careful analysis of the <sup>1</sup>H n.m.r. spectrum of the reaction mixture, the signals of (**4b**) being subtracted. A second aliquot of the crude reaction mixture dissolved in water-saturated chloroform was kept at room temperature for 10 days. Inspection of the <sup>1</sup>H n.m.r. spectrum of the solution then showed, in addition to the signals of the epoxide (**4b**) and the ethylene (**7b**), the signals of the benzoylacetate (**8b**), the benzoylmalonate (**8a**),<sup>15</sup> the monomethyl oxalate (**9**),<sup>16</sup> and polymeric material. Solvent was removed from the solution under reduced pressure, and the residue subjected to silica gel chromatography; the results obtained were identical with those obtained when the reaction mixture was immediately chromatographed.

An aliquot of the crude reaction mixture of the furan (**1c**) was chromatographed on silica gel. Elution with light petroleum–diethyl ether (17:3, v/v) yielded the benzoylacetone (**8c**) [20%, formed by hydrolysis of the keto ester (**5c**) on contact with the adsorbent] and the ethylene (**7c**) (6%). Elution with light petroleum–diethyl ether (7:3, v/v) and diethyl ether gave the epoxide (**4c**) (42%) and polymeric material (30%), successively. The benzoylacetone (**8c**) was identified by comparison with an authentic sample. The ethylene (**7c**) was identified by comparison with a sample obtained by reduction with diethyl sulphide of the methoxy hydroperoxide (**2c**), according to the procedure previously reported.<sup>2</sup> Physical, spectral, and analytical data of the compounds (**4c**) and (**7c**) are reported in Table 1. A second aliquot was dissolved in water-saturated chloroform and kept at room temperature for 10 days. Inspection of the <sup>1</sup>H n.m.r. spectrum then showed, in addition to the signals of the epoxide (**4c**) and the ethylene (**7c**), the signals of the benzoylacetone (**8c**), the monomethyl oxalate (**9**),<sup>16</sup> and polymeric material. Solvent was removed from the solution under reduced pressure, and the residue subjected to silica gel chromatography; the results obtained were identical with those obtained when the reaction mixture was immediately chromatographed. Spectral data for the keto ester (**5c**) (Table 1) were recorded for a sample obtained as follows. Most of the solvent was removed under reduced pressure from a carbon tetrachloride solution obtained, as above reported, by dye-sensitized photo-oxygenation of the furan (**1c**). In this way the epoxide (**4c**), which is hardly soluble in this solvent, separated in the solid state. The suspension was filtered and the resulting solution was rapidly chromatographed on a short column of silica gel. Elution with light petroleum–diethyl ether (1:1, v/v) gave the keto ester (**5c**) (90% pure).

*Dye-sensitized Photo-oxygenation of the 2-Methoxyfuran (1a) in Methanol.*—The furan (**1a**) (1 mmol) was oxygenated in dry methanol at the concentrations of  $2 \times 10^{-2}$  M and  $5 \times 10^{-3}$  M in the presence of Methylene Blue ( $3.6 \times 10^{-4}$  mmol), as above reported for the carbon tetrachloride solution, at  $-70$ ,  $-40$ ,  $-20$ , and  $10$  °C. After completion of the reaction (4–5 h), the solution was kept at the reaction temperature for some hours and then warmed at room temperature. After removal of the

methanol under reduced pressure, the <sup>1</sup>H n.m.r. and <sup>13</sup>C n.m.r. spectra of the residue were recorded. No spectral evidence was obtained to support the presence of the hemiperacetal (**17a**) the <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra showing only the signals of the methoxy hydroperoxide (**2a**), the epoxide (**4a**), the keto ester (**5a**)≡(**6a**), the ethylene (**7a**), and the methoxyhydroperoxide (**18**). Spectral data for (**18**), reported in Table 1, were deduced from inspection of the <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra of the reaction mixture obtained at  $-70$  °C, the signals of the known products being rejected. At  $-70$  °C formation of (**18**) increased while the yields of (**2a**) lessened. The composition of the reaction mixtures, deduced by <sup>1</sup>H n.m.r. spectroscopy, was confirmed by silica gel chromatography. Elution with light petroleum–diethyl ether (9:1, v/v) gave the lactone (**19**) derived from quantitative hydrolysis of the methoxy hydroperoxide (**18**) on contact with the adsorbent. Elution with light petroleum–diethyl ether (4:1, v/v) yielded the benzoylmalonate (**8a**),\* the ethylene (**7a**), the epoxide (**4a**), and the methoxy hydroperoxide (**2a**) successively. The structure of the lactone (**19**) was assigned on the basis of spectral and analytical data (Table 1). The products (**8a**), (**7a**), (**4a**), and (**2a**) were identified by comparison with authentic samples.

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\* Formed by hydrolysis of the keto ester (**5a**)≡(**6a**) on contact with the adsorbent.

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