

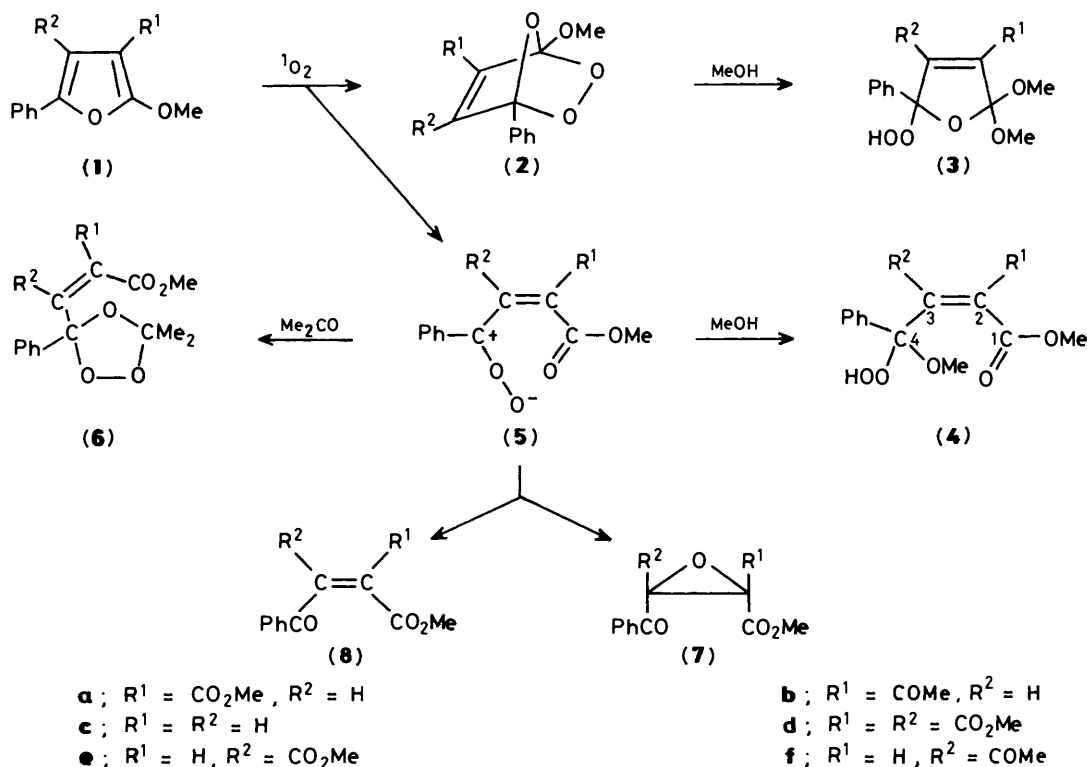
## Photosensitized Oxidation of Furans. Part 13.<sup>1</sup> Trapping Reactions of the Carbonyl Oxides Obtained from Some 2-Methoxy-5-phenylfurans

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The dye-sensitized photo-oxygenation in methanol of the 2-methoxy-5-phenylfurans (**1a—c**), unsubstituted at C-4 with electron-withdrawing groups, leads to the hemiperacetals (**4a—c**). The reaction provides the first incontrovertible evidence for carbonyl oxide intermediacy in sensitized photo-oxygenation of heterocyclic systems. Further supporting evidence is also reported. In polar non-participating solvents carbonyl oxides (**5a—c**) partly rearrange to the epoxides (**7a—c**).

Both synthetic and mechanistic studies of the dye-sensitized photo-oxygenation of furans have provided convenient routes to several multifunctional compounds, *via* furan endo-peroxides.<sup>1,2</sup> The latter generally react with primary and secondary alcohols to give alkoxy hydroperoxides, *e.g.* (**3**), or products which are believed to arise from these compounds.<sup>2b,3</sup> Alternatively, they fail to add alcohols at all; this is the case with electron-deficient endo-peroxides<sup>2a,†</sup> whose behaviour confirms the suggested addition pathway.<sup>2b</sup>

We have now found that dye-sensitized photo-oxygenation of 2-methoxy-5-phenylfurans (**1a—c**) in anhydrous methanol at  $-40^{\circ}\text{C}$ , quantitatively gives  $\alpha$ -methoxy hydroperoxides (**4a—c**). The latter are hemiperacetals structurally related to the  $\alpha$ -alkoxyalkyl hydroperoxides which have been obtained by ozonolysis of alkenes in an alcoholic solvent *via* the carbonyl oxides.<sup>5</sup> Therefore, formation of the  $\alpha$ -methoxy hydroperoxides (**4a—c**) can be rationalized in terms of trapping of the carbonyl oxides (**5a—c**) by methanol. The nature of these dipolar



The numeration on the structure (**4**) is used to simplify the reading of the n.m.r. data.

† Dimethyl 1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]hept-5-ene-5,6-dicarboxylate<sup>4</sup> under the usual conditions does not add methanol.

‡ When the oxygenation in acetone was carried out on the furan (**1c**), trioxolane (**6c**) was not detected. Only the products isolated from the reaction carried out in non-participating solvent were obtained (see below).

intermediates was confirmed by carrying out the sensitized photo-oxygenation of the furans (**1a, b**) at  $-40^{\circ}\text{C}$  in acetone to give the 1,2,4-trioxolanes (**6a, b**), in addition to the products which were obtained from the carbonyl oxides (**5a** and **b**) in non-participating solvents (see below).‡ The trioxolanes (**6a, b**) were isolated from the reaction mixtures by silica gel chromatography. In contrast, in the sensitized photo-oxygenation

**Table 1.** Product distribution in the dye-sensitized photo-oxygenation of the furans (1a–c) in nitromethane at –25 °C

Substrate	Concentration (M × 10 <sup>2</sup> )	Reaction time (min)	Yields (%) <sup>a</sup>			
			(7)	(8)	(9)	Polymeric material <sup>b</sup>
(1a)	2	90	26	46	—	20
(1a)	10	90	13	48	—	33
(1b)	2	90	43	33	15	7
(1b)	10	90	21	40	14	20
(1c)	2	150	5	27	—	47 <sup>c</sup>
(1c)	10	450	Trace	50	—	37 <sup>c</sup>

<sup>a</sup> Deduced on the basis of the <sup>1</sup>H n.m.r. spectrum and confirmed by silica gel chromatography. <sup>b</sup> Calculated on the basis of the molecular weight of the starting furan + O<sub>2</sub>/2. <sup>c</sup> Percentage yield includes a small amount of a yet unidentified compound.

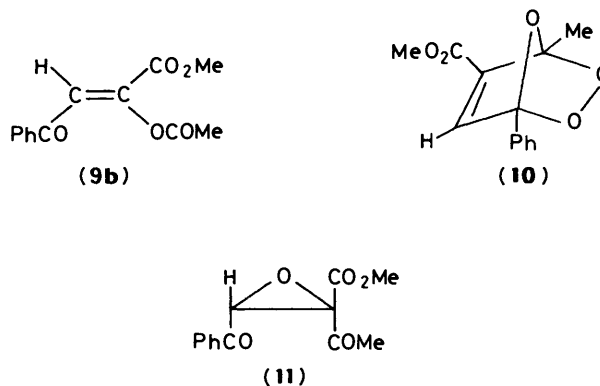
mixtures of the furans (1d–f) in methanol and in acetone no products such as the hemiperacetals (4) and trioxolanes (6), respectively, were detected (<sup>1</sup>H n.m.r.). In particular, in methanol the normal methanolysis<sup>2b,3</sup> of the *endo*-peroxides (2d–f) was observed giving the 5-hydroperoxy-2,2-dimethoxy-2,5-dihydrofurans (3d–f) which were purified by silica gel chromatography.

On the basis of these results it is clear that the unusual behaviour of the furans (1a–c) is a peculiarity of the 2-alkoxyfurans which have no electron-withdrawing group at the C-4 position. On the other hand, by the suggested mechanism<sup>2b</sup> the peroxides (2a–c) should react with methanol more easily than (2d–f), the developing cation being more stable. Therefore, the experimental results can be interpreted assuming that, owing to the presence of the alkoxy group at the C-1 position and the hydrogen atom at the C-5 position, the cleavage rates of the *endo*-peroxides (2a–c) to carbonyl oxides (5a–c) are higher than the reaction rates with methanol. Alternatively, it must be assumed that, depending on the particular substituents in the transition states formed in the reactions of singlet oxygen with furans (1a–c), one of the new bonds is almost completely formed while the other is very weak. Therefore, the transition states can be regarded as weakly perturbed zwitterions formed by combination of the diene and the dienophile at only one point in each, as recently suggested for some Diels–Alder reactions involving unsymmetrical dienes.<sup>6</sup> The perturbed zwitterions should collapse very readily to carbonyl oxides. This alternative hypothesis is also supported by a recent study on the mechanism of furan *endo*-peroxide formation.<sup>2c</sup>

However, the aforementioned reactions represent the first incontrovertible evidence for the carbonyl oxide intermediacy in the sensitized photo-oxygenation of heterocyclic systems.<sup>7–9</sup>

A few years ago it was suggested that *endo*-peroxides of the 2,5-diphenylfurans in aprotic polar solvents rearrange into *cis*-diaroyl epoxides *via* dipolar intermediates.<sup>9,\*</sup> Thus, in order to examine the fate of the carbonyl oxides (5a–c) in a polar non-participating solvent, the dye-sensitized photo-

oxygenation of the furans (1a–c) was carried out in nitromethane at a lower temperature compatible with the freezing point of this solvent. In no case were we able to detect intermediates. Table 1 shows the percentage yields of the products obtained using 2 × 10<sup>–2</sup> M and 0.1 M solutions of the furans (1a–c). An increase in the concentration of the furans (1a–c) only increased the amount of the ethylenes (8a–c) and/or polymeric material. Quantification was made on the basis of the <sup>1</sup>H n.m.r. spectra of the reaction mixtures and confirmed by chromatography on silica gel, which allowed the isolation of the epoxides (7a–c), ethylenes (8a–c), and the enol



ester (9b). The results show that in polar non-participating solvent the carbonyl oxides (5a–c) rearrange into the epoxides (7a–c), thus confirming that these compounds under the aforementioned conditions are formed *via* dipolar intermediates.† That the epoxides (7) are formed by oxygen transfer from the carbonyl oxides (5) to the ethylenes (8), however, can be excluded. In fact, methyl (*E*- and/or (*Z*)-2-acetyl-3-benzoyl-2,3-epoxypropionate were not detected when the sensitized photo-oxygenation of the furan (1a) was carried out in the presence of a mixture of methyl (*E*)-2-acetyl-3-benzoylacrylate and its *Z*-isomer. The high yield of the ethylenes (8a–c) (Table 1) can be rationalized considering the increase in yield when the reactions are carried out at higher concentration. In our opinion ethylene formation can be explained in two ways:‡ (a) through oxygenation, by carbonyl oxides (5a–c), of the yet unoxidized furans (1a–c), the latter behaving as trapping reagents;§ (b) through dipolar dimeric carbonyl oxides which could decompose to carbonyl compounds [ethylenes (8a–c)] and oxygen, as previously suggested for monosubstituted carbonyl oxides.<sup>5a</sup> The presence of the enol ester (9b) in the reaction mixture of the thermal conversion of the carbonyl oxide (5b) must be ascribed to the presence of the acetyl group, in that enol esters such as (9b) were not detected in the oxygenation mixture

\* Cf. Ref. 7 and 8.

† The low yields of the epoxide (7c) may be due to the lower stability of the carbonyl oxide (5c) relative to (5a, b).

‡ The further possibility that the carbonyl oxides (5a–c) react with small amounts of water, accidentally present in the reaction mixture, to give  $\alpha$ -hydroxy hydroperoxides which decompose into ethylenes (8a–c) must be discarded. In fact, control experiments showed that the quantity of compounds (8) in the reaction mixture does not vary when the solvent is saturated with water. Control experiments allowed exclusion of the possibility that compounds (8) were formed by triplet oxygen oxygenation.<sup>10</sup>

§ It is to be noted that owing to the withdrawing substituent position, carbonyl oxides (5a–c) could also behave as electrophilic oxidants.<sup>11</sup>

Table 2. Physical, spectral, and analytical data for the new products

Product	M.p. (°C)	$\nu_{\max}$ (CHCl <sub>3</sub> )/ cm <sup>-1</sup>	$\delta_{\text{H}}$ (CDCl <sub>3</sub> )	$\delta_{\text{C}}$ (CDCl <sub>3</sub> )/p.p.m.	Found (%) (Required)			
					Formula	C	H	O <sub>act.</sub>
(1a)	78—80 <sup>a</sup>		3.88 (3 H, s, CO <sub>2</sub> Me), 4.12 (3 H, s, OMe), 6.87 (1 H, s, 4-H), and 7.2—7.7 (5 H, m, Ph) <sup>b</sup>		C <sub>13</sub> H <sub>12</sub> O <sub>4</sub> (232.23)	67.1 (67.23)	5.0 (5.21)	
(1b)	96—98 <sup>a</sup>		2.43 (3 H, s, COMe), 4.28 (3 H, s, OMe), 6.95 (1 H, s, 4-H), and 7.2—7.7 (5 H, m, Ph) <sup>b</sup>		C <sub>13</sub> H <sub>12</sub> O <sub>3</sub> (216.23)	72.4 (72.21)	5.65 (5.59)	
(1c)	51—52 <sup>a</sup>		3.95 (3 H, s, OMe), 5.24 (1 H, d, <i>J</i> 4.2 Hz, 3-H), 6.53 (1 H, d, <i>J</i> 4.2 Hz, 4-H), and 7.2—7.7 (5 H, m, Ph) <sup>b</sup>		C <sub>11</sub> H <sub>10</sub> O <sub>2</sub> (174.19)	75.7 (75.84)	5.8 (5.79)	
(1e)	44—46 <sup>a</sup>		3.90 (3 H, s, CO <sub>2</sub> Me), 4.00 (3 H, s, OMe), 5.72 (1 H, s, 3-H), and 7.3—8.2 (5 H, m, Ph) <sup>b</sup>		C <sub>13</sub> H <sub>12</sub> O <sub>4</sub> (232.23)	67.1 (67.23)	5.2 (5.21)	
(1f)	58—60 <sup>a</sup>		2.38 (3 H, s, COMe), 3.93 (3 H, s, OMe), 5.58 (1 H, s, 3-H), and 7.3—8.1 (5 H, m, Ph) <sup>b</sup>		C <sub>13</sub> H <sub>12</sub> O <sub>3</sub> (216.23)	72.1 (72.21)	5.55 (5.59)	
(3d)	Oil	3 680, 3 400, 1 738, and 1 680	3.50 and 3.61 (6 H, 2 × s, 2 × OMe), 3.80 and 3.85 (6 H, 2 × s, 2 × CO <sub>2</sub> Me), 7.35—7.8 (5 H, m, Ph), and 9.40 (1 H, br s, OOH)	51.0, 52.3, 52.7, and 52.8 (4 × q, 4 × OMe), 112.5 (s, C-5), 121.3 (s, C-2), 126.5 (d, C-3 and C-5 of Ph), 128.3 (d, C-2 and C-6 of Ph), 129.7 (d, C-4 of Ph), 135.0 (s, C-3), 137.2 (s, C-1 of Ph), 140.5 (s, C-4), and 161.3 and 162.5 (2 × s, 2 × CO <sub>2</sub> )	C <sub>16</sub> H <sub>18</sub> O <sub>9</sub> (354.30)	54.2 (54.24)	5.25 (5.12)	4.0 (4.5)
(3e)	Oil	3 500, 3 300, 1 732, and 1 656	3.47 and 3.51 (6 H, 2 × s, 2 × OMe), 3.72 (3 H, s, CO <sub>2</sub> Me), 6.94 (1 H, s, 3-H), 7.3—7.8 (5 H, m, Ph), and 8.90 (1 H, br s, OOH)	50.3, 51.4, and 52.0 (3 × q, 3 × OMe), 113.9 (s, C-5), 121.1 (s, C-2), 126.8 (d, C-3 and C-5 of Ph), 127.9 (d, C-2 and C-6 of Ph), 129.1 (d, C-4 of Ph), 136.0 (s, C-1 of Ph), 137.2 (d, C-3), 137.6 (s, C-4), and 161.6 (s, CO <sub>2</sub> )	C <sub>14</sub> H <sub>16</sub> O <sub>7</sub> (296.27)	56.75 (56.75)	5.3 (5.44)	5.0 (5.4)
(3f)	Oil	3 570, 3 500, and 1 695	2.30 (3 H, s, COMe), 3.48 and 3.54 (6 H, 2 × s, 2 × OMe), 6.85 (1 H, s, 3-H), 7.3—7.8 (5 H, m, Ph), and 9.07 (1 H, br s, OOH)	28.6 (q, COMe), 50.5 and 51.6 (2 × q, 2 × OMe), 114.5 (s, C-5), 121.1 (s, C-2), 126.7 (d, C-3 and C-5 of Ph), 128.3 (d, C-2 and C-6 of Ph), 129.4 (d, C-4 of Ph), 135.9 (s + d, C-1 of Ph and C-3), 143.9 (s, C-4), and 194.1 (s, CO)	C <sub>14</sub> H <sub>16</sub> O <sub>6</sub> (280.27)	59.8 (59.99)	5.6 (5.75)	5.0 (5.7)
(4a)	Oil	3 520, 3 300, 1 735, and 1 660	3.29 (3 H, s, OMe), 3.80 and 3.93 (6 H, 2 × s, 2 × CO <sub>2</sub> Me), 7.06 (1 H, s, 3-H), 7.3—7.75 (5 H, m, Ph), and 8.12 (1 H, br s, OOH)	50.4, 52.3, and 52.5 (3 × q, 3 × OMe), 105.3 (s, C-4), 126.5 (d, C-3 and C-5 of Ph), 128.5 (d, C-2 and C-6 of Ph), 129.1 (d, C-4 of Ph), 135.7 (s + s, C-1 of Ph and C-2), 143.4 (d, C-3), and 163.6 and 166.6 (2 × s, 2 × CO <sub>2</sub> )	C <sub>14</sub> H <sub>16</sub> O <sub>7</sub> (296.27)	56.95 (56.75)	6.0 (5.44)	4.9 (5.4)

Table 2 (continued)

Product	M.p. (°C)	$\nu_{\max}$ (CHCl <sub>3</sub> )/ cm <sup>-1</sup>	$\delta_H$ (CDCl <sub>3</sub> )	$\delta_C$ (CDCl <sub>3</sub> )/p.p.m.	Formula	Found (%) (Required)		
						C	H	O <sub>act.</sub>
(4b)	116—118 <sup>c</sup>	3 600, 3 400, 1 737, and 1 679	2.29 (3 H, s, COMe), 3.25 (3 H, s, OMe), 3.86 (3 H, s, CO <sub>2</sub> Me), 6.73 (1 H, s, 3-H), 7.3—7.5 (5 H, m, Ph), and 8.96 (1 H, br s, OOH)	26.1 (q, Me), 50.5 and 52.5 (2 × q, 2 × OMe), 105.5 (s, C-4), 126.5 (d, C-3 and C-5 of Ph), 128.7 (d, C-2 and C-6 of Ph), 129.3 (d, C-4 of Ph), 135.6 and 135.7 (2 × s, C-1 of Ph and C-2), 142.5 (d, C-3), 168.0 (s, CO <sub>2</sub> ), and 195.0 (s, CO)	C <sub>14</sub> H <sub>16</sub> O <sub>6</sub> (280.27)	59.8 (59.99)	5.7 (5.75)	4.8 (5.7)
(4c)	Oil	3 510, 3 280, 1 730, and 1 655	3.28 (3 H, s, OMe), 3.74 (3 H, s, CO <sub>2</sub> Me), 5.90 and 6.02 (2 H, 2 × d, $J_{cis}$ 12.9 Hz, 2-H and 3-H), 7.3—7.6 (5 H, m, Ph), and 9.55 (1 H, br s, OOH)	50.1 and 51.7 (2 × q, 2 × OMe), 106.0 (s, C-4), 121.1 (d, C-2), 126.4 (d, C-3 and C-5 of Ph), 128.2 (d, C-2 and C-6 of Ph), 128.6 (d, C-4 of Ph), 137.7 (s, C-1 of Ph), 138.4 (d, C-3), and 167.7 (s, CO <sub>2</sub> )	C <sub>12</sub> H <sub>14</sub> O <sub>5</sub> (238.23)	60.3 (60.50)	5.85 (5.92)	6.2 (6.7)
(6a)	Oil	1 735 and 1 655	1.47 and 1.54 (6 H, 2 × s, 2 × Me), 3.76 (6 H, s, 2 × OMe), 7.09 (1 H, s, CH), and 7.2—7.65 (5 H, m, Ph)	23.0 and 24.9 (2 × q, 2 × Me), 52.2 and 52.7 (2 × q, 2 × OMe), 106.9 (s, C-5), 111.2 (s, C-3), 126.3 (d, C-3 and C-5 of Ph), 128.5 (d, C-2 and C-6 of Ph), 129.7 (d, C-4 of Ph), 135.1 (s + s, C-1 of Ph and olefinic C), 142.9 (d, olefinic CH), and 163.5 and 165.3 (2 × s, 2 × CO <sub>2</sub> )	C <sub>16</sub> H <sub>18</sub> O <sub>7</sub> (322.30)	59.55 (59.62)	5.5 (5.63)	4.9 (4.96)
(6b)	Oil	1 735, 1 679, and 1 655	1.50 and 1.56 (6 H, 2 × s, 2 × Me), 2.33 (3 H, s, COMe), 3.78 (3 H, s, CO <sub>2</sub> Me), 6.90 (1 H, s, CH), and 7.3—7.6 (5 H, m, Ph)	22.9, 24.9, and 26.6 (3 × q, 3 × Me), 52.2 (q, OMe), 107.0 (s, C-5), 111.3 (s, C-3), 126.3 (d, C-3 and C-5 of Ph), 128.6 (d, C-2 and C-6 of Ph), 129.8 (d, C-4 of Ph), 135.0 and 135.7 (2 × s, C-1 of Ph and olefinic C), 141.4 (d, olefinic CH), 164.5 (s, CO <sub>2</sub> ), and 194.3 (s, CO)	C <sub>16</sub> H <sub>18</sub> O <sub>6</sub> (306.30)	62.95 (62.74)	5.75 (5.92)	4.9 (5.2)
(7a)	Oil	1 735 and 1 694	3.71 and 3.84 (6 H, 2 × s, 2 × OMe), 4.68 (1 H, s, CH), and 7.35—8.0 (5 H, m, Ph)		C <sub>13</sub> H <sub>12</sub> O <sub>6</sub> (264.23)	59.2 (59.09)	4.6 (4.58)	
(7c)	102—103 <sup>d</sup>	1 752 and 1 690	3.65 (3 H, s, OMe), 3.90 and 4.23 (2 H, 2 × d, $J_{cis}$ 4.7 Hz, 2 × CH), and 7.4—8.2 (5 H, m, Ph)		C <sub>11</sub> H <sub>10</sub> O <sub>4</sub> (206.19)	64.1 (64.07)	4.8 (4.89)	
(8a)	Oil	1 735, 1 671, and 1 625	3.80 and 3.88 (6 H, 2 × s, 2 × OMe), and 7.35—8.0 (m, Ph) and 7.88 (s, CH) together 6 H		C <sub>13</sub> H <sub>12</sub> O <sub>5</sub> (248.23)	62.7 (62.90)	4.7 (4.87)	
(8c)	62—63 <sup>d</sup>	1 728 and 1 673	3.59 (3 H, s, OMe), 6.29 and 6.91 (2 H, 2 × d, $J_{cis}$ 12.1 Hz, 2 × CH), and 7.4—8.0 (5 H, m, Ph)		C <sub>11</sub> H <sub>10</sub> O <sub>3</sub> (190.19)	69.4 (69.46)	5.2 (5.30)	

<sup>a</sup> Recrystallization solvent, light petroleum (b.p. 40—70 °C). <sup>b</sup> Recorded on a Varian EM-360. <sup>c</sup> Recrystallization solvent, diethyl ether. <sup>d</sup> Recrystallization solvent, hexane.

of compounds (1a) or (1c). However, the suggested hypothesis that the carbonyl oxide (5b) cyclises to the isomeric endoperoxide (10), which rearranges into the enol ester (9b), as previously observed,<sup>10</sup> must also be excluded since if this were so, the isomeric epoxide (11) should also be obtained.<sup>3</sup>

The previously known compounds were identified by straightforward comparison of their i.r. and <sup>1</sup>H n.m.r. spectra with those of authentic samples. The structures of the new products were assigned on the basis of elemental analyses and spectral data (Table 2). In the methoxy hydroperoxides (3) the location of the two methoxy groups was ascertained by long-range <sup>13</sup>C-<sup>1</sup>H shift correlated 2D n.m.r. spectra (COLOC).<sup>12</sup> In fact, the experiment performed on compound (3d) showed correlation between C-2 ( $\delta$  121.3) and the two methoxy signals resonating at  $\delta$  3.55 and 3.67, thus indicating that both methoxy groups are linked to the same carbon atom. The stereochemistry of compounds (4b) and (6b) was assigned by a series of n.O.e. difference experiments. In particular, in compound (4b) the irradiation at  $\delta$  2.29 (COMe) caused enhancement of the signal at  $\delta$  6.73 (CH); in compound (6b) irradiation at  $\delta$  2.33 (COMe) caused enhancement of the signal at  $\delta$  6.90 (CH).

As regards the synthetic applications, this new method for the preparation of carbonyl oxides represents a convenient entry to the synthesis of several classes of functionalized compounds.

## Experimental

M.p.s are uncorrected. I.r. spectra were recorded with chloroform as solvent on a Perkin-Elmer 399 spectrophotometer. <sup>1</sup>H and <sup>13</sup>C N.m.r. spectra were recorded on a Bruker WH-270 or a Varian XL-200 spectrometer, unless otherwise stated, using deuteriochloroform as solvent and tetramethylsilane as internal standard. Methanol, acetone, and nitromethane 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.

Methyl 2-methoxy-5-phenylfuran-3-carboxylate (1a) and methyl 2-methoxy-5-phenylfuran-4-carboxylate (1e) were prepared according to a procedure previously reported<sup>13</sup> starting from 5-methoxy-4-methyl-2-phenyloxazole and methyl propiolate; silica gel chromatography of the reaction mixture with benzene as eluant gave (1e) (35%) and (1a) (26%) successively. 3-Acetyl-2-methoxy-5-phenylfuran (1b) and 4-acetyl-2-methoxy-5-phenylfuran (1f) were prepared according to the procedure reported for compound (1a) starting from 5-methoxy-4-methyl-2-phenyloxazole and butyn-2-one; silica gel chromatography of the reaction mixture, with benzene as eluant gave (1f) (35%) and (1b) (15%) successively. Dimethyl 2-methoxy-5-phenylfuran-3,4-dicarboxylate (1d)<sup>14</sup> was prepared according to the procedure reported for (1a), starting from 5-methoxy-4-methyl-2-phenyloxazole and dimethyl acetylenedicarboxylate; silica gel chromatography of the reaction mixture with light petroleum–diethyl ether (9:1 v/v) as eluant gave compound (1d) (70%). 2-Methoxy-5-phenylfuran (1c) was prepared and purified (70%) according to the procedure reported for 2-ethoxy-5-phenylfuran,<sup>15</sup> starting from 2,2-dimethoxy-5-phenyl-2,3-dihydrofuran.<sup>16</sup> Physical, spectral, and analytical data for the furans (1a–c) and (1e–f) are listed in Table 2.

*General Procedure for the Photosensitized Oxygenation of the 2-Methoxyfurans (1a–f) in Methanol.*—A  $2 \times 10^{-2}$  M solution of the furan (1) (1 mmol) in methanol was irradiated with a halogen-Superphot lamp (Osram, 650 W) in the presence of Methylene Blue ( $8 \times 10^{-3}$  mmol). During the irradiation, dry oxygen was bubbled through the solution which was maintained at –40 °C. Progress of the reaction was checked by periodically monitoring (<sup>1</sup>H n.m.r.) furan disappearance.

The oxygenation of the furans (1a–c) was complete within 120, 60, and 180 min respectively. After removal of the methanol, inspection of the <sup>1</sup>H n.m.r. spectra showed only the presence of the hemiperacetals (4a–c). The residue was taken up in dry ether, the suspension filtered to remove the Methylene Blue, and the filtrate evaporated to give quantitatively pure (4a–c). All attempts to separate (4a–c) from the Methylene Blue chromatographically failed since they partly polymerize and partly hydrolyse on contact with the absorbents.

Oxygenation of the furans (1d–f) was complete within 120 min [5 h for (1d)]. The solutions were heated at room temperature (18–22 °C). After 30 min, the methanol was removed under reduced pressure and the <sup>1</sup>H n.m.r. spectra of the mixtures showed the presence of the methoxy hydroperoxides (3d–f) with no trace of the hemiperacetals such as (4). Chromatography on a short column of silica gel, using light petroleum–diethyl ether (4:1 v/v) as eluant, led to the methoxy hydroperoxides (3d–f) (70–75%).

Physical, spectral, and analytical data of the hemiperacetals (4a–c) and the methoxy hydroperoxides (3d–f) are listed in Table 2.

*General Procedure for the Photosensitized Oxygenation of the 2-Methoxyfurans (1a–f) in Acetone.*—The photosensitized oxygenation was carried out according to the procedure reported above for the methanol solutions. When inspection of the <sup>1</sup>H n.m.r. spectrum of the solution showed complete conversion of the furan, the acetone was removed under reduced pressure.

Inspection of the <sup>1</sup>H n.m.r. spectra of the residue of the furan (1a, b) reaction mixtures showed the presence of the trioxolanes (6a, b) and the products which were identified by comparison with the spectra of the products obtained by photosensitized oxygenation of the furans (1a, b) in nitromethane. The trioxolanes (6a, b) were isolated by silica gel chromatography of the reaction mixtures of (1a, b), eluting with light petroleum–diethyl ether (85:15 v/v), in 30 and 12% yields respectively. Physical, spectral, and analytical data of (6a, b) are reported in Table 2.

Inspection of the <sup>1</sup>H n.m.r. spectrum of the residue of the reaction mixture of the furan (1c) showed only the presence of the products obtained when nitromethane was used as solvent (see below). They were identified by comparison with the <sup>1</sup>H n.m.r. spectrum of the photosensitized oxygenation mixture of (1c) in nitromethane.

Products such as the trioxolanes (6d–f) were absent (<sup>1</sup>H n.m.r.) from the reaction mixtures of the furans (1d–f).

*General Procedure for the Photosensitized Oxygenation of the 2-Methoxyfurans (1a–c) in Nitromethane.*—The photosensitized oxygenation was performed at –25 °C according to the procedure reported above, using  $2 \times 10^{-2}$  M and 0.1 M solutions. When inspection of the <sup>1</sup>H n.m.r. spectrum of the solution showed complete conversion of the furan, the solvent was removed under reduced pressure and the residue 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, are shown in Table 1.

Quantification of the reaction mixture of the furan (1a) was based on the relative areas of the signals at  $\delta$  4.68 [CH of (7a)], 7.88 [CH of (8a)], and methoxy signals. The crude reaction mixture was chromatographed on silica gel. Elution with light petroleum–diethyl ether (4:1 v/v) and diethyl ether gave, successively, ethylene (8a), epoxide (7a), and polymeric materials. The physical, spectral, and analytical data for compounds (7a) and (8a) are reported in Table 2. When the photosensitized oxygenation of the furan (1a) was carried out as described above

using nitromethane saturated with water as solvent, the same results were obtained. When the irradiation was carried out as described above but in absence of Methylene Blue, the furan (**1a**) was quantitatively recovered.

Quantification of the reaction mixture of the furan (**1b**) was based on the relative areas of the signals at  $\delta$  2.10 [COMe of (**9b**)], 2.31 [COMe of (**7b**)], 2.47 [COMe of (**8b**)], and methoxy signals. The crude reaction mixture was chromatographed on silica gel. Elution with light petroleum–diethyl ether (4:1 v/v) and (1:1 v/v), and diethyl ether, gave successively, enol ester (**9b**),<sup>10</sup> ethylene (**8b**),<sup>3</sup> epoxide (**7b**),<sup>17</sup> and polymeric materials.

Quantification of the reaction mixture of the furan (**1c**) was based on the relative areas of the doublets at  $\delta$  6.29 [CH of (**8c**)], 4.23 [CH of (**7c**)], and methoxy signals (signals attributable to an unidentified product were also present). The crude reaction mixture was chromatographed on silica gel. Elution with light petroleum–diethyl ether (85:15 v/v) and (4:1 v/v), and diethyl ether gave successively an unidentified product (5–10%), the ethylene (**8c**), the epoxide (**7c**), and polymeric materials. The epoxide (**7c**) was further purified by t.l.c. (benzene–diethyl ether, 4:1 v/v). The physical, spectral, and analytical data for compounds (**7c**) and (**8c**) are reported in Table 2.

*Photosensitized Oxygenation of Methyl 2-Methoxy-5-phenyl-furan-3-carboxylate (1a) in Nitromethane, in the Presence of a Mixture of Methyl (Z)-2-Acetyl-3-benzoylacrylate (8b) and its E-Isomer.*—To a nitromethane solution of the furan (**1a**) ( $2 \times 10^{-2}$ M; 50 ml) was added the ethylene (**8b**) and its *E*-isomer (together 1 mmol). The solution was photo-oxygenated at  $-25^\circ\text{C}$  according to the procedure reported above. After 90 min inspection of the  $^1\text{H}$  n.m.r. spectrum of the reaction mixture, obtained by removal of the solvent at reduced pressure, showed only signals for ethylene (**8b**) and its *E*-isomer, and for products derived from the photosensitized oxygenation of the furan (**1a**) in nitromethane. The mixture was chromatographed on silica gel. Elution with light petroleum–diethyl ether (4:1 v/v) and diethyl ether gave successively the ethylene (**8b**) and its *E*-isomer, the ethylene (**8a**), the epoxide (**7a**), and polymeric material. The ethylene (**8b**) and its *E*-isomer were recovered quantitatively; the ethylene (**8a**), the epoxide (**7a**), and polymeric material in the yields reported in Table 1 (solution  $2 \times 10^{-2}$ M).

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