Photosensitized Oxidation of Furans. Part 1. Synthesis and Properties of Furan *endo*-Peroxides

By **M. Liliana Graziano, M. Rosaria Iesce,** and **Rachele Scarpati,*** Istituto di Chimica Organica e Biologica dell'Università, 80134 Napoli, Italy

Photosensitized oxidation of 3-methoxycarbonylfurans (1) at −15 °C yields quantitatively furan *endo*-peroxides (2) which are stable at this temperature under strictly anhydrous conditions. At room temperature in absence of solvent and moisture, within 15—20 days, they give epoxides (3) as the major products. Reduction, methanolysis, and hydrolysis of the *endo*-peroxides (2) have been investigated.

DYE-SENSITIZED photo-oxidations of alkyl- and aryl-substituted furans have been widely studied and it has been assumed that the 1,4-addition of the singlet oxygen leads to furan *endo*-peroxides.[1] These compounds, which can be seen as mono-ozonides of cyclobutadienes, are unstable and have been isolated up to now in only few cases.[2,3] Therefore some ambiguities associated with their hydrolysis and thermal conversion remained unresolved.

In order to obtain more stable furan *endo*-peroxides we have carried out the dye-sensitized photo-oxidation of furans substituted with an electron-withdrawing group at position 3. This choice was made on the basis that delocalization of the π-electrons of the furan *endo*-peroxide structure by an electron-withdrawing substituent would ensure that the reactivity of this system lay between that of the mono-ozonides of cyclobutadiene derivatives and of the more stable ozonides of cyclobutene derivatives.[4] There are few reports describing the behaviour towards singlet oxygen of furans substituted at position 3 and/or 4 with electron-withdrawing groups. The only reported studies in this area are those of Kock, who observed a decrease in reactivity in the presence of a formyl or carboxy-substituent on the furan system,[5] and of Rio who incidentally carried out the dye-sensitized photo-oxidation of the 3-ethoxycarbonyl-5-methyl-2,4-diphenylfuran at room temperature in methanol remarking that the methoxyhydroperoxy-2,5-dihydrofuran obtained showed unusual behaviour.[6]

In this paper we report the results obtained using 3-methoxycarbonyl-2-methyl-5-phenylfuran (1a) and 3-methoxycarbonyl-2,5-dimethylfuran (1b). The photo-oxidation of (1a) was accomplished in anhydrous chloroform at −15 °C with Methylene Blue as a sensitizer using a halogen-superphot lamp (Osram 650 W). The reaction was periodically sampled and the sample analysed by ^{1}H n.m.r. spectroscopy. After the signals of the starting material had disappeared (2 h), the ^{1}H n.m.r. spectrum showed the presence of only one compound which was isolated as a white solid in quantitative yield and characterized as the furan *endo*-peroxide (2a) on the basis of active-oxygen determination and spectral data detailed in the Experimental section.

The *endo*-peroxide (2a) is stable at −15 °C *under strictly anhydrous conditions*. At room temperature, in the absence of solvent and moisture, after 15 days it was completely transformed (^{1}H n.m.r.). From the reaction mixture, silica gel chromatography allowed the isolation of methyl (*E*)-2-acetyl-3-benzoyl-2,3-epoxypropionate (3a) (62%) and of a mixture of methyl (*E*)-2-acetyl-3-benzoylacrylate (4a) and its *Z*-isomer (5a) (altogether 5%), apart from a mixture of gummy materials. Structure (3a) was assigned on the basis of elemental analyses and spectral data detailed in the Experimental section, and a negative test for peroxide with acidified KI. In particular, the *E*-configuration was supported by the ^{1}H n.m.r. solvent effect:[7] the singlet due to acetyl protons, which appeared at δ 2.33 in deuteriochloroform, remained unchanged in hexadeuteriobenzene. A series of nuclear Overhauser effect (NOE) difference experiments, performed on a Fourier transform 270-MHz spectrometer with the aid of an ASPECT 2000 microprogram, provided further evidence for the assigned configuration. In fact, in the ^{1}H n.m.r. spectrum of the epoxide in $CDCl_3$, irradiation at δ 2.33 (COMe) left the signal at δ 4.73 (CH) unchanged.† Acrylates (4a) and (5a) were identified by comparison of their i.r. and ^{1}H n.m.r. spectra with those of the compounds obtained by reduction of (2a) (see below). The mixture of gummy materials gave a positive test for peroxide with acidified KI and showed very complex i.r. and ^{1}H n.m.r. spectra (see Experimental section).

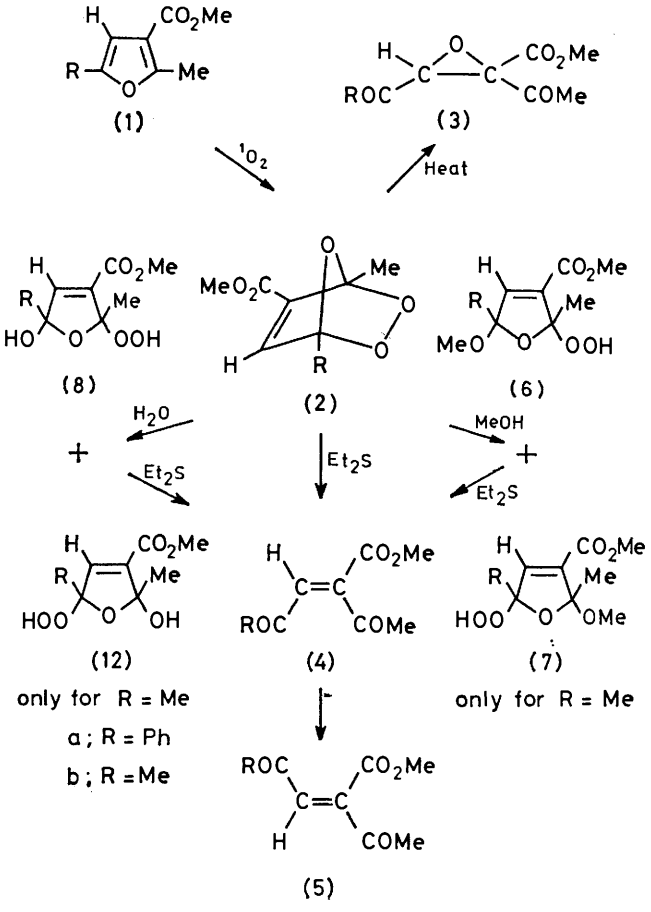
The *endo*-peroxide (2a) was reduced by diethyl sulphide,‡ at 0 °C within 1 h, into *E*-isomer (4a) which partly converted into the *Z*-isomer (5a). After 12 h the ^{1}H n.m.r. spectrum, on the basis of the integration of the methoxy-singlets, showed that the *E* : *Z* ratio was 5 : 4 with no further changes over a period of time. The *E*-isomer (4a) partly isomerizes into (5a) on contact with silica gel, alumina, and polyamide. The acrylates (4a) and (5a) were isolated as a mixture by silica gel chroma-

† In the ^{1}H n.m.r. spectrum in $CDCl_3$ of the *Z*-isomer of (3a) [δ ($CDCl_3$) 2.31 (3 H, s, COMe), 3.65 (3 H, s, CO_2Me), 4.45 (1 H, s, CH), and 7.35—8.05 (5 H, m, aromatic); (C_6D_6) 1.80 (3 H, s, COMe), 3.15 (3 H, s, CO_2Me), 3.90 (1 H, s, CH), and 6.85—7.90 (5 H, m, aromatic)], obtained from (2a) by a different way as will be reported in the near future, irradiation at δ 2.31 (COMe) caused the enhancement of the signal at δ 4.45 (CH).

‡ Before using the diethyl sulphide reduction [8] we applied the triphenylphosphine technique, which we have used in similar cases,[9] obtaining only the starting furans (1a). The reduction by trialkyl phosphite of 2-ene-1,4-diones to furan has been recently reported.[10]

tography and all the attempts to separate them by chromatographic methods failed. Structural assignments of the two isomers were made on the basis of elemental analyses and spectral properties (particularly ^{1}H n.m.r. solvent effect [7] and NOE) of their mixture as detailed in the Experimental section.

Addition of anhydrous methanol to the *endo*-peroxide (2a) at 0 °C gave quantitatively only one compound. Active-oxygen determination and elemental and spectral data, reported in the Experimental section, agree with structure (6a) as well as with structure (7a). The latter was excluded on the basis of the fully coupled ^{13}C n.m.r. spectrum. C-2 appeared as a multiplet at δ 115.09 which was simplified into a quartet (*J* 4.5 Hz) and



into a doublet (*J* 8.4 Hz) by irradiation at *H*C-4 and at H_3C-C-2 frequencies respectively while it was completely unaffected by irradiation on the frequency of the acetalic H_3C-O group. On the other hand C-5 appeared as a complex multiplet which was partially simplified by irradiation at *H*C-4 and acetalic H_3C-O group frequencies, thus pointing out that the structure of 2-hydroperoxy-5-methoxy-3-methoxycarbonyl-2-methyl-5-phenyldihydrofuran (6a) * is to be assigned to the compound obtained by methanolysis of (2a). Methoxyhydroperoxide (6a) can be obtained in quantitative yield also by sensitized photo-oxidation at −15 °C of the furan (1a) in anhydrous methanol, as previously observed for alkylfurans.[11] The methoxyhydroperoxide (6a) is stable at room temperature under neutral conditions and is readily reduced by diethyl sulphide [12] into the *E*-isomer (4a).

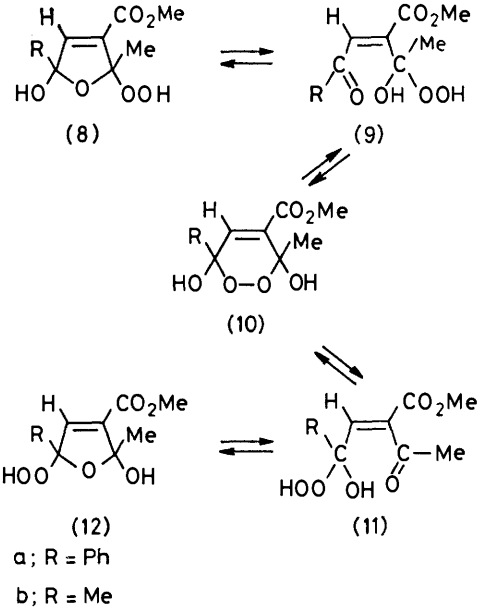
The *endo*-peroxide (2a) is sensitive to hydrolysis: when it was kept at room temperature in conditions not strictly anhydrous, *e.g.* in an n.m.r. tube in deuteriochloroform, after a few hours the ^{1}H n.m.r. spectrum showed signals attributable to hydroxyhydroperoxy-compounds. In an attempt to isolate the hydrolysis products, the *endo*-peroxide (2a) was kept at 0 °C in acetone–water solution. After 2 h † the ^{1}H n.m.r. spectrum of the reaction mixture showed, in addition to the signals of (3a), (4a), and (5a), and of the gummy materials, singlets attributable to several peroxy-compounds (see Experimental section). The latter signals underwent remarkable modifications over a period of time (broadened signals appeared). All the attempts to separate the peroxy-compounds by chromatographic methods failed because they polymerize in contact with the absorbent. However, useful information for the assignment of their structures was obtained by investigating the crude reaction mixture soon after the signals of (2a) had disappeared in the ^{1}H n.m.r. spectrum. In fact, inspection of this spectrum showed that the molar ratio (3a) : (4a) + (5a) : peroxy-compounds was *ca.* 6 : 1 : 8. Addition of diethyl sulphide followed by silica-gel chromatography allowed the isolation of (3a) and (4a) + (5a) in *ca.* 6 : 9 molar ratio. These results clearly indicate that the peroxy-compounds are reduced by diethyl sulphide to (4a). On the basis of the results of the reaction of (2a) with methanol and of the spectral and chemical properties of the reaction mixture of (2a) with water, it seems reasonable to assume that the key step of the hydrolysis is the addition of water to (2a) to form 2-hydroperoxy-5-hydroxy-3-methoxycarbonyl-2-methyl-5-phenyldihydrofuran (8a). This compound, as a hemiacetal, could be in equilibrium with (9a), (10a), (11a), and (12a). Since (9a) and (11a) might react also intermolecularly, the above hypothesis would also account for the modifications of the ^{1}H n.m.r. spectrum of the hydrolysis mixture after several days. Not only have equilibria similar to (9) ⇌ (10) ⇌ (11) previously been observed, but there have also been reports that in compounds like (9) or (11) the addition of the hydroperoxy-group to the carbonyl group tends to occur intermolecularly to give polymeric peroxides.[13]

Furan (1b), upon dye-sensitized photo-oxidation, behaved just like (1a) and furan *endo*-peroxide (2b) was isolated in quantitative yield. The latter is stable at −15 °C under anhydrous conditions. At room temperature in the absence of solvent and moisture, after 20 days it gave a mixture, the ^{1}H n.m.r. spectrum of which showed, in addition to broadened signals, the presence of epoxypropionate (3b). Reduction of (2b) by diethyl

* The stereochemistry of (6a) has not been investigated.

† Conversion of (2a) into (3a) takes place more rapidly in solution than in the absence of solvent.

sulphide gave, in very good yield, methyl (*E*)-2,3-diacetylacrylate (4b) which was partly converted into the *Z*-isomer (5b). Both (4b) and (5b) polymerize with time. All attempts to separate the epoxide (3b) or the acrylates (4b) and (5b) by chromatographic methods failed because of their polymerization in contact with the absorbent. Therefore structural assignments were made on the basis of spectral properties of the crude mixtures (see Experimental section). The addition of anhydrous



methanol to the *endo*-peroxide (2b) was slower than with (2a); it gave quantitatively 2-hydroperoxy-5-methoxy-3-methoxycarbonyl-2,5-dimethyldihydrofuran (6b) and 5-hydroperoxy-2-methoxy-3-methoxycarbonyl-2,5-dimethyldihydrofuran (7b) in nearly equal amounts (^{1}H n.m.r.). Since all attempts at separation of the products failed, structural assignments were made on the basis of elemental analyses, active-oxygen determination, and spectral and chemical properties of the mixture. *endo*-Peroxide (2b) reacted with water, more slowly than (2a), to give hydroxyhydroperoxides which were converted into (4b) by addition of diethyl sulphide. On the basis of the results of the reaction of (2b) with methanol, in this case the addition of water could give 2-hydroperoxy-5-hydroxy-3-methoxycarbonyl-2,5-dimethyldihydrofuran (8b) and 5-hydroperoxy-2-hydroxy-3-methoxycarbonyl-2,5-dimethyldihydrofuran (12b) which should be in equilibrium through (9b), (10b), and (11b).

The above results indicate that furan *endo*-peroxides like (2) can be obtained in quantitative yield by dye-sensitized photo-oxidation of 3-methoxycarbonylfurans (1) at −15 °C. The high hydrolytic reactivity of *endo*-peroxides (2) makes a detailed study on their thermal conversion very difficult. Nevertheless it is evident that the epoxides (3), which may be produced by intra- or inter-molecular epoxidation, are the most significant products deriving from this reaction. Formation of epoxides was observed occasionally in the sensitized-photo-oxidation of tetra-arylfurans.[2,14] Reaction of *endo*-peroxides (2) with methanol or water can be viewed as a nucleophilic opening by attack on an α carbon to give the methoxyhydroperoxides or the hydroxyhydroperoxides respectively. This mechanistic interpretation is supported by substituent effects on methanolysis. In fact, in the case of (2a) the nucleophilic attack occurs exclusively on the benzyl carbon atom and only the 5-methoxy-2-hydroperoxide (6a) is obtained; in the case of (2b) a decrease in reactivity is observed, with respect to (2a), and in addition to the 5-methoxy-2-hydroperoxide (6b) the 2-methoxy-hydroperoxide (7b) is formed.

EXPERIMENTAL

M.p.s are uncorrected. I.r. spectra were measured with chloroform as solvent, unless otherwise stated, on a Perkin-Elmer 399 spectrophotometer. ^{1}H N.m.r. spectra were recorded with deuteriochloroform as solvent, unless otherwise stated, on a Perkin-Elmer R 12 A or on a Bruker W. H. 270 with tetramethylsilane as standard. ^{13}C N.m.r. spectra were recorded on a Bruker W. H. 270 with tetramethylsilane as standard. Nuclear Overhauser effects were measured on a Bruker W. H. 270 Fourier transform spectrometer with the aid of an ASPECT 2000 microprogram which allowed direct automatic accumulation of NOE difference FIDs; 3% $CDCl_3$ degassed solutions were used. Chloroform used in the oxidation reactions was anhydrous and ethanol-free. Silica gel 0.50—0.20 mm (Merck) and light petroleum b.p. 30—50 °C were used for column chromatography.

3-Methoxycarbonyl-2-methyl-5-phenylfuran (1a) was prepared from methyl phenacylacetoacetate by dehydration with phosphoric acid ester.[15] Silica gel chromatography (elution with light petroleum–ether, 19 : 1 v/v) gave (1a) (95%), m.p. 55—56 °C (Found: C, 72.05; H, 5.5. $C_{13}H_{12}O_3$ requires C, 72.21; H, 5.59); $\nu_{max.}$ 1 715 cm^{-1}; ^{1}H n.m.r. δ 2.62 (3 H, s, Me), 3.82 (3 H, s, OMe), 6.88 (1 H, s, CH), and 7.20—7.80 (5 H, m, Ph).

3-Methoxycarbonyl-2,5-dimethylfuran (1b) was prepared following the method of Stevenson.[16] Silica-gel chromatography [elution with light petroleum–ether (19 : 1 v/v)] gave (1b) (80%) as a colourless liquid (Found: C, 62.05; H, 6.3. $C_8H_{10}O_3$ requires C, 62.32; H, 6.54); $\nu_{max.}$ 1 713 cm^{-1}; ^{1}H n.m.r. δ 2.22 (3 H, s, 5-Me), 2.51 (3 H, s, 2-Me), 3.78 (3 H, s, OMe), and 6.21 (1 H, s, CH).

Photosensitized Oxidation of Furan (1a) *into the Furan* endo-*Peroxide* (2a).—A solution of (1a) (216 mg, 1 mmol) and Methylene Blue (3 mg, 8 × 10^{-3} mmol) in dry chloroform (10 ml) was irradiated with a halogen-superphot lamp (Osram 650 W). During the irradiation, dry oxygen was bubbled through the solution which was cooled at −15 °C. The reaction was complete within 2 h (^{1}H n.m.r.). After removal of the chloroform *in vacuo*, the residue was taken up in dry ether. The suspension was filtered to remove Methylene Blue and the solution evaporated. All the procedure was carried out at −15 °C. In this way pure *furan* endo-*peroxide* (2a) was quantitatively isolated as a white solid, m.p. 78 °C (decomp.) (Found: O_{active} 5.9. $C_{13}H_{12}O_5$ requires 6.4%); $\nu_{max.}$ 1 725 (C=O), 1 610 (C=C), and 860 cm^{-1} (O–O); ^{1}H n.m.r. δ 2.08 (3 H, s, Me), 3.80 (3 H, s, COOMe), 7.28 (1 H, s, CH), and 7.35—7.90 (5 H, m, aromatic); ^{13}C n.m.r. δ 13.1 (q, Me), 52.1 (q, OMe), 112.7 and

113.2 (2 × s, C-2 and C-5), 127.5 and 129.0 (2 × d, C-2, C-6 and C-3, C-5 of Ph group), 131.4 (d, C-4 of Ph group), 138.8 (s, C-3), 138.8 (s, C-1 of Ph group), 139.3 (d, C-4), and 162.2 (s, C=O).

Thermal Conversion of endo-*Peroxide* (2a).—*endo*-Peroxide (2a) (307 mg, 1.24 mmol) was kept under strictly anhydrous conditions at room temperature. After 15 days an inspection of the ^{1}H n.m.r. spectrum showed that (2a) was entirely converted into the epoxide (3a) and the acrylates (4a) and (5a); furthermore broadened signals appeared in the range of the methyl absorption. The mixture was chromatographed on silica gel (15 g). Elution with light petroleum–ether (4 : 1 v/v) gave (4a) and (5a) (14 mg, 5%, identified by comparison of i.r. and ^{1}H n.m.r. spectra with those of the authentic samples), and (3a) (194 mg, 62%) successively. Elution with ether gave gummy materials (73 mg).

Epoxide (3a) is a colourless liquid (Found: C, 63.05; H, 5.1. $C_{13}H_{12}O_5$ requires C, 62.90; H, 4.87%); $\nu_{max.}$ 1 760 (CO_2Me), 1 730 (COMe), and 1 703 cm^{-1} (COPh); δ ($CDCl_3$) 2.33 (3 H, s, COMe), 3.82 (3 H, s, CO_2Me), 4.73 (1 H, s, CH), and 7.35—8.05 (5 H, m, aromatic); δ (C_6D_6) 2.30 (3 H, s, COMe), 3.28 (3 H, s, CO_2Me), 4.68 (1 H, s, CH), and 6.85—7.90 (5 H, m, aromatic).

The gummy materials gave a positive test for peroxide with acidified KI, and the i.r. spectrum revealed the presence of several OH (3 650—3 400 cm^{-1}), C=O (1 750—1 700 cm^{-1}), C=C (1 675—1 650 cm^{-1}, and O–O (870—850 cm^{-1}) functions; the ^{1}H n.m.r. spectrum showed broadened signals at δ 1.1—1.9, 3.5—3.9, and 7.0—8.2.

Reduction of endo-*Peroxide* (2a) *by Diethyl Sulphide.*—To a 2% solution of (2a) (250 mg, 1 mmol) in dry chloroform pre-cooled at 0 °C was added diethyl sulphide (0.21 ml, 2 mmol) and the solution was kept at 0 °C After 1 h it was washed with water, in order to remove the diethyl sulphoxide, and dried. Removal of the chloroform and the unchanged diethyl sulphide *in vacuo* gave the E-*acrylate* (4a) as a liquid; $\nu_{max.}$ (CCl_4) 1 740 (CO_2Me), 1 715 (COMe), 1 675 (COPh), and 1 620 cm^{-1} (C=C); δ ($CDCl_3$) 2.49 (3 H, s, COMe), 3.87 (3 H, s, CO_2Me), 7.40—7.60 (3 H, m, 3,4,5-PhH), 7.78 (1 H, s, CH), and 7.80—8.10 (2 H, m, 2,6-PhH); (C_6D_6) 2.32 (3 H, s, COMe), 3.28 (3 H, s, CO_2Me), 6.85—7.20 (3 H, m, 3,4,5-PhH), and 7.55 and 7.55—7.80 (3 H, s and m, CH and 2,6-PhH). A NOE-difference experiment in $CDCl_3$ showed that irradiation at δ 2.49 left the signal at δ 7.78 unchanged.

A ^{1}H n.m.r. spectrum recorded after 12 h showed the presence of (4a) and (5a) in *ca.* 5 : 4 molar ratio (on the basis of the relative areas of the two methoxy-singlets). The mixture was chromatographed on silica gel (15 g). Elution with light petroleum–ether (4 : 1 v/v) gave an inseparable mixture of *E*- (4a) and *Z*-isomer (5a) (200 mg, 85%) in a molar ratio 5 : 4 (^{1}H n.m.r.) (Found: C, 67.0; H, 5.3. $C_{13}H_{12}O_4$ requires C, 67.23; H, 5.21%); $\nu_{max.}$ (CCl_4) 1 740 (CO_2Me), 1 715 (COMe), 1 675 (COPh), and 1 620 cm^{-1} (C=C); δ for *Z*-isomer (5a) ($CDCl_3$) 2.47 (3 H, s, COMe), 3.76 (3 H, s, CO_2Me), and 7.65 (1 H, s, CH); (C_6D_6) 1.99 (3 H, s, COMe), 3.37 (3 H, s, CO_2Me), and 7.29 (1 H, s, CH); the phenyl hydrogens of (5a) were not assigned since their signals and those of (4a) overlap each other. A NOE-difference experiment in $CDCl_3$ showed that irradiation at δ 2.47 caused the enhancement of the signal at δ 7.65 (CH). The mixture of (4a) and (5a) was also obtained when *E*-acrylate (4a) was chromatographed on silica gel, alumina, and polyamide.

Addition of Methanol to the endo-*Peroxide* (2a).—The *endo*-peroxide (2a) (248 mg, 1 mmol) was dissolved in dry methanol (12.5 ml) pre-cooled at 0 °C and the solution was kept at 0 °C under strictly anhydrous conditions. When the reaction was complete (1 h), methanol was removed *in vacuo* and the residue was filtered through a short column of silica gel. Elution with light petroleum–ether (4 : 1 v/v) gave quantitatively the *methoxyhydroperoxide* (6a) as a colourless liquid (Found: C, 59.7; H, 5.9; O_{active} 5.5. $C_{14}H_{16}O_6$ requires C, 59.99; H, 5.75; O_{active} 5.7%); $\nu_{max.}$ 3 690 and 3 525 (OOH), 1 730 (C=O), 1 660 (C=C), and 855 cm^{-1} (O–O); ^{1}H n.m.r. δ 1.79 (3 H, s, Me), 3.24 (3 H, s, OMe), 3.75 (3 H, s, CO_2Me), 6.99 (1 H, s, CH), 7.25—7.65 (5 H, m, aromatic), and 8.65 (1 H, s, OOH); ^{13}C n.m.r. δ 21.14 (q, Me), 51.17 (q, acetal OMe), 51.98 (q, ester OMe), 109.01 (s, C-5), 115.09 (s, C-2), 126.48 (d, C-3 and C-5 of Ph group), 128.71 (d, C-2 and C-6 of Ph group), 128.98 (d, C-4 of Ph group), 133.18 (s, C-3), 137.43 (s, C-1 of Ph group), 143.91 (d, C-4), and 161.90 (s, C=O).

Similar results were obtained by sensitized photo-oxidation of (1a) (216 mg, 1 mmol) in dry methanol (12.5 ml) under the conditions used for the photo-oxidation of (1a) in chloroform. The reaction was complete within 5 h.

Reduction of the methoxyhydroperoxide (6a) by diethyl sulphide, carried out as above described for *endo*-peroxide (2a), gave the *acrylate* (4a). The reaction was complete within 15 min; yield 85%.

Addition of Water to the endo-*Peroxide* (2a).—The *endo*-peroxide (2a) (248 mg, 1 mmol) was dissolved in acetone–water (6 ml; 4 : 1 v/v) pre-cooled at 0 °C. The solution was kept at 0 °C for 2 h, after which work-up gave a mixture (176 mg) the ^{1}H n.m.r. spectrum of which showed, in addition to the presence of (3a), (4a), (5a), and gummy materials, singlets at δ 1.65, 1.75, and 1.77 (Me), 3.80, 3.85, and 3.88 (CO_2Me), 3.59, 4.37, and 4.75 (OH), 6.96, 7.00, 7.03, and 7.22 (=CH), and 9.44, 10.49, and 10.60 (OOH) assigned to the *peroxy-compounds* (8a)—(12a). Molar ratio (3a) : (4a) + (5a) : (8a) to (12a) was *ca.* 6 : 1 : 8, on the basis of relative areas of the singlets at δ 4.73 [CH of (3a)], 2.47 and 2.49 [COMe of (4a) and (5a)], 6.96—7.22 [=CH of (8a) to (12a)]. The reaction mixture was dissolved in chloroform (8 ml) and treated with diethyl sulphide (0.12 ml, 1.28 mmol). After 3 h the solution was washed with water and dried. Removal of the solvent and of the unchanged diethyl sulphide *in vacuo* gave a residue which was analysed by ^{1}H n.m.r. spectroscopy [molar ratio (3a) : (4a) + (5a) was *ca.* 6 : 9] and chromatographed on silica gel (8 g). Elution with light petroleum–ether (4 : 1 v/v) gave (4a) + (5a) (65 mg, 28%) and (3a) (45 mg, 18%) successively.

When the mixture obtained by hydrolysis was kept at room temperature, the ^{1}H n.m.r. spectrum, recorded after several days, showed that the signals assigned to (8a)—(12a) had disappeared and, in addition to the signals of (3a), (4a), and (5a), only broadened signals appeared. Silica-gel chromatography allowed only the isolation of (3a) and (4a) + (5a).

Photosensitized Oxidation of Furan (1b) *into the Furan* endo-*Peroxide* (2b).—Oxidation was accomplished on 230 mg (1.5 mmol) of (1b) as described above for (1a). Pure endo-*peroxide* (2b) was quantitatively isolated as a colourless liquid (Found: O_{active} 8.1. $C_8H_{10}O_5$ requires 8.6%); $\nu_{max.}$ 1 725 (C=O), 1 613 (C=C), and 862 cm^{-1} (O–O); ^{1}H n.m.r. δ 1.82 (3 H, s, 5-Me), 1.98 (3 H, s, 2-Me), 3.78 (3 H, s, OMe), and 6.93 (1 H, s, CH); ^{13}C n.m.r. δ 12.8 and 13.2 (2 × q, 2 × Me), 51.9 (q, OMe), 111.2 and 112.2 (2 × s, C-2

and C-5), 138.0 (s, C-3), 140.3 (d, C-4), and 162.1 (s, C=O).

Thermal Conversion of the endo-*Peroxide* (2b).—The *endo*-peroxide (2b) was kept under strictly anhydrous conditions in the absence of solvent at room temperature. After 20 days the ^{1}H n.m.r. spectrum showed, in addition to broadened signals, singlets at δ 2.24, 2.37, 3.85, and 4.07 with relative areas *ca.* 3 : 3 : 3 : 1 * which were assigned respectively to 2 × COMe, CO_2Me, and CH of the *epoxide* (3b) by comparison with the ^{1}H n.m.r. spectrum of the crude mixture of the thermal conversion of (2a); yield of (3b) was *ca.* 30%. Attempts to isolate (3b) by chromatographic methods were unsuccessful: in fact, silica-gel chromatography gave only inseparable mixtures of (3b) and gummy materials, the ^{1}H n.m.r. spectrum of which showed broadened signals. Alumina or polyamide chromatography gave only small amounts of gummy materials, the ^{1}H n.m.r. spectrum of which showed broadened signals.

Reduction of the endo-*Peroxide* (2b) *by Diethyl Sulphide.*—To a 2% solution of (2b) (186 mg, 1 mmol) in dry chloroform was added diethyl sulphide (0.21 ml, 2 mmol). The solution was kept at room temperature for 2 h after which work-up gave the E-*acrylate* (4b) (160 mg, 94%) as a colourless liquid; $\nu_{max.}$ 1 725 (CO_2Me), 1 700 (COMe), and 1 635 cm^{-1} (C=C); δ 2.31 and 2.38 (6 H, 2 × s, 2 × COMe), 3.82 (3 H, s, CO_2Me), and 7.02 (1 H, s, CH). The ^{1}H n.m.r. spectrum recorded after 12 h showed, in addition to broadened signals in the range of the methyl and methoxy-absorptions, the presence of (4b) and (5b) in *ca.* 5 : 4 molar ratio (on the basis of the relative areas of the two olefinic singlets); δ for the Z-*isomer* (5b) 2.32 and 2.36 (6 H, 2 × s, 2 × COMe), 3.85 (3 H, s, CO_2Me), and 6.94 (1 H, s, CH). The ^{1}H n.m.r. spectrum recorded after 15 days showed only broadened signals. Silica gel, alumina, or polyamide chromatography of (4b) gave only compounds the ^{1}H n.m.r. spectra of which showed broadened signals.

Addition of Methanol to the endo-*Peroxide* (2b).—The *endo*-peroxide (2b) (186 mg, 1 mmol) was dissolved in dry methanol (9 ml) and the solution was kept at room temperature under strictly anhydrous conditions. When the reaction was complete (3 h), methanol was removed *in vacuo* and the residue was analysed by ^{1}H n.m.r. spectroscopy; the molar ratio (6b) : (7b) was *ca.* 1 : 1. Some attempts to separate (6b) from (7b) by chromatography on silica gel, alumina, or polyamide failed, the mixture was filtered through a short column of silica gel. Elution with light petroleum–ether (7 : 3; v/v) gave quantitatively a mixture of the *methoxyhydroperoxides* (6b) and (7b) as a colourless liquid (Found: C, 49.55; H, 6.2; O_{active} 6.9. $C_9H_{14}O_6$ requires C, 49.54; H, 6.47; O_{active} 7.3%); $\nu_{max.}$ 3 690 and 3 530 (OOH), 1 730 (C=O), 1 665 and 1 653 (C=C), and 860 cm^{-1} (O–O); δ 1.51 and 1.53 (6 H, 2 × s, 2 × Me), 1.65 (6 H, s, 2 × Me), 3.36 (6 H, s, 2 × OMe), 3.80 (6 H, s, 2 × CO_2Me), 6.78 and 6.82 (2 H, 2 × s, 2 × CH), and 8.75 (2 H, br s, 2 × OOH).

Reduction of the mixture of methoxyhydroperoxides (6b) and (7b) by diethyl sulphide, carried out as described above for the *endo*-peroxide (2b), gave the *acrylate* (4b) in 92% yield. The reaction was complete within 90 min.

* The determination of the areas cannot be rigorous owing to the presence of broadened signals in the range of the methyl and methoxy absorptions.

† Trace amounts of (4b) were present.

Addition of Water to the endo-*Peroxide* (2b).—The *endo*-peroxide (2b) (186 mg, 1 mmol) was dissolved in acetone–water (5 ml; 4 : 1 v/v) and the solution was kept at room temperature for 6 h. Work-up gave the *peroxy-compounds* (8b)—(12b) † (140 mg, 70%) as a liquid (Found: O_{active}, 6.7. $C_8H_{12}O_6$ requires O_{active}, 7.8%); $\nu_{max.}$ 3 690 and 3 530 (OOH), 3 580 and 3 400 (OH), 1 725 (C=O), 1 650 and 1 605 (C=C), and 860 cm^{-1} (O–O); δ 1.51, 1.57, 1.58, 1.61, 1.63, 1.68 and 2.21 (altogether 6 H, singlets, Me), 3.81 and 3.84 (altogether 3 H, singlets, CO_2Me), 3.99, 4.12, and 4.95 (altogether 1 H, singlets, OH), 6.67, 6.78, 6.82, and 6.85 (altogether 1 H, singlets, =CH), 8.40 and 9.15 (altogether 1 H, singlets, OOH).

Reduction of the peroxy-compounds (8b)—(12b) by diethyl sulphide, carried out as above described for the *endo*-peroxide (2b), required 12 h. After this time, the ^{1}H n.m.r. spectrum of the reaction mixture showed, in addition to broadened signals in the range of the methyl and methoxy absorptions, the presence of the E-*acrylate* (4b) and the Z-*acrylate* (5b) in *ca.* 5 : 4 molar ratio.

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