Photosensitized Oxidation of Furans. Part 16.[1] Selective Formation and Chemical Properties of 3*H*-1,2-Dioxoles: a New Class of Cyclic Peroxides

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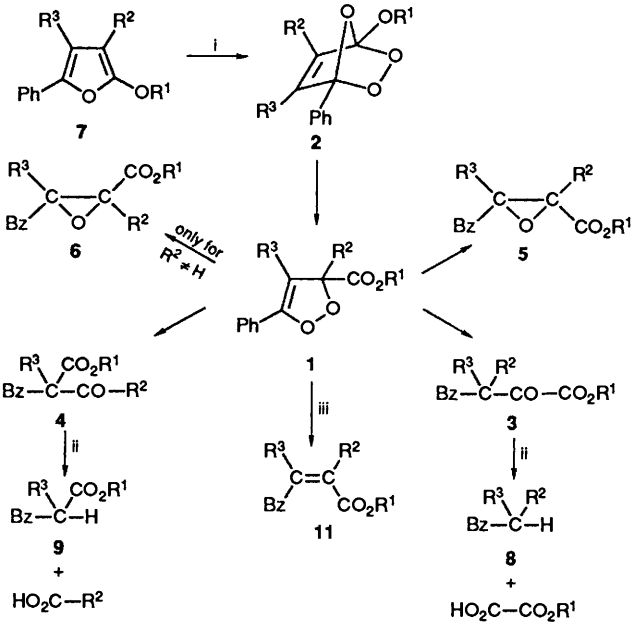
Direct evidence is provided for the selective formation of the 3*H*-1,2-dioxoles **1** by thermal conversion of the furan *endo*-peroxides **2** substituted at C-1 with an alkoxy substituent and at C-5 with an electron-withdrawing group. The thermally unstable dioxoles **1** when heated give, by concerted rearrangements, in addition to the keto esters **3** and **4**, the epoxides **5**, or **5** and **6**. Those like **1c–e**, which are disubstituted at C-3, yield the two stereoisomeric epoxides **5c–e** and **6c–e**, while dioxoles **1a** and **1b**, which bear a hydrogen atom at C-3, give stereospecifically the epoxides **5a** and **b**. The stereospecificity of the latter reaction is suggested to be due to the preferential conformation **10**, which the peroxides **1a,b** assume on formation from the related *endo*-peroxides. Some other chemical properties of the new class of peroxides are reported.

Some years ago we invoked the 3*H*-1,2-dioxoles **1a–c**† as intermediates in the thermal conversion of the 1-methoxy-2,3,7-trioxabicyclo[2.2.1]hept-5-enes **2a–c** into the keto esters **3a**, **b**, **4b** and **3c≡4c**, although we excluded their intermediacy in the formation of the epoxides **5a–c**‡, the isomeric epoxides **6a** and **6b**§ having never been detected.[3] Subsequently, spectral evidence for the 3*H*-1,2-dioxole **1d** intermediacy was found in the thermal conversion, at −60 °C in an apolar solvent,¶ of the *endo*-peroxide **2d**.[1] Furthermore, it was observed that although compound **1d** rearranges into the keto ester **4d** it leads mainly to the stereoisomeric epoxides **5d** and **6d**.[1] On the other hand, the 1-methoxytrioxabicycloheptenes **2** unsubstituted at C-5 and bearing an electron-withdrawing group at C-6 lead selectively to carbonyl oxides[4] whilst the peroxides **2** bearing an electron-donating group at C-5 and an electron-withdrawing substituent at C-6 rearrange quantitatively into furanodioxetanes.[5]

Therefore, it was desirable to confirm the intermediacy of the dioxoles **1a–c** in the thermal conversion of the *endo*-peroxides **2a–c** as well as to gain information concerning the stereospecific formation of the epoxides **5a**, **b**.

Results and Discussion

We carried out tetraphenylporphyrin-sensitized photooxygenation of the furans **7a–c** and **7e** in $CDCl_3$–$CFCl_3$ at −80 °C (Scheme 1). After 90 min ^1H and ^{13}C NMR spectra of the reaction mixtures, recorded at −80 °C, showed the presence of only the *endo*-peroxides **2a–c** and **2e** (Table 1). The subsequent rearrangements starting from the latter (Scheme 1) were evidenced by NMR spectroscopic analyses at various times and temperatures. The *endo*-peroxides **2a** and **2b** at −60 °C led quantitatively to the dioxoles **1a** and **1b**. The latter at −40 °C rearranged into the keto esters **3a** and **4a** and the epoxide **5a** and into the keto ester **3b** and the epoxide **5b**, respectively.‖ These results show that, in contrast with our previous assumption,[3] both the keto esters and the epoxides are formed from the *endo*-peroxides **2** *via* the dioxoles **1**. However, a careful spectral analysis confirmed that the epoxides **6a,b** were not formed.** Conversion of the *endo*-peroxides **2c** and **2e**, which are more thermally stable than the peroxides **2a,b**,†† into the dioxoles **1c** and **1e** started at −25 °C. The latter, in turn, at this temperature rearranged into the keto ester **3c≡4c** and the epoxide **5c≡6c** and into the keto esters **3e** and **4e** and the epoxides **5e** and **6e**, respectively. Within 24 h the *endo*-peroxides **2c** and **2e** and the dioxoles **1c** and **1e** disappeared nearly simultaneously and almost equimolecular quantities of the thermal conversion products were only present in the reaction mixtures. Quantification of the thermal conversion products of the *endo*-peroxide



a; R¹ = Me R² = H R³ = CO_2Me
b; R¹ = Me R² = H R³ = Ac
c; R¹ = Me R² = R³ = CO_2Me
d; R¹ = Me R² = Ph R³ = H
e; R¹ = Et R² = R³ = CO_2Me

Scheme 1 *Reagents:* i, $^1O_2$; ii, H_3O^+; iii, $(Ph)_3P$

† 3*H*-1,2-Dioxoles have not been reported previously in the literature.[2]
‡ *In the thermal conversion of the endo*-peroxides **2a–c** almost equimolecular quantities of the keto esters and of the epoxides **5a–c** were formed.[3]
§ It is to be noted that **6c≡5c**.
¶ In polar solvents the main product was the carbonyl oxide.[1]
‖ The keto esters and the epoxides were obtained in the same yields when the dye-sensitized photooxygenation of **7a,b** was carried out at −20 °C in CCl_4, $CHCl_3$ and $MeNO_2$.[3]

** Independent synthesis of the isomers **5a,b** and **6a,b** (see Experimental section) provided final evidence for this datum.
†† As observed in similar cases,[6] there is a connection between the instability of the furan *endo*-peroxides and the electron density in the bicyclic unsaturated ring.

Table 1 Physical, spectral and analytical data for the products derived from the dye-sensitized photooxygenation of the furans **7a–c,e**

Compd.	M.p. (°C)	ν_{max}/cm^{-1} ($CHCl_3$)	δ_H[$CDCl_3$–$CFCl_3$ (1:1)] (*J* values in Hz)	δ_C[$CDCl_3$–$CFCl_3$ (1:1)]
1a			3.78 and 3.91 (6 H, 2 × s, 2 × OMe), 6.04 (1 H, s, CH), 7.40–7.90 (5 H, m, Ph)	52.3 and 53.5 (2 × q, 2 × OMe), 84.1 (d, C-3), 98.6 (s, C-4), 121.7 (s, C-1 of Ph), 128.3, 130.3 and 132.6 (3 × d, CH of Ph), 156.9 (s, C-5), 162.6 and 169.3 (2 × s, 2 × CO_2)
1b			2.06 (3 H, s, Me), 3.92 (3 H, s, OMe), 6.13 (1 H, s, CH), 7.50–7.80 (5 H, m, Ph)	28.1 (q, Me), 53.3 (q, OMe), 85.5 (d, C-3), 113.0 (s, C-4), 122.5 (s, C-1 of Ph), 129.1, 130.3 and 132.5 (3 × d, CH of Ph), 162.7 (s, C-5), 169.2 (s, CO_2), 191.7 (s, CO)
1c			3.73 (s, OMe)[a]	
1e			1.38 (t, *J* 6.9, Me), 3.73 and 3.86 (2 × s, 2 × OMe), 4.36 (q, *J* 6.9, OCH_2)[b]	
2a			3.71 and 3.84 (6 H, 2 × s, 2 × OMe), 7.23 (1 H, s, CH), 7.40–7.70 (5 H, m, Ph)	52.5 and 54.0 (2 × q, 2 × OMe), 110.1 (s, C-4), 125.3 (s, C-1), 126.2, 128.3 and 130.6 (3 × d, CH of Ph), 128.2 (s, C-1 of Ph), 138.2 (s, C-5), 137.9 (d, C-6), 161.7 (s, CO_2)
2b			2.37 (3 H, s, Me), 3.84 (3 H, s, OMe), 7.16 (1 H, s, CH), 7.40–7.70 (5 H, m, Ph)	27.7 (q, Me), 53.9 (q, OMe), 110.1 (s, C-4), 125.1 (s, C-1), 128.3, 129.0 and 136.5 (3 × d, CH of Ph), 130.6 (s, C-1 of Ph), 143.3 (d, C-6), 145.3 (s, C-5), 193.2 (s, CO)
2c			3.71, 3.88 and 3.93 (9 H, 3 × s, 3 × OMe), 7.40–7.70 (5 H, m, Ph)[c]	53.0, 53.3 and 54.7 (3 × q, 3 × OMe), 109.8 (s, C-4), 124.5 (s, C-1), 126.4, 128.7 and 131.2 (3 × d, CH of Ph), 127.4 (s, C-1 of Ph), 136.6 and 140.4 (2 × s, C-5 and C-6), 160.6 and 161.4 (2 × s, 2 × CO_2)
2e			1.41 (3 H, t, *J* 7.3, Me), 3.71 and 3.95 (6 H, 2 × s, 2 × OMe), 4.25 (2 H, m, OCH_2),[d] 7.40–7.70 (5 H, m, Ph)	15.1 (q, Me), 53.3 and 53.6 (2 × q, 2 × OMe), 64.3 (t, OCH_2), 109.6 (s, C-4), 124.3 (s, C-1), 126.3, 128.7 and 131.2 (3 × d, CH of Ph), 127.3 (s, C-1 of Ph), 137.8 and 139.0 (2 × s, C-5 and C-6), 161.1 and 161.3 (2 × s, 2 × CO_2)
3e + **4e**[e]			1.17 (t, *J* 7.1, Me), 1.35 (t, *J* 7.1, Me), 3.77 (s, 2 × OMe), 3.78 (s, OMe), 3.89 (s, OMe), 4.28 (m, OCH_2),[d] 4.37 (m, OCH_2)[d,f]	78.7 and 78.8 (2 × s, 2 × C_{quat}), 183.4 and 183.5 (2 × s, 2 × CO), 190.5 (s, 2 × *C*OPh)[g]
5e[h]	oil	1758 1697	1.06 (3 H, t, *J* 7.1, Me), 3.78 and 3.91 (6 H, 2 × s, 2 × OMe), 4.08 (2 H, q, *J* 7.1, OCH_2), 7.30–8.10 (5 H, m, Ph)[f]	13.4 (q, Me), 53.4 and 54.1 (2 × q, 2 × OMe), 63.5 (t, OCH_2), 63.7 and 65.8 (2 × s, 2 × $C_{epoxidic}$), 128.8 and 134.5 (2 × d, CH of Ph), 133.8 (s, C-1 of Ph), 162.4, 162.7 and 164.1 (3 × s, 3 × CO_2), 186.7 (s, CO)[f]
6a[i]	oil	1759 1692	3.78 and 3.87 (6 H, 2 × s, 2 × OMe), 3.95 (1 H, s, CH), 7.40–8.10 (5 H, m, Ph)[f]	53.1 and 53.6 (2 × q, 2 × OMe), 56.4 (d, CH), 64.3 (s, $C_{epoxidic}$), 128.9, 129.3 and 134.6 (3 × d, CH of Ph), 133.4 (s, C-1 of Ph), 164.4 and 165.2 (2 × s, 2 × CO_2), 188.7 (s, CO)[f]
6b[j]	oil	1757 1732 1687	2.45 (3 H, s, Me), 3.85 (3 H, s, OMe), 3.92 (1 H, s, CH), 7.40–8.10 (5 H, m, Ph)[f]	28.0 (q, Me), 53.2 (q, OMe), 57.1 (d, CH), 69.7 (s, $C_{epoxidic}$), 128.9, 129.8 and 134.7 (3 × d, CH of Ph), 135.5 (s, C-1 of Ph), 165.8 (s, CO_2), 189.8 (s, *C*OPh), 199.0 (s, *C*OMe)[f]
6e[k]	104–106[l]	1759 1692	1.37 (3 H, t, *J* 7.1, Me), 3.65 and 3.79 (6 H, 2 × s, 2 × OMe), 4.38 (2 H, q, *J* 7.1, OCH_2), 7.30–8.10 (5 H, m, Ph)[f]	13.8 (q, Me), 53.6 and 53.9 (2 × q, 2 × OMe), 62.9 (t, OCH_2), 63.7 and 66.0 (2 × s, 2 × $C_{epoxidic}$), 128.9 and 134.5 (2 × d, CH of Ph), 133.6 (s, C-1 of Ph), 162.1, 163.1 and 163.9 (3 × s, 3 × CO_2), 186.9 (s, CO)[f]
9e[m]	oil	1758 1682	1.24 (3 H, t, *J* 7.1, Me), 3.80 (3 H, s, OMe), 4.27 (2 H, q, *J* 7.1, OCH_2), 5.31 (1 H, s, CH), 7.35–7.90 (CH, m, Ph)[f]	13.9 (q, Me), 53.3 (q, OMe), 61.6 (d, CH), 62.5 (t, OCH_2), 128.5, 129.0 and 134.2 (3 × d, CH or Ph), 129.8 (s, C-1 of Ph), 164.7 and 165.2 (2 × s, 2 × CO_2), 188.8 (s, CO)[f]

[a] The other hydrogens were not assigned since their signals and those of the products present in the mixture overlap. [b] No integration nor assignment of the phenyl hydrogens was possible since their signals and those of the products present in the mixture overlap. [c] The chemical shifts reported in Ref. 3 were measured with a Varian EM-360 spectrometer in carbon tetrachloride. [d] The methylene hydrogens are diastereotopic. [e] In *ca.* 1:1 molar ratio in addition to the epoxides **5e** and **6e**. Therefore only selected signals of the mixture of **3e** and **4e** are reported for both ^1H and ^{13}C NMR spectra. [f] Recorded in deuteriochloroform. [g] Recorded in deuterioacetone. [h] Found: C, 57.2; H, 4.8. $C_{16}H_{16}O_8$ requires C, 57.14; H, 4.80%. [i] Found: C, 59.1; H, 4.6. $C_{13}H_{12}O_6$ requires C, 59.09; H. 4.58%. [j] Found: C, 62.2; H, 4.8. $C_{13}H_{12}O_5$ requires C, 62.09; H, 4.87%. [k] Found: C, 57.3; H, 4.7. $C_{16}H_{16}O_8$ requires C, 57.14; H, 4.80%. [l] Recrystallization solvent mixture light petroleum–diethyl ether. [m] Found: C, 62.4; H, 5.6. $C_{13}H_{14}O_5$ requires C, 62.39; H, 5.64%.

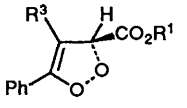
2e, *via* **1e**, was confirmed by chromatography of the reaction mixture on silica gel, which gave results similar to those observed for the *endo*-peroxide **2c**.[3] Known compounds were identified by comparison with authentic samples. The structures of the new products were assigned on the basis of elemental analysis and/or spectral data, reported in Table 1. The stereochemistry of the two epoxides **5e** and **6e** was assigned by comparison in the two isomers of the chemical shifts of the geminal alkoxycarbonyl groups.* As regards compounds **3e** and **4e**, which are difficult to isolate owing to their ready hydrolysis (see Experimental section), it was not possible to assign the NMR signals to each of them since they are similar in structure and are present in the reaction solution in *ca.* 1:1 molar ratio. Therefore, Table 1 reports the ^1H and ^{13}C NMR data of the mixture, the signals of the epoxides **5e** and **6e** being subtracted. The ^1H NMR data of the dioxoles **1c**, **e** (Table 1) were deduced by a careful analysis of the ^1H NMR spectra of the conversion mixtures of the *endo*-peroxides **2c,e**, periodically recorded at −25 °C, the signals of the other products being subtracted.†

The thermal conversion of the *endo*-peroxide **2a** into the dioxole **1a** as well as those of the latter and of the *endo*-peroxide **2e** into the thermally stable products were uninfluenced by 2,6-di-*tert*-butyl-*p*-cresol. Similar results were also obtained when the thermal rearrangements of the dioxole **1a** and of the *endo*-peroxide **2e** were carried out, respectively, at −40 and −25 °C

* In the *E*-isomer **5e** the signals of the ethoxycarbonyl group [δ 4.08 (OCH_2) and 1.06 (Me)] undergo upfield shifts with respect to those for the *Z*-isomer **6e** [δ 4.38 (OCH_2) and 1.37 (Me)] owing to the anisotropy of the aromatic ring in the benzoyl group which is on the same side. On the other hand, it is the singlet of the methoxycarbonyl group in isomer **6e** (δ 3.65) which undergoes the upfield shift with respect to that for isomer **5e** (δ 3.91).

† Only one methoxy signal was evidenced for the dioxole **1c** owing to the crowding of the signals in the region of the methoxy resonances.

using polar solvents, such as [$^2H_3$]acetonitrile and [$^2H_4$]-methanol.* These results confirm our previous assumption[3] of the concertedness of the rearrangement of the *endo*-peroxides **2** into the dioxoles **1**. Also it is reasonable to assume that both the rearrangements of the dioxoles **1** into the keto esters **3** and **4** and into the epoxides **5**, or **5** and **6** proceed *via* concerted processes, the first involving the 1,5 shift of the alkoxycarbonyl group or, in preference, that of the hydrogen atom.† As regards the epoxide formation, the dioxoles **1d** and **1e**, disubstituted at C-3, yield both the stereoisomeric epoxides **5d,e** and **6d,e**, while the dioxoles **1a** and **1b**, which at C-3 bear a hydrogen atom, give stereospecifically the epoxides **5a,b**. A possible explanation of the unexpected stereospecificity is that the dioxoles **1a,b** on formation from the *endo*-peroxides **2a,b** assume the less crowded conformations **10a,b**‡ and collapse into the epoxides



10a, b

5a,b without undergoing conformational isomerization. In contrast, the dioxoles **1c–e** are conformationally mobile systems having comparable crowding of the two groups at C-3 and lead to both the isomeric epoxides **5c–e** and **6c–e**.§ It is also possible that the ring inversion for the dioxoles **1a,b** is prevented by intramolecular non-bonding interaction between the carbonyl oxygen of the substituent at C-4 and the hydrogen atom at C-3. Indeed, the C–H bond is heavily polarized owing to the presence, on the carbon atom, of both the electron-withdrawing group and the oxygen substituent.¶ The dioxole **1a** in solvents such as methanol or acetonitrile once again rearranges stereospecifically into the epoxide **5a**. However, it is known that sometimes the extent of intramolecular hydrogen bonding is independent of the solvent.[10]

Since the dioxoles **1** are the first examples of this ring system, it seemed of interest to study their chemical reactivity. Although a considerable limitation to this investigation was imposed by the low temperature of conversion of the peroxides **1**, it had been observed that the dioxoles **1a** and **1d** are unreactive towards both water, even in the presence of hydrochloric acid, and methanol at −60 °C. At this temperature triphenylphosphine slowly reacts with the dioxoles **1** and at room temperature triphenylphosphine oxide and the ethylenes (*E*)-**11a**[11],‖ and (*Z*)-**11d**[1] were respectively obtained. A little of the rearrangement products were present in the reaction mixture of the peroxide **1d**.

In conclusion, the above and the previous[1,4,5] results show that the thermal conversion of the *endo*-peroxides of the 2-alkoxyfurans takes different courses in connection with the electron-density distribution in the bicyclic unsaturated ring, dramatically depending on the nature as well as on the position of the substituents. In particular, the dioxoles **1** can be formed when a partial positive charge is located at C-6, substitution at C-5 with an electron-withdrawing group making the formation *selective*.

* This solvent was used only for the dioxole **1a** since the *endo*-peroxide **2e** adds methanol in the same manner as compounds **2a–c**.[7]

† The preferential shift of the hydrogen atom was also observed for the 3*H*-1,2,4-dioxazoles.[8]

‡ The Dreiding models show that the hydrogen atom at C-3 and the substituent at C-4 are roughly in the same plane.

§ Under the experimental conditions used the conformational interconversion is too fast to be observed by NMR spectroscopy.

¶ There are many examples of the non-bonding interaction of O and activated C–H groups in the literature.[9] In nearly all cases, the C–H bond is adjacent to either an electron-withdrawing group or some other activating group, which serves to influence the polarization of the C–H bond.

Experimental

IR spectra were recorded on a Perkin-Elmer 1760X-FT spectrophotometer with chloroform as solvent. ^1H and ^{13}C NMR spectra were recorded with Bruker AC-270 or AM-400 spectrometers using deuteriochloroform–trichlorofluoromethane (1:1) as solvents, unless otherwise stated, and tetramethylsilane as internal standard. The solvents used in the photooxygenation reactions were anhydrous. Silica gel 0.05–0.20 mm (Merck), and light petroleum (b.p. 40–70 °C) were used for column chromatography. TLC was performed on layers (1 mm thickness) of silica gel (Whatman Silica gel PK6F). Tetraphenylporphyrin (TPP) (Fluka) was used without purification.

Dye-sensitized Photooxygenation of the Furans **7a–c,e**.—Solutions 5 × 10^{-2} mol dm^{-3} of the furans **7a–c**[7] and **7e**[13] (1 mmol) in $CDCl_3$–$CFCl_3$ (1:1) were 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 solutions which were kept at −80 °C. Periodically the solutions were monitored (^1H NMR) for the disappearance of the furans. When the reactions were complete (90 min), the ^1H NMR spectra, recorded at −80 °C, showed the presence of the only *endo*-peroxides **2a–c,e** whose spectral data are reported in Table 1.

Thermal Conversion of the endo-*Peroxides* **2a,b**.—The samples of the *endo*-peroxides **2a** and **2b** were warmed to −60 °C. After 10 h for compound **2a** and 5 h for compound **2b** the ^1H and ^{13}C NMR spectra (Table 1) showed the presence of only the dioxoles **1a** and **1b**, respectively. Similar results were obtained when the thermal conversion of the *endo*-peroxide **2a** was carried out at −60 °C in the presence of 2,6-di-*tert*-butyl-*p*-cresol.

The samples of the dioxoles **1a** and **1b** in $CDCl_3$–$CFCl_3$ were warmed at −40 °C. Within 3 h they were converted into the keto esters **3a** and **4a** and the epoxide **5a** and into the keto ester **3b** and the epoxide **5b**, respectively. The molar ratios (^1H NMR) of the compounds obtained were very similar to those previously observed.[3] Similar results were obtained either when the conversion of the dioxole **1a** was carried out in the presence of 2,6-di-*tert*-butyl-*p*-cresol at −40 °C or when, after removal of $CDCl_3$–$CFCl_3$ at reduced pressure at −60 °C, the rearrangement of the dioxole **1a** was carried out in [$^2H_4$]methanol or in [$^2H_3$]acetonitrile at −40 °C.

Synthesis of the Isomeric Epoxides **5a,b** *and* **6a,b**.—Compounds **5a,b** and **6a,b** were obtained according to a procedure previously reported for different functionalized oxiranes[14] starting from the parent ethylenes **11a** and **11b**, respectively, by *tert*-butyl hydroperoxide oxygenation in the presence of triethylamine. Slow silica gel chromatography of the reaction mixture of the ethylene **11a** [eluent light petroleum–diethyl ether (17:3)] led to the epoxides **5a**[3] (40%) and **6a** (23%). Silica gel chromatography of the reaction mixture of the ethylene **11b** [eluent light petroleum–diethyl ether (17:3)] followed by TLC chromatography [eluent light petroleum–diethyl ether (4:1)] gave the epoxides **5b**[3] (38%) and **6b** (16%). The physical, spectral and analytical data for compounds **6a,b** are reported in Table 1.

The *E*-ethylenes **11a**[11] and **11b**[3] were prepared according to the procedure previously reported for different acylethylenes[15] by diethyl sulfide reduction of the related 2-hydroperoxy-5,5-dimethoxy-2-phenyldihydrofurans.[7] Silica gel chromatography, using light petroleum–diethyl ether (4:1) as eluent, gave

‖ Indeed, the dioxole **1a** at −60 °C led to an unidentified compound, presumably a phosphorane,[12] which at room temperature smoothly yielded triphenylphosphine oxide and the ethylene **11a**.

the ethylene **11a**[11] (98%) and the ethylene **11b**[3] (95%), respectively.

Thermal Conversion of the endo-*Peroxides* **2c,e**.—Samples of the *endo*-peroxides **2c** and **2e** when warmed to −25 °C underwent conversion into the dioxoles **1c** and **1e** which, in turn, rearranged into the epoxide **5c≡6c** and keto ester **3c≡4c** and into the epoxides **5e** and **6e** and the keto esters **3e** and **4e**, respectively. Within 24 h the conversions of the *endo*-peroxides **2c** and **2e** and of the dioxoles **1c** and **1e** were complete and the molar ratio (^{1}H NMR) of the products obtained from **2c** was very similar to those previously observed.[3] The molar ratio of the epoxides **5e** and **6e** and the keto esters **3e** and **4e**, obtained in the thermal conversion of the peroxide **2e**, was *ca.* 1:1:1:1.

The remainder of the solution of the *endo*-peroxide **2e** was warmed to room temperature. After 30 min the ^{1}H and ^{13}C NMR spectra of the mixture was recorded. The solvents were then removed at reduced pressure and the residue chromatographed on silica gel. Elution with light petroleum–diethyl ether (17:3, v/v) yielded ethyl methyl benzoylmalonate **9e** [20%, formed by hydrolysis of the keto ester **4e** on contact with the adsorbent], dimethyl benzoylmalonate **8e**[16] [22%, formed by hydrolysis of the keto ester **3e** on contact with the adsorbent] and a mixture of the epoxides **5e** and **6e** [together 50%, *ca.* 1:1 molar ratio by ^{1}H NMR] successively. From the mixture of the two isomeric epoxides **5e** and **6e** the latter was separated in the solid form by crystallization from light petroleum–diethyl ether. The epoxide **5e** was obtained by evaporation of the filtrate under reduced pressure and slow chromatography of the residue on silica gel (eluent light petroleum–diethyl ether, 17:3 v/v).

The physical, analytical and/or spectral data for the dioxoles **1c** and **1e**, for the epoxides **5e** and **6e** and for the malonate **9e** are reported in Table 1. The latter also reports the spectral data of the mixture of the keto esters **3e** and **4e** which were deduced by the ^{1}H and ^{13}C NMR spectra of the reaction mixture, kept at room temperature for 30 min, the signals of the epoxides **5e** and **6e** being subtracted. Similar results were obtained either when the thermal conversion of the *endo*-peroxide **2e** was carried out in the presence of 2,6-di-*tert*-butyl-*p*-cresol at −25 °C or when, after removal of $CDCl_3$–$CFCl_3$ at reduced pressure at −40 °C, the conversion was carried out at −25 °C in [$^2H_3$]acetonitrile.

Chemical Behaviour of the Dioxoles **1a,d**.—To a 5 × 10^{-2} mol dm^{-3} (0.5 cm^3) solution of the dioxole **1a** in $CDCl_3$–$CFCl_3$ (1:1, v/v), kept at −60 °C, [$^2H_4$]methanol (0.5 cm^3), precooled at −60 °C, was added and the resulting mixture was kept at this temperature. After 3 h the ^{1}H NMR spectrum, recorded at −60 °C, showed the dioxole **1a** to be unchanged.

To a 5 × 10^{-2} mol dm^{-3} solution (0.1 cm^3) of the dioxole **1a** in $CDCl_3$–$CFCl_3$ (1:1 v/v), kept at −60 °C, was added a solution (0.5 cm^3) of [$^2H_6$]acetone–[$^2H_2$]oxide (50:1 v/v), precoooled at −60 °C, and the resulting mixture was kept at this temperature. After 3 h the ^{1}H NMR spectrum, recorded at −60 °C, showed the dioxole **1a** to be unchanged.

To a 5 × 10^{-2} mol dm^{-3} solution (0.1 cm^3) of the dioxole **1a** in $CDCl_3$–$CFCl_3$ (1:1 v/v), kept at −60 °C, was added a solution (0.5 cm^3) of [$^2H_6$]acetone–[$^2H_2$]oxide–38% [$^2H_1$]-hydrochloric acid (50:1:1 v/v/v), precooled at −60 °C, and the resulting mixture was kept at this temperature. After 3 h, the ^{1}H NMR spectrum, recorded at −60 °C, showed the dioxole **1a** to be unchanged.

To a 5 × 10^{-2} mol dm^{-3} solution (10 cm^3, 0.5 mmol) of the dioxole **1a** in $CDCl_3$–$CFCl_3$ (1:1, v/v), kept at −60 °C, was added a $CDCl_3$ solution of triphenylphosphine (5 cm^3, 0.75 mmol), precooled at −60 °C and the resulting mixture was kept at this temperature. Periodically the solution was monitored (^{1}H NMR) at −60 °C for the disappearance of the dioxole **1a**. After some minutes the signals of the dioxole **1a** declined while singlets at δ 3.70 and 3.85, attributable to a phosphorane, appeared. After 12 h only the latter signals and those of the ethylene **11a** were present. The mixture was warmed to room temperature. After a few minutes only the presence of the ethylene **11a** was observed (^{1}H NMR). Removal of the solvent at reduced pressure gave a residue which was chromatographed on silica gel. Elution with light petroleum–diethyl ether (19:1, 4:1 v/v) and diethyl ether–methanol (19:1, v/v) gave triphenylphosphine (38%), the ethylene **11a**[11] (90%) and triphenylphosphine oxide (62%) successively.

The dioxole **1d**, obtained by thermal conversion at −60 °C of the related *endo*-peroxide **2d**,[1] was submitted to the same reactions as for the dioxole **1a** and gave similar results, except for the presence of some amounts of its thermal conversion products[1] in the reaction mixtures.

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