Photosensitized Oxidation of Furans. Part 4.[1] Influence of the Substituents on the Behaviour of the *endo*-Peroxides of Furans

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A comparison of the behaviour of *endo*-peroxides of the β-furoic esters (1a, b and d—f) and of the furans (1c or g), with the same 2,5-substituents, shows that the thermal instability of these compounds is related to the electron density in the bicyclic unsaturated ring. This also accounts for the higher stability of the alkyl-substituted *endo*-peroxides (1a—c) as compared with that of the aryl-substituted derivatives (1d—g), as well as for the different course of the thermal conversion in the two series.

ALTHOUGH the photosensitized oxidation of furans has been extensively studied, the behaviour of the postulated intermediate *endo*-peroxides in organic solvents other than alcohols has not yet been well defined.[2] Before our preliminary publication[3] only a number of apparently isolated facts concerning the thermal conversion of the singlet-oxygen–furan adducts had been reported. Wasserman *et al.*[4] and Lutz *et al.*[5] observed that the photosensitized oxidation of tetraphenylfuran in aqueous acetone led to *cis*-dibenzoylstilbene oxide and an enol benzoate.† Subsequently Trozzolo *et al.*[6] obtained, at —70 °C, a singlet-oxygen–2,5-diphenylfuran adduct which, at room temperature in aprotic solvents, regenerated the starting furan. Later Adam *et al.*[7] obtained, in carbon tetrachloride, the *endo*-peroxide of 2,5-dimethylfuran ([1]H n.m.r. evidence) which, by solvent removal, afforded polymeric products. In order to attempt a rationalization of the aforementioned data we have investigated the thermal conversion of suitably substituted furan *endo*-peroxides which were isolated or unequivocally identified by spectral data.

We have succeeded in isolating some of the epidioxydihydrofuran (1), substituted with an electron-withdrawing group at the 5-position, by photosensitized oxidation of the parent furans (2).[8] On the basis that delocalization of the π-electrons in the furan *endo*-peroxide structure, caused by electron-withdrawing substituents, would ensure that the reactivity of this system lay between that of mono-ozonides of cyclobutadiene derivatives and of the more stable ozonides of cyclobutene derivatives,[9] we have extended the photosensitized oxidation to a series of 3- and 3,4-furoic esters with 2,5-alkyl or -aryl substituents. The new *endo*-peroxides (1a, e, and f) were obtained in quantitative yields by Methylene Blue photosensitized oxidation of the corresponding furans, and isolated as previously described for the peroxides (1b and d).[8] Structures (1) were assigned on the basis of active-oxygen determination and the spectral data are summarized in Table 1. *endo*-Peroxides (1a, e, and f), isolated at —15 °C, undergo conversions at higher temperatures, the reaction pathway depending to some extent on the experimental conditions but chiefly on the structure of the starting

compounds. In order to gain information concerning these transformations, the stabilities of the new and of the hitherto known[8] *endo*-peroxides of the β-furoic esters were compared among themselves and with those of the *endo*-peroxides (1c and g) [from 2,5-dimethylfuran (2c)[7] and 2,5-diphenylfuran (2g),[6] respectively]. The peroxide (1g) was prepared by a modification of the procedure used for compound (1c),[7] which involves the

a; R[1] = R[2] = Me, R[3] = R[4] = CO₂Me
b; R[1] = R[2] = Me, R[3] = CO₂Me, R[4] = H
c; R[1] = R[2] = Me, R[3] = R[4] = H
d; R[1] = Me, R[2] = Ph, R[3] = CO₂Me, R[4] = H
e; R[1] = R[2] = Ph, R[3] = R[4] = CO₂Me
f; R[1] = R[2] = Ph, R[3] = CO₂Et, R[4] = H
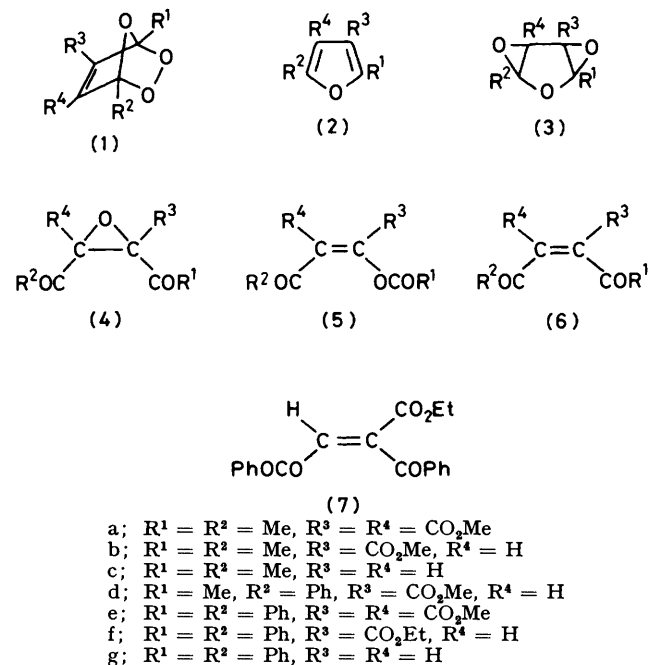g; R[1] = R[2] = Ph, R[3] = R[4] = H

photo-oxidation of the parent furan in carbon tetrachloride using tetraphenylporphin as sensitizer. Owing to the known difficulties in the isolation of *endo*-peroxides without electron-withdrawing groups,[6,7] the carbon tetrachloride solutions, which showed the presence only of compounds (1c or g) ([1]H n.m.r. evidence), were used directly. In Table 2 the times required for the completion of the reaction at —25,‡ 4, and 77 °C ([1]H n.m.r.), and the proportions of the conversion products at 4 and 77 °C, are reported. Quantification of the reaction products was made on the basis of the [1]H n.m.r. spectra of

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† Lutz *et al.* were able to isolate the diepoxide in addition to the aforementioned products.[5]

‡ For the fairly stable *endo*-peroxides (1) only the percentages of unchanged material after 75 d are reported.

TABLE 1

Physical, spectral, and analytical data of products derived from oxidation of the furans (2a, c, e—g)

Product	M.p./°C	$\nu_{max.}$(CHCl₃)/cm⁻¹	δ(¹H) (CDCl₃) (J/Hz)	δ(¹³C) (CDCl₃)/p.p.m.	Formula	Analysis (%) Found (Required)		
						C	H	O (Active)
(1a)	Oil	1 722, 1 635	1.92 (6 H, s, 2 × Me), 3.80 (6 H, s, 2 × CO₂Me)	12.39 (q, 2 × Me), 52.45 (q, 2 × OMe), 111.90 (s, C-1 and -4), 138.98 (s, C-5 and -6), 161.68 (s, 2 × CO₂)	$C_{10}H_{12}O_7$			6.72 (6.56)
(1c) [a]		3 080, 2 990, 2 940, 1 450, 1 390, 1 330, 1 210 [b]	1.75 (6 H, s, 2 × Me), 6.20 (2 H, s, 2 × CH) [b]					
(1e)	58 (decomp.)	1 730, 1 638	3.68 (6 H, s, 2 × CO₂Me), 7.30—7.85 (10 H, m, aromatic)	52.34 (q, 2 × OMe), 113.29 (s, C-1 and -4), 126.83 and 128.49 (2 × d, 2 × C-2 and 2 × C-6, 2 × C-3 and 2 × C-5 of Ph groups), 130.86 (d, 2 × C-4 of Ph groups), 134.25 (s, 2 × C-1 of Ph groups), 140.59 (s, C-5 and -6), 161.55 (s, 2 × CO₂)	$C_{20}H_{16}O_7$			4.4 (4.3)
(1f)	42 (decomp.)	1 718, 1 615	1.12 (3 H, t, J 7, Me), 4.07 (2 H, q, J 7, CO₂CH₂), 7.35—7.85 (11 H, m, CH and aromatic)		$C_{19}H_{16}O_5$			4.4 (4.9)
(1g) [c]		3 070, 3 040, 1 450, 1 335, 1 010, 940, 908 [b]	6.81 (2 H, s, 2 × CH), 7.25—7.85 (10 H, m, aromatic) [b]					
(3c)			1.58 (6 H, s, 2 × Me), 3.35 (3 H, s, 2 × CH) [b]					
(3e)			3.65 (s, OMe) [a]	52.65 (q, 2 × OMe), 65.64 (s, C-1 and -2), 99.32 (s, C-4 and -6), 126.99 and 128.28 (2 × d, 2 × C-2 and 2 × C-6, 2 × C-3 and 2 × C-5 of Ph groups), 130.31 (d, 2 × C-4 of Ph groups), 134.96 (s, 2 × C-1 of Ph groups), 163.11 (s, 2 × CO₂)				
(4f)	68—69 [c]	1 745, 1 685	1.21 (3 H, t, J 7, Me), 4.26 (2 H, q, J 7, CO₂CH₂), 4.80 (1 H, s, CH), 7.30—8.10 (10 H, m, aromatic)		$C_{19}H_{16}O_5$	69.94 (70.36)	4.69 (4.98)	
(5e)	Oil	1 735, 1 670, 1 602	3.79 and 3.85 (6 H, 2 × s, 2 × OMe), 7.25—8.15 (10 H, m, aromatic)	53.13 and 53.24 (2 × q, 2 × OMe), 126.12 (s, C=CO), 128.55, 128.87, 129.31 and 130.24 (4 × d, 2 × C-2 and 2 × C-6, 2 × C-3 and 2 × C-5 of Ph groups), 134.27 and 134.32 (2 × d, 2 × C-4 of Ph groups), 133.75 and 137.48 (2 × s, 2 × C-1 of Ph groups), 144.19 (s, C=CO), 161.22, 162.80, and 163.12 (3 × s, 3 × CO₂), 188.74 (s, CO)	$C_{20}H_{16}O_7$	65.42 (65.21)	4.31 (4.38)	

(5f) Oil; 1732, 1675, 1601; 1.32 (3 H, t, J 7, Me), 4.31 (2 H, q, J 7, CO$_2$CH$_2$), 7.39 and 7.30—8.10 (11 H, s and m, CH and aromatic) [b]; 13.95 (q, Me), 62.45 (t, OCH$_2$), 121.47 (d, CH), 128.49, 128.71, 129.04, and 130.35 (4 × d, 2 × C-2 and 2 × C-6, 2 × C-3 and 2 × C-5 of Ph groups), 133.67 and 133.84 (2 × d, 2 × C-4 of Ph groups), 134.43 and 137.16 (2 × s, 2 × C-1 of Ph groups), 144.90 (s, C=CO), 161.63 and 163.92 (2 × s, 2 × CO$_2$), 189.20 (s, CO); C$_{19}$H$_{16}$O$_5$; 69.87 (70.36), 5.16 (4.98)

(6e) 137—139[e]; 1730, 1670, 1598; 3.79 (6 H, s, 2 × OMe), 7.30—8.00 (10 H, m, aromatic); C$_{20}$H$_{16}$O$_6$; 67.57 (68.18), 4.55 (4.58)

(6f) 82—83[e]; 1720, 1668, 1615; 1.18 (3 H, t, J 7, Me), 4.25 (2 H, q, J 7, CO$_2$CH$_2$), 7.35—8.10 (10 H, m, aromatic), 8.15 (1 H, s, CH); C$_{19}$H$_{16}$O$_4$; 73.79 (74.01), 5.17 (5.23)

(7) 1.22 (3 H, t, J 7, Me), 4.17 (2 H, q, J 7, CO$_2$CH$_2$), 8.66 (1 H, s, CH) [b,d]; 13.95 (q, Me), 61.48 (t, OCH$_2$), 126.5 (s, C=CO), 128.49, 128.71, 129.04, and 130.35 (4 × d, 2 × C-2 and 2 × C-6, 2 × C-3 and 2 × C-5 of Ph groups), 133.67 and 134.62 (2 × d, 2 × C-4 of Ph groups), 134.21 and 136.87 (2 × s, 2 × C-1 of Ph groups), 147.27 (d, CH), 161.65 and 164.12 (2 × s, 2 × CO$_2$), 190.10 (s, CO)

[a] Lit.,[7] δ (CCl$_4$) 1.70 and 6.02. [b] In CCl$_4$. [c] Known product,[6] but i.r. and [1]H n.m.r. data are new. [d] The phenyl hydrogens were not assigned since their signals and those of products present in the mixture overlap. [e] Recrystallization solvent, light petroleum (b.p. 40—70 °C).

TABLE 2

Thermal conversion of *endo*-peroxides (1)

Reaction conditions [a]

Substrate	At −25 °C		At 4 °C							At 77 °C						
	Reaction time[b]	Unchanged peroxide (%)	Reaction time[b]	Yields (%)[c]						Reaction time[b] (min)	Yields (%)[c]					
				(2)	(3)	(4)[d]	(5)	(6)[d]	Polymeric material[e]		(2)	(3)	(4)[d]	(5)	(6)[d]	Polymeric material[e]
(1a)	75 d	Unchanged	150 d		50*				50	70		100*				
(1b)	75 d	80	120 d						100	60		100*[f]				
(1c)	75 d	50	12 d						100	20	20	45*				55
(1d)	75 d	45	20 d			32	3	12	38	15			9	4	7	53
(1e)	75 d	80	35 d	5	22*		15	3		15	50	30*		16	3	
(1f)	75 d	Completely changed[g]	3 d	43		34	9[h]	3	11	15	57		10	9[h]	3	12
(1g)	12 h	Completely changed[g]	4 h	27		34	16	20		15	50		14	17	18	

[a] Using a 4% carbon tetrachloride solution. [b] Required for the completion of the reaction ([1]H n.m.r.). [c] Deduced on the basis of the [1]H n.m.r. spectrum and confirmed by silica-gel chromatography, unless marked *. [d] On the basis of the previous results[8] it is reasonable to assume that the epoxides (4) and diacylethylenes (6) are formed in *cis*-configuration. [e] Calculated on the basis of the molecular weight of the starting furan + O$_2$/2. [f] In the light of the present results, we re-examined the thermal conversion of the peroxide (1b) in the absence of solvent at room temperature;[8] in this case, in addition to the epoxide (4b) and polymeric material, small amounts of the diepoxide (3b) were also detected in the reaction mixture. [g] Proportions of the reaction products are similar to those reported for the conversion at 4 °C. [h] Percentage yield includes the isomer ethyl 2-benzoyl-3-benzoyloxypropenoate (7).

the reaction mixture and confirmed, unless otherwise stated, by chromatography on silica gel. The hitherto known compounds were identified by straightforward comparison of their i.r. and ^{1}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 (summarized in Table 1). The structures of compounds (3c and e), which would have been very difficult to isolate because of the high hydrolytic reactivity and tendency to polymerization of the diepoxides (3), were deduced from the ^{13}C and ^{1}H n.m.r. spectra of the reaction mixtures.

The behaviour of the *endo*-peroxides (1a—g) provides evidence for the proposal that the complexity of reactions of singlet-oxygen with furanic systems is not due to the diverse modes of attack of the singlet-oxygen on the substrate,[10] but rather to the multiplicity of paths available for the decomposition of the initially formed *endo*-peroxide. On the other hand, comparison of the times required for the thermal conversion shows that, when the 2,5-substituents are identical in nature, the *endo*-peroxides of 3,4-furoic diesters are thermally more stable than those of 3-furoic esters, which in turn are more stable than those of furans without 3,4-substituents. Moreover, alkyl-substituted *endo*-peroxides are thermally more stable than aryl-substituted derivatives. Therefore it seems clear that there is a connection between the driving force which determines the instability of a furan *endo*-peroxide and the electron density in the bicyclic unsaturated ring. Furthermore, the thermal conversions of the two series, especially at 77 °C, take different courses, aryl-substituted *endo*-peroxides yielding mainly furans (2), epoxides (4),* and enol esters (5), while alkyl-substituted compounds give the diepoxides (3).[3] The aryl-substituted *endo*-peroxides might be expected to give products (2), (4), and (5) since in these products a greater resonance stabilization can occur than is allowed in the starting *endo*-peroxide. On the other hand, alkyl-substituted *endo*-peroxides rearrange into diepoxides because in this case conversion into the products (2), (4), and (5) is not satisfactorily assisted by resonance stabilization.

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 Bruker WH 270 spectrometer with tetramethylsilane as internal standard. ^{13}C N.m.r. spectra were recorded on a Bruker WH 270 spectrometer in deuteriochloroform solutions with tetramethylsilane as internal standard. The chloroform used in the oxidation reactions was anhydrous and free of ethanol and the carbon tetrachloride used was anhydrous. Silica gel [0.05—0.20 mm (Merck)] and light petroleum (b.p. 30—50 °C) were used for column chromatography.

* As an exception the *endo*-peroxide (1e) in addition to (2e) and (5e) yielded the diepoxide (3e) instead of the epoxide (4e).

Dimethyl 2,5-diphenylfuran-3,4-dicarboxylate (2e) was prepared by saponification of the diethyl diester[11] followed by methylation, with diazomethane, of the acid obtained. Silica-gel chromatography (elution with light petroleum–diethyl ether, 17 : 3 v/v) gave compound (2e) (75%), m.p. 83—84 °C (Found: C, 71.35; H, 4.8. $C_{20}H_{16}O_5$ requires C, 71.42; H, 4.80%); $v_{max.}$ (CCl$_4$) 1 725 cm^{-1}; δ 3.85 (6 H, s, 2 × CO$_2$Me) and 7.30—8.00 (10 H, m, aromatic).

Preparation of the endo-*Peroxides* (1a), (1e), *and* (1f).—A solution (2%) of dimethyl 2,5-dimethylfuran-3,4-dicarboxylate (2a)[12] (1 mmol) and Methylene Blue (8 × 10^{-3} mmol) in dry chloroform was irradiated with a halogen-superphot lamp (Osram, 650 W). During the irradiation, dry oxygen was bubbled through the solution which was kept at −15 °C. The reaction was complete within 1 h (^{1}H n.m.r.). After removal of the chloroform under reduced pressure, the residue was taken up in dry diethyl ether. The suspension was filtered to remove Methylene Blue and the solution evaporated. All these procedures were carried out at −15 °C. Thus pure endo-(*dimethyl 2,5-epidioxy-2,5-dihydro-2,5-dimethylfuran-3,4-dicarboxylate*) (1a) was quantitatively isolated. The endo-*peroxides* (1e and f) were prepared, as described for compound (1a), from the furans (2e) and (2f),[13] respectively. Physical, spectral, and analytical data for the *per*oxides (1a, e, and f) are shown in Table 1.

Preparation of endo-2,5-*Epidioxy-2,5-dihydro-2,5-diphenylfuran* (1g).—A solution (3.5%) of 2,5-diphenylfuran (2g)[14] (1 mmol) in dry carbon tetrachloride, after addition of tetraphenylporphin (3.6 × 10^{-4} mmol), was oxidized as described above. After 20 min the ^{1}H n.m.r. spectrum of the reaction mixture showed only the presence of the peroxide (1g). The spectral data of this compound are shown in Table 1.

General Procedure for the Thermal Conversion of the endo-*Peroxides* (1).—Thermal conversion was carried out on a solution (4%) of the *endo*-peroxides (1) (1 mmol) in dry carbon tetrachloride under strictly anhydrous conditions at −25, 4, and 77 °C. The solution was periodically sampled and the sample analyzed by ^{1}H n.m.r. spectroscopy. The results are shown in Table 2. The composition of the reaction mixture, which was deduced on the basis of the ^{1}H n.m.r. spectrum, was confirmed by silica-gel chromatography, except where shown otherwise (Table 2).

Thermal Conversion of the endo-*Peroxide* (1a) *at* 77 °C.—Dimethyl 2,3:4,5-diepoxy-2,3,4,5-tetrahydro-2,5-dimethylfuran-3,4-dicarboxylate (3a)[3] was quantitatively isolated from the refluxed carbon tetrachloride solution by removal of the solvent under reduced pressure. It partly polymerizes and partly undergoes hydrolysis on contact with silica gel, alumina, or polyamide; moreover it polymerizes with time and is hydrolyzed by atmospheric moisture.

Thermal Conversion of endo-(*Methyl 2,5-Epidioxy-2,5-dihydro-2,5-dimethylfuran-3-carboxylate*) (1b).—At −25 °C, after 75 d, inspection of the ^{1}H n.m.r. spectrum of the reaction mixture showed the signals of the peroxide (1b)[8] in addition to broadened signals from polymeric materials. Quantification of unchanged starting material (1b) was based on the relative areas of its olefinic singlet and the methoxy-singlets of the components of the mixture.

At 4 °C the ^{1}H n.m.r. spectrum, recorded after 15 d, showed, in addition to the signals from the peroxide (1b) and polymeric material, signals from methyl 2,3:4,5-diepoxy-2,3,4,5-tetrahydro-2,5-dimethylfuran-3-carboxylate (3b), identified by comparison (^{1}H n.m.r.) with an authentic sample.[3]

The diepoxide (3b) was quantitatively isolated from the refluxed carbon tetrachloride solution by removal of the solvent under reduced pressure. Its behaviour is exactly analogous to that of compound (3a).

Thermal Conversion of endo-2,5-*Epidioxy*-2,5-*dihydro*-2,5-*dimethylfuran* (1c).—A carbon tetrachloride solution (4%) of the peroxide (1c),[7] obtained from the furan (2c) (1 mmol), was kept at −25 °C. After 75 d inspection of the [1]H n.m.r. spectrum showed signals from compound (1c) in addition to broadened signals from polymeric materials. Quantification of unchanged starting material (1c) was based on the relative areas of its singlets and the broadened signals of the polymers.

After 20 min under reflux, inspection of the [1]H n.m.r. spectrum of a solution of compound (1c) showed that it had been entirely converted into 2,3:4,5-diepoxy-2,3,4,5-tetrahydro-2,5-dimethylfuran (3c) and polymeric material. Quantification of compound (3c) was based on the relative areas of its singlets and broadened signals of the polymeric material. All attempts to isolate the diepoxide (3c) by chromatographic methods failed since it partly polymerizes and partly undergoes hydrolysis on contact with the absorbent. Its [1]H n.m.r. spectral data are listed in Table 1.

Thermal Conversion of endo-(*Methyl* 2,5-*Epidioxy*-2,5-*dihydro*-2-*methyl*-5-*phenylfuran*-3-*carboxylate*) (1d).—At −25 °C, after 75 d, inspection of the [1]H n.m.r. spectrum of the solution showed the presence of compounds (1d), methyl 2-acetyl-3-benzoyl-2,3-epoxypropanoate (4d), methyl 2-acetoxy-3-benzoylpropenoate (5d), and methyl 2-acetyl-3-benzoylpropenoate (6d), identified by comparison ([1]H n.m.r.) with authentic samples,[8,15] in addition to polymeric materials. Quantification of unchanged starting material (1d) was based on the relative areas of the methyl singlets of the products present in the mixture.

At 4 °C, after 20 d, inspection of the [1]H n.m.r. spectrum of the solution showed that compound (1d) had been entirely converted into the products (2d), (4d), (5d), and (6d) and polymeric material. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel (10 g). Elution with light petroleum–diethyl ether (19 : 1 v/v) gave methyl 2-methyl-5-phenylfuran-3-carboxylate (2d) (10 mg, 5%), while light petroleum–diethyl ether (4 : 1 v/v) gave, successively, the enol ester (5d) (8 mg, 3%), the acrylate (6d) (27 mg, 12%), and the epoxide (4d) (79 mg, 32%). With acetone as eluant polymeric material (88 mg, 38%) was obtained. All the compounds were identified by comparison (i.r. and [1]H n.m.r.) with authentic samples.[8,15]

At 77 °C, after 15 min, inspection of the [1]H n.m.r. spectrum showed that the peroxide (1d) had been entirely converted into compounds (2d), (4d), (5d), and (6d), and polymeric material. After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel (10 g). Elution with light petroleum–diethyl ether (19 : 1 v/v) gave the furan (2d) (43 mg, 20%), and light petroleum–diethyl ether (4 : 1 v/v) gave, successively, compounds (5d) (10 mg, 4%), (6d) (16 mg, 7%), and (4d) (23 mg, 9%). Elution with acetone gave polymeric material (123 mg, 53%). All the products were identified by comparison (i.r. and [1]H n.m.r.) with authentic samples.[8,15]

Thermal Conversion of endo-(*Dimethyl* 2,5-*Epidioxy*-2,5-*dihydro*-2,5-*diphenylfuran*-3,4-*dicarboxylate*) (1e).—At −25 °C, after 75 d, inspection of the [1]H n.m.r. spectrum showed the presence of compound (1e) in addition to small amounts of dimethyl 2,5-diphenylfuran-3,4-dicarboxylate (2e), di-

methyl 3-benzoyl-2-benzoyloxybutene-1,4-dioate (5e), and dimethyl 2,3:4,5-diepoxy-2,3,4,5-tetrahydro-2,5-diphenylfuran-3,4-dicarboxylate (3e), identified by comparison with the [1]H n.m.r. spectrum of the conversion mixture of compound (1e) at 77 °C.

At 4 °C, after 30 d, inspection of the [1]H n.m.r. spectrum of the solution showed that compound (1e) was entirely converted into the products (2e), (3e), (5e), and (6e). The diepoxide (3e) was identified by comparison of the [1]H n.m.r. spectrum of the reaction mixture with that of the mixture obtained by refluxing the peroxide (1e); its quantification was based on the relative areas of the methoxy-singlets of the products present in the mixture. After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel (15 g). Elution with light petroleum–diethyl ether (17 : 3 v/v) gave, successively, the furan (1e) (144 mg, 43%) and a mixture of the enol ester (5e) and hydrolytic products derived from the diepoxide (3e) (78 mg). Elution with light petroleum–diethyl ether (7 : 3 v/v) gave dimethyl 1,2-dibenzoylbutene-1,4-dioate (6e) (10 mg, 3%), and with acetone gave polymeric materials derived from compound (3e) (71 mg). Separate chromatography on silica gel (5 g) eluting with benzene gave pure compound (5e) (55 mg, 15%). The diepoxide (3e) also undergoes hydrolysis and polymerization on contact with other adsorbents. The physical, spectral, and analytical data of compounds (5e) and (6e) are listed in Table 1.

At 77 °C, after 15 min, inspection of the [1]H n.m.r. spectrum showed that the peroxide (1e) was entirely converted into compounds (2e), (3e), (5e), and (6e). Quantification was based on the relative areas of the methoxy-singlets from the products present in the mixture. In order to obtain spectral data for the diepoxide (3e) (shown in Table 1), after removal of the solvent, the [13]C n.m.r. spectrum of the mixture was recorded and the signals for products (2e), (5e), and (6e) were rejected. The mixture was chromatographed on silica gel (15 g). Elution with light petroleum–diethyl ether (17 : 3 and 7 : 3 v/v) and acetone gave, successively, the furan (2e) (168 mg 50%), a mixture of the enol-ester (5e) and hydrolytic products deriving from the diepoxide (3e) (105 mg), compound (6e) (10 mg, 3%), and polymeric materials (70 mg), also from compound (3e). Separate chromatography on silica gel (5 g), eluting with benzene, gave pure enol ester (5e) (60 mg, 16%). All the compounds isolated were identified by comparison (i.r. and [1]H n.m.r.) with those obtained by the thermal conversion of the peroxide (1e) at 4 °C.

Thermal Conversion of endo-(*Ethyl* 2,5-*Epidioxy*-2,5-*dihydro*-2,5-*diphenylfuran*-3-*carboxylate*) (1f).—At −25 °C, after 75 d, inspection of the [1]H n.m.r. spectrum of the solution showed that compound (1f) had been entirely converted into ethyl 2,5-diphenylfuran-3-carboxylate (2f), ethyl 2,3-dibenzoyl-2,3-epoxybutanoate (5f), ethyl 3-benzoyl-2-benzoyloxypropenoate (7), and ethyl 2,3-dibenzoylpropenoate (6f); these were identified by comparison ([1]H n.m.r.) with authentic samples isolated from the thermal conversion of the peroxide (1f) at 4 °C. The proportions of the products are similar to those obtained from the conversion at 4 °C as shown by comparison of the [1]H n.m.r. spectra of the conversion mixtures at −25 and 4 °C.

At 4 °C, after 3 d, inspection of the [1]H n.m.r. spectrum showed that the peroxide (1f) was entirely converted into the products (2f), (4f), (5f), (6f), and (7). The mixture, after removal of the solvent under reduced pressure, was chromatographed on silica gel (15 g). Elution with light

petroleum–diethyl ether (19 : 1 v/v) gave the furan (2f) (96 mg, 33%), identified by comparison (i.r. and ^{1}H n.m.r.) with an authentic sample,[13] while light petroleum–diethyl ether (4 : 1 v/v) gave, successively, a mixture of isomers (5f) and (7) (29 mg, 9%), the ester (6f) (10 mg, 3%), and the epoxide (4f) (110 mg, 34%). Elution with acetone gave polymeric material (33 mg, 11%). All attempts to separate the isomers (5f) and (7) by chromatographic methods failed. Therefore the structural assignment of the two isomers was made on the basis of elemental analyses and spectral properties of the mixture (Found: C, 69.85; H, 5.15. $C_{19}H_{16}O_5$ requires C, 70.36; H, 4.98%). In particular, the isomer (5f) was identified by comparison of the ^{1}H and ^{13}C n.m.r. spectra of the mixture with those of an authentic sample obtained from the peroxide (1f) by an alternative route. The physical, spectral, and analytical data of compounds (4f), (5f), (6f), and (7) are listed in Table 1.

At 77 °C, after 15 min, inspection of the ^{1}H n.m.r. spectrum showed that the peroxide (1f) had been entirely converted into the products (2f), (4f), (5f), (6f), and (7). The mixture, after removal of the solvent under reduced pressure, was chromatographed on silica gel (10 g). Elution with light petroleum–diethyl ether (19 : 1 and 4 : 1 v/v) and acetone gave successively, the furan (2f) (166 mg, 57%), a mixture of the isomers (5f) and (7) (30 mg, 9%), the ester (6f) (10 mg, 3%), the epoxide (4f) (32 mg, 10%), and polymeric materials (36 mg, 12%). All the compounds were identified by comparison (i.r. and ^{1}H n.m.r.) with those obtained by the thermal conversion of the peroxide (1f) at 4 °C.

Thermal Conversion of the endo-*Peroxide* (1g).—A carbon tetrachloride solution (4%) of the peroxide (1g),[6] obtained from the furan (2g) [14] (1 mmol), was kept at −25 °C. Within 12 h compound (1g) had been entirely converted (^{1}H n.m.r.) into the furan (2g), 1,2-dibenzoyl-1,2-epoxyethane (4g), 2-benzoylvinyl benzoate (5g), and 1,2-dibenzoylethylene (6g); these were identified by comparison (^{1}H n.m.r.) with authentic samples isolated from the thermal conversion at 4 °C. The proportions of the products are similar to those obtained for the conversion at 4 °C, as shown by comparison of the ^{1}H n.m.r. spectra of the mixtures from the conversion at −25 and 4 °C.

When the solution was kept at 4 °C, the peroxide (1g) was entirely converted (^{1}H n.m.r.) within 4 h into the products (2g), (4g), (5g), and (6g). The mixture, after removal of the solvent under reduced pressure, was chromatographed on silica gel (10 g). Elution with light petroleum–diethyl ether (19 : 1 v/v) gave, successively, the furan (2g) (60 mg, 27%) and a mixture of *cis*- and *trans*-isomeric enol esters (5g) (40 mg, 16%).*

Elution with light petroleum–diethyl ether (7 : 3 v/v) gave

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* The *trans*-enol ester [16] is formed by isomerization of the initially formed *cis*-isomer [olefinic hydrogen signals at δ (CCl₄) 6.23 (d, *J* 8 Hz) and 7.90 (d, *J* 8 Hz)].

cis-1,2-dibenzoylethylene (6g) [17] (48 mg, 20%), while light petroleum–diethyl ether (1 : 1 v/v) gave the epoxide (4g) [18] (86 mg, 34%).

When the solution was refluxed, the peroxide (1g) was entirely converted (^{1}H n.m.r.) within 10 min into the products (2g), (4g), (5g), and (6g). After removal of the solvent under reduced pressure, the mixture was chromatographed on silica gel (10 g). Elution with light petroleum–diethyl ether (19 : 1, 7 : 3, and 1 : 1 v/v) gave, successively, the furan (2g) (110 mg, 50%), *cis*- and *trans*-enol esters (5g) (41 mg, 17%), the olefin (6g) (42 mg, 18%), and the epoxide (4g) (35 mg, 14%). The *trans*-enol ester (5g), *cis*-1,2-dibenzoylethylene (6g), and the epoxide (4g) were identified by comparison (i.r. and ^{1}H n.m.r.) with authentic samples.[16–18]

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