

Photosensitized Oxidation of Furans. Part 12.¹ Solvent Effects in Thermal Rearrangement of the 2,5-Peroxides of 2,5-Unsubstituted Furans

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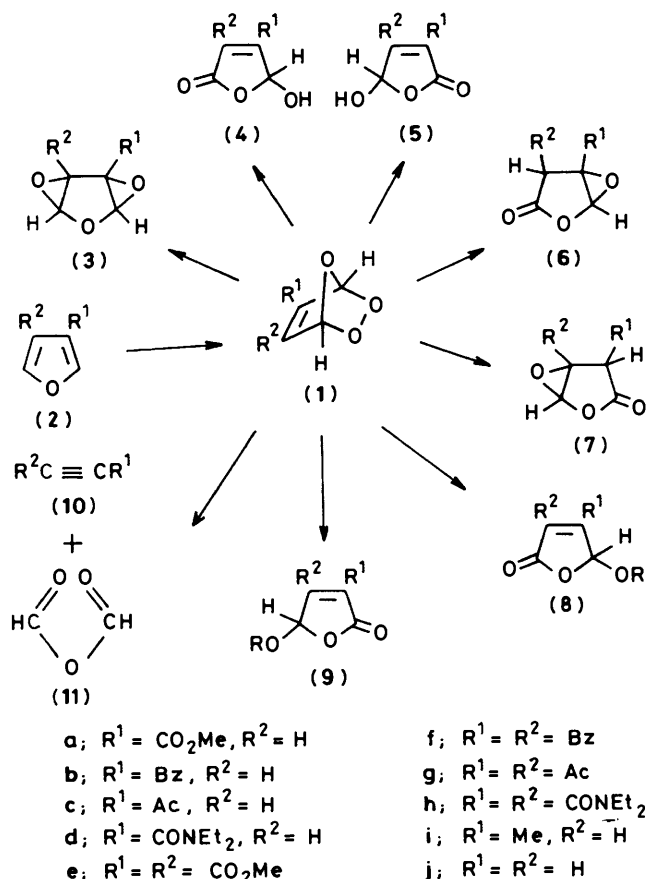
The formation, thermal stability, and modes of thermal rearrangement of the 2,5-peroxides (**1a—i**) of 2,5-unsubstituted furans are reported. In apolar solvents the main product of thermal rearrangement is the *cis* diepoxide (**3**) accompanied by the epoxyfuranones (**6**) and (**7**). These rearrangements are thought to proceed *via* concerted processes, although no distinction can be made between them and rearrangements *via* diradicals. In basic solvents the 5-hydroxyfuran-2(5*H*)-ones (**4**) and (**5**) are isolated in high yields. In this case the rearrangements are explained by assuming ion pairs, (**18**), as intermediates.

Little was known about the thermal rearrangements of singlet oxygen-2,5-unsubstituted furan adducts²⁻⁶ before our preliminary communication which dealt with methyl 2,3,7-trioxabicyclo[2.2.1]hept-5-ene-5-carboxylate (**1a**).⁷ In that paper we reported that the peroxide (**1a**), obtained by dye-sensitized photo-oxygenation at -40°C of the furan (**2a**), at 35°C in apolar solvents leads to methyl 3,5,7-trioxatricyclo[4.1.0.0^{2,4}]-heptane-1-carboxylate (**3a**). In contrast, in basic solvents (**1a**) rearranges into methyl 2-hydroxy-5-oxo-2,5-dihydrofuran-3-carboxylate (**4a**), whereas the formation of methyl 3-oxo-2,6-dioxabicyclo[3.1.0]hexane-5-carboxylate (**6a**), the minor product of the two reactions, is independent of the solvent. On the basis that no interconversions of compounds (**3a**), (**4a**) or (**6a**) were observed under the reaction conditions, that the product ratios were invariant with concentration, and that the reaction course was uninfluenced by 2,6-di-*t*-butyl-*p*-cresol addition, we suggested that the thermal isomerization processes involve intramolecular *synchronous* rearrangements with, in particular, the solvent-assisted breakage of the C-H₂ bond to induce formation of the furanone (**4a**). (According to the Dewar terminology,⁸ however, we should have used the term *concerted* rearrangement in that we meant that in the reorganization of bonds the bond-breaking and bond-making processes do not take place in unison.)

At the same time Gollnick *et al.*⁹ isolated and identified by ¹H n.m.r. spectroscopy the 2,5-peroxide of the furan (**1j**), which in apolar solvents at room temperature rearranges to a mixture of the diepoxide (**3j**) and epoxyfuranone (**6j**)≡(**7j**) and in alcohols leads to a mixture of the epoxyfuranone (**6j**)≡(**7j**), furanone (**4j**)≡(**5j**), and alkoxyfuranone (**8j**)≡(**9j**). They suggested that the thermal rearrangement reactions of the peroxide (**1j**) in apolar solvents are initiated by homolytic cleavage of the O-O bond to yield a diradical and that in alcohols this cleavage competes with two polar processes of (**1j**) with the alcohol.

Successively, we prepared a series of peroxides, (**1a, b, d—h**), of 2,5-unsubstituted furans with electron-withdrawing substituents at position(s) 3 or 3,4 and pointed out a pathway for the synthesis of 3-, 4-, or 3,4-functionalized furanones (**4**) and (**5**).¹ In the Scheme 1 the paths for the thermal conversions of the peroxides (**1**) are shown.

In order to gain more mechanistic insight into the thermal reactions of the peroxides of 2,5-unsubstituted furans, we have now investigated the dynamic chemistry of some of them, suitably 3- or 3,4-substituted,† in various organic solvents. Table 1



Scheme 1.

shows the percentage yields of the thermal conversion products of the bicyclic peroxides (**1b—i**) at 35°C in chloroform. The latter was used as an apolar solvent prototype after control experiments showing that the reactions can be carried out in different apolar solvents without substantial alteration of the results. Quantification of the reaction products was made on the basis of the ¹H n.m.r. spectra and confirmed by chromatography on silica gel, compatible with the products stability. In Table 1 are also reported the percentage yields of the thermal conversion products of the peroxides (**1c, h**) carried out in deuteriochloroform. The evaluation was made on the basis of the ¹H n.m.r. spectra recorded before rearrangement of the peroxides was complete. For the peroxides (**1a, b, d, f, g**), the

† As the information on the 3-methylfuran-singlet oxygen adduct was fragmentary,^{2-4,6} we have taken into consideration also the behaviour of the peroxide (**1i**), which was obtained by Methylene Blue sensitized photo-oxygenation of the furan (**2i**) at -40°C and identified on the basis of its ¹H n.m.r. spectrum (Table 2).

Table 1. Thermal rearrangement of the peroxides (1a—i) in chloroform at 35 °C

Substrate	Conversion time (min)	Yields (%) ^a						Polymeric material ^b
		(3)	(4)	(5)	(6)	(7)	(10)	
(1a) ⁷	70 ^c	80			11			9
(1b)	30 ^c	65			10			25
(1c)	20 ^c	60			15			25
(1c) ^d	10 ^e	60 ^f		25 ^f	15 ^f			Trace ^f
(1d)	45 ^c	30	7	40	Trace			20
(1e)	150 ^c	40	60 ^g					
(1f)	30 ^c	15	45 ^g				40	
(1g)	15 ^c	40	50 ^g					10
(1h)	30 ^c	20	48 ^g		12 ^h		20	
(1h) ^d	20 ^e	20	15 ^g		45 ^{f,h}		20	
(1i)	5 ^c	53			18	23		7

^a Deduced on the basis of the ¹H n.m.r. spectrum and confirmed by silica gel chromatography (compatible with product stability). ^b Calculated on the basis of the molecular weight of the starting furan + O₂/2. ^c Time required for the completion of the conversion (¹H n.m.r.). ^d Conversion carried out in deuteriochloroform. ^e At this time the peroxide was present in ca. 10% (¹H n.m.r.). ^f Deduced on the basis of the ¹H n.m.r. spectrum and evaluated on the changed peroxide. ^g (4)≡(5). ^h (6h)≡(7h).

Table 2. Spectral and analytical data for the products derived from oxygenation of the furans (2b—i)

Product	ν _{max} (CHCl ₃)/ cm ⁻¹	δ _H (CDCl ₃) (J/Hz)	Formula	Found (%) (Required)	
				C	H
(1c)		2.37 (3 H, s, CH ₃), 6.57 (1 H, s, 1-H), 6.77 (1 H, s, 4-H), 6.92 (1 H, s, 6-H)			
(1i)		2.01 (3 H, d, CH ₃), 6.16 (1 H, m, 6-H), 6.23 and 6.30 (2 H, 2 s, 4- and 1-H)			
(3b)	1 678	4.34 (1 H, d, <i>J</i> 1.5, 2-H), 5.67 (2 H, m, 4- and 6-H), 7.40—8.10 (5 H, m, ArH)	C ₁₁ H ₈ O ₄ (204.17)	64.7 (64.92)	3.95 (3.91)
(3c)	1 710	2.12 (3 H, s, CH ₃), 4.31 (1 H, d, <i>J</i> 1.8, 2-H), 5.58 (1 H, dd, <i>J</i> 1.8 and 2.6, 4-H), 5.71 (1 H, d, <i>J</i> 2.6, 6-H)			
(3d)		3.95 (1 H, s, 2-H), 5.58 (2 H, s, 4- and 6-H) ^a			
(3e)		3.82 (6 H, s, 2 × OCH ₃), 5.81 (2 H, s, 4- and 6-H)	C ₈ H ₈ O ₇ (216.10)	44.45 (44.72)	3.75 (3.75)
(3f)		5.87 (s, 4- and 6-H) ^b			
(3g)		2.21 (6 H, s, 2 × CH ₃), 5.69 (2 H, s, 4- and 6-H)			
(3h)		5.68 (s, 4- and 6-H) ^a			
(4i)		2.10 (3 H, d, <i>J</i> 1.4, CH ₃), 5.82 (1 H, q, <i>J</i> 1.4, 3-H), 6.01 (1 H, s, 5-H)	C ₅ H ₆ O ₃ (114.10)	52.8 (52.63)	5.3 (5.30)
(5i) ^c		1.89 (3 H, d, <i>J</i> 1.4, CH ₃), 6.12 (1 H, d, <i>J</i> 1.4, 5-H), 6.87 (1 H, m, 4-H)			
(6b)	1 815	3.04 (dd, <i>J</i> 1.1 and 19.1) and 3.61 (d, <i>J</i> 19.1) (together 2 H, 4-H), 5.77 (1 H, d, <i>J</i> 1.1, 1-H), 7.4—8.1 (5 H, m, ArH)	C ₁₁ H ₈ O ₄ (204.17)	64.7 (64.92)	3.95 (3.91)
(6c)	1 818	2.14 (3 H, s, CH ₃), 2.90 (dd, <i>J</i> 1.1 and 22.7) and 3.70 (d, <i>J</i> 22.7) (together 2 H, 4-H), 5.73 (1 H, d, <i>J</i> 1.1, 1-H)			
(6d)	1 710	2.91 (1 H, d, <i>J</i> 20.3, 4-H), 5.62 (1 H, s, 1-H) ^d			
(6h)≡(7h)		4.90 (1 H, s, 4-H), 5.56 (1 H, s, 1-H) ^a			

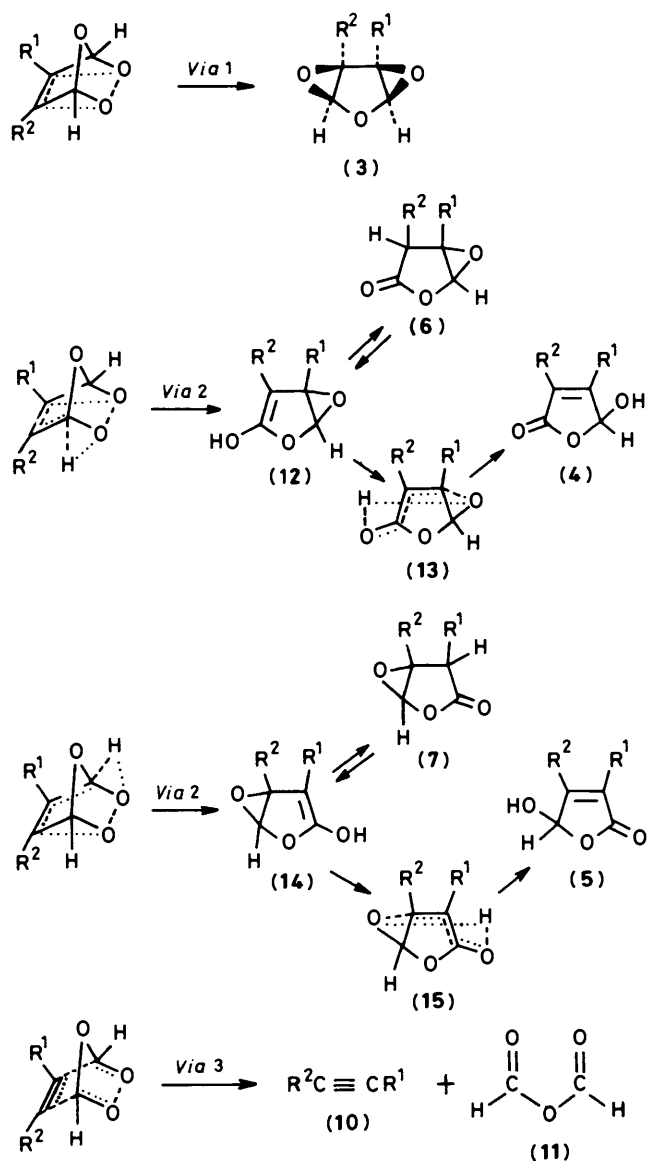
^a The ethyl hydrogens were not assigned since their signals and those of products present in the mixture overlap. ^b The phenyl hydrogens were not assigned since their signals and those of products present in the mixture overlap. ^c Known product, ^d but ¹H n.m.r. data are new. ^e The other 4-H and ethyl hydrogens were not assigned since their signals and those of products present in the mixture overlap.

transient species were too unstable to be quantified, whilst with the peroxides (1e, i) no transient species were detected.* For sake of completeness, in Table 1 are also summarized previously reported data on the thermal conversion of the peroxide (1a).⁷ The hitherto known compounds were identified by comparison with authentic samples. The structures of the new products (3b), (3e), and (6b) were assigned on the basis of elemental analyses and spectral data (see Table 2). The structures of the peroxides (1c) and (1i), which are thermally very unstable, were deduced on the basis of their ¹H n.m.r. spectra (see Table 2). Compounds

(3c, d, f—h) and (6c, d) are very difficult to isolate owing to their ready hydrolysis and tendency to polymerize. Therefore, structures (3d, f—h), and (6d) were deduced from the ¹H n.m.r. spectra of the reaction mixtures, the signals of known compounds being subtracted. Structures of (3c) and (6c) were deduced by careful analysis of i.r. and ¹H n.m.r. spectra of their mixture; Table 2 reports the spectral data so deduced. The *X*-ray structure analysis of (3a) confirms its *cis* configuration.¹⁰

The results reported in Table 1 are consistent with both the previously suggested mechanisms of thermal rearrangement in apolar solvents of the peroxides (1a)⁷ and (1j).⁹ In fact compounds (3)—(7), (10), and (11) can be formed whether by transition states which have *diradical character*, via three

* In thermal conversion of the peroxide (1e), the epoxide (6e)≡(7e) was detected when deuterionitromethane was used as solvent.



Scheme 2. --- Bond-breaking and ···· bond-making

different concerted pathways, as shown in Scheme 2,* or by diradicals (16) and (17),† as previously suggested.⁹ Therefore



* Intermediate formation of the enols (12) or (14) was taken into account since migration of hydrogen is hard when hydrogen is transferred from one carbon atom to another, less hard when it takes place from a carbon to a heteroatom, and easiest when it takes place between two heteroatoms.⁸ However, tautomerization of (12) or (14) to (6) or (7) is normally much faster than migration of the hydrogen from the enol oxygen to the epoxy oxygen to give (4) or (5); in fact in the reaction mixture of the peroxides (1a–c) and (1f) no furanones (4a–c) and (4f) or (5f) were detected (*vide infra*).

† In this case a 1,2-carbon-carbon hydrogen shift should be possible and the epoxides (6) and (7) should form directly. However the equilibria (6) \rightleftharpoons (12) and (7) \rightleftharpoons (14) are still effective (*vide infra*).

the problem falls within the classical mechanistic dilemma of distinguishing between normal spin-conserved diradical and concerted paths.¹¹ Because the reaction course of the peroxide (1a) is uninfluenced by 2,6-di-*t*-butyl-*p*-cresol⁷ we are inclined towards the concerted mechanism, a hypothesis which is to be tested by work at present in progress. In any case, it is noteworthy that acetylene derivatives are formed only for (1f) and (1h) when appreciable steric hindrance, deriving from bulky R¹ and R² substituents, makes difficult the formation of C–O σ bonds. Moreover, when the substituents R¹ and R² on the peroxide (1) are methyl and hydrogen, in addition to the diepoxide (3i), both the epoxides (6i) and (7i) are obtained and no furanones (4i) and (5i) are formed because the equilibria (6i) \rightleftharpoons (12i) and (7i) \rightleftharpoons (14i) lie well over to the left.‡ In contrast, when R¹ = R² are electron-withdrawing groups, the furanones (4e–h) \rightleftharpoons (5e–h) replace the epoxides (6e–h) \rightleftharpoons (7e–h) which, though not isolated, were detected (¹H n.m.r.) in the reaction mixture as transient species changing into (4e–h) \rightleftharpoons (5e–h). It is evident that, when R¹ and R² contain a multiple bond which can be in conjugation with the enolic double bond, enol forms are stabilized and tautomers (6) \rightleftharpoons (7) and (12) \rightleftharpoons (14) are interconverted. Thus, migration of the hydrogen from the enol oxygen to the epoxy oxygen, with reorganization of the bonds, as reported in (13) \rightleftharpoons (15), leads to (4e–h) \rightleftharpoons (5e–h). These interpretations account for the results obtained in thermal conversion of the peroxides (1a–c) where R¹ is an electron-withdrawing group and R² is a hydrogen. In these cases, in addition to the diepoxides (3a–c), the epoxides (6a–c) and polymeric material are obtained.§ However, in the reaction mixture the furanones (5a–c) were detected (¹H n.m.r.) as transient species, which rapidly undergo polymerization. It is evident that the furanones (5a–c) are formed from the epoxides (7a–c) which behave as epoxides (6e–h) \rightleftharpoons (7e–h). The suggested mechanism also allows the elucidation of the ambiguities associated with the behaviour of the peroxide (1d), where R¹ is a bulky and weakly electron-withdrawing substituent and R² is a hydrogen. As reported for (1f, h) appreciable steric hindrance makes formation of the C–O σ bond on the carbon atom bearing the bulky substituent difficult; therefore, low yields of the diepoxide (3d) and only trace amount of the epoxide (6d) are formed. The latter derives from the related enol form (12d) which in preference collapses, *via* (13d), into the furanone (4d), this compound, unlike (6d), being without strain. The main product of the thermal conversion of the peroxide (1d) is the furanone (5d) which is formed, by the enol form (14d), *via* (15d), from epoxide (7d),¶ the latter being without steric hindrance. The furanone (5d) owing to the bulkiness of its substituent undergoes polymerization only slowly and can, in contrast to (5a–c), be isolated.

We now report some observations made during the synthetic work¹ on the thermal rearrangement of the peroxides (1) in basic solvents. (1) In no case was the diepoxide (3) detected in the reaction mixture. (2) Rearrangements of the peroxides (1b) and (1d–h) into the furanones (4b), (4d–h), and (5d), which were carried out for convenience in acetone¹ can also be carried out in all the basic solvents used for the peroxide (1a),⁷ without substantial alteration of the results. || (3) In both chloroform and

‡ Similar results were previously obtained when R¹ = R² = H, the peroxide (1j) giving only the epoxide (6j) \rightleftharpoons (7j), in addition to (3j).⁹

§ The epoxides (6a–c), like the epoxides (6i), (7i), and (6j) \rightleftharpoons (7j), do not interconvert into the enol form (12a–c), and no furanones (4a–c) are formed.

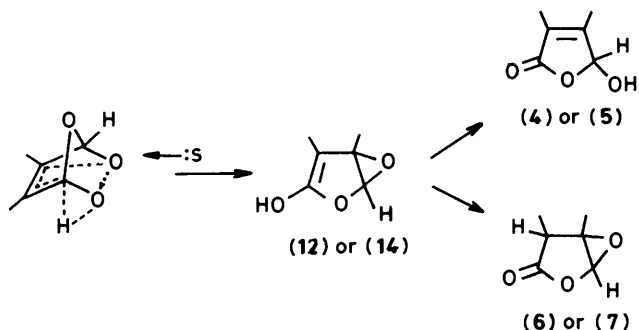
¶ The epoxide (7d), in contrast to (7a–c), is detectable in the reaction mixture the diethylamide group moving the equilibrium (7d) \rightleftharpoons (14d) only a little to the right.

|| Occasionally small amounts of acetylenic compounds and formic anhydride were detected.

acetone the epoxide (6h)⇌(7h) was the transient species (¹H n.m.r.) which rapidly collapses to the furanone (4h)⇌(5h). On the basis of the above observations, we have carried out the thermal conversion of the peroxides (1a—i) at 35 °C in acetone and Table 3 reports the percentage yields of the products so obtained. Quantification of the reaction products was made on the basis of the ¹H n.m.r. spectra of the crude reaction mixture and confirmed by chromatography on silica gel, unless otherwise stated. Since the furanones (4b, c) and (5a—c) easily polymerize, thermal conversions of the peroxides (1a—c) were also carried out in deuterioacetone. In Table 3 are reported the percentage yields of the reaction products evaluated on the basis of the ¹H n.m.r. spectra recorded before complete conversion of the peroxides (1a—c). Although the conversions for the peroxides (1d—i) were also carried out in deuterioacetone, only in the case of (1h) were we able to detect a transient species [(6h)⇌(7h)].* The spectral and analytical data for the new product (4i) are reported in Table 2.

A control experiment showed that the diepoxides (3) were unchanged under the reaction conditions: this allows us to exclude the possibility that the polymeric material reported in Table 3 is due to solvent-dependent polymerization of (3). Radical or concerted mechanisms as reported for thermal conversion of (1) in apolar solvents can, therefore, be discarded.

On the basis of the general properties of peroxides,^{12,13} two different mechanisms could accommodate the observed behaviour of the peroxides (1) in electron-rich solvents. The electrophilic behaviour of peroxides on reaction with electron pair donors is well known.¹² However the possibility that the electron-rich solvents act as nucleophilic catalysts by attack on a peroxy oxygen (Scheme 3) may be excluded. In fact, control experiments showed that the 2,5-peroxide of dimethyl 2,5-dimethylfuran-3,4-dicarboxylate in acetone behaves exactly as in carbon tetrachloride,¹⁴ to give quantitatively the diepoxide: this shows that the nature of the solvent does not influence the O—O breakage. It is also known that in the presence of weak bases, peroxides possessing α-hydrogens can undergo the Kornblum–De la Mare reaction.¹⁵ This process is generally assumed to involve an intramolecular carbanion displacement. Therefore, it is conceivable that the peroxides (1) in basic solvents form the 'intimate' ion pair (18), which evolves to give the products reported in Table 3, *via* (20) and/or (19), as shown



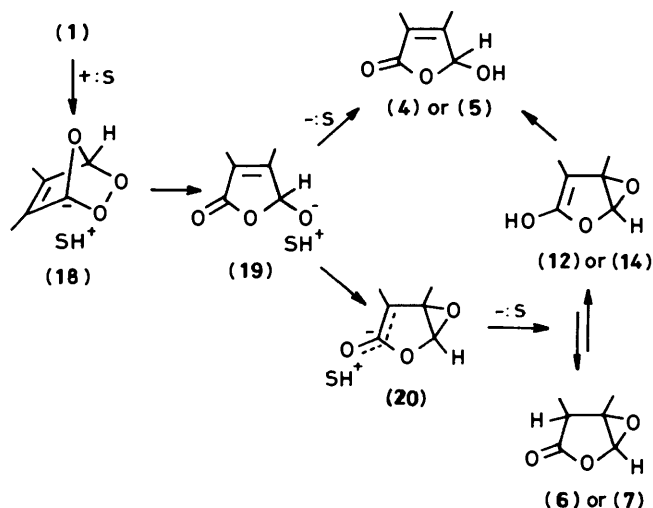
Scheme 3.

in Scheme 4, where we designate the basic solvent as :S. This interpretation accounts for: (1) the behaviour of the peroxides

* Evidently with the peroxides (1d—g) the equilibria (7) ⇌ (14) lies well over to the right (see Scheme 3).

† This observation is evident for (1a) (Table 3) in that in this case only the furanone (5a) polymerizes. The furanones (4b,c) and (5b,c) both polymerize; however on the basis of the data obtained in deuteriochloroform it is possible to envisage this as a general pattern of behaviour.

(1a—c) which preferentially rearrange into the furanones (4a—c) and the epoxides (6a—c), since between the ion pairs (18) the one having higher resonance stabilization is preferentially operative; ‡ (2) the behaviour of the peroxide (1i) which gives the epoxide (7i) as the main product (Table 3), ‡ in that the methyl group inductive effect opposes the formation of the ion pair (18) which should give (6i); (3) the behaviour of the peroxides (1e—g) and (1a—d) from which the epoxides (6e—g)⇌(7e—g) and (7a—d) respectively were unrecovered confirming the aforementioned remarks on the keto–enol equilibrium.



Scheme 4.

In conclusion, 2,5-peroxides (1) of 2,5-unsubstituted furans can be considered as key intermediates in the synthesis of several compound types such as the diepoxides (3), the furanones (4) and (5),¹ and the epoxides (6) and (7). It is noteworthy that the diepoxides (3) are structurally related to cotepoxide, a well-known anticancer agent,¹⁶ and the epoxides (6) and (7) with compounds which play a significant role both in biochemistry and in phytochemistry.¹⁷

Experimental

I.r. spectra were recorded on a Perkin-Elmer 399 spectrophotometer with chloroform as solvent. ¹H n.m.r. spectra were recorded with deuteriochloroform as solvent, unless otherwise stated, on a Varian EM-360 or a Bruker WH-270 spectrometer with tetramethylsilane as internal standard. The chloroform used in the oxygenation reactions was anhydrous and free of ethanol; the acetone and the carbon tetrachloride were anhydrous. Silica gel 0.05–0.20 mm (Merck) and light petroleum (b.p. 30–50 °C) were used for column chromatography.

The previously unreported peroxides (1c) and (1i) were prepared in deuteriochloroform in quantitative yields starting from the furan (2c)¹⁸ and (2i)¹⁹ according to the procedure previously described for similar peroxides.¹ § Owing to their high instability, particularly of (1i), they were not isolated and only ¹H n.m.r. data are reported in Table 2.

Thermal Conversion of the 2,3,7-Trioxabicyclo[2.2.1]hept-5-enes (1a—i) in Chloroform.—An 0.1M solution of the peroxides (1) in dry chloroform, obtained by sensitized photo-

‡ The epoxide (3i) is evidently formed by the mechanism which is operative in an apolar solvent.

§ Reaction time for (2c): 3 h, for (2i): 4 h (¹H n.m.r.).

Table 3. Thermal rearrangement of the peroxides (1a–i) in acetone at 35 °C

Substrate	Conversion time (min)	Yields (%) ^a					Polymeric material ^b
		(3)	(4)	(5)	(6)	(7)	
(1a) ⁷	30 ^c		50		18		30
(1a) ^d	20 ^e		50 ^f	30 ^f	20 ^f		Trace ^f
(1b)	10 ^c		30		10		60
(1b) ^d	5 ^e		38 ^f	32 ^f	10 ^f		20 ^f
(1c)	10 ^c						100
(1c) ^d	5 ^e		30 ^f	30 ^f	10 ^f		30 ^f
(1d)	20 ^c		30	45	13		12
(1e)	50 ^c		80 ^g				20
(1f)	20 ^c		98 ^g				2
(1g)	8 ^c		85 ^g				15
(1h)	20 ^c		95 ^g				5
(1i)	2 ^c	13	2	4	12	40	27

^a Deduced on the basis of the ¹H n.m.r. spectrum and confirmed by silica gel chromatography (compatible with product stability). ^b Calculated on the basis of the molecular weight of the starting furan + O₂/2. ^c Time required for the completion of the conversion (¹H n.m.r.). ^d Conversion carried out in deuterioacetone. ^e At this time the peroxide was present in *ca.* 10% (¹H n.m.r.). ^f Deduced on the basis of the ¹H n.m.r. spectrum and evaluated on the changed peroxide. ^g (4)≡(5).

oxygenation of the furans (2) in this solvent according to the procedure previously described in acetone,¹ was warmed at 35 °C and kept at this temperature under strictly anhydrous conditions until complete disappearance of (1) (¹H n.m.r.). Removal of the solvent under reduced pressure gave a mixture which was analysed by ¹H n.m.r. spectroscopy. The conversion times and the composition of the mixture, deduced on the basis of the ¹H n.m.r. spectrum and confirmed by silica-gel chromatography (compatible with the product stability), are shown in Table 1. When deuteriochloroform was used as reaction solvent, the spectral analysis (¹H n.m.r.) was carried out before the peroxides (1) disappeared.

Quantification of the mixture resulting from rearrangement of the peroxide (1a) was based on the relative areas of the signals at δ 4.27 [2-H of (3a)], 5.75 [1-H of (6a)], and methoxy signals.⁷ An aliquot of the crude reaction mixture was chromatographed on silica gel. Elution with light petroleum–diethyl ether (4:1, v/v) and diethyl ether yielded, successively, the epoxide (6a) and polymeric material. The diepoxide (3a) was isolated from a second aliquot of the crude reaction mixture by crystallization from light petroleum (b.p. 40–70 °C). The ¹H n.m.r. spectrum of the deuteriochloroform solution showed some more signals at δ 6.20 and 7.95 [5-H and 4-H of (5a)] which rapidly disappeared.

Quantification of the mixture resulting from rearrangement of the peroxide (1b) was based on the relative areas of the signals at δ 4.34 [2-H of (3b)], 3.04 and 3.61 [4-H of (6b)], and aromatic signals. An aliquot of the crude reaction mixture was chromatographed on silica gel. Elution with light petroleum–diethyl ether (4:1, v/v) and diethyl ether gave, successively, pure epoxide (6b) as an oil (Table 2) and polymeric material. From a second aliquot of the crude reaction mixture, by dissolution in diethyl ether, a mixture of (3b) and (6b) in *ca.* 6:1 molar ratio was obtained. Spectral data for (3b) were obtained from the ¹H n.m.r. spectrum of the mixture, signals due to (6b) being rejected, and the analytical data from elemental analysis of this mixture of isomers (Table 2). The ¹H n.m.r. spectrum of the deuteriochloroform solution showed another signal at δ 6.37 [5-H of (5b)], which rapidly disappeared.

Quantification of mixture resulting from rearrangement of the peroxide (1c) was based on the relative areas of the signals at δ 4.31 [2-H of (3c)], 2.90 and 3.70 [4-H of (6c)], and methyl signals. From the crude reaction mixture, by dissolution in diethyl ether, a mixture of (3c) and (6c) in *ca.* 4:1 molar ratio was obtained. The spectral data of the diepoxide (3c) and of the

epoxide (6c) (Table 2) were deduced by careful analysis of the i.r. and ¹H n.m.r. spectra of this mixture. The ¹H n.m.r. spectrum of the deuteriochloroform solution showed some more signals at δ 2.57 (Me), 6.24 (5-H), and 7.82 (4-H) of (5c) which rapidly disappeared (Table 1).

Quantification of the mixture resulting from rearrangement of the peroxide (1d) was based on the relative areas of the signals at δ 3.95 [2-H of (3d)], 6.10 [5-H of (4d)], 6.20 [5-H of (5d)], and the methyl signals. The crude reaction mixture was chromatographed on silica gel. Elution with light petroleum–diethyl ether (4:1, v/v), diethyl ether, and ethyl acetate gave, successively, (4d) and (5d) (identified by comparison with authentic samples¹), and polymeric material. The epoxide (6d) was identified by comparison (¹H n.m.r.) of the reaction mixture with that obtained from (1d) in acetone. The spectral data for the diepoxide (3d) (Table 2) were deduced from the ¹H n.m.r. spectrum of the reaction mixture, the signals of (4d)–(6d) being subtracted. The ¹H n.m.r. spectrum of the deuteriochloroform solution showed some more signals at δ 4.11 and 5.60 [4-H and 1-H of (7d)] which rapidly decreased while those of (5d) increased.

Quantification of the reaction mixture of the peroxide (1e) was based on the relative areas of the signals at δ 5.81 [2-H of (3e)], 6.42 [5-H of (4e)≡(5e)], and the methoxy signals. From the crude reaction mixture, by dissolution in diethyl ether, a mixture of (3e) and (4e)≡(5e) in *ca.* 3:2 molar ratio was obtained. The spectral data of (3e) (Table 2) were deduced from the ¹H n.m.r. spectrum of this mixture, the signals of (4e)≡(5e) being subtracted.¹ The analytical data for (3e) (Table 2) were obtained from elemental analysis of this mixture of isomers.*

Quantification of the reaction mixture of the peroxide (1f) was based on the relative areas of signals at δ 5.87 [4-H of (3f)], 6.87 [5-H of (4f)≡(5f)], and the aromatic signals. The crude reaction mixture was chromatographed on silica gel. Elution with light petroleum–diethyl ether (1:1→1:4, v/v) and diethyl ether gave successively (10f), (4f)≡(5f),¹ and polymeric material. Dibenzoylacetylene (10f) was obtained as a red-orange solid, m.p. 109–111 °C (lit.,²⁰ 110–111 °C); ν_{\max} (CCl₄) 1 655 cm⁻¹ (C=O); δ_{H} 7.50–7.85 (6 H, m, 2 × 3,4,5-ArH) and 8.10–8.45

* When deuterionitromethane was used as the reaction solvent, ¹H n.m.r. spectrum of the solution showed, in addition to the signals for the peroxide (1e), the diepoxide (3e), and the furanone (4e)≡(5e), singlets at δ 4.57 (4-H) and 5.85 (1-H) for the epoxide (6e)≡(7e); these were slowly (10 h) converted into those for (4e)≡(5e).

(4 H, m, 2 × 2,6-ArH). The spectral data for the diepoxide (**3f**) (Table 2) were deduced from the ¹H n.m.r. spectrum of the reaction mixture, the signals for (**4f**)=(**5f**) and (**10f**) being subtracted. The ¹H n.m.r. spectrum of the deuteriochloroform solution showed further signals at δ 8.82 [formic anhydride (**11**)] and at δ 5.79 and 5.73 [1-H and 4-H of (**6f**)=(**7f**)] which rapidly disappeared. On distillation of the solution at room temperature (1 mmHg), volatile compound (**11**) co-distilled with the deuteriochloroform and was identified by comparison (¹H n.m.r.) with an authentic sample.²¹ The distillation residue was composed of (**3f**), (**4f**)=(**5f**), and (**10f**) in percentage yields similar to those reported in Table 1 (¹H n.m.r.).

Quantification of the reaction mixture for the peroxide (**1g**) was based on the relative areas of the signals at δ 6.36 [5-H of (**4g**)=(**5g**)] and 5.69 [4-H of (**3g**)], and the methyl signals. The spectral data for the diepoxide (**3g**) (Table 2) were deduced from the ¹H n.m.r. spectrum of the mixture, the signals of (**4g**)=(**5g**) being rejected.¹ The ¹H n.m.r. spectrum of the deuteriochloroform solution showed further signals at δ 5.54 and 5.41 [1-H and 4-H of (**6g**)=(**7g**)] which rapidly disappeared.

Quantification of the reaction mixture for the peroxide (**1h**) was based on the relative areas of the signals at δ 5.68 [4-H of (**3h**)], 6.45 [5-H of (**4h**)=(**5h**)], 4.90 [4-H of (**6h**)=(**7h**)], and the methyl signals. The crude reaction mixture was chromatographed on silica gel. Elution with light petroleum–diethyl ether (3:7, v/v), diethyl ether, and acetone gave successively the acetylene (**10h**), m.p. 64–65 °C (lit.,²² m.p. 65 °C) and the furanone (**4h**)=(**5h**).¹ The singlets at δ 4.90 and 5.56 were assigned to the epoxide (**6h**)=(**7h**) (Table 2) since they were slowly converted into those for (**4h**)=(**5h**). Spectral data for (**3h**) (Table 2) were obtained by subtraction of the signals arising from (**4h**)=(**5h**), (**6h**)=(**7h**), and (**10h**). The ¹H n.m.r. spectrum of the deuteriochloroform solution showed the data reported in Table 1.

Quantification of the reaction mixture for the peroxide (**1i**) was based on the relative areas of the signals at δ 5.30 [6-H of (**3i**)], 5.43 [1-H of (**6i**)], 5.60 [1-H of (**7i**)], and the methyl signals. The products (**3i**), (**6i**), and (**7i**) were identified by comparison (¹H n.m.r.) with authentic samples.³

Thermal Rearrangement of the 2,3,7-Trioxabicyclo[2.2.1]-hept-5-enes (1a–i) in Acetone.—A 0.1M solution of the peroxides (**1**) in dry acetone, obtained by sensitized photooxygenation of the furans (**2**)¹ was treated according to the procedure above reported for the chloroform solutions. The conversion time and the composition of the mixtures, deduced on the basis of the ¹H n.m.r. spectrum and confirmed by silica-gel chromatography (compatible with the product stability) are reported in Table 3. When the deuterioacetone was used as reaction solvent, the spectral analysis (¹H n.m.r.) was carried out before the peroxides (**1**) disappeared (Table 3). In these cases, the products obtained were identified by comparison of the ¹H n.m.r. spectrum of the reaction mixture with those of authentic samples recorded in deuterioacetone. The diepoxides (**3**), obtained by thermal rearrangement of (**1**) in chloroform, were recovered unchanged when their acetone solution was kept at 35 °C for a time equal to the reaction time.

Quantification of the reaction mixture of the peroxide (**1a**) was based on the relative areas of the signals at δ 6.41 [5-H of (**4a**)], 5.75 [1-H of (**6a**)], and the methoxy signals.⁷ The ¹H n.m.r. spectrum of the deuterioacetone solution showed further signals at δ 8.11 and 6.33 [4-H and 5-H of (**5a**)], which rapidly disappeared.

Quantification of the reaction mixture for the peroxide (**1b**) was based on the relative areas of the signals at δ 6.62 [3-H of (**4b**)¹], 5.77 [1-H of (**6b**)], and the aromatic 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 the epoxide (**6b**) identified by comparison (i.r. and ¹H n.m.r. spectra) with a sample obtained by thermal conversion of (**1b**) in chloroform, and polymeric material. The ¹H n.m.r. spectrum of the deuterioacetone solution showed a further signal at δ 6.67 [5-H of (**5b**)] which rapidly disappeared.

Analysis of the ¹H n.m.r. spectrum of the reaction mixture for the peroxide (**1c**) showed the presence of only polymeric material. The ¹H n.m.r. spectrum of the deuterioacetone solution showed the data reported in Table 3 [(**4c**): signals at δ 6.18 and 6.58 (5-H and 3-H); (**5c**): signals at δ 5.97 and 7.72 (5-H and 4-H)].

Quantification of the reaction mixture for the peroxide (**1d**) was based on the relative areas of the signals at δ 6.10 [5-H of (**4d**)], 6.20 [5-H of (**5d**)], 5.62 [1-H of (**6d**)], and the methyl signals. The crude mixture was chromatographed on silica gel. Elution with light petroleum–diethyl ether (1:4, v/v), diethyl ether, and ethyl acetate gave successively (**4d**),¹ (**5d**),¹ and polymeric material. The spectral data for (**6d**), reported in Table 2, were deduced from the ¹H n.m.r. spectrum of the reaction mixture, the signals for (**4d**) and (**5d**) being subtracted.

Quantification of the reaction mixture for the peroxides (**1e**), (**1f**), (**1g**), and (**1h**) was based on the relative areas of the 5-H singlets of (**4e–h**)=(**5e–h**) and the methoxy, aromatic, methyl, and ethyl signals respectively.¹ The ¹H n.m.r. spectrum of (**1h**) in deuterioacetone solution showed further signals at δ 5.07 and 6.03 [4-H and 1-H of (**6h**)=(**7h**)] which rapidly decreased while those of (**4h**)=(**5h**) increased.

Quantification of the reaction mixture for the peroxide (**1i**) was based on the relative areas of the signals at δ 5.30 [6-H of (**3i**)], 5.43 [1-H of (**6i**)], 5.60 [1-H of (**7i**)], and the methyl signals. Quantification of the furanones (**4i**) and (**5i**) was difficult since their signals and those of the polymeric material present overlapped. The products (**3i**), (**6i**), and (**7i**) were identified by comparison (¹H n.m.r.) with authentic samples.³ The crude reaction mixture was chromatographed on silica gel. Elution with light petroleum–diethyl ether (1:4, v/v) and diethyl ether gave successively a mixture of the furanones (**4i**) and (**5i**)⁶ in ca. 1:2 molar ratio and polymeric material. The unreported spectral data of (**5i**) are listed in Table 2. The spectral data of (**4i**) were deduced from an ¹H n.m.r. spectrum of a mixture of it with (**5i**) signals due to the latter being subtracted; analytical data were also obtained by elemental analysis of the mixture (Table 2).

Thermal Rearrangement of the 2,5-Peroxide of Dimethyl 2,5-Dimethylfuran-3,4-dicarboxylate in Acetone and in Carbon Tetrachloride at 55 °C.—Two 0.1M solutions of the title peroxide, in acetone and in carbon tetrachloride respectively, were kept at 55 °C. The solution were periodically analysed by ¹H n.m.r. spectroscopy. The thermal rearrangement proceeded in the same way for both solutions. The time required for the completion of the reaction was the same (10 h) and after this time, in both solutions the peroxide was quantitatively converted into dimethyl 4,6-dimethyl-3,5,7-trioxatricyclo-[4.1.0.0.2.4]heptane-1,2-dicarboxylate, identified by comparison with an authentic sample.²³

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