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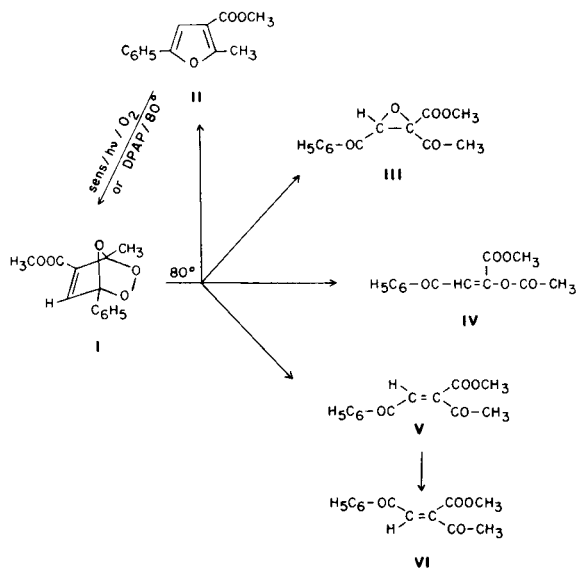
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Thermal conversion of furan *endo*-peroxide I, obtained by photosensitized oxidation of furan II, yields very similar results to those of the oxidation of the furan II by thermally generated singlet oxygen, showing that also in the latter case the *endo*-peroxide I is the key intermediate. A mechanistic interpretation of the furan II-singlet oxygen reaction is reported.

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We have previously shown that photosensitized oxidation of 3-methoxycarbonylfurans at  $-15^{\circ}$  yields quantitatively furan *endo*-peroxides which are stable at this temperature under strictly anhydrous conditions (1). In a first approach we assumed that the singlet oxygen attacks the furan-diene system by 1,4-cycloaddition as previously suggested in the cases of alkyl- and aryl-substituted furans, which lead to unstable furan *endo*-peroxides (2). However, since it is known that furans substituted with electron-withdrawing groups generally do not react as diene compounds (3), the possibility that the light, besides causing the formation of the singlet oxygen, induces the reaction which leads to *endo*-peroxides is now taken into consideration.



If the reaction is light-induced, as concerted suprafacial (4 + 2) photocycloadditions are forbidden by the Woodward-Hoffman selection rules (4), a mechanism different from the 1,4-cycloaddition could take place. In order to clarify if the formation of 5-methoxycarbonyl-4-methyl-1-phenyl-2,3,7-trioxabicyclo[2.2.1]hept-5-ene (I) occurs by a normal 1,4-cycloaddition of the singlet oxygen to

the 3-methoxycarbonyl-2-methyl-5-phenylfuran (II) or not, the behaviour of II towards the thermally generated singlet oxygen was investigated. A source of singlet oxygen, 9,10-diphenylanthracene 9,10-peroxide (DPAP), was chosen which decomposes in refluxing benzene to produce the active oxygenation species (5).

Initially, in order to gain information concerning the stability of the *endo*-peroxide I in the reaction conditions, I, prepared as previously described (1), was refluxed in anhydrous benzene. After 15 minutes it was completely transformed ( $^1\text{H}$  nmr). From the reaction mixture, silica gel chromatography allowed the isolation of furan II, of methyl (*E*)-2-acetyl-3-benzoyl-2,3-epoxypropionate (III), of methyl 2-acetyloxy-4-oxo-4-phenylbutenoate (IV) and of a mixture of methyl (*E*)-2-acetyl-3-benzoylacrylate (V) and its *Z*-isomer (VI) [altogether 3% (6)], apart from a mixture of polymeric materials.

Yields of the isolated products are listed in the Table. The identification of the products was confirmed by comparison of their chromatographic and spectral properties with those previously reported (1,7). Formation of the furan II indicates that *endo*-peroxide I in part reverts back to the starting furan by liberation of singlet oxygen. A similar behaviour was observed by Trozzolo for the 2,5-diphenylfuran-singlet oxygen adduct (8). All the other products obtained by thermal decomposition of I at  $80^{\circ}$  were also isolated when thermal conversion was carried out at room temperature although, as expected, the ratio epoxide III to polymeric materials was rather different (1,7). Very similar results were obtained when the decomposition of the *endo*-peroxide I was carried out in the presence of DPAP (*cf.* Table).

The oxidation of the furan II, using DPAP as a singlet oxygen donor, was accomplished at  $80^{\circ}$  in refluxing anhydrous benzene in the dark until the  $^1\text{H}$  nmr spectrum of the oxidation mixture showed the complete consumption of the starting furan II. The reaction was complete after 90 hours. Silica gel chromatography allowed the isolation of epoxide III and enol ether IV, apart from a

Table  
Thermal Conversion of *Endo*-peroxide I and  
Singlet Oxygen Oxidation of Furan II at 80°

Reaction Conditions (a)	Reaction Time	Products and % Yields (b)			
		II	III	IV	V+VI
I	15 minutes	20	9	2	6
I, DPAP molar ratio 1:2	15 minutes	20	10	2	6
II, DPAP molar ratio 1:2	90 hours	-	29	4	-
II, DPAP molar ratio 1:2	20 hours	(c)	27(d)	4(d)	4(d)

(a) Using a 2% refluxing benzene solution. (b) Compounds listed are the only products present in appreciable amounts in the reaction mixtures, in addition to the polymeric materials. The yields were deduced on the basis of the <sup>1</sup>H nmr spectrum of the reaction mixture and confirmed by silica gel chromatography. (c) Sixty percent of the starting II was recovered. (d) Calculated on the basis of the furan which was not recovered.

mixture of polymeric materials. In these conditions acrylates V and/or VI were not detected, however control experiments demonstrated that these compounds, in the presence or not of DPAP, by heating at 80° in refluxing benzene slowly undergo thermal polymerization. Therefore, in order to verify if V was also formed in the DPAP oxidation of II, the reaction was interrupted after 20 hours. Under these conditions the 60% of the starting furan II was recovered, however silica gel chromatography allowed the isolation of the acrylates V and VI in addition to III, IV and polymeric materials. The yields of the isolated products under both of the reaction conditions are listed.

The above results point out that the thermal conversion of the furan *endo*-peroxide I yields similar results to the oxidation of the furan II by thermally generated singlet oxygen, showing that also in the latter case the *endo*-peroxide I is the key intermediate. Therefore the presence of light is not essential for the formation of I and it can also be concluded that in the case of the 3-methoxy-carbonylfurans the uptake of singlet oxygen involves 1,4-cycloaddition to the furan ring.

The observed higher yields of III in the DPAP oxidation of the furan II at 80° with respect to the thermal conversion of I at 80° are consistent with an *endo*-peroxide I to epoxide III intramolecular rearrangement rather than with an intermolecular oxygen transfer (1). Unfortunately all of the attempts to carry out a kinetic control in this direction failed since the high hydrolytic reactivity of I makes a detailed study very difficult.

## EXPERIMENTAL

Ir spectra were measured with chloroform as the solvent on a Perkin Elmer 399 spectrophotometer; <sup>1</sup>H nmr spectra were recorded with

deuteriochloroform as the solvent, unless otherwise stated, on a Perkin Elmer R 12 A or on a Bruker W. H. 270 with TMS as the internal standard. Benzene used in the reactions was anhydrous. Silica gel 0.05-0.20 mm (Merk) and light petroleum bp 30-50° were used for column chromatography.

### Thermal Conversion of *endo*-peroxide I at 80°.

A 2% solution of I (1) (228 mg, 0.92 mmole) in dry benzene was refluxed under strictly anhydrous conditions. After 15 minutes I was completely transformed (<sup>1</sup>H nmr) and the solvent was removed under reduced pressure. Inspection of the <sup>1</sup>H nmr spectrum showed the presence of II, III, IV, V and polymeric materials. The mixture was chromatographed on silica gel (10 g). Elution with benzene/light petroleum (1:1; v/v) gave furan II (40 mg, 20%), elution with benzene/ether (9:1; v/v) gave the enol ether IV (3 mg, 2%), acrylates V and VI (12 mg, 6%) and epoxide III (21 mg, 9%), successively. Elution with acetone yielded polymeric materials (118 mg). Ir and <sup>1</sup>H nmr spectra of the compounds matched those of the authentic samples (1,7).

Similar results were obtained when the thermal conversion of I was carried out in the presence of DPAP (molar ratio I:DPAP, 1:2).

### Oxidation of Furan II by DPAP Thermal Decomposition.

A 2% solution of II (1) (175 mg, 0.81 mmole) in dry benzene, after addition of DPAP (2c) (586 mg, 1.62 mmoles), was refluxed in the dark under strictly anhydrous conditions. The reaction was periodically sampled and the samples analyzed by <sup>1</sup>H nmr. The oxidation was complete within 90 hours. Inspection of the <sup>1</sup>H nmr spectrum of the reaction mixture showed the presence of III, IV and polymeric materials. After removal of the solvent under reduced pressure the residue was chromatographed on silica gel (40 g). Elution with benzene/light petroleum (1:1; v/v) gave a mixture of DPAP and 9,10-diphenylanthracene, elution with benzene/ether (9:1; v/v) gave enol ether IV (8 mg, 4%) and epoxide III (58 mg, 29%) successively. Elution with acetone gave polymeric materials (136 mg). Ir and <sup>1</sup>H nmr spectra of the compounds matched those of the authentic samples (1,7).

When the oxygenation (II 196 mg, DPAP 666 mg) was interrupted after 20 hours and the solvent was removed under reduced pressure, inspection of the <sup>1</sup>H nmr spectrum showed the presence of II, III, IV, V and polymeric materials. The mixture was chromatographed on silica gel (40 g). Elution with benzene/light petroleum (1:1; v/v) yielded a mixture of DPAP and 9,10-diphenylanthracene and, successively, furan II (117 mg, 60%). Elution with benzene/ether (9:1; v/v) gave enol ether IV (4 mg, 4%), acrylates V and VI (4 mg, 4%) and epoxide III (25 mg, 27%) successively. Elution with acetone gave polymeric materials (52 mg).

### Behaviour of Acrylate V under the Oxidation Conditions.

A 2% solution of V (92 mg), after addition of DPAP (289 mg), was refluxed in the dark. After 90 hours the solvent was removed under reduced pressure and the residue was chromatographed on silica gel (20 g). Elution with benzene/light petroleum (1:1; v/v) yielded DPAP and 9,10-diphenylanthracene. Elution with benzene/ether (9:1; v/v) yielded acrylates V and VI (60 mg, 65%). Elution with acetone gave polymeric materials (25 mg).

Similar results were obtained when V was refluxed in the absence of DPAP.

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(6) As previously observed (1), the *E*-isomer V partly isomerizes into the *Z*-isomer VI by standing at room temperature or on contact with the chromatographic absorbant.

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