Carbonyl Oxide Chemistry. Part 2.† Substituent and Solvent Effects on the Chemical Behaviour of Carbonyl Oxides

M. Rosaria Iesce, Flavio Cermola, M. Liliana Graziano and Rachele Scarpati*
Dipartimento di Chimica Organica e Biologica dell'Università di Napoli Federico II, via Mezzocannone 16, 80134 Napoli, Italy

Comparison of the behaviour in polar and apolar solvents at various concentrations of the monoaryl carbonyl oxides **1** bearing an electron-withdrawing or an electron-donating group, respectively, on the aryl substituent is reported. The results are consistent with the conversion pathways reported in Scheme 1 and show that the electron-donating group increases the intramolecular oxygen-transfer potential of the system. It is also proposed that under some experimental conditions the carbonyl oxides so substituted mainly isomerize into dioxiranes **11**.

Carbonyl oxides, as typical 1,3-dipoles, participate in the cycloaddition chemistry which is characteristic of this class of reactive intermediates.[2] Considerable effort in both theoretical[3] and experimental[4] fields has been directed towards the characterisation of the oxidation chemistry of these highly reactive peroxides, to establish the pertinence of these processes to biological oxygenations[5] and to problems in atmospheric environmental chemistry.[6] However, methods used for generation of these elusive species are not appropriate for investigation in this field, owing to the possible involvement of other oxidant species and of side reactions.‡

Recently, we developed a method for the synthesis of the carbonyl oxides **1** from the 2-methoxyfurans **2**, *via* the 1-methoxy-4-phenyl-2,3,7-trioxabicyclo[2.2.1]hept-5-enes **3**,[1] in order to study the cycloaddition reactions of carbonyl oxides,[1,2] which represents a very convenient alternative to the previously suggested routes.[2] In the course of our work in this field, we frequently observed the stereospecific formation of the *Z*-acylalkenes **4** and the *Z*-epoxides **5**,§ which we suggested were derived from the carbonyl oxides **1** by oxygen-transfer reactions.[1,7]

In order to establish whether the new preparative method might be used to investigate the reactivity of carbonyl oxides as oxygen-transfer agents, in this preliminary study we clarify the dynamic chemistry of the carbonyl oxides **1b–d** in polar and apolar non-participating solvents at various concentrations. We therefore prepared the *endo*-peroxides **3b, d** and ascertained their quantitative opening into the carbonyl oxides **1b, d**. The choice of the latter was made on the basis that the electronic state of the molecules could affect the 1,3-dipolar character, as opposed to the oxygen transfer potential of the system.[8],¶

Results and Discussion

We carried out the tetraphenylporphyrin-sensitized photooxygenation of the furans **2b** and **2d** at −70 °C in $CDCl_3$–$CFCl_3$, according to the procedure previously reported for the furan **2c**.[1] After 90 min, the ^1H NMR spectra of the reaction mixtures, recorded at −70 °C, showed the presence of only the *endo*-peroxides **3b** and **3d**, respectively (Scheme 1). The latter, by addition of anhydrous methanol (precooled at −70 °C), led to the α-methoxy hydroperoxides **6b, d** which were by far the major products. Compounds **6b, d** were obtained quantitatively by Methylene Blue-sensitized photooxygenation of the furans **2b, d** in methanol, both at −70 °C and at −20 °C, thereby showing that the rearrangement of the *endo*-peroxides **3b, d** into the carbonyl oxides **1b, d** under these conditions is quantitative.

In order to gain further mechanistic insight into the behaviour of the carbonyl oxides **1** in the absence of co-reactants, the dye-sensitized photooxygenation of the furans **2b–d** was carried out at −20 °C,** and at various concentrations in nitromethane and carbon tetrachloride†† (typical polar aprotic and apolar solvents, respectively). Table 1 shows the yields (%) of the conversion products obtained using 0.1, 5×10^{-2} and 5×10^{-3} mol dm^{-3} solutions, deduced on the basis of ^1H NMR spectroscopy and/or by silica gel chromatography of the reaction mixtures.‡‡ The previously known compounds were identified by straightforward comparison of their IR and ^1H NMR spectra with those of authentic samples. The structures of the new products were assigned on the basis of elemental analyses and/or spectral data (Table 2).

The data reported in Table 1 show that the carbonyl oxides **1b, c** in nitromethane at high and medium concentrations led mainly to the alkenes **4b, c**, in addition to the epoxides **5b, c** and very small amounts of the cycloadducts **7b, c** and **8b, c**. Compounds **7b, c**, and **8b, c** were evidently formed by the cycloaddition of the carbonyl oxides **1b, c** to the double bond of the *endo*-peroxides **3b, c** and to the ketone group of the epoxides **5b, c** respectively. The mode of formation of the alkenes **4**, which

† Part 1, ref. 1(*a*).

‡ Generally, it is not possible to identify the actual oxygen-transfer agent in alkene ozonation reactions; ozone, 1,2,3-trioxolane, 1,2,4-trioxolane and carbonyl oxide are all potential oxygen-transfer agents, and all co-exist under ozonolysis conditions. On the other hand, in the oxidation of diazo compounds by singlet oxygen, the possibility that side reactions which do not involve the carbonyl oxide are dominant must be taken into account. In fact, singlet oxygen reacts with cyclohexene to give a product distribution similar to that obtained for this alkene in the presence of diazofluorene.[2]

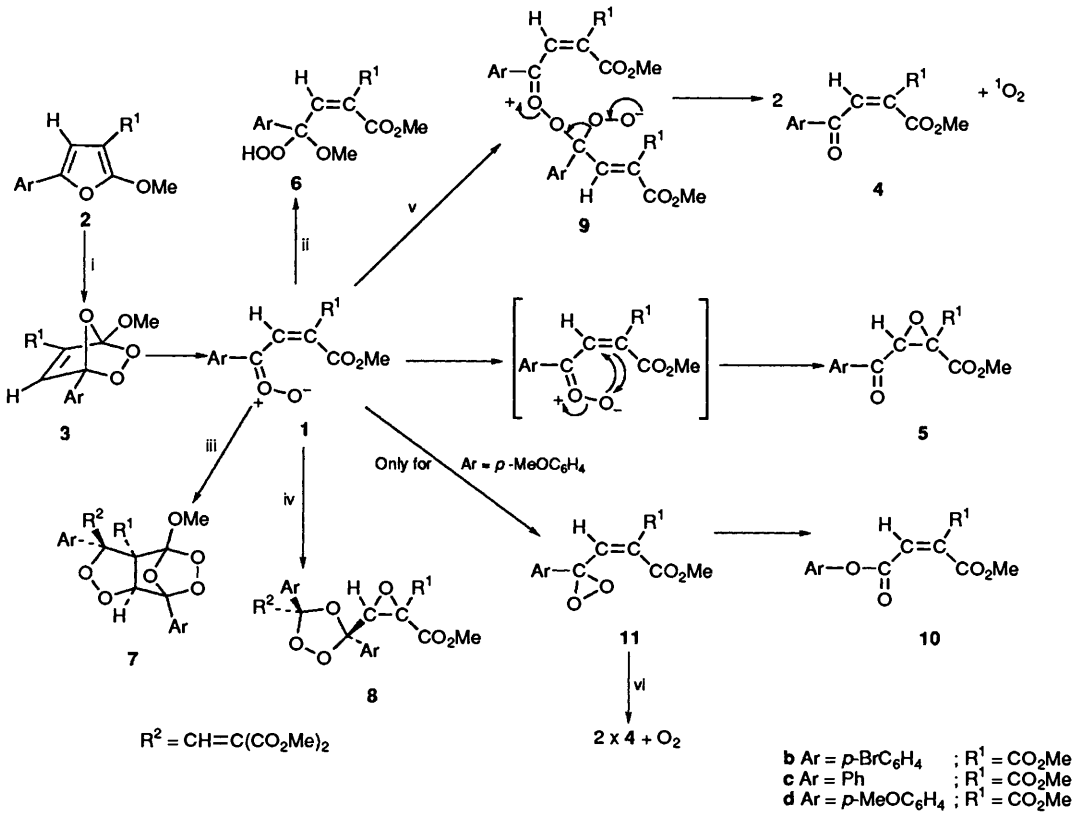
§ The carbonyl oxide **1a** leads stereospecifically to the *Z*-acylalkene **4a** and *Z*-epoxide **5a**[7] (Scheme 1 where for **a** Ar = Ph and R^1 = Ac).

¶ Attempts to prepare methyl 1-methoxy-4-(*p*-nitrophenyl)-2,3,7-trioxabicyclo[2.2.1]hept-5-ene-6-carboxylate **3e** were unsuccessful owing to the low solubility of the starting furan **2e** (Scheme 1 where for **e** Ar = *p*-$NO_2C_6H_4$ and R^1 = CO_2Me) at low temperature in all the solvents used.

** The lowest temperature compatible with the freezing point of the solvents used.

†† We previously reported some data on the behaviour of the carbonyl oxide **1c** in these solvents.[1,7] However, the reactions were carried out with different objectives and the results were not significant in this context.

‡‡ In no case were we able to detect the 1,2,4,5-tetraoxanes, the so-called carbonyl oxide dimers,[2] even when the thermal conversion of the *endo*-peroxides **3** was carried out in $CDCl_3$–$CFCl_3$ at −60 °C. These conditions were examined since it was recently reported that the amount of acetone diperoxide increases as the temperature of the ozonolysis of tetramethylethylene is lowered.[9]



Scheme 1 *Reagents:* i, $^1O_2$; ii, MeOH; iii, **3**; iv, **5**; v, **1**; vi, **11**

are the ketone compounds related to the carbonyl oxides **1**, can be assumed to be similar to that occurring during the decay of a variety of diaryl-substituted carbonyl oxides which decompose *via* a bimolecular pathway into the related diaryl ketones.[10] However, as the amounts of the alkenes **4b**, **c** were closely dependent on the solvent polarity (see below), we suggest a dipolar dimeric carbonyl oxide, *e.g.* **9b**, **c**, as a reaction intermediate. This pathway has been confirmed by trapping the singlet oxygen formed together with the alkene **4c**, the reaction being depicted in Scheme 1.* In nitromethane at low concentration the proportions of compounds **4c** and **5c** were reversed, and the bimolecular cycloadditions of **1c**, which led to compounds **7c** and **8c**, were prevented completely. The changes were less significant in the case of the carbonyl oxide **1b** owing to its high 1,3-dipolar character (shown by the presence of the cycloadduct **8b**) and a more dilute solution was necessary in order to observe an inversion of the proportions of **4b** and **5b** (Table 1). The increasing yields of the epoxides **5b**, **c** in dilute solutions suggest that the latter are formed by an intramolecular oxygen transfer as shown in Scheme 1. Consistent with this assumption is the previously observed stereospecific formation of the epoxide **5a**.[7] Intramolecular cycloadditions of carbonyl oxides are known,[2,12] and in some cases intramolecular oxygen transfer has been suggested as the pathway for the final products.[13] In the case of the carbonyl oxides **1b**, **c**, owing to the electronic state of the molecules, the intramolecular oxygen transfer becomes significant only when the bimolecular reactions are unfavourable.

In carbon tetrachloride at high and medium concentrations the formation of the alkenes **4b**, **c** was minimized, the dipolar dimeric carbonyl oxides **9b**, **c** being scarcely stabilized in the apolar solvent. Under these conditions cycloaddition of the carbonyl oxides **1b**, **c** to the dipolarophiles present in the reaction mixtures was favoured[14] and the main products were compounds **7b**, **c** and **8b**, **c**, confirming the results obtained for **1c** in 2×10^{-2} mol dm^{-3} solution of the apolar solvent.[1] However, at very low concentration, the bimolecular cycloadditions of the carbonyl oxides **1b**, **c** were in competition with the formation of the epoxides **5b**, **c**,† thus confirming the intramolecular mechanism suggested for the formation of the latter.

These mechanistic observations were confirmed by some aspects of the behaviour of the carbonyl oxide **1d**. Apart from the ester **10d**, the products obtained for **1d** were similar in nature to those obtained from the carbonyl oxides **1b**, **c**. However, in polar nitromethane the intramolecular formation of the epoxide **5d** greatly prevailed over that of the alkene **4d** even at high concentrations, as the data reported in Table 1 show. Evidently, in spite of the positive influence of the solvent polarity, the formation of the dipolar dimeric carbonyl oxide **9d** is made difficult owing to the delocalization of the positive charge on the *p*-MeOC$_6$H$_4$ substituent of the carbonyl oxide **1d**. This delocalization, which reduces the 1,3-dipolar character of the carbonyl oxide **1d**, could be also partly‡ responsible for the small amount of the cycloadduct **7d** in apolar carbon tetrachloride. It is significant that in the apolar solvent at

* The trapping of singlet oxygen was effected by adding, to the reaction mixture of the *endo*-peroxide **3c**, 9,10-diphenylanthracene which led to the related 9,10-peroxide.[11] The latter was detected in the reaction mixture by ^{1}H NMR and by HPLC (see Experimental section).

† The main products would again appear to be the cycloadducts **7b**, **c**. However, it is to be noted that, in order to obtain the real amounts of the epoxides **5b**, **c**, it is necessary to add those of the cycloadducts **8b**, **c**.

‡ The low amount of the adduct **7d** can also be ascribed to the low concentration of the unstable *endo*-peroxide **3d** in the reaction mixtures. Indeed, control experiments showed that the peroxide **3d** is thermally less stable than **3b**, **c** (see Experimental section).

Table 1 Yields of the products of thermal conversion of the peroxides **3b–d** at −20 °C

Substrate	Ar	Solvent	Concentration/ mol dm^{-3}	Yield (%)[a] 4	5	7	8	10
3b	*p*-BrC_6H_4	$MeNO_2$	0.1	71	17	—	12	—
3c	Ph			67	22	5	6	—
3d	*p*-$MeOC_6H_4$			30	61	—	4	5
3b	*p*-BrC_6H_4		5×10^{-2}	67	20	5	8	—
3c	Ph			65	24	5	6	—
3d	*p*-$MeOC_6H_4$			19	75	1	1	4
3b	*p*-BrC_6H_4		5×10^{-3}	67[b]	33[b]	—	Trace	—
3c	Ph			46	54	—	—	—
3d	*p*-$MeOC_6H_4$			21	77	—	—	2
3b	*p*-BrC_6H_4	CCl_4	0.1	5	—	86	9	—
3c	Ph			11	5	67	17	—
3d	*p*-$MeOC_6H_4$			42	17	20	18	3
3b	*p*-BrC_6H_4		5×10^{-2}	6	—	85	9	—
3c	Ph			13	5	59	23	—
3d	*p*-$MeOC_6H_4$			23	20	33	21	3
3b	*p*-BrC_6H_4		5×10^{-3}	12	14	47	27	—
3c	Ph			15	19	38	28	—
3d	*p*-$MeOC_6H_4$			15	58	16	9	2

[a] Deduced on the basis of ^{1}H NMR spectra and/or by silica gel chromatography. [b] When the reaction was carried out at a concentration of 2.5×10^{-3} mol dm^{-3}, yields were: **4b** 45 and **5b** 55%, respectively.

high and medium concentrations, in contrast with the carbonyl oxides **1b**, **c**, the carbonyl oxide **1d** still added to the carbonyl group of the epoxide **5d** to only a moderate extent although the latter was present in the mixtures at much higher concentration.

Unexpectedly in the apolar solvent at high concentrations, the amount of the alkene **4d** was considerable. This result is not in accordance with the above remarks on the formation of the alkenes **4** *via* the dipolar dimeric carbonyl oxides **9**. Indeed, formation of **9d**, which is disfavoured in nitromethane, would be prevented in the apolar solvent. One plausible explanation for the observation of a large amount of **4d** is closely related to the formation of the aryl ester **10d**. The formation of both compounds should be explained if the carbonyl oxide **1d** *partly* isomerizes into the dioxirane **11d**. Although for many carbonyl oxides the dioxirane formation seems to be ruled out, some special cases exist where ring closure might be favourable[2] and *ab initio* calculations indicate that the isomerization is facilitated by the presence of π-donors.[15] In this connection the isomerization of the carbonyl oxide **1d** into the dioxirane **11d** could be assisted by the *p*-$MeOC_6H_4$ substituent. On the other hand, although dioxirane chemistry still appears to be in its initial stages, the most well established aspects of the reactivity of bisubstituted dioxiranes are: (a) electrophilic oxygen transfer, (b) production of esters and (c) decomposition into dioxygen and ketone compounds.[16] The last reaction could become the main transformation of the dioxirane **11d** in the apolar solvent at high concentration. The data reported in Table 1 also show that the formation of the ester **10d** is a peculiarity of the carbonyl oxide **1d**. Indeed, the esters **10b**, **c** were never detected in the reaction mixtures of the carbonyl oxides **1b**, **c**, whose structures rule out a rearrangement to the dioxiranes **11b**, **c**. Finally, at first glance the large amount of the epoxide **5d** produced at low concentration would suggest an intramolecular oxygen transfer of the dioxirane part of the molecule on the unsaturated chain. However, the structural characteristic of this chain should involve a nucleophilic oxygen transfer.* Therefore, we are inclined to ascribe the result to an oxygen transfer of the carbonyl oxide **1d** before it isomerizes into the dioxirane **11d**. The presence in the reaction mixtures of the cycloadduct **7d** (though not in comparable amount with **7b**, **c**) and of the cycloadduct **8d** supports this hypothesis.

According to the previously reported remarks about the relative energetics of some processes involving carbonyl oxides,[2] we tentatively suggest that the carbonyl oxides **1** are formed from the *endo*-peroxides **3** with considerable excess of internal energy. In apolar carbon tetrachloride at high concentration the carbonyl oxide **1d** retains sufficient energy to ensure that isomerization to the dioxirane **11d** assisted by the π-donor substituent is possible. Of course, the exothermicity of this cyclization implies that the dioxirane **11d** will be formed with a large amount of internal energy so that it will react further to give the alkene **4d** or will rearrange to the ester **10d**. When the concentration of the carbonyl oxide **1d** in carbon tetrachloride is very low, the collisional deactivation from the solvent makes the dioxirane **11d** formation difficult, the latter being largely supplanted by the intramolecular oxygen transfer leading to the epoxide **5d**. At medium concentration the balance between the difficulty of dioxirane **11d** formation and stabilization of the apolar *endo*-peroxide **3d** in the apolar solvent favours the bimolecular cycloaddition to the latter of the carbonyl oxide **1d**, explaining the formation of the cycloadduct **7d**. The formation of the ester **10d** in the nitromethane solutions shows that also in this solvent the dioxirane **11d** is formed although the isomerization might have been expected to occur to a lesser extent, the carbonyl oxide **1d** being stabilized in the more polar medium.†

Conclusion

It has been established that a π-donor group on the phenyl substituent of the carbonyl oxide **1** considerably increases the intramolecular oxygen transfer of the latter *versus* the 1,3-cycloaddition. Moreover, it is possible that, under some experimental conditions, the carbonyl oxide thus substituted mainly isomerizes into the dioxirane **11**, the extent of isomerization being related to concentration and solvent polarity. Whether this hypothesis is valid and whether some

* It is to be noted that diethyl maleate cannot be epoxidized even with the more highly reactive dioxiranes.[16e]

† The methylene carbonyl oxide has a calculated dipole moment of 5.4 D while that of the related dioxirane is 3.1 D, which should be reflected in a difference in ground-state solvation in polar and apolar solvents.[3]

suitably substituted carbonyl oxides **1** can be used as intermolecular oxygen transfer agents will be ascertained through further studies which are currently under way.

Experimental

IR spectra were recorded on a Perkin-Elmer 1760 X-FT spectrophotometer with chloroform as solvent. ^1H and ^{13}C NMR spectra were recorded with Bruker AC-270 or AM-400 spectrometers using deuteriochloroform as solvent, unless otherwise stated, and tetramethylsilane as internal standard. *J* Values are given in Hz. The mass spectrum of compound **10d** was recorded on a Kratos MS 80 spectrometer. HPLC was performed on a Varian 5000 instrument equipped with a Varichrom UV detector. The solvents used in the photooxygenation reactions were anhydrous. Silica gel 0.06–0.20 mm (Merck) and light petroleum (b.p. 40–70 °C) were used for column chromatography. TLC was performed on silica gel layers (Whatman PK6F). Tetraphenylporphyrin (TPP) and Methylene Blue (MB) (Fluka) were used without purification.

The furans **2b**, **d**, **e** were prepared according to a procedure previously reported for different furans,[17] starting from methyl propiolate and the 2-aryl-5-methoxy-4-methyloxazoles, the latter being obtained by cyclization of the methyl *N*-aroyl-2-aminopropionates with phosphorus pentachloride[17] and used without purification. Silica gel chromatography of the reaction mixtures gave **2b** (25%) and **2d** (23%) by elution with light petroleum–diethyl ether (9:1 v/v) and **2e** (25%) by elution with light petroleum–diethyl ether (7:3 v/v), respectively. Physical, spectroscopic and analytical data for the furans **2b**, **d**, **e** are listed in Table 2.

General Procedure for the Photosensitized Oxygenation of the 2-Methoxyfurans **2b** *and* **2d** *in Methanol.*—A solution of each of the furans **2b** and **2d** (5×10^{-3} mol dm^{-3}; 1 mmol) in methanol was irradiated with a halogen-superphot lamp (Osram, 650 W) in the presence of MB (8×10^{-3} mmol). During the irradiation, dry oxygen was bubbled through each solution which was maintained at −70 and −20 °C, respectively. Progress of each reaction was checked by periodically monitoring (^1H NMR) of furan disappearance. When each reaction was complete (90 min), the methanol was removed under reduced pressure. Each residue, which showed the presence of only the hemiperacetals **6b** and **6d** respectively (^1H NMR), was taken up in dry ether and the respective suspensions filtered to remove MB. Evaporation of each filtrate gave, respectively, quantitatively pure **6b** and **6d**. All attempts to separate compounds **6b** and **6d** from the MB chromatographically failed since compounds **6** partly polymerize and partly hydrolyse on contact with the adsorbents. Physical, spectroscopic, and analytical data of the hemiperacetals **6b**, **d** are listed in Table 2.

General Procedure for the Photosensitized Oxygenation of the 2-Methoxyfurans **2b** *and* **2d** *in* $CDCl_3$–$CFCl_3$.—A solution of each of the furans **2b** and **2d** (5×10^{-2} mol dm^{-3}; 1 mmol) in $CDCl_3$–$CFCl_3$ (3:1) was photo-oxygenated in the presence of TPP (3.6×10^{-4} mmol) at −70 °C according to the procedure reported above for the methanol solutions and previously reported for the furan **2c**.[1] When the reaction was complete (90 min), a sample was transferred from the reaction apparatus to the spectrometer, the probe temperature being −70 °C. Inspection of the ^1H NMR spectra showed the presence of only the *endo*-peroxides **3b** and **3d** (Table 2). Upon raising the probe temperature to −60 °C for **3d** and to −40 °C for **3b**,* the signals of **3b** and **3d** decreased. After 3 h compounds **3b** and **3d** had been completely converted into the compounds obtained when nitromethane was used as solvent (see below).

To a second aliquot (4 cm^3) of each of the solutions of the *endo*-peroxides **3b** and **3d** at −70 °C, methanol (3 cm^3) precooled at this temperature was added and the solutions were maintained at −70 °C. After 90 min the solutions were warmed to room temp. and the solvents were removed under reduced pressure. The ^1H NMR spectra of the residues showed, in addition to small amounts of compounds **4b** and **4d** and **5b** and **5d**, the α-methoxy-hydroperoxides **6b** and **6d**. Compounds **4b** and **4d**, **5b** and **5d**, **6b** and **6d** were identified by comparison with authentic samples.

Photosensitized Oxygenation of the 2-Methoxyfurans **2b–d** *in Nitromethane and Carbon Tetrachloride.*—The reactions were performed at −20 °C according to the procedure reported above, using 0.1, 5×10^{-2} and 5×10^{-3} mol dm^{-3} solutions of each of the furans **2b–d** (1 mmol) in nitromethane (sensitizer MB) and in carbon tetrachloride (sensitizer TPP). For the furan **2b** a 2.5×10^{-3} mol dm^{-3} solution in nitromethane was also used. When inspection of the ^1H NMR spectra showed complete conversion of the furans **2** (90 min), the lamp was switched off and the oxygen flow was stopped. After 3 h, the solvents were removed at room temp. under reduced pressure and the residues analysed by ^1H NMR spectroscopy. The composition of the reaction mixtures, deduced on the basis of the ^1H NMR spectra, was confirmed by isolation of the products by silica gel chromatography and is reported in Table 1.

Quantification of the reaction mixtures of the furan **2b** was based on the relative areas of the singlets at δ_H 4.63 (CH of the epoxide **5b**), 5.55 (CH of the tricyclic compound **7b**), 6.99 (olefinic CH of the trioxolane **8b**). No integration of signals of the alkene **4b** was possible since they and those of the other products present in the mixtures overlap. Therefore the crude reaction mixtures were chromatographed on silica gel. Elution with light petroleum–diethyl ether (17:3, 4:1, 3:2 v/v) gave, successively, the alkene **4b**, the epoxide **5b**, the tricyclic compound **7b** and the trioxolane **8b**.† The amounts of the alkene **4b**, reported in Table 1, were estimated correlating its chromatographic yields to those of the epoxide **5b**. Compounds **4b**, **7b**, and **8b** were recrystallized from hexane. The physical, spectroscopic and analytical data for compounds **4b**, **5b**, **7b** and **8b** are reported in Table 2.

Quantification of the reaction mixtures of the furan **2c** was based on the relative areas of the singlets at δ_H 4.68 (CH of the epoxide **5c**), 5.64 (CH of the tricyclic compound **7c**), 7.07 (olefinic CH of the trioxolane **8c**), 7.88 (CH of the alkene **4c**).[1a,7] The crude reaction mixtures, chromatographed on silica gel as reported above for the reaction mixtures obtained by starting from the furan **2b**, confirmed the quantification and gave the compounds **4c**, **5c**, **7c** and **8c**, which were identified by comparison with authentic samples.[1a,7]

Quantification of the reaction mixtures of the furan **2d** was based on the relative areas of the singlets at δ_H 4.02 (epoxide CH of the trioxolane **8d**), 4.68 (CH of the epoxide **5d**), 5.65 (CH of the tricyclic compound **7d**) and 7.86 (CH of the alkene **4d**). The ester **10d** was present in the reaction mixtures but no integration

* When the conversion of the *endo*-peroxide **3b** was carried out at −60 °C, after 10 h the ^1H NMR spectrum of the reaction mixture showed the presence of almost 50% of unchanged **3b**. Similar behaviour showed the peroxide **3c**. In no case were we able to detect the 1,2,4,5-tetraoxanes.

† Some amounts (*ca.* 2–3%) of a compound, presumably a stereoisomer of **7b**, were present in the reaction mixtures in carbon tetrachloride at high and medium concentrations. This product was obtained by silica gel chromatography as an inseparable mixture together with the cycloadduct **7b** and its spectroscopic data [δ_H 3.22, 3.64, 3.77 and 4.00 (4 × s, 4 × OMe), 5.71 (s, CH), 7.12 (s, olefinic CH) and 7.20–7.70 (m, 2 × Ar)] were deduced by ^1H NMR spectrum of this mixture, the signals of **7b** being subtracted.

Table 2 Physical, spectroscopic and analytical data of the new products

Product	M.p. (T/°C)	ν_{max}/cm^{-1} ($CHCl_3$)	δ_H($CDCl_3$; J-values in Hz)	Formula	Found (%)[e]/(Required) C	H	N
2b	108–112[a]	1707	3.84 and 4.22 (6 H, 2 × s, 2 × OMe), 6.88 (1 H, s, CH), 7.30–7.60 (4 H, m, Ar)	$C_{13}H_{11}BrO_4$ (311.13)	50.2 (50.18)	3.6 (3.56)	
2d	106–107[a]	1704	3.82, 3.83 and 4.19 (9 H, 3 × s, 3 × OMe), 6.70 (1 H, s, CH), 6.91 (2 H, d, J 9.0, 3- and 5-H of Ar) and 7.47 (2 H, d, J 9.0, 2- and 6-H of Ar)	$C_{14}H_{14}O_5$ (262.25)	64.2 (64.11)	5.4 (5.38)	
2e	161–165[b]	1713	3.85 and 4.26 (6 H, 2 × s, 2 × OMe), 7.13 (1 H, s, CH), 7.64 (2 H, d, J 8.8, 2- and 6-H of Ar) and 8.24 (2 H, d, J 8.8, 3- and 5-H of Ar)	$C_{13}H_{11}NO_6$ (277.23)	56.1 (56.32)	4.1 (4.00)	4.9 (5.05)
3b			3.89 and 3.93 (6 H, 2 × s, 2 × OMe), 7.43 (1 H, s, CH) and 7.50–7.70 (4 H, m, Ar)[c]				
3d			3.91 (6 H, s, 2 × OMe), 3.98 (3 H, s, OMe), 7.04 (2 H, d, J 8.8, 3- and 5-H of Ar), 7.57 (1 H, s, CH), 7.69 (2 H, d, J 8.8, 2- and 6-H of Ar)[c]				
4b	120–122[a]	1736, 1673, 1626	3.83 and 3.90 (6 H, 2 × s, 2 × OMe), 7.66 (2 H, d, J 8.8, 3- and 5-H of Ar), 7.82 (1 H, s, CH) and 7.83 (2 H, d, J 8.8, 2- and 6-H of Ar)	$C_{13}H_{11}BrO_5$ (327.13)	47.8 (47.73)	3.4 (3.39)	
4d	Oil	1734, 1666	3.81 (3 H, s, OMe), 3.88 (6 H, s, 2 × OMe), 6.96 (2 H, d, J 9.0, 3- and 5-H of Ar), 7.86 (1 H, s, CH), 7.95 (2 H, d, J 9.0, 2- and 6-H of Ar)	$C_{14}H_{14}O_6$ (278.25)	60.2 (60.43)	5.2 (5.07)	
5b	Oil	1752, 1697	3.74 and 3.92 (6 H, 2 × s, 2 × OMe), 4.63 (1 H, s, CH), 7.66 (2 H, d, J 8.8, 3- and 5-H of Ar) and 7.86 (2 H, d, J 8.8, 2- and 6-H of Ar)	$C_{13}H_{11}BrO_6$ (343.13)	45.7 (45.50)	3.3 (3.23)	
5d	Oil	1757, 1686	3.74, 3.89 and 3.90 (9 H, 3 × s, 3 × OMe), 4.68 (1 H, s, CH), 6.98 (2 H, d, J 9.0, 3-and 5-H of Ar), 7.99 (2 H, d, J 9.0, 2 and 6-H of Ar)	$C_{14}H_{14}O_7$ (294.25)	57.2 (57.14)	4.9 (4.80)	
6b	Oil	3511, 3350, 1734, 1660	3.25 (3 H, s, OMe), 3.76 and 3.87 (6 H, 2 × s, 2 × CO_2Me), 6.90 (1 H, s, CH), 7.30–7.60 (4 H, m, Ar), 8.94 (1 H, br s, OOH)	$C_{14}H_{15}BrO_7$* (375.18)	44.9 (44.82)	4.1 (4.03	
6d	Oil	3510 3300, 1734, 1660	3.23 (3 H, s, OMe), 3.75, 3.81 and 3.87 (9 H, 3 × s, 3 × OMe), 6.89 (2 H, d, J 9.0, 3- and 5-H of Ar), 6.94 (1 H, s, CH), 7.38 (2 H, d, J 9.0, 2- and 6-H of Ar), 8.98 (1 H, br s, OOH)	$C_{15}H_{18}O_8$† (326.29)	55.0 (55.21)	5.6 (5.56)	
7b	62–64[a]	1742, 1655	3.39, 3.68, 3.79 and 3.90 (12 H, 4 × s, 4 × OMe), 5.55 (1 H, s, CH), 7.20–7.60 (8 H, m, 2 × Ar), 7.71 (1 H, s, olefinic CH)	$C_{26}H_{22}Br_2O_{12}$ (686.27)	45.3 (45.50)	3.3 (3.23)	
7d	Oil	1741, 1654	3.35, 3.66, 3.83 and 3.92 (12 H, 4 × s, 4 × OMe), 3.78 (6 H, s, 2 × OMe), 5.65 (1 H, s, CH), 6.84 and 6.96 (4 H, 2 × d, J 9.0, 3- and 5-H of two Ar), 7.30 and 7.50 (4 H, 2 × d, J 9.0, 2- and 6-H of two Ar), 7.78 (1 H, s, olefinic CH)	$C_{28}H_{28}O_{14}$ (588.50)	57.3 (57.14)	4.9 (4.80)	
8b	52–55[a]	1741, 1673	3.52, 3.63, 3.76 and 3.77 (12 H, 4 × s, 4 × OMe), 3.95 (1 H, s, epoxide CH), 6.99 (1 H, s, olefinic CH), 7.40–7.70 (8 H, m, 2 × Ar)	$C_{26}H_{22}Br_2O_{12}$ (686.27)	45.5 (45.50)	3.4 (3.23)	
8d	Oil	1742, 1652	3.47, 3.63, 3.76 and 3.78 (12 H, 4 × s, 4 × OMe), 3.84 (6 H, s, 2 × OMe) 4.02 (1 H, s, epoxide CH), 6.93 (4 H, 2 × d, J 9.0, 3- and 5-H of two Ar), 7.09 (1 H, s, olefinic CH), 7.53 and 7.70 (4 H, 2 × d, J 9.0, 2- and 6-H of two Ar)	$C_{28}H_{28}O_{14}$ (588.50)	57.3 (57.14)	4.9 (4.80)	
10d[d]	Oil	1737, 1673	3.80, 3.88 and 3.89 (9 H, 3 × s, 3 × OMe), 6.89 and 7.05 (4 H, 2 × d, J 9.0, Ar) and 7.09 (1 H, s, CH)	$C_{14}H_{14}O_7$ (294.25)	57.3 (57.14)	4.9 (4.80)	

[a] Recrystallization solvent hexane. [b] Recrystallization solvent chloroform–hexane. [c] Recorded in $CDCl_3$–$CFCl_3$ (3:1 v/v). [d] δ_C($CDCl_3$) 53.1, 53.4 and 55.6 (3 × q, 3 × OMe), 114.6 and 121.9 (2 × d, CH of Ar), 130.0 (d, *C*H=C), 139.5 (s, CH=*C*), 143.6 and 157.7 (2 × s, C-1 and C-4 of Ar) and 162.3, 162.5 and 164.5 (3 × s, 3 × CO_2); m/z 294 (M^+, 3%), 171 (100) and 123 (30). [e] Active oxygen [O_{act}: Found (requires): * 3.8 (4.3) and † 4.3 (4.9)].

was possible since its signals and those of the other products present in the mixtures overlap. The crude reaction mixtures were chromatographed on silica gel. Elution with light petroleum–diethyl ether (9:1, 17:3, 4:1, 3:2 v/v) gave, successively, the ester **10d**, the alkene **4d**, the epoxide **5d**, the tricyclic compound **7d** and the trioxolane **8d**. The amounts of the ester **10d**, reported in Table 1, were estimated correlating its chromatographic yields to those of the epoxide **5d**. Further purification by TLC [benzene for **4d**, **5d** and **10d** and benzene–diethyl ether (19:1) for **7d** and **8d**] gave pure **4d**, **5d**, **7d**, **8d** and **10d**, whose physical, spectroscopic, and analytical data are reported in Table 2.

Trapping of Singlet Oxygen in Thermal Conversion of the endo-*Peroxide* **3c**.—A solution of the furan **2c** (5×10^{-2} mol dm^{-3}; 0.5 mmol) in $CDCl_3$–$CFCl_3$ (3:1) was photooxygenated at −70 °C according to the procedure reported above for the furans **2b** and **2d**. When the reaction was complete, the lamp was switched off and the oxygen flow was replaced by a nitrogen flow while the solution was kept at −70 °C in the dark. After 30 min a solution of 9,10-diphenylanthracene (0.5 mmol) in $CDCl_3$ (10 cm^3), pre-cooled at −70 °C and degassed, was added. The resulting mixture was warmed at −20 °C and kept at this temperature in the dark. After 24 h, the solvents were

removed under reduced pressure at room temp. The ^1H NMR spectrum of the reaction mixture showed, in addition to the signals of compounds **4c**, **5c**, **7c** and **8c** and of 9,10-diphenylanthracene, a multiplet at δ_H 7.19 typical of 9,10-diphenyl-9,10-epidioxy-9,10-dihydroanthracene.† HPLC Chromatography on a Whatman Partisil 10 (10 μm) column (flow rate 0.5 cm^3 min^{-1}) with a mobile phase of *tert*-butyl methyl ether–hexane (1:19 v/v) yielded successively 9,10-diphenylanthracene (R_t 8 min), its peroxide (R_t 13 min) and the products **4c**, **5c**, **7c** and **8c**. All the products were identified by comparison (R_t) with authentic samples.[1a]

Acknowledgements

This work was financially supported by Progetto Finalizzato del CNR (Rome) Chimica Fine 2 and by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (M.U.R.S.T). The NMR spectra were taken at the Centro di Metodologie Chimico Fisiche, Università di Napoli Federico II (Mr. V. Piscopo).

† The ^1H NMR spectrum in $CDCl_3$–$CFCl_3$ (3:1) of this peroxide, prepared according to a known procedure,[18] shows 2 multiplets at δ_H 7.19 (8 H, 2 × Ar) and 7.50–7.75 (10 H, 2 × Ph).

References

1 (*a*) M. R. Iesce, M. L. Graziano, F. Cermola, G. Cimminiello and R. Scarpati, *Gazz. Chim. Ital.*, 1990, **120**, 629; (*b*) M. L. Graziano, M. R. Iesce, F. Cermola, F. Giordano and R. Scarpati, *J. Chem. Soc., Chem. Commun.*, 1989, 1608.
2 W. H. Bunnelle, *Chem. Rev.*, 1991, **91**, 335 and references therein.
3 R. D. Bach, A. L. Owensby, J. L. Andrés and H. B. Schlegel, *J. Am. Chem. Soc.*, 1991, **113**, 7031.
4 W. Adam, W. Haas and B. B. Lohray, *J. Am. Chem. Soc.*, 1991, **113**, 6202.
5 C. T. Walsh and Y. C. J. Chen, *Angew. Chem. Int. Ed. Engl.*, 1988, **27**, 333; T. A. Dix and S. J. Benkovic, *Acc. Chem. Res.*, 1988, **21**, 101.
6 S. Kumar and R. W. Murray, *J. Am. Chem. Soc.*, 1984, **106**, 1040 and references therein.
7 M. L. Graziano, M. R. Iesce, G. Cimminiello and R. Scarpati, *J. Chem. Soc., Perkin Trans. 1*, 1988, 1699.
8 K. H. Houk and K. Yamaguchi, in *1,3-Dipolar Cycloaddition Chemistry*, ed. A. Padwa, Wiley, New York, 1984, vol. 2, p. 407 and references therein; D. Cremer and C. W. Bock, *J. Am. Chem. Soc.*, 1986, **108**, 3375 and references therein.
9 R. W. Murray, W. Kong and S. N. Rajadhyaksha, *J. Org. Chem.*, 1993, **58**, 315.
10 J. C. Scaiano, W. G. McGimpsey and H. L. Casal, *J. Org. Chem.*, 1989, **54**, 1612; M. Girard and D. Griller, *J. Phys. Chem.*, 1986, **90**, 6801.
11 A. J. Bloodworth and H. J. Eggelte, in *Singlet O_2*, ed. A. A. Frimer, CRC Press, Boca Raton, FL., 1985, vol. 2, p. 173.
12 W. H. Bunnelle and S. Lee, *J. Am. Chem. Soc.*, 1992, **114**, 7577; M. Casey and A. J. Culshaw, *Synlett.*, 1992, 214.
13 N. Nakamura, M. Nojima and S. Kusabayashi, *J. Am. Chem. Soc.*, 1986, **108**, 4671; 1987, **109**, 4969; R. W. Murray and R. Banavali, *Tetrahedron Lett.*, 1983, **24**, 2327.
14 R. Huisgen, in *1,3-Dipolar Cycloaddition Chemistry*, ed. A. Padwa, Wiley, New York, 1984, vol. 1, p. 1.
15 D. Cremer, T. Schmidt, J. Gauss and T. P. Radhakrishnan, *Angew. Chem. Int. Ed. Engl.*, 1988, **27**, 427.
16 (*a*) R. Curci, in *Adv. in Oxygenated Processes*, ed. A. L. Baumstark, JAI Press, London, 1990, vol. 2, p. 1; (*b*) R. W. Murray, *Chem. Rev.*, 1989, **89**, 1187; (*c*) W. Adam, R. Curci and J. O. Edwards, *Acc. Chem. Res.*, 1989, **22**, 205; (*d*) W. Adam, R. Curci, M. E. Gonzalez-Nunez and R. Mello, *J. Am. Chem. Soc.*, 1991, **113**, 7654; (*e*) R. W. Murray, M. Singh and R. Jeyaraman, *J. Am. Chem. Soc.*, 1992, **114**, 1346; (*f*) M. Singh and R. W. Murray, *J. Org. Chem.*, 1992, **57**, 4263; (*g*) P. Bovicelli, P. Lupattelli, E. Mincione, T. Principe and R. Curci, *J. Org. Chem.*, 1992, **57**, 2182; (*h*) R. Curci, M. Fiorentino, C. Fusco, R. Mello, F. P. Ballistreri, S. Failla and G. A. Tomaselli, *Tetrahedron Lett.*, 1992, **33**, 7929; (*i*) J. K. Crandall and T. Reix, *J. Org. Chem.*, 1992, **57**, 6759.
17 H. Gotthardt, R. Huisgen and H. O. Bayer, *J. Am. Chem. Soc.*, 1970, **92**, 4340.
18 R. W. Denny and A. Nickon, in *Organic Reactions*, ed. J. Wiley and Sons, New York, 1973, vol. 20, p. 185.

Paper 3/01493B
Received 15*th March* 1993
Accepted 27*th August* 1993