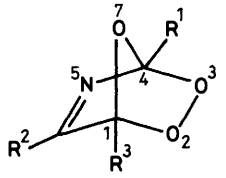
Dioxazole and Dioxetane Intermediates in the Thermal Rearrangement of *endo*-Peroxides obtained by Dye-sensitized Photo-oxygenation of 2-Alkoxyoxazoles

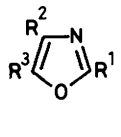
M. Liliana Graziano, M. Rosaria Iesce, Guido Cimminiello, and Rachele Scarpati*
Dipartimento di Chimica Organica e Biologica, Università di Napoli, Via Mezzocannone 16, 80134 Napoli, Italy
Michelangelo Parrilli
Istituto di Chimica, Università della Basilicata, Via N. Sauro 85, 85100 Potenza, Italy

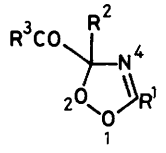
Singlet oxygen reacts with 2-alkoxyoxazoles (**2c,d**) leading to *endo*-peroxides (**1c,d**), which easily rearrange into dioxazoles (**3c,d**) and dioxetanes (**4c,d**). Both give carbamates (**5c,d**) *via* imino anhydrides (**7c,d**). When the reaction is carried out in alcohols at −60 °C only the dioxetanes (**4c,d**) are obtained. These compounds, which are the first examples of a bicyclic system of this type, at higher temperatures add methanol to give 2,5-dihydro-oxazoles (**9c,d**) and already at −60 °C react with diethyl sulphide to give the imines (**10c,d**).

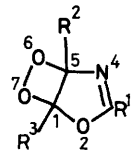
Although the dye-sensitized photo-oxygenation of oxazoles has many applications in organic synthesis,[1] some uncertainty remains as to the mechanism of the reaction. Recently Gollnick *et al.* isolated and characterized at low temperatures *endo*-peroxides of oxazoles bearing hydrogen, methyl, and/or phenyl groups as substituents, *e.g.* (**1a**).[2] These results confirm that the *endo*-peroxide (**1**) is the intermediate in dye-sensitized photo-oxygenation of 5-alkoxyoxazoles, *e.g.* (**2b**). We recently suggested this hypothesis on the basis of the comparable behaviour of singlet oxygen towards 2-alkoxyfurans carrying an electron-withdrawing group at C-4 which lead to 3*H*-1,2-dioxoles *via* furan *endo*-peroxides,[3] and towards the 5-alkoxyoxazoles which lead to 3*H*-1,2,4-dioxazoles, *e.g.* (**3b**).[4]† The formation of the 3*H*-1,2-dioxole by furan *endo*-peroxide thermal rearrangement is a peculiarity related to the position of the alkoxy group with respect to the electron-withdrawing group. Not only do other α-alkoxyfurans[5,6] behave differently from the aforementioned but also those carrying hydrogen, methyl, or phenyl groups as α-substituents.[7] To see whether the position of the methoxy group with respect to the nitrogen atom can influence the course of the reaction, we have investigated the behaviour of 2-methoxy-4-methyl-5-phenyloxazole (**2c**)‡ and checked again, this time at low temperatures, the behaviour of 2-methoxy-4,5-diphenyl-oxazole (**2d**)[8] towards singlet oxygen.

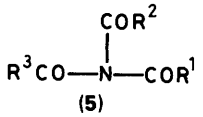
The reaction on the oxazole (**2c**) was carried out in $CDCl_3$–$CFCl_3$ (3:1) at −60 °C using tetraphenylporphyrin as sensitizer. When the reaction was complete (4 h, ^1H NMR), a sample was transferred from the reaction apparatus into the spectrometer. ^1H and ^{13}C NMR spectra, recorded at −60 °C, showed the presence of 4-methoxy-6-methyl-1-phenyl-2,3,7-trioxa-5-azabicyclo[2.2.1]hept-5-ene (**1c**), of 3-benzoyl-5-methoxy-3-methyl-1,2,4-dioxazole (**3c**), and of 3-methoxy-5-methyl-1-phenyl-2,6,7-trioxa-4-azabicyclo[3.2.0]hept-3-ene (**4c**) in *ca.* 3:1:0.3 molar ratio. The spectra of the sample kept at −60 °C after 4 h were substantially unchanged. The structure (**1c**) was deduced from the ^1H and ^{13}C NMR spectra of the reaction mixture, the signals of the minor products (**3c**) and (**4c**) being subtracted; data are reported in the Table. By raising the probe temperature to −40 °C, the signal intensities of the *endo*-peroxide (**1c**) decreased while those of the dioxazole (**3c**) and of the dioxetane (**4c**) increased. When the conversion of (**1c**) was complete, only the dioxazole (**3c**) and the dioxetane (**4c**) were present in a *ca.* 3:1 molar ratio. Since the molar ratio (**3c**):(**4c**) was the same as that observed at −60 °C, the fact that both (**3c**) and (**4c**) appeared in the sample checked by NMR at −60 °C must be the result of the thermal rearrangement of (**1c**) which occurred during the transfer of the sample in the spectrometer. Compounds (**3c**) and (**4c**) could not be isolated since both undergo thermal rearrangement into methyl *N*-acetyl-*N*-benzoylcarbamate (**5c**).[4a] However, the dioxetane (**4c**) was identified by comparing the spectra of the mixture with those of an authentic

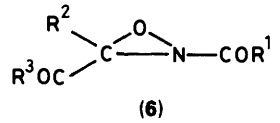

(1)


(2)


(3)


(4)

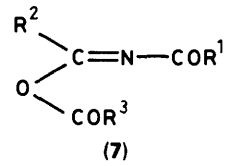

(5)

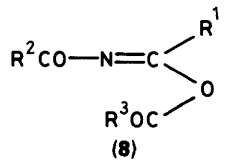

(6)

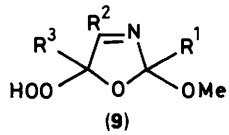
	R^1	R^2	R^3
a;	Ph	Me	H
b;	Ph	Me	OMe
c;	OMe	Me	Ph
d;	OMe	Ph	Ph
e;	Ph	CH_2Ph	OMe

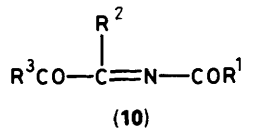
† Control experiments have now shown that when the tetraphenylporphyrin-sensitized photo-oxygenation of the 5-methoxyoxazole (**2b**) is carried out in $CDCl_3$–$CFCl_3$ (3:1) at −80 °C, the *endo*-peroxide (**1b**) is detectable by analysis of the ^1H NMR spectrum recorded at this temperature (Table). The *endo*-peroxide (**1b**) readily rearranges into the dioxazole (**3b**).

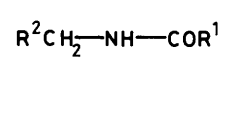
‡ This choice was made on the basis that the methyl presence should enable us to determine the product structures by ^1H and ^{13}C NMR spectral analysis.

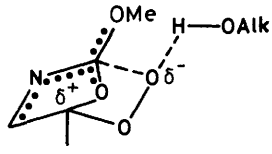

(7)

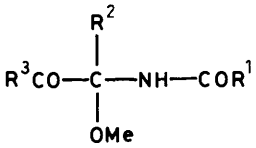

(8)

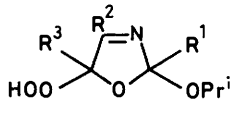

(9)


(10)


(11)


(12)


(13)


(14)

	R^1	R^2	R^3
a;	Ph	Me	H
b;	Ph	Me	OMe
c;	OMe	Me	Ph
d;	OMe	Ph	Ph
e;	Ph	CH_2Ph	OMe

sample (see below) and the structure of the dioxazole (**3c**)* was deduced by ^1H and ^{13}C spectral analysis of the photo-oxygenation mixture kept at −40 °C, the signals of (**4c**) being subtracted. The spectral data of (**3c**) so obtained are reported in the Table. Methanol or isopropyl alcohol precooled to −60 °C was added to the photo-oxygenation mixture of (**2c**) in $CDCl_3$–$CFCl_3$ at the same temperature and the mixture was kept at −60 °C for 3 h. After solvent removal at −40 °C the ^1H and ^{13}C NMR spectra showed the presence of (**3c**) and (**4c**) in the molar ratio *ca.* 1:3.3. Accordingly, when the sensitized photo-oxygenation was carried out at −60 °C in methanol or isopropyl alcohol, the dioxetane (**4c**) was quantitatively obtained and isolated by evaporation of the solvent at −40 °C under reduced pressure. The structure (**4c**) was assigned on the basis of the spectral data and of the active oxygen and molecular weight determinations (Table). On the basis of the results obtained, it is evident that alcohols play a special role in *endo*-peroxide (**1c**) rearrangement since they strongly favour the dioxetane (**4c**) formation. To see whether this role is related to solvent polarity, we carried out the sensitized photo-oxygenation of (**2c**) in deuterioacetone and in deuterioacetonitrile at −40 °C: the dioxetane (**4c**) was always formed in <15% yield, while the major product was the dioxazole (**3c**). This suggests that it is the protic character of alcohols which influences the reaction course.

The dioxazole (**3c**), obtained as major product at −40 °C in $CDCl_3$–$CFCl_3$ and in a greater amount in deuterioacetone, yields the carbamate (**5c**) quantitatively within a few minutes at room temperature. It is to be noted that also in methanol the rearrangement into (**5c**) was the only transformation observed. When the rearrangement was carried out in $CDCl_3$–$CFCl_3$ at −10 °C a transient imino anhydride was displayed (^1H NMR) which, on the basis of the NMR data reported in the Table, could have either of the isomeric structures (**7c**) or (**8c**). The latter was ruled out in view of the results obtained in the case of the oxazole (**2d**) (see below).

The dioxetane (**4c**) in $CDCl_3$ was quite stable at −5 °C whereas at room temperature within 5 days it rearranged quantitatively into the carbamate (**5c**).† It reacted with methanol at 4 °C to give quantitatively 5-hydroperoxy-2,2-dimethoxy-4-methyl-5-phenyldihydro-oxazole (**9c**), which was isolated by silica gel chromatography. The structure (**9c**) was assigned on the basis of the analytical and spectral data reported in the Table.

Several years ago, we detected in the ^1H NMR spectrum of the dye-sensitized photo-oxygenation mixture of the oxazole (**2d**) at −15 °C two transient intermediates both of which led to methyl *N*,*N*-dibenzoylcarbamate (**5d**) at room temperature.[8]‡ On the basis of the chemical behaviour of this reaction mixture, we were able to assign the structure of the imino anhydride (**7d**) to the product which showed a methoxy singlet at δ 3.73 ($CDCl_3$);§ also, on the basis of the behaviour of the oxazole (**2b**), we suggested a dioxazole structure for the peroxide with the methoxy singlet at δ 4.25 ($CDCl_3$).§ In the light of the results obtained with the oxazole (**2c**), we have now re-examined the sensitized photo-oxygenation of the oxazole (**2d**) by carrying out the reaction at −60 °C. The results were similar to those obtained using (**2c**). The Table reports ^1H and ^{13}C NMR data for (**1d**), (**3d**), (**4d**), (**7d**), and (**9d**). The genesis and the ^{13}C spectrum indicate a dioxetane structure for the peroxide (**4d**) instead of the dioxazole structure which had been suggested.[8] This compound is less thermally stable and reacts with methanol more easily than (**4c**). Therefore, we obtained dioxetane (**4d**) using isopropyl alcohol as protic solvent. In contrast, the imino anhydride (**7d**), which is more stable than (**7c**), can be obtained in solution at a purity of *ca.* 80%. Its catalytic hydrogenolysis led to methyl *N*-benzylcarbamate (**11d**)[13] and benzoic acid, thus ruling out the alternative structure (**8**) for the imino anhydrides obtained. It is interesting that the imino anhydride (**7d**) can be obtained by thermal rearrangement starting from either the dioxazole (**3d**) or the dioxetane (**4d**) (see Experimental section).

The peroxides (**4c,d**), which are the first examples of a bicyclic system of this type, show unusual dioxetane behaviour: by thermal rearrangement they give the imino anhydrides (**7c,d**) and by methanolysis the 2,5-dihydro-oxazoles (**9c,d**), instead of the expected cleavage products (**8c,d**).[14] Compounds (**7**) and (**9**) have the expected structures of products obtained starting from *endo*-peroxides.¶ To examine the possibility of mutual

* On the basis of the behaviour of (**3c**) and by analogy with the thermal rearrangement of the α-alkoxyfuran *endo*-peroxides, which always partly lead to epoxides,[3,5] the structure of 3-benzoyl-1-methoxycarbonyl-3-methyloxaziridine (**6c**)[9] was an alternative possibility. However, we excluded it, the ^1H and ^{13}C data of (**3c**) being closer to those of (**3e**)[4b] (Table), whose structure was ascertained by X-ray analysis,[10] than those for oxaziridine.[11]

† It was not possible to display any transient intermediate. However, in the case of the dioxetane (**4d**) the intermediate formation of the imino anhydride (**7d**) was displayed (see below).

‡ In the reaction mixture a small amount of the imine (**10d**) was also present, probably formed by triplet oxygen oxidation of the oxazole (**2d**). Oxidation by ground state molecular oxygen of alkoxyoxazoles is known to give imines as a major product.[12] Control experiments have now shown that a suitable oxygen stream minimizes or prevents imine (**10d**) formation.

§ The 3.73 and 4.25 values, which in the Table correspond to δ 3.76 and 4.33 respectively, at that time were obtained with a Perkin-Elmer R12A spectrometer.[8]

¶ Furan *endo*-peroxides under suitable conditions give 2-acyl enol esters.[15] Generally, they add alcohols to give 2,5-dihydrofurans.[16]

Table. Physical, spectral, and analytical data for the products derived from dye-sensitized photo-oxygenation of the oxazoles (**2b–e**)

Product	M.p. (°C)	$\nu_{max}(CHCl_3)$/ cm^{-1}	$\delta_H(CDCl_3)$	$\delta_C(CDCl_3)$/ppm
(**1b**)			2.40 (3 H, s, Me), 3.94 (3 H, s, OMe), 7.40–7.70 (5 H, m, Ph)[a]	
(**1c**)			2.19 (3 H, s, Me), 3.93 (3 H, s, OMe), 7.30–7.70 (5 H, m, Ph)[a]	15.5 (q, Me), 55.4 (q, OMe), 108.3 (s, C-1), 129.7 (s, C-4), 125.6, 129.0, 131.1 (3 × d, CH of Ph), 135.4 (s, C-1 of Ph), 177.8 (s, C-6)[a,b]
(**1d**)			3.97 (3 H, s, OMe), 7.20–7.70 (10 H, m, 2 × Ph)[a]	53.3 (q, OMe), 108.4 (s, C-1), 127.4 (s, C-4), 128.2, 128.9 and 130.7 (3 × d, CH, of the two Ph), 132.5, and 133.0 (2 × s, C-1 of the two Ph), 168.2 (s, C-6)[a,b]
(**3c**)			1.88 (3 H, s, Me), 4.04 (3 H, s, OMe), 7.50–8.30 (5 H, m, Ph)[a]	24.2 (q, Me), 60.1 (q, OMe), 110.1 (s, C-3), 128.5, 130.2, and 133.8 (3 × d, CH of Ph), 132.3 (s, C-1 of Ph), 160.2 (s, C-5), 194.7 (s, CO)[a,b]
(**3d**)			4.09 (3 H, s, OMe), 7.40–8.30 (10 H, m, 2 × Ph)[a]	60.2 (q, OMe), 110.5 (s, C-3), 161.1 (s, C-5), 192.1 (s, CO)[a,b,c]
(**3e**)[d]	57–59 (lit.,[4b] 57–59)			41.6 (t, CH_2), 52.8 (q, OMe), 108.9 (s, C-3), 121.8 (s, C-1 of 5-Ph), 127.0, 127.9, 128.4, 130.5, and 132.7 (5 × d, CH of the two Ph), 132.9 (s, C-1 of Ph), 160.1 (s, C-5), 167.9 (s, CO_2)[a,b]
(**4c**)[e]	Oil	1 656	1.44 (3 H, s, Me), 4.15 (3 H, s, OMe), 7.30–7.80 (5 H, m, Ph)	20.2 (q, Me), 58.7 (q, OMe), 111.0 (s, C-5), 117.7 (s, C-1), 126.7, 128.8, and 130.7 (3 × d, CH of Ph), 134.4 (s, C-1 of Ph), 168.5 (s, C-3)[b]
(**4d**)			.4.33 (3 H, s, OMe), 7.10–7.80 (10 H, m, 2 × Ph)	59.1 (q, OMe), 111.5 (s, C-5), 118.8 (s, C-1), 126.4, 126.6, 128.1, 128.3, 130.5, and 130.7 (6 × d, CH of the two Ph), 131.5 and 134.0 (2 × s, C-1 of the two Ph), 169.3 (s, C-3)[b]
(**7c**)			2.43 (3 H, br s, Me), 3.81 (3 H, br s, OMe)[a,f,g]	
(**7d**)			3.76 (3 H, s, OMe), 7.30–8.20 (10 H, m, 2 × Ph)[a]	53.6 (q, OMe), 128.8, 128.9, 130.4, and 133.2 (4 × d, CH of the two Ph), 129.9 and 134.4 (2 × s, C-1 of the two Ph), 154.4 (s, C=N), 159.3 (s, NCO_2), 162.3 (s, CO_2)[a]
(**9c**)[h]	Oil	3 689 3 480 1 681	2.08 (3 H, s, Me), 3.61 and 3.62 (6 H, 2 × s, 2 × OMe), 7.30–7.60 (5 H, m, Ph), 9.15 (1 H, br s, OOH)	14.2 (q, Me), 51.3, and 52.2 (2 × q, 2 × OMe), 115.6 (s, C-5), 130.9 (s, C-2), 126.3, 128.5, and 129.7 (3 × d, CH of Ph), 133.7 (s, C-1 of Ph), 174.3 (s, C-4)
(**9d**)[i]	104–105[j]	3 650 3 460 1 635	3.53 and 3.67 (6 H, 2 × s, 2 × OMe), 7.16–8.00 (10 H, m, 2 × Ph), 9.24 (1 H, br s, OOH)	51.3 and 52.6 (2 × q, 2 × OMe), 115.5 (s, C-5), 129.1 (s, C-2), 126.3, 128.5, 129.3, 129.6, and 132.1 (5 × d, CH of the two Ph), 130.5 and 135.0 (2 × s, C-1 of the two Ph), 170.4 (s, C-4)
(**10c**)			2.32 (3 H, s, Me), 3.85 (3 H, s, OMe), 7.30–8.10 (5 H, m, Ph)	25.4 (q, Me), 53.3 (q, OMe), 129.6, 130.0, and 133.6 (3 × d, CH of Ph), 133.0 (s, C-1 of Ph), 161.5 (s, CO_2), 169.4 (s, CN), 191.6 (s, CO)
(**10d**)			3.61 (3 H, s, OMe), 7.20–8.10 (10 H, m, 2 × Ph)	53.3 (q, OMe), 128.7, 129.2, 133.2, and 134.5 (4 × d, CH of the two Ph), 132.4 and 133.7 (2 × s, C-1 of the two Ph), 161.7 (s, CO_2), 172.1 (s, CN), 194.0 (s, CO)
(**13c**)[k]	64–65[j]	3 406 1 735 1 683	1.94 (3 H, s, Me), 3.20 (3 H, s, OMe), 3.73 (3 H, s, CO_2Me), 6.69 (1 H, br s, NH), 7.37–8.35 (5 H, m, Ph)	24.3 (q, Me), 51.3 and 51.9 (2 × q, 2 × OMe), 88.8 (s, C_q), 128.6, 130.2, and 133.8 (3 × d, CH of Ph), 132.5 (s, C-1 of Ph), 154.4 (s, CO_2), 197.2 (s, CO)
(**13d**)[l]	74–75[j]	3 400 1 735 1 680	3.34 (3 H, s, OMe), 3.57 (3 H, s, CO_2Me), 6.10 (1 H, br s, NH), 7.10–8.20 (10 H, m, 2 × Ph)	51.0 and 51.8 (2 × q, 2 × OMe), 90.2 (s, C_q), 126.0, 128.1, 128.2, 130.5, and 133.5 (5 × d, CH of the two Ph), 132.3 and 138.8 (2 × s, C-1 of the two Ph), 153.8 (s, CO_2), 194.9 (s, CO)
(**14d**)[m]	Oil	3 655 3 465 1 635	1.26 and 1.36 (6 H, 2 × d, *J* 6.7 Hz, 2 × Me), 3.50 (3 H, s, OMe), 4.64 (1 H, h, *J* 6.7 Hz, OCH), 7.16–8.05 (10 H, m, 2 × Ph), 9.26 (1 H, br s, OOH)	23.5 and 24.0 (2 × q, 2 × Me), 51.4 (q, OMe), 68.7 (d, OCH), 115.2 (s, C-5), 129.3 (s, C-2), 126.3, 128.4, 129.2, 129.5, and 131.9 (5 × d, CH of the two Ph), 130.7 and 135.0 (2 × s, C-1 of the two Ph), 169.6 (s, C-4)

[a] Recorded in $CDCl_3/CFCl_3$ (3:1). [b] The ^{13}C chemical shift assignment of quaternary carbons was obtained by long range C–H heteronuclear selective decoupling experiments. [c] The phenyl carbons were not assigned since their signals and those of the products present in the mixture overlap. [d] Known product[4b], but ^{13}C NMR data are new. [e] M.W. (benzene f.p. depression) 207 (required 221). Found: O_{act} 6.8. $C_{11}H_{11}NO_4$ requires O_{act} 7.2%. [f] The phenyl hydrogens were not assigned since their signals and those of the products present in the mixture overlap. [g] When the spectrum was recorded at −50 °C the signals separate in two sharp singlets each (δ 2.40 and 2.46, 3.80, and 3.91 respectively) showing that at higher temperature a rapid interconversion *syn*/*anti* occurs. [h] Found: C, 56.8; H, 5.9; N, 5.4; O_{act} 6.0. $C_{12}H_{15}NO_5$ requires C, 56.91; H, 5.97; N, 5.53; O_{act} 6.3%. [i] Found: C, 64.6; H, 5.3; N, 4.5; O_{act} 4.9. $C_{17}H_{17}NO_5$ requires C, 64.75; H, 5.43; N, 4.44; O_{act} 5.1%. [j] Recrystallization solvent, hexane. [k] Found: C, 60.5; H, 6.4; N, 6.0. $C_{12}H_{15}NO_4$ requires C, 60.75; H, 6.37; N, 5.90%. [l] Found: C, 67.9; H, 5.8; N, 6.3. $C_{17}H_{17}NO_4$ requires C, 68.21; H, 5.73; N, 4.68%. [m] Found: C, 66.3; H, 6.0; N, 4.2; O_{act} 4.3. $C_{19}H_{21}NO_5$ requires C, 66.46; H, 6.16; N, 4.08; O_{act} 4.7%.

conversion between *endo*-peroxides (**1c,d**) and dioxetanes (**4c,d**) and of a higher reactivity of (**1c,d**) responsible for the observed reactions, we carried out the diethyl sulphide reduction of (**4c,d**) at −60 °C. Within a few minutes the dioxetanes (**4c,d**) gave, quantitatively, the unusual dioxetane reduction products,[14] the imines (**10c,d**). These also had the structure expected of a product obtained by diethyl sulphide reduction of *endo*-peroxides.* However, when diethyl sulphide was added under the same conditions to the mixtures obtained by dye-sensitized

* Furan *endo*-peroxides give 1,2-diacylethylenes by diethyl sulphide reduction.[17]

photo-oxygenation of (**2c,d**) at −60 °C in $CDCl_3$–$CFCl_3$ [consisting of the *endo*-peroxides (**1c,d**), the dioxazoles (**3c,d**), and the dioxetanes (**4c,d**)] within a few minutes only the dioxetanes (**4c,d**) gave the imines (**10c,d**). The *endo*-peroxides (**1c,d**) were still unchanged after 30 min* showing that they are not directly involved in the reduction of the dioxetanes (**4c,d**).

Therefore, it is likely that the particular behaviour of the dioxetanes (**4c,d**) is due to their unusual structure. It is to be noted that other exceptions to the usual dioxetane cleavage have been claimed and several examples in which alcohols add to the dioxetanes have been reported.[14]

The results above show that singlet oxygen attacks the α-alkoxyoxazoles as well as the α-alkoxyfurans[3,6] univocally in a 1,4-fashion to give thermally unstable *endo*-peroxides. The *endo*-peroxides deriving from the 5-alkoxyoxazoles [*e.g.* (**1b**)], rearrange into compounds [*e.g.* (**3b**)] carrying the original alkoxy group as an alkoxycarbonyl group. *Endo*-Peroxides (**1c,d**) deriving from 2-alkoxyoxazoles, owing to the position of the nitrogen with respect to the alkoxy group, rearrange into the dioxazoles (**3c,d**) and dioxetanes (**4c,d**) because both conversions are satisfactorily assisted by resonance stabilization (conjugation of the unshared electrons on two oxygen atoms with the carbon–nitrogen double bond). Protic solvents promote only the dioxetane formation. We explain this result by assuming that in these solvents formation of a hydrogen-bonded peroxide group can stabilize the developing positive charge, as shown in (**12**). This favours dioxetane formation over dioxazole formation. This explanation is currently being examined in further studies.

Experimental

IR spectra were recorded on a Perkin-Elmer 1760X-FT spectrophotometer with chloroform as solvent. ^1H and ^{13}C NMR spectra were recorded with Bruker AC-270 or AM-400 spectrometers using deuteriochloroform as solvent, unless otherwise stated, and tetramethylsilane as internal standard. The solvents used in the photo-oxygenation reactions were anhydrous. Silica gel 0.05–0.20 mm (Merck) or neutral alumina (Fluka), and light petroleum (b.p. 30–50 °C) were used for column chromatography.

2-Methoxy-4-methyl-5-phenyloxazole (**2c**) was prepared according to the procedure previously reported,[18] starting from phenylpropyne and methoxycarbonylazide. Alumina B-III chromatography of the reaction mixture with light petroleum–diethyl ether (41:1, v/v) as eluant gave (**2c**) (70%) as an oil (Found: C, 69.75; H, 5.8; N, 7.6. $C_{11}H_{11}NO_2$ requires C, 69.82; H, 5.86; N, 7.40%. δ_H 2.35 (3 H, s, Me), 4.09 (3 H, s, OMe), and 7.20–7.60 (5 H, m, Ph).

Dye-sensitized Photo-oxygenation of the 2-*Methoxyoxazole* (**2c**) *in Aprotic Solvents and Thermal Conversions of the Mixtures obtained.*—A 0.1M solution of the oxazole (**2c**) (1 mmol) in $CDCl_3$–$CFCl_3$ (3:1) was irradiated with a halogen-superphot lamp (Osram, 650 W) in the presence of tetraphenylporphyrin (3.6×10^{-4} mmol). During the irradiation, dry oxygen was bubbled through the solution which was kept at −60 °C. Periodically the solution was monitored (^1H NMR) for disappearance of the oxazole (**2c**). When the reaction was complete (4 h), a sample was transferred from the reaction apparatus to the spectrometer (probe temperature −60 °C) and the ^1H and ^{13}C NMR spectra were recorded at this temperature. The analysis of the ^1H NMR spectrum showed the presence of the *endo*-peroxide (**1c**), the dioxazole (**3c**), and the dioxetane (**4c**) in *ca.* 3:1:0.3 molar ratio on the basis of the relative areas of the methoxy signals. After 4 h this ratio was essentially unchanged. The spectral data of the *endo*-peroxide (**1c**) (Table) were deduced from the data of the reaction mixture spectra, the signals of (**3c**) and (**4c**) being subtracted. When the probe temperature was raised to −40 °C, the signals of the *endo*-peroxide (**1c**) declined while those of the dioxazole (**3c**) and of the dioxetane (**4c**) increased. After 3 h, in the sample of the reaction mixture kept at −40 °C only (**3c**) and (**4c**) were present in *ca.* 3:1 molar ratio.†

The dioxetane (**4c**) was identified by comparison of the ^1H and ^{13}C NMR spectra of this mixture with those of an authentic sample, obtained by dye-sensitized photo-oxygenation of (**2c**) in methanol at −40 °C. The spectral data of the dioxazole (**3c**) (Table) were obtained from those of the reaction mixture recorded at −40 °C, the signals of (**4c**) being subtracted. When the probe temperature was raised to −10 °C, it was observed that the dioxazole (**3c**) rearranged into the imino anhydride (**7c**) and the latter into the carbamate (**5c**). After 3 h, in the sample of the reaction mixture kept at −10 °C, only the dioxetane (**4c**), the anhydride (**7c**), and the carbamate (**5c**) were present in *ca.* 1:2.2:0.8 molar ratio, based on the relative areas of the methyl signals. The carbamate (**5c**) was identified by comparison (^1H NMR spectrum) with an authentic sample.[4a] The spectral data of the anhydride (**7c**) (Table) were deduced from the ^1H NMR spectrum of the sample kept at −10 °C for 3 h, the signals of the dioxetane (**4c**) and of the carbamate (**5c**) being subtracted. After 10 h in the sample kept at −10 °C only the dioxetane (**4c**) and the carbamate (**5c**) were present in *ca.* 1:3 molar ratio. When this sample was kept at room temperature and periodically analysed by ^1H NMR spectroscopy, after 5 days only the presence of the carbamate (**5c**) was observed.

The remainder of the photo-oxygenation at −60 °C mixture was kept at room temperature. After 5 days the solvents were removed under reduced pressure and the residue was chromatographed on silica gel (10 g). Elution with light petroleum–diethyl ether (9:1 v/v) gave the carbamate (**5c**) (95%), which was identified by comparison with an authentic sample.[4a]

A 0.1M solution of the oxazole (**2c**) (0.5 mmol) in deuterioacetone was photo-oxygenated at −40 °C using Methylene Blue as sensitizer (1.8×10^{-4} mmol) according to the procedure followed when $CDCl_3$–$CFCl_3$ were used as solvents. After 4 h, the ^1H NMR spectrum of the reaction solution, recorded at −40 °C, showed the presence of the dioxazole (**3c**) and the dioxetane (**4c**) in *ca.* 9:1 molar ratio. When the reaction solution was kept at room temperature, within a few minutes in the mixture only (**4c**) and (**5c**) were present in *ca.* 1:9 molar ratio.

When the photo-oxygenation of the oxazole (**2c**) was carried out at −40 °C in deuterioacetonitrile, according to the procedure followed when the deuterioacetone was used as solvent, the ^1H NMR spectrum of the mixture recorded at −40 °C showed the presence of the dioxazole (**3c**) and the dioxetane (**4c**) in *ca.* 7:1 molar ratio.

Dye-sensitized Photo-oxygenation of the 2-*Methoxyoxazole* (**2c**) *at* −60 °C *in Protic Solvents and Thermal Conversion of the Dioxetane* (**4c**) *obtained.*—A 0.1M solution of the oxazole (**2c**) (0.5 mmol) in methanol was irradiated at −60 °C as above reported when deuterioacetone was used as solvent. When the reaction was complete (4 h), removal of the solvent at −40 °C

* After 10 days in the reaction mixtures only the imines (**10c,d**) were present. The dioxazoles (**3c,d**), which as well as (**1c,d**) were still unchanged after 30 min at −60 °C, are reduced to the imines (**10c,d**) at −40 °C within 12 h; therefore, at present, it is still uncertain whether the *endo*-peroxides (**1c,d**) were reduced to or preferentially rearranged into the dioxazoles (**3c,d**) and dioxetanes (**4c,d**). Further investigation is in progress to clarify this point.

† The same result was obtained carrying out the reaction at −40 °C.

under reduced pressure afforded the pure dioxetane (**4c**). Physical, spectral, and analytical data, and molecular weight determination are reported in the Table. The same results were obtained when the photo-oxygenation was carried out at −40 °C and when isopropyl alcohol was used as solvent at −60 and −40 °C. A dioxetane (**4c**) solution in deuteriochloroform was kept at −5 °C; after 5 days a ^{1}H NMR spectrum was superimposable on that of the starting solution. When a 0.1 molar solution of the dioxetane (**4c**) (0.5 mmol) in deuteriochloroform was kept at room temperature and periodically analysed by ^{1}H NMR spectroscopy, after 5 days it was observed that only the carbamate (**5c**) was present; this was obtained (95%) by removal of the solvent under reduced pressure and by chromatography of the residue on silica gel (5 g), using light petroleum–diethyl ether (9:1 v/v) as eluant. It was identified by comparison with an authentic sample.[4a]

Chemical Behaviour of the endo-*Peroxide* (**1c**).—To an aliquot (1.5 ml) of a 0.1M photo-oxygenation mixture in $CDCl_3$–$CFCl_3$ of the oxazole (**2c**) obtained as above reported at −60 °C [(**1c**):(**3c**):(**4c**) in *ca.* 3:1:0.3 molar ratio] methanol (1.5 ml), precooled to −60 °C, was added and the solution was kept at this temperature. After 4 h, the solvents were removed at −40 °C and reduced pressure and the ^{1}H NMR spectrum, recorded at this temperature, showed the presence of the dioxazole (**3c**) and the dioxetane (**4c**) in *ca.* 1:3.3 molar ratio. The same results were obtained when isopropyl alcohol was used.

To a second aliquot (5 ml) of the above photo-oxygenation mixture diethyl sulphide (1.5 mmol), precooled to −60 °C, was added and the resulting mixture was kept at −60 °C. After 30 min, the ^{1}H NMR spectrum showed the presence of the *endo*-peroxide (**1c**), the dioxazole (**3c**), and the imine (**10c**) (see below) in the molar ratio 3:1:0.3 on the basis of the relative areas of the methyl signals. After 10 days, in addition to the diethyl sulphide and the diethyl sulphoxide, only the imine (**10c**) was present. It was identified by comparison with the compound obtained by diethyl sulphide reduction of the dioxetane (**4c**) and quantified (95%) by methanol addition as described below.

Chemical Behaviour of the Dioxazole (**3c**).—To an aliquot (5 ml) of a 0.1M photo-oxygenation solution of the oxazole (**2c**) in acetone obtained at −40 °C as above described [(**3c**):(**4c**) in *ca.* 9:1 molar ratio], methanol (5 ml), precooled at −40 °C, was added and the resulting solution was kept at this temperature for 3 h and then at 4 °C for 12 h. Removal of the solvents at reduced pressure and chromatography of the residue on silica gel (5 g), using as eluant light petroleum–diethyl ether (9:1 and 4:1 v/v), successively yielded the carbamate (**5c**) (85%) and the dihydro-oxazole (**9c**) (10%). The latter was identified by comparison with the product obtained from pure (**4c**) (^{1}H NMR).

To a second aliquot (5 ml) of the above photo-oxygenation mixture in acetone, diethyl sulphide (1.5 mmol), precooled at −40 °C, was added and the resulting mixture was kept at this temperature for 12 h. After removal of the solvent and of the unchanged diethyl sulphide, the ^{1}H NMR spectrum of the residue showed, in addition to the diethyl sulphoxide, only the presence of the imine (**10c**). The latter was identified by comparison with the compound obtained by diethyl sulphide reduction of the dioxetane (**4c**) and quantified (95%) by methanol addition as described below.

Chemical Behaviour of the Dioxetane (**4c**).—A 0.1M solution of the dioxetane (**4c**) (0.5 mmol) in methanol was kept at 4 °C. After 12 h, removal of the methanol under reduced pressure afforded a mixture which was chromatographed on silica gel (7 g). Elution with light petroleum–diethyl ether (9:1, 4:1 v/v) gave small amounts of the carbamate (**5c**) and the dihydro-oxazole (**9c**) (85%) successively. The physical, spectral, and analytical data for (**9c**) are listed in the Table. The same results were obtained when the photo-oxygenation solution of (**2c**) in methanol, obtained at −60 °C as reported above, was kept at 4 °C for 12 h.

To a 0.1M solution of the dioxetane (**4c**) (0.5 mmol) in chloroform, diethyl sulphide (1.5 mmol) was added and the mixture was kept at 4 °C for 10–15 min.* Removal of the solvent and of the unchanged diethyl sulphide under reduced pressure at room temperature yielded the imine (**10c**). All attempts to purify the imine (**10c**) by chromatographic methods failed since it undergoes hydrolysis to methyl carbamate and 1-phenylpropane-1,2-dione on contact with the absorbents. The ^{1}H and ^{13}C NMR spectral data of (**10c**)† (Table) were deduced for the reaction mixture, the signals of the diethyl sulphoxide being subtracted. Quantification of the imine (**10c**) was obtained by immediately adding dry methanol (5 ml) to the reduced mixture at room temperature. After 12 h, the solvents were removed under reduced pressure and the residue chromatographed on silica gel (5 g). Elution with light petroleum–diethyl ether (7:3, v/v) afforded 2-methoxy-2-(*N*-methoxycarbonylamino)-1-phenylpropanone (**13c**) (95%). The physical, spectral, and analytical data for this compound are reported in the Table.

Dye-sensitized Photo-oxygenation of the 2-*Methoxyoxazole* (**2d**) *in Aprotic Solvents and Thermal Conversions of the Mixtures obtained.*—A 0.1M solution of the oxazole (**2d**)[8] (0.5 mmol) in $CDCl_3$–$CFCl_3$ (3:1) was irradiated at −60 °C as described for (**2c**). When the reaction was complete (4 h) a sample was transferred from the reaction apparatus to the spectrometer (probe temperature −60 °C) and the ^{1}H and ^{13}C NMR spectra were recorded at this temperature. The analysis of the ^{1}H NMR spectrum showed the presence of the *endo*-peroxide (**1d**), the dioxazole (**3d**), and the dioxetane (**4d**) in *ca.* 3:1:1 molar ratio on the basis of the methoxy signals. After 4 h this ratio was substantially unchanged. The spectral data of the *endo*-peroxide (**1d**) (Table) were deduced from those of the reaction mixture, the signals of (**3d**) and (**4d**) being subtracted. When the probe temperature was raised to −40 °C, the signals of the *endo*-peroxide (**1d**) declined, while those of the dioxazole (**3d**) and the dioxetane (**4d**) increased. After 2 h at −40 °C only (**3d**) and (**4d**) in *ca.* 1:1 molar ratio were present in the solution. The dioxetane (**4d**) was identified by comparison of the ^{1}H and ^{13}C NMR spectra of this mixture, recorded at −40 °C, with those of an authentic sample obtained by photo-oxygenation of (**2d**) in isopropyl alcohol at −60 °C (see below). The spectral data of the dioxazole (**3d**) were obtained from those of the reaction mixture, the signals of (**4d**) being subtracted. When the probe temperature was raised to −10 °C, it was observed that both the dioxazole and the dioxetane rearranged to the imino anhydride (**7d**); the latter then rearranged more slowly into the carbamate (**5d**). After 18 h the ^{1}H NMR spectrum of the sample showed the presence of (**4d**) and (**7d**) in *ca.* 1:1 molar ratio, in addition to small amounts of the carbamate (**5d**). After 3 days the ^{1}H NMR spectrum showed the presence of the imino anhydride (**7d**) and the carbamate (**5d**) in *ca.* 4:1 molar ratio. The carbamate (**5d**) was identified by comparison (^{1}H NMR spectrum) with an authentic sample.[8] The spectral data of the imino anhydride (**7d**) (Table) were obtained by ^{1}H and ^{13}C NMR spectra of the mixture kept at −10 °C for 3 days, the signals of the carbamate (**5d**) being subtracted. When the photo-

* Dioxetane (**4c**) reacts rapidly with diethyl sulphide already at −60 °C.
† The imine (**10c**) slowly undergoes alteration.

oxygenation mixture, obtained at −60 °C, was kept at room temperature, only the carbamate (**5d**) was detectable after 12 h. It was obtained (90%) by removal of the solvents under reduced pressure and chromatography on silica gel (3 g), using light petroleum–diethyl ether (9:1, v/v) as eluant. The carbamate (**5d**) was identified by comparison (NMR) with an authentic sample.[8]

A 0.1M solution of the oxazole (**2d**) (0.5 mmol) in deuterioacetone was photo-oxygenated at −40 °C as described for (**2c**). After 4 h the ^{1}H NMR spectrum of the reaction mixture, recorded at −40 °C, showed the presence of the dioxazole (**3d**) and the dioxetane (**4d**) in *ca.* 3:1 molar ratio. When the solution was kept for 18 h at −10 °C the ^{1}H NMR spectrum, recorded at this temperature, showed the presence of the dioxetane (**4d**) and the imino anhydride (**7d**) in *ca.* 3:1 molar ratio, together with small amounts of the carbamate (**5d**). After 3 days the ^{1}H NMR spectrum showed the presence of (**7d**) and (**4d**) in *ca.* 4:1 molar ratio.

When the photo-oxygenation of the oxazole (**2d**) was carried out at −40 °C in deuterioacetonitrile as described for (**2c**) for 4 h, the ^{1}H NMR spectrum of the mixture, recorded at −40 °C, showed the presence of the dioxazole (**3d**) and the dioxetane (**4d**) in *ca.* 2:1 molar ratio.

Dye-sensitized Photo-oxygenation of the 2-*Methoxyoxazole* (**2d**) *at* −60 °C *in Protic Solvents and Thermal Conversion of the Dioxetane* (**4d**) *obtained.*—A 0.1M solution of the oxazole (**2d**) (0.5 mmol) in isopropyl alcohol was irradiated at −60 °C as described for (**2c**). When the reaction was complete (4 h), removal of the solvent at −40 °C under reduced pressure afforded the pure dioxetane (**4d**). Spectral data, recorded at −40 °C, are reported in the Table. A 0.1M solution of the dioxetane (**4d**) in deuteriochloroform was kept at room temperature and periodically analysed by ^{1}H NMR spectroscopy. After 4 h inspection of the ^{1}H NMR spectrum showed the presence of the imino anhydride (**7d**) and the carbamate (**5d**) in *ca.* 1:1 molar ratio. After 12 h only (**5d**) was detectable and this was obtained (90%) by removal of the solvent and chromatography on silica gel (3 g) using light petroleum–diethyl ether (9:1 v/v) as eluant. The carbamate (**5d**) was identified by comparison with an authentic sample.[8]

The photo-oxygenation of the oxazole (**2d**) (0.5 mmol) in methanol was carried out at −60 °C as described for the isopropyl alcohol solution. After 4 h, removal of the solvent at −40 °C under reduced pressure from a sample of the reaction mixture and inspection of the ^{1}H NMR spectrum (recorded at −40 °C) of the residue showed the presence of the dihydro-oxazole (**9d**), in addition to some amount of the dioxetane (**4d**). After 6 h only (**9d**) was detectable.

t

Chemical Behaviour of the endo*Peroxide* (**1d**).—To an aliquot (1.5 ml) of a 0.1M photo-oxygenation solution of the oxazole (**2d**) in $CDCl_3$–$CFCl_3$, obtained at −60 °C as above described [(**1d**):(**3d**):(**4d**) in *ca.* 3:1:1 molar ratio] isopropyl alcohol (1.5 ml), precooled to −60 °C, was added and the resulting solution was kept at this temperature. After 4 h, removal of the solvents at −40 °C under reduced pressure gave a mixture consisting of the dioxazole (**3d**) and the dioxetane (**4d**) in *ca.* 1:4 molar ratio (^{1}H NMR spectrum recorded at −40 °C). When methanol (1.5 ml) instead of isopropyl alcohol was added and the procedure described above was followed a mixture consisting of the dioxazole (**3d**), the dioxetane (**4d**), and the dihydro-oxazole (**10d**) in *ca.* 1:2:2 molar ratio was obtained.

To a second aliquot (3 ml) of the above photo-oxygenation mixture diethyl sulphide (1 mmol), precooled to −60 °C, was added and the resulting mixture was kept at −60 °C. After 30 min, the ^{1}H NMR spectrum showed the presence of the *endo*-peroxide (**1d**), the dioxazole (**3d**), and the imine (**10d**) (see below) in the molar ratio 3:1:1 on the basis of the relative areas of the methoxy signals. After 10 days, in addition to the diethyl sulphide and the diethyl sulphoxide, only the imine (**10d**) was present. This was identified by comparison with the compound obtained by diethyl sulphide reduction of the dioxetane (**4d**) and quantified (95%) by methanol addition as described below.

Chemical Behaviour of the Dioxazole (**3d**).—To an aliquot (5 ml) of a 0.1M photo-oxygenation solution of the oxazole (**2d**) in acetone obtained at −40 °C as above reported [(**3d**):(**4d**) in *ca.* 3:1 molar ratio], methanol (5 ml), precooled at −40 °C, was added and the resulting solution was kept at this temperature for 4 h and then at room temperature for 12 h. Removal of the solvents at room temperature and reduced pressure, and chromatography of the residue on silica gel (5 g) using light petroleum–diethyl ether (9:1, 4:1 v/v) as eluant, yielded successively the carbamate (**5d**) (73%) and the dihydro-oxazole (**9d**) (22%).

To a second aliquot (5 ml) of the above photo-oxygenation mixture in acetone, diethyl sulphide (1.5 mmol), precooled to −40 °C, was added and the resulting mixture was kept at this temperature for 12 h. After removal of the solvent and of the unchanged diethyl sulphide, an ^{1}H NMR spectrum of the residue showed, in addition to the diethyl sulphoxide, only the presence of the imine (**10d**). The latter was identified by comparison with the compound obtained by diethyl sulphide reduction of the dioxetane (**4d**) and quantified (90%) by methanol addition as described below.

Chemical Behaviour of the Dioxetane (**4d**).—A 0.1M solution of the dioxetane (**4d**) (0.5 mmol) in methanol was kept at −40 °C. After 4 h, removal of the methanol under reduced pressure afforded a residue which was chromatographed on silica gel (7 g). Elution with light petroleum–diethyl ether (4:1 v/v) gave the dihydro-oxazole (**9d**) (90%), the physical, spectral, and analytical data for which are listed in the Table.

A 0.1M isopropyl alcohol solution of (**4d**) (5 ml) was kept at −30 °C. After 3 days, the isopropyl alcohol was removed under reduced pressure and the residue was chromatographed on silica gel (7 g). Elution with light petroleum–diethyl ether (9:1, 4:1 v/v) afforded successively the carbamate (**5d**) (10%) and 5-hydroperoxy-2-methoxy-4,5-diphenyl-2-isopropoxy-2,5-dihydro-oxazole (**14d**) (80%), the physical, spectral, and analytical data for which are reported in the Table. The stereochemistry of this compound has not been investigated.

To a 0.1M chloroform solution of (**4d**) (5 ml) diethyl sulphide (1.5 mmol), precooled to −20 °C, was added and the resulting mixture was kept at −20 °C for 10–15 min.* Removal of the solvent and of the unchanged diethyl sulphide under reduced pressure at room temperature yielded, in addition to diethyl sulphoxide, only the imine (**10d**). All attempts to purify the imine (**10d**) by chromatographic methods failed since it undergoes hydrolysis to methyl carbamate and benzil on contact with the absorbents. The spectral data for (**10d**) were deduced from the ^{1}H and ^{13}C NMR spectra of the reduction mixture, the signals of the diethyl sulphoxide being subtracted. Quantification of the imine (**10d**) was obtained by adding dry methanol (5 ml) to the reduction mixture. After 12 h, the methanol was removed and the residue was chromatographed on silica gel (5 g). Elution with light petroleum–diethyl ether (7:3, v/v) afforded the adduct (**13d**) (87%). The physical, spectral, and analytical data for (**13d**) are reported in the Table.

Catalytic Hydrogenolysis of the Imino Anhydride (**7d**).—A

* The dioxetane (**4d**) reacts rapidly with diethyl sulphide already at −60 °C.

mixture consisting of (**7d**) and (**5d**) in *ca.* 4:1 molar ratio, obtained by carrying out the photo-oxygenation of (**2d**) (0.5 mmol) in acetone at −40 °C and by keeping the solution at −10 °C for 3 days, was hydrogenated at −5 °C and 1.2 atm in the presence of 10% C-Pd catalyst (33 mg) for 5 h. The catalyst was filtered off and the acetone was evaporated and replaced by chloroform. The solution was extracted with $NaHCO_3$ to recover the benzoic acid (50%) and dried on calcium sulphate. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel (10 g). Elution with light petroleum–diethyl ether (9:1, 4:1 v/v) afforded successively the carbamate (**5d**) (30%) and *N*-benzylcarbamate (**11d**) (50%) identified by comparison with an authentic sample.[13]

Dye-sensitized Photo-oxygenation of the 5-Methoxyoxazole (**2b**).—A 0.1M solution of the oxazole (**2b**)[4a] (1 mmol) in $CDCl_3$–$CFCl_3$ (3:1) was irradiated at −80 °C as described for (**2c**). When the reaction was complete (2 h) a sample was transferred from the reaction apparatus to the spectrometer (probe temperature −80 °C) and the ^1H NMR spectrum was recorded at this temperature. A spectral analysis showed the presence of the *endo*-peroxide (**1b**) and the dioxazole (**3b**) in *ca.* 1:2 molar ratio on the basis of the methyl signals. The spectral data of (**1b**) (Table) were deduced from those of the reaction mixture, the signals of (**3b**) being subtracted. When the probe temperature was raised to −40 °C, the signals of the *endo*-peroxide (**1b**) readily declined, while those of the dioxazole (**3b**) increased. After 30 min, in the solution kept at −40 °C only (**3b**) was present; it was identified by comparison with an authentic sample.[4a]

Acknowledgements

This work has been financially supported by the Ministero Pubblica Istruzione and by Progetto Finalizzato del C.N.R. (Rome) Chimica Fine e Secondaria 2. The NMR spectra were taken at the Centro di Metodologie Chimico Fisiche, Università di Napoli (I. Giudicianni).

References

1 (*a*) H. H. Wasserman, K. E. McCarthy, and K. S. Prowse, *Chem. Rev.*, 1986, **86**, 845 and references therein; (*b*) M. L. Graziano, A. Carotenuto, M. R. Iesce, and R. Scarpati, *Tetrahedron Lett.*, 1977, 447; (*c*) M. L. Graziano, M. R. Iesce, and R. Scarpati, *J. Heterocycl. Chem.*, 1979, **16**, 129.
2 K. Gollnick and S. Koegler, *Tetrahedron Lett.*, 1988, **29**, 1003, 1007.
3 M. L. Graziano, M. R. Iesce, G. Cimminiello, and R. Scarpati, *J. Chem. Soc. Perkin Trans. 1*, 1989, 241.
4 (*a*) M. L. Graziano, M. R. Iesce, A. Carotenuto, and R. Scarpati, *J. Heterocycl. Chem.*, 1977, **14**, 261; (*b*) M. L. Graziano, M. R. Iesce, A. Carotenuto, and R. Scarpati, *Synthesis*, 1977, 572.
5 M. L. Graziano, M. R. Iesce, G. Cimminiello, and R. Scarpati, *J. Chem. Soc., Perkin Trans. 1*, 1988, 1699.
6 M. L. Graziano, M. R. Iesce, F. Cermola, F. Giordano, and R. Scarpati, *J. Chem. Soc., Chem. Commun.*, 1989, 1608.
7 (*a*) M. L. Graziano and R. Scarpati, *J. Chem. Soc., Chem. Commun.*, 1985, 124 and references therein; (*b*) M. L. Graziano, M. R. Iesce, A. Cinotti, and R. Scarpati, *J. Chem. Soc., Perkin Trans. 1*, 1987, 1833.
8 M. L. Graziano, M. R. Iesce, and R. Scarpati, *J. Heterocycl. Chem.*, 1978, **15**, 1205.
9 E. Schmitz, *Adv. Heterocycl. Chem.*, 1979, **24**, 63.
10 Unpublished results.
11 (*a*) W. B. Jennings, V. E. Wilson, D. R. Boyd, and P. B. Coulter, *Org. Magn. Reson.*, 1983, **21**, 279; W. B. Jennings, S. P. Watson, and D. R. Boyd, *J. Chem. Soc., Chem. Commun.*, 1988, 931.
12 M. L. Graziano, A. Carotenuto, M. R. Iesce, and R. Scarpati, *J. Heterocycl. Chem.*, 1977, **14**, 1215.
13 J. W. Baker, *J. Chem. Soc.*, 1927, 565.
14 For a comprehensive review, see W. Adam, 'The Chemistry of Functional Groups, Peroxides', ed. S. Patai, J. Wiley, New York, 1983, p. 829.
15 M. L. Graziano, M. R. Iesce, B. Carli, and R. Scarpati, *Synthesis*, 1982, 736.
16 (*a*) M. L. Graziano, M. R. Iesce, and R. Scarpati, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1955; (*b*) K. Gollnick and A. Griesbeck, *Tetrahedron*, 1985, **41**, 2057.
17 M. L. Graziano, M. R. Iesce, B. Carli, and R. Scarpati, *Synthesis*, 1983, 125.
18 R. Huisgen and H. Blaschke, *Chem. Ber.*, 1965, **98**, 2985.

Paper 9/02188D
Received 24*th May* 1989
Accepted 3rd *August* 1989