Synthesis of Stable 3,6-Epidioxypyrazin-2-ones and α-Oxo Imides by Photo-oxygenation of Pyrazin-2-ones with Singlet Oxygen

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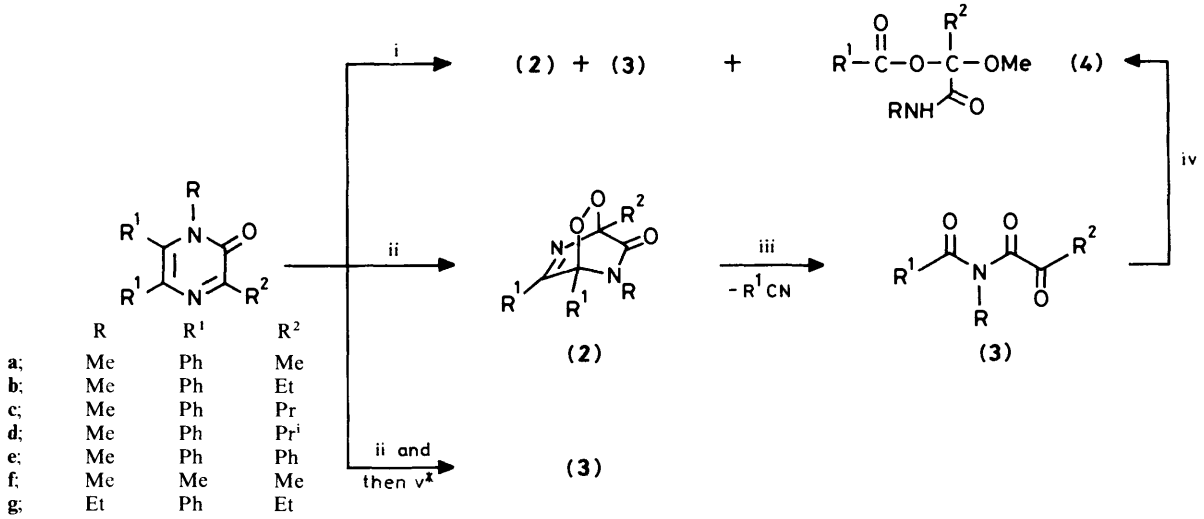
Irradiation of the pyrazin-2-ones (**1**) in methanol under oxygen gave the 3,6-epidioxypyrazin-2-ones (**2**), the *N*-alkyl-*N*-acyl-α-oxo amides (**3**), and the unusual products, *N*-alkyl-α-acyloxy-α-methoxy amides (**4**). The mechanism for the formation of these photoproducts is discussed. Furthermore, thermal or photochemical treatment of the 3,6-epidioxypyrazinones (**2**), which could be readily obtained by the reaction of (**1**) and singlet oxygen, gave the *N*-alkyl-*N*-acyl-α-oxo amides (**3**) and this reaction would provide a useful synthetic method for the α-oxo imides (**3**).

We previously reported that dye-sensitized photo-oxygenation of the pyrazin-2-ones (**1**; R^2 = H), which have no substituents at the 3-position, gave stable 3,6-epidioxypyrazin-2-ones† (**2**; R^2 = H)[1a,b] and that these, when irradiated in alcohol, gave the unusual amide derivative (**4**; R^2 = H).[1b] The α-oxo imide (**3**; R^2 = H), although not isolated, was assumed to be an intermediate for the transformation of (**2**) to (**4**). We have now investigated the photo-oxygenation of a range of 3-substituted pyrazin-2-ones more fully and report here the isolation of the intermediate α-oxo imides (**3**) and the behaviour of the epidioxypyrazinones (**2**).

Results and Discussion

Photochemical Reactions of the Pyrazin-2-ones (**1**) *under an Oxygen Atmosphere.*—Irradiation of a solution of the pyrazin-2-ones (**1**) in methanol under oxygen gave the 3,6-epidioxypyrazin-2-ones (**2**), the *N*-alkyl-*N*-acyl-α-oxo amides (**3**), and the *N*-alkyl-α-acyloxy-α-methoxy amides (**4**) (Scheme 1, i). The structures of these photoproducts were elucidated on the basis of their spectroscopic properties and elemental analyses. The i.r. spectrum of the epidioxypyrazinones (**2**) showed a carbonyl stretching band at 1 695—1 710 cm^{-1}, while that of the starting pyrazin-2-ones (**1**) showed it at around 1 640 cm^{-1}. The ^{13}C n.m.r. spectrum of (**2**) showed, *inter alia*, signals at δ_C 89.6—90.4 (s, C-6/C-3), 90.9—93.1 (s, C-3/C-6), 170.0—170.3 (s, C=NH), and 178.1—178.2 p.p.m. (s, CO). The ^{13}C n.m.r. spectrum of the α-oxo imides (**3**) showed carbonyl singlets at δ_C 170.6—171.3, 173.1—173.5, and 187.3—201.1 p.p.m. The i.r. spectrum of (**4**) showed absorptions characteristic of amide (1 670—1 690 cm^{-1}), ester carbonyl (1 725—1 740 cm^{-1}), and amine (3 350—3 440 cm^{-1}). A reasonable reaction path for the formation of these photoproducts (**2**)—(**4**) is presented in Scheme 2. In this the epidioxypyrazinone (**2**)‡ formed initially gives upon irradiation the α-oxo imide (**3**) by electrocyclic ring opening and loss of the corresponding nitrile; methanol attack at the carbonyl carbon of (**3**) then yields the amide (**4**). In order to gain some evidence for this reaction path, we studied the synthesis and reactions of the epidioxypyrazinone (**2**) and α-oxo imides (**3**).



	R	R^1	R^2
a;	Me	Ph	Me
b;	Me	Ph	Et
c;	Me	Ph	Pr
d;	Me	Ph	Pr^i
e;	Me	Ph	Ph
f;	Me	Me	Me
g;	Et	Ph	Et

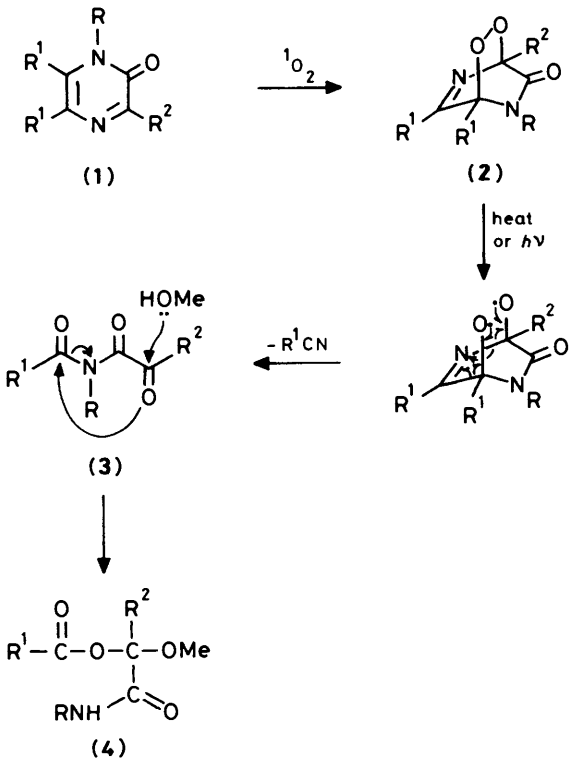
Scheme 1. *Reagents:* i, *hν*,O_2 in MeOH; ii, $^1O_2$ in CH_2Cl_2; iii, *hν* or heat or CoTPP; iv, heat in MeOH; v, *hν* in CH_2Cl_2

* One-pot reaction.

The Photo-oxygenation of the Pyrazin-2-ones (**1**) *with Singlet Oxygen.*—Irradiation of an oxygenated solution of the pyrazin-2-ones (**1**) in dichloromethane in the presence of Methylene

† Also called pyrazin-2-one 3,6-*endo*-peroxides

‡ The formation of the epidioxypyrazinone can be explained in terms of the photo-oxygenation of the pyrazin-2-one, which can act as its own sensitizer, with singlet oxygen.[1b]



Scheme 2.

Blue as a sensitizer with visible light at room temperature for 2 h gave the epidioxypyrazin-2-ones (**2**) in high isolated yields (Scheme 1, ii). The epidioxypyrazinones (**2**) thus obtained were stable in the solid state but decomposed to yield the α-oxo imides (**3**) in 21—47% yields on photolysis in dichloromethane with a high-pressure mercury lamp under argon for 3 h at room temperature (Scheme 1, v).

Synthesis of the N-*Alkyl*-N-*acyl*-α-*oxo Amides* (**3**) *by the Photochemical or Thermal Decomposition of the* 3,6-*Epidioxypyrazin*-2-*ones* (**2**).—Although many papers concerning the preparation of the symmetrical imides have been reported,[3] to our knowledge, those of the unsymmetrical imides, α-oxo imides, are few.[4] Since the α-oxo imides (**3**) were isolated by the photochemical decomposition of the epidioxypyrazinones (**2**) as described above, we studied the synthesis of (**3**) in detail. The α-oxo imides (**3**) were also obtained by a one-pot reaction in similar yields when the pyrazin-2-ones (**1**) were photo-oxygenated with singlet oxygen in dichloromethane under the same conditions as described above and then photolysed under argon with >3 000 Å light. On the other hand, thermal decomposition of the epidioxypyrazinones (**2**) gave the α-oxo imides (**3**) in fair yields. The 3,6-epidioxypyrazin-2-ones (**2**) were heated to reflux in toluene to give the α-oxo imides (**3**), accompanied by the corresponding nitriles. In the case of 3,6-epidioxy-1-methyl-3,5,6-triphenylpyrazin-2-one (**2e**), *N*-methyl-*N*-benzoyl-α-phenylglyoxylamide (**3e**) and starting pyrazin-2-one (**1e**) were produced in 20 and 60% yields, respectively, with the concomitant formation of singlet oxygen when (**2e**) was refluxed in toluene. The singlet oxygen thus generated was trapped with 1,3-diphenylisobenzofuran[5] to give 1,2-dibenzoylbenzene and phenyl *o*-benzoylbenzoate and the pyrazin-2-one (**1e**). Furthermore, when the epidioxypyrazinones (**2**) were heated neat above their melting points, the α-oxo imides (**3**) were obtained in high yields. In recent years, a high-yield catalytic rearrangement of 1,4-epidioxy bicyclic compounds was found with cobalt *meso*-tetraphenylporphine (CoTPP) by Foote *et al.*[6] This sequence represents a synthetically useful route from 1,3-diene to diepoxides under mild conditions. We have applied this method for the synthesis of the α-oxo imides by the mild decomposition of (**2**) (Scheme 1, iii). The 3,6-epidioxypyrazin-2-ones (**2**) were treated with 5 mol% CoTPP to give the α-oxo imides (**3**) in high yields, along with the corresponding nitriles. Furthermore, *N*-methyl-*N*-benzoyl-α-phenylglyoxylamide (**3e**) was also obtained by treatment of the epidioxypyrazinone (**2e**) with trifluoroacetic acid or boron trifluoride–diethyl ether. Therefore, the 3,6-epidioxypyrazin-2-ones (**2**), which can be easily obtained in a stable form by the reaction of the pyrazin-2-ones (**1**) with singlet oxygen, would be useful precursors for the synthesis of the α-oxo imides (**3**). In order to establish the photochemical reaction pathway as shown in Scheme 2, in which the α-oxo imides (**3**) are attacked by methanol to give the amides (**4**); the α-oxo imides (**3**) were heated in methanol at 45 °C to yield the expected amide derivatives (**4**). Consequently, the formation of these unusual photoproducts arises *via* the intermediate (**2**) initially produced by the reaction of the pyrazin-2-ones (**1**) with singlet oxygen followed by O–O bond fission, addition of methanol, and rearrangement, accompanied by elimination of nitrile.

Experimental

M.p.s and b.p.s are uncorrected and measured with a Yanaco micromelting point apparatus and a Buchi Kugelrohr distillation apparatus, respectively. I.r. spectra were recorded on JASCO IRA-1 and Hitachi 260-30 spectrophotometers. ^{1}H and ^{13}C N.m.r. spectra were run on JEOL FX-90Q (90 MHz) and FX-100 (100 MHz) spectrometers in $CDCl_3$ as solvent using tetramethylsilane as internal standard. Mass spectra were measured with a Hitachi M-80 spectrometer.

Starting Materials.—The pyrazin-2-ones (**1a**—**e,g**) were prepared by alkylation[1b] of the corresponding pyrazin-2-ols which were prepared by literature[8,9] methods and the pyrazin-2-one (**1f**) was prepared by the method of Furrer.[10]

Alkylation of the Pyrazin-2-*ols.*—To a stirred solution of the pyrazin-2-ol (1 ml) and sodium methoxide [from sodium (1.2 mol) and MeOH (30 mol)] in methanol (50 ml) was added dropwise dimethyl sulphate (or diethyl sulphate) (1.2 mol) at room temperature; the reaction mixture was then refluxed for 2 h. After this it was concentrated under reduced pressure, poured into 10% aqueous HCl, and extracted with dichloromethane. The extract was washed with 10% aqueous sodium hydrogen carbonate and water, dried ($MgSO_4$), and evaporated to provide a residue which when chromatographed on a silica gel column with benzene–ethyl acetate (10:1—2:1) as eluant gave the pyrazin-2-ones.

1,3-Dimethyl-5,6-diphenylpyrazin-2-one (**1a**) (55%), m.p. 169—170 °C (Found: C, 78.25; H, 5.8; N, 10.1. $C_{18}H_{16}N_2O$ requires C, 78.25; H, 5.85; N, 10.15%); $\nu_{max.}$(KBr) 1 640 cm^{-1} (C=O); δ_H 2.58 (3 H, s), 3.29 (3 H, s), and 7.10—7.39 (10 H, m); δ_C 21.1 (q), 33.9 (q), 126.8 (s), 127.7 (d), 128.2 (d), 128.9 (d), 129.3 (d), 130.1 (d), 132.3 (s), 132.6 (s), 136.5 (s), 137.9 (s), 155.2 (s), and 155.9 (s).

3-Ethyl-1-methyl-5,6-diphenylpyrazin-2-one (**1b**) (76%), m.p. 145—146 °C (Found: C, 78.75; H, 6.3; N, 9.7. $C_{19}H_{18}N_2O$ requires C, 78.6; H, 6.25; N, 9.65%); $\nu_{max.}$(KBr) 1 640 cm^{-1} (C=O); δ_H 1.34 (3 H, t), 2.97 (2 H, q), 3.29 (3 H, s), and 7.03—7.40 (10 H, m); δ_C 10.9 (q), 27.0 (t), 33.8 (q), 126.7 (d), 127.6 (d), 128.2 (d), 129.0 (d), 129.3 (d), 139.1 (d), 132.1 (s), 132.7 (s), 136.1 (s), 138.1 (s), 155.6 (s), and 158.8 (s).

1-Methyl-5,6-diphenyl-3-propylpyrazin-2-one (**1c**) (39%),

Table 1. Photoreaction of the pyrazin-2-ones (**1**) under oxygen

Pyrazinone	R	R^1	R^2	Yield (%) (2)	(3)	(4)
(**a**)	Me	Ph	Me	12	24	18
(**b**)	Me	Ph	Et	10	31	10
(**d**)	Me	Ph	Pr^i	9	28	11
(**e**)	Me	Ph	Ph	10	48	0

m.p. 124.5–126 °C (Found: C, 78.85; H, 6.6; N, 9.2. $C_{20}H_{29}N_2O$ requires C, 78.9; H, 6.6; N, 9.2%); $\nu_{max.}$(KBr) 1 640 cm^{-1} (C=O); δ_H 1.06 (3 H, t), 1.67—2.05 (2 H, m), 2.93 (2 H, t), 3.29 (3 H, s), and 7.03—7.40 (10 H, m); δ_C 14.2 (q), 20.1 (t), 33.9 (q), 35.7 (t), 126.7 (d), 127.6 (d), 128.2 (d), 128.9 (d), 129.3 (d), 130.1 (d), 132.1 (s), 132.7 (s), 136.2 (s), 138.1 (s), 155.6 (s), and 157.9 (s).

3-Isopropyl-1-methyl-5,6-diphenylpyrazin-2-one (**1d**) (57%), m.p. 165—166.5 °C (Found: C, 78.9; H, 6.6; N, 9.25. $C_{20}H_{20}N_2O$ requires C, 78.9; H, 6.6; N, 9.2%); $\nu_{max.}$(KBr) 1 640 cm^{-1} (C=O); δ_H 1.33 (6 H, d, *J* 6.8 Hz), 3.29 (3 H, s), 3.60 (1 H, sept., *J* 6.8 Hz), and 7.03—7.41 (10 H, m); δ_C 20.2 (q), 30.9 (d), 33.8 (q), 126.6 (d), 127.5 (d), 129.0 (d), 129.2 (d), 130.1 (d), 131.7 (d), 132.8 (s), 135.9 (s), 138.1 (s), 155.1 (s), and 161.7 (s).

1-Methyl-3,5,6-triphenylpyrazin-2-one (**1e**) (33%), m.p. 181.5—182 °C (Found: C, 81.9; H, 5.45; N, 8.2. $C_{23}H_{18}N_2O$ requires C, 81.65; H, 5.35; N, 8.25%); $\nu_{max.}$(KBr) 1 640 cm^{-1} (C=O); δ_H 3.36 (3 H, s), 7.05—7.49 (13 H, m), and 8.41—8.55 (2 H, m); δ_C 34.3 (q), 126.8 (d), 127.5 (d), 127.8 (d), 128.9 (d), 129.2 (d), 129.5 (d), 129.9 (d), 132.5 (s), 132.7 (s), 136.1 (s), 137.6 (s), 137.9 (s), 149.6 (s), and 155.0 (s).

1,3,5,6-Tetramethylpyrazin-2-one (**1f**) (47%), m.p. 74—76 °C (lit.,[10] 77—78 °C); $\nu_{max.}$(KBr) 1 635 cm^{-1} (C=O); δ_H 2.30 (6 H, s), 2.41 (3 H, s), and 3.53 (3 H, s); δ_C 15.6 (q), 19.9 (q), 20.4 (q), 30.8 (q), 127.6 (s), 131.3 (s), 151.9 (s), and 155.9 (s).

1,3-Diethyl-5,6-diphenylpyrazin-2-one (**1g**) (20%), m.p. 134.5—136 °C (Found: C, 78.9; H, 6.65; N, 9.2. $C_{20}H_{20}N_2O$ requires C, 78.9; H, 6.6; N, 9.2%); $\nu_{max.}$(KBr) 1 640 cm^{-1} (C=O); δ_H 1.15 (3 H, t), 1.35 (3 H, t), 2.97 (2 H, q), 3.88 (2 H, q), and 7.03—7.42 (10 H, m); δ_C 10.9 (q), 13.6 (q), 26.9 (t), 41.2 (t), 126.6 (d), 127.5 (d), 128.6 (d), 129.2 (d), 130.3 (d), 132.2 (s), 132.5 (s), 135.9 (s), 138.1 (s), 154.8 (s), and 159.2 (s).

General Procedure for the Photochemical Reactions of the Pyrazin-2-ones (**1a,b,d,e**) *under an Oxygen atmosphere.*—A solution of the pyrazin-2-one (**1**) (200 mg) in methanol (50 ml) was irradiated in a Pyrex vessel with a high-pressure mercury lamp (450 W) under oxygen at room temperature. After removal of the solvent, the residue was chromatographed on a silica gel column with benzene–ethyl acetate (29:1—1:1) or chloroform–acetone–ethanol (100:5:1) to yield the corresponding epidioxypyrazinone (**2**), α-oxo imide (**3**), and amide derivatives (**4**). The yields of products (**2**)—(**4**) are given in Table 1.

The epidioxypyrazinone (**2a**), m.p. 103—104.5 °C (Found: C, 69.85; H, 5.25; N, 9.05. $C_{18}H_{16}N_2O_3$ requires C, 70.1; H, 5.25; N, 9.1%); $\nu_{max.}$(KBr) 1 710 (C=O) and 1 605 cm^{-1} (C=N); δ_H 1.96 (3 H, s), 2.63 (3 H, s), and 6.90—7.41 (10 H, m); δ_C 17.5 (q), 29.1 (q), 90.1 (s), 90.9 (s), 127.4 (d), 127.9 (d), 128.1 (d), 128.4 (d), 129.9 (s), 130.1 (d), 130.3 (d), 134.3 (s), 170.3 (s), and 178.2 (s); *m/z* (c.i.) 309 ($M^+ + 1$).

The α-oxo imide (**3a**), b.p. 107 °C at 2 mmHg (Found: C, 64.5; H, 5.4; N, 6.95. $C_{11}H_{11}NO_3$ requires C, 64.4; H, 5.4; N, 6.8%); $\nu_{max.}$(film) 1 680br cm^{-1} (C=O); δ_H 2.38 (3 H, s), 3.26 (3 H, s), and 7.37—7.89 (5 H, m); δ_C 25.8 (q), 32.9 (q), 128.8 (d), 128.9 (d), 133.0 (d), 133.8 (s), 171.3 (s), 173.5 (s), and 194.4 (s).

The amide (**4a**), oil (Found: C, 60.75: H, 6.4; N, 5.85. $C_{12}H_{15}NO_4$ requires C, 60.75; H, 6.35; H, 5.9%); $\nu_{max.}$($CHCl_3$) 3 440 (NH), 1 725 (CO_2), and 1 690 cm^{-1} (C=O); δ_H 1.76 (3 H, s), 2.92 (3 H, d, *J* 4.9 Hz), 3.45 (3 H, s), 6.86 (1 H, br s, exchangeable with D_2O), 7.16—7.61 (3 H, m), and 8.00—8.15 (2 H, m); δ_C 21.0 (q), 26.2 (q), 50.6 (q), 100.0 (s), 128.4 (d), 130.0 (d), 130.1 (d), 133.5 (s), 170.0 (s), and 171.2 (s).

The epidioxypyrazinone (**2b**), m.p. 109—110 °C (Found: C, 70.55; H, 5.6; N, 8.65. $C_{19}H_{18}N_2O_3$ requires C, 70.8; H, 5.6; N, 8.7%); $\nu_{max.}$(KBr) 1 705 (C=O) and 1 590 cm^{-1} (C=N); δ_H 1.29 (3 H, t), 2.08—2.66 (2 H, m), 2.62 (3 H, s), and 6.90—7.59 (10 H, m); δ_C 6.9 (q), 24.2 (t), 29.0 (q), 89.9 (s), 92.1 (s), 127.7 (d), 128.1 (d), 128.3 (d), 128.8 (d), 129.9 (d), 130.2 (d), 134.4 (s), 170.2 (s), and 178.2 (s); *m/z* (c.i.) 323 ($M^+ + 1$).

The α-oxo imide (**3b**), b.p. 94 °C at 2 mmHg (Found: C, 65.75; H, 5.95; N, 6.4. $C_{12}H_{13}NO_3$ requires C, 65.75; H, 5.95; N, 6.4%); $\nu_{max.}$(film) 1 680 (C=O) and 1 600 cm^{-1} (C=N); δ_H 1.08 (3 H, t), 2.76 (2 H, q), 3.25 (3 H, s), and 7.38—7.68 (5 H, m); δ_C 6.6 (q), 31.7 (t), 32.7 (q), 128.4 (d), 128.6 (d), 132.6 (d), 132.9 (s), 171.3 (s), 173.3 (s), and 197.7 (s).

The amide (**4b**), m.p. 102—104 °C (Found: C, 61.9; H, 6.85; N, 5.5. $C_{13}H_{17}NO_4$ requires C, 62.15; H, 6.8; N, 5.55%); $\nu_{max.}$(KBr) 3 390 (NH), 1 720 (CO_2), and 1 670 cm^{-1} (C=O); δ_H 0.88 (3 H, t), 2.20 (2 H, q), 2.91 (3 H, d, *J* 4.9 Hz), 3.39 (3 H, s), 6.83 (1 H, br s), 7.28—7.57 (3 H, m), and 8.00—8.13 (2 H, m); δ_C 6.8 (q), 25.7 (q), 26.0 (t), 49.8 (q), 102.2 (s), 128.2 (d), 129.5 (d), 129.8 (d), 133.2 (s), 163.9 (s), and 168.6 (s); *m/z* (c.i.) 252 ($M^+ + 1$).

The epidioxypyrazinone (**2d**), m.p. 105—106.5 °C (Found: C, 71.2; H, 6.05; N, 8.3. $C_{20}H_{20}N_2O_3$ requires C, 71.4; H, 6.0; N, 8.3%); $\nu_{max.}$(KBr) 1 695 (C=O) and 1 605 cm^{-1} (C=N); δ_H 1.22 (3 H, d, *J* 6.8 Hz), 1.40 (3 H, d, *J* 6.8 Hz), 2.50—2.83 (1 H, m), 2.61 (3 H, s), and 6.90—7.68 (10 H, m); δ_C 15.6 (q), 17.3 (q), 28.8 (q), 29.9 (d), 89.6 (s), 93.1 (s), 127.6 (d), 128.2 (d), 128.7 (d), 129.8 (d), 130.0 (d), 134.6 (s), 170.0 (s), and 178.2 (s); *m/z* (c.i.) 337 ($M^+ + 1$).

The α-oxo imide (**3d**), b.p. 120 °C at 2 mmHg (Found: C, 66.95; H, 6.5; N, 5.9. $C_{13}H_{15}NO_3$ requires C, 66.95; H, 6.5; N, 6.0%); $\nu_{max.}$(film) 1 680br cm^{-1} (C=O); δ_H 1.24 (6 H, d, *J* 6.8 Hz), 2.81—3.16 (1 H, m), 3.24 (3 H, s), and 7.18—7.69 (5 H, m); δ_C 17.6 (q), 33.1 (q), 37.5 (d), 128.6 (d), 128.8 (d), 132.8 (s), 132.8 (s), 171.3 (s), 173.5 (s), and 201.1 (s).

The amide (**4d**), m.p. 95—97 °C (Found: C, 63.3; H, 7.25; N, 5.25. $C_{14}H_{19}NO_4$ requires C, 63.4; H, 7.2; N, 5.25%); $\nu_{max.}$(KBr) 3 350 (NH), 1 740 (CO_2), and 1 670 cm^{-1} (C=O); δ_H 1.01 (3 H, d, *J* 6.8 Hz), 1.22 (3 H, d, *J* 6.8 Hz), 2.56 (1 H, sept., *J* 6.8 Hz), 6.73 (1 H, br s, exchangeable with D_2O), 7.27—7.66 (3 H, m), and 8.02—8.13 (2 H, m); δ_C 16.4 (q), 16.8 (q), 25.9 (q), 31.9 (d), 50.2 (q), 102.9 (s), 128.4 (d), 129.9 (d), 133.2 (s), 164.2 (s), and 167.5 (s); *m/z* (c.i.) 266 ($M^+ + 1$).

The epidioxypyrazinone (**2e**), m.p. 130—131 °C (Found: C, 74.3; H, 4.9; N, 7.45. $C_{23}H_{18}N_2O_3$ requires C, 74.6; H, 4.9; N, 7.55%); $\nu_{max.}$(KBr) 1 705 (C=O) and 1 605 cm^{-1} (C=N); δ_H 2.71 (3 H, s), 7.00—7.63 (13 H, m), and 7.95—8.11 (2 H, m); δ_C 29.6 (q), 90.4 (s), 91.9 (s), 127.8 (d), 128.1 (d), 128.3 (d), 129.3 (d), 130.1 (d), 130.3 (d), 134.6 (s), 170.0 (s), and 178.1 (s); *m/z* (c.i.) 371 ($M^+ + 1$).

The α-oxo imide (**3e**), m.p. 89—90 °C (Found: C, 71.85; H, 4.9; N, 5.15. $C_{16}H_{13}N_3$ requires C, 71.9; H, 4.9; N, 5.25%); $\nu_{max.}$(KBr) 1 670br cm^{-1} (C=O); δ_H 3.34 (3 H, s), 7.10—7.62 (8 H, m), and 7.84—7.93 (2 H, m); δ_C 33.1 (q), 128.6 (d), 129.3 (d), 133.9 (d), 170.6 (s), 173.1 (s), and 187.3 (s).

Photo-oxygenation of the Pyrazin-2-ones (**1a—g**) *with Singlet Oxygen.*—An oxygenated solution of the pyrazin-2-one (**1**) (200 mg) in dichloromethane (50 ml) in the presence of Methylene Blue (MB) (*ca.* 2 mg) as a sensitizer was irradiated in a Pyrex tube with a halogen lamp for 2 h at room temperature. After removal of the solvent under reduced pressure, the residue was

Table 2. The yield of the 3,6-epidioxypyrazin-2-one (**2**) derived from the reaction of (**1**) and singlet oxygen

	R	R^1	R^2	Yield (%)
a	Me	Ph	Me	85
b	Me	Ph	Et	83
c	Me	Ph	Pr	86
d	Me	Ph	Pr^i	80
e	Me	Ph	Ph	96
f	Me	Me	Me	80
g	Et	Ph	Et	68

Table 3. The yield of the α-oxo imides (**3**) obtained by the decomposition of the epidioxypyrazinones (**2**)

				Yield of (**3**) (%)			
					Thermolysis		
	R	R^1	R^2	Photolysis	Neat	Ref./toluene	CoTPP
a	Me	Ph	Me	33	95	70	93
b	Me	Ph	Et	47	95	50	71
c	Me	Ph	Pr	21			
d	Me	Ph	Pr^i	21	95	46	94
e	Me	Ph	Ph	44	95	20(60)[a]	92
e					(90)[b]		
e					(90)[c]		
f	Me	Me	Me	52			
g	Et	Ph	Et	40			

[a] 1-Methyl-3,5,6-triphenylpyrazin-2-one (**1e**). [b] Treatment of (**2e**) with trifluoroacetic acid. [c] Treatment of (**2e**) with boron trifluoride–diethyl ether.

chromatographed on a silica gel column with benzene–ethyl acetate (4:1—9:1) as eluant to yield the epidioxypyrazinone (**2**). The yields of (**2**) are given in Table 2.

The epidioxypyrazinone (**2c**), m.p. 98—99.5 °C (Found: C, 71.4; H, 6.0; N, 8.35. $C_{20}H_{20}N_2O_3$ requires C, 71.4; H, 6.0; N, 8.3%); $\nu_{max.}$(KBr) 1 715, 1 705 (C=O), and 1 615 cm^{-1} (C=N); δ_H 1.06 (3 H, t), 1.61—2.05 (2 H, m), 2.11—2.47 (2 H, m), 2.62 (3 H, s), and 6.90—7.59 (10 H, m); δ_C 14.6 (q), 15.9 (t), 29.0 (q), 32.9 (t), 89.8 (s), 91.9 (s), 127.7 (d), 128.1 (d), 128.3 (d), 128.6 (d), 129.9 (d), 130.1 (d), 134.4 (s), 170.3 (s), and 178.1 (s); *m/z* (c.i.) 337 ($M^+ + 1$).

The epidioxypyrazinone (**2f**), m.p. 89—90 °C (Found: C, 51.95; H, 6.8; N, 15.5. $C_8H_{12}N_2O_3$ requires C, 52.15; H, 6.55; N, 15.2%); $\nu_{max.}$(KBr) 1 700 (C=O) and 1 630 cm^{-1} (C=N); δ_H 1.74 (3 H, s), 1.76 (3 H, s), 2.26 (3 H, s), 2.97 (3 H, s); δ_C 14.9 (q), 17.3 (q), 20.2 (q), 26.2 (q), 86.5 (s), 90.4 (s), 169.3 (s), and 178.1 (s); *m/z* (c.i.) 185 ($M^+ + 1$).

The epidioxypyrazinone (**2g**), m.p. 96—97 °C (Found: C, 71.25; H, 6.0; N, 8.3. $C_{20}H_{20}N_2O_3$ requires C, 71.4; H, 6.0; N, 8.3%); $\nu_{max.}$(KBr) 1 710 (C=O) and 1 600 cm^{-1} (C=N); δ_H 0.88 (3 H, s), 1.28 (3 H, t), 2.01—2.56 (2 H, m), 2.63—3.14 (1 H, m), 3.32—3.86 (1 H, m), and 6.87—7.56 (10 H, m); δ_C 6.9 (q), 13.7 (q), 24.2 (t), 37.8 (t), 90.1 (s), 92.1 (s), 127.7 (d), 128.0 (d), 128.1 (d), 129.8 (d), 130.0 (d), 134.7 (s), 169.9 (s), and 178.4 (s); *m/z* (c.i.) 337 ($M^+ + 1$).

Synthesis of the α-Oxo Imides (**3**) *by Decomposition of the Epidioxypyrazinones* (**2**): (*See Table 3*).—(i) *Photolysis of* (**2**). A solution of the epidioxypyrazinone (**2**) (200 mg) in dichloromethane (50 ml) was irradiated with a high-pressure mercury lamp (450 W) through a Pyrex filter under argon at room temperature for 3 h. After removal of the solvent, the residue was chromatographed on a silica gel column with benzene–ethyl acetate (4:1—30:1) to give the α-oxo imide (**3**), together with the corresponding nitrile.

The α-oxo imide (**3c**), b.p. 97 °C at 2 mmHg (Found: C, 67.05; H, 6.45; N, 6.0. $C_{13}H_{15}NO_3$ requires C, 66.95; H, 6.5; N, 6.0%); $\nu_{max.}$(film) 1 670br cm^{-1} (C=O); δ_H 0.93 (3 H, t), 1.44—1.81 (2 H, m), 2.72 (2 H, t), 3.24 (3 H, s), and 7.17—7.68 (5 H, m); δ_C 13.3 (q), 16.0 (t), 32.8 (q), 40.0 (t), 128.5 (d), 128.6 (d), 132.6 (d), 132.9 (s), 171.3 (s), 173.3 (s), and 197.0 (s).

The α-oxo imide (**3f**), oil (Found: C, 50.6; H, 6.55; N, 9.6. $C_6H_9NO_3$ requires C, 50.35; H, 6.35; N, 9.8%); $\nu_{max.}$(film) 1 680br cm^{-1} (C=O); δ_H 2.33 (6 H, s) and 3.25 (3 H, s); δ_C 23.0 (q), 25.5 (q), 30.0 (q), 170.3 (s), 173.7 (s), and 193.7 (s).

The α-oxo imide (**3g**), oil (Found: C, 66.65; H, 6.55; N, 5.75. $C_{13}H_{15}NO_3$ requires C, 66.95; H, 6.5; N, 6.0%); $\nu_{max.}$(film) 1 680br cm^{-1} (C=O); δ_H 0.98 (3 H, t), 1.22 (3 H, t), 2.70 (2 H, q), 3.82 (2 H, q), and 7.31—7.65 (5 H, m); δ_C 6.8 (q), 13.6 (q), 31.7 (t), 40.7 (t), 128.2 (d), 128.9 (d), 132.6 (d), 134.3 (s), 171.0 (s), 173.7 (s), and 198.0 (s).

(ii) *Thermal decomposition of* (**2**). (*a*) The epidioxypyrazinone (**2**) (50 mg) when heated in a sealed tube above its melting point for several minutes and then worked up yielded the corresponding α-oxo imide (**3**). (*b*) A solution of the epidioxypyrazinone (**2**) (100 mg) in toluene (20 ml) was refluxed for 3 h under argon and worked up to give the corresponding α-oxo imide (**3**).

(iii) *The reaction of the epidioxypyrazinone* (**2**) *with CoTPP.* A solution of the epidioxypyrazinone (**2**) (100 mg) and 5 mol% CoTPP, prepared according to the literature method previously described,[6,7] in dichloromethane (40 ml) was stirred at room temperature for 4 h and then worked up to give the corresponding α-oxo imide (**3**).

(iv) *Reaction of the epidioxypyrazinone* (**2e**) *with trifluoroacetic acid or boron trifluoride–diethyl ether.* A solution of (**2e**) (100 mg) and a few drops of trifluoroacetic acid or boron trifluoride–diethyl ether in dichloromethane (20 ml) was stirred at room temperature for 30 min and worked up to give the α-oxo imide (**3e**).

Table 4. The yield of the amides (**4**) by methanolysis of the α-oxo imides (**3**).

	R	R^1	R^2	Yield (%)
a	Me	Ph	Me	26 (14)[a]
b	Me	Ph	Et	43 (20)
d	Me	Ph	Pr^i	18 (33)
e	Me	Ph	Ph	0 (90)

[a] Recovered (**3**).

Thermal Conversion of α-Oxo Imides (**3**) *into the Amides* (**4**) *in Methanol.*—A solution of the α-oxo imide (**3a**) (100 mg) in methanol (10 ml) was heated at 45 °C for 10 h and then worked up to give the amide (**4**), together with unchanged (**3**). The yields of (**4**) are given in Table 4.

Trapping Experiment of Singlet Oxygen with 1,3-*Diphenylisobenzofuran.*—A solution of the epidioxypyrazinone (**2e**) (185 mg, 0.5 mmol) and 1,3-diphenylisobenzofuran (134 mg, 0.5 mmol) in toluene (30 ml) was refluxed for 3 h under argon. After removal of the solvent, the residue was chromatographed under similar conditions to those described above to give the α-oxo imide (**3e**) (trace), 1,2-dibenzoylbenzene (52%), phenyl *o*-benzoylbenzoate (16%), and 1-methyl-3,5,6-triphenylpyrazin-2-one (**1e**) (47%).

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