Photochemical Reactions of Pyrazin-2(1*H*)-ones

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Irradiation of 1-alkyl-5,6-diarylpyrazin-2(1*H*)-ones (1a—c) in alcohol under oxygen gave *N*-alkyl-acetamide derivatives (2a—e) in 21—69% yield. The formation of acetamide derivatives (2) arises *via* the endoperoxide intermediates (3), initially produced by the reaction of the pyrazin-2(1*H*)-ones (1), which act as their own sensitizer, with singlet oxygen followed by O–O bond fission, alcohol addition, and rearrangement accompanied by the elimination of the corresponding nitrile derivative. The pyrazin-2(1*H*)-ones (1a–d) rapidly reacted with singlet oxygen to afford the stable endoperoxides (3a—d). On the other hand, the pyrazin-2(1*H*)-ones (1a—d) were inert to the photolysis in benzene or methanol under argon.

Although the photochemistry of heterocycles possessing an amide functional group, *e.g.*, 2-pyridones,[1] uracil derivatives,[2] *etc.* has been extensively studied, that of the conjugated cyclohexadienone system containing two nitrogen atoms (*e.g.*, pyrimidinones, pyrazinones, and pyridazinones) has received little attention. Previously, we reported the photochemical electrocyclization of 1,4,6-trisubstituted pyrimidin-2(1*H*)-ones to give 2-oxo-1,3-diazabicyclo[2.2.0]hex-5-enes,[3] photochemical ring opening of *N*-arylpyrimidin-2(1*H*)-ones,[4] and hydrogen-atom-abstraction reactions of 1-alkyl-4,6-diphenylpyrimidin-2(1*H*)-ones.[5] Photochemical alcohol addition of 4,6-dimethylpyrimidin-2-ol, pyrimidin-2-ol, and 1-methyl-4-methylaminopyrimidin-2(1*H*)-one was reported by Pfoertner,[6] Kanaoka *et al.*,[6] and Schetler and his co-workers.[7] Furthermore, photochemical ring-contraction of pyrimidin-4(1*H*)-ones and the pyridazin-3(1*H*)-ones was reported by Nagata and his co-workers [8] and Tsuchiya *et al.*[9] Herein we report the photochemical reactions of the pyrazin-2(1*H*)-ones (1a—d). Details of an *X*-ray crystallographic analysis of a photoproduct (2a) are also presented.

Results and Discussion

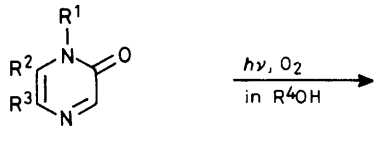
*Photochemical Reactions of the Pyrazin-*2(1H)*-ones* (1) *under Oxygen.*—1-Alkylpyrazin-2(1*H*)-ones (1a—d) were inert to the photolysis in benzene or methanol under argon.† However, when the pyrazin-2(1*H*)-one (1a) was irradiated in methanol in a Pyrex vessel with a high-pressure mercury lamp under oxygen at room temperature for 5 h and then purified through silica gel column chromatography, benzonitrile and a white crystalline solid, $C_{11}H_{13}NO_4$, which gave a negative peroxide test, were obtained in 45 and 60% yield, respectively. The i.r. spectrum of the solid showed absorptions at 3 430, 1 725, 1 690, and 1 450 cm^{-1} assignable to secondary amine, benzoyloxy, amide carbonyl, and amide II band absorptions, respectively. The ^1H n.m.r. spectrum showed signals at δ 2.89 (3 H, d, changed to singlet on the addition of D_2O), 3.60 (3 H, s), 6.18 (1 H, s), and 6.7 (1 H, br s, exchangeable with D_2O) due to methylamino, methoxy, methine, and amine protons, respectively, in addition to signals due to aromatic protons. Furthermore, the ^{13}C n.m.r. spectrum displayed signals at δ_C 26.0 (q, NCH_3), 57.5 (q, OCH_3), 94.1 (d, methine C), 165.8 (s, NCO), and 166.4 p.p.m. (s, CO_2), in addition to aromatic carbon peaks. This photoproduct was treated with potassium hydroxide in methanol to give methyl benzoate and unidentified materials. Thus, the photoproduct was characterized as 1-benzoyloxy-1-methoxy-*N*-methylacetamide (2a). Furthermore, the structure of compound (2a) was confirmed by *X*-ray structural analysis (see later).

Irradiation of the pyrazin-2(1*H*)-ones (1a—c) in alcohol under the same conditions as described above gave the acetamide derivatives (2b—e) in 21—69% yield. The structures of the photoproducts (2b and e) were assigned on the basis of their spectroscopic properties (see Experimental section). The acetamide products (2c and d) decomposed at 40 °C at 10^{-3} mmHg to give benzoic acid and unidentified materials. The formation of the photoproducts (2) was presumed to arise *via* the endoperoxide (3) followed by O–O bond fission upon irradiation, then addition of alcohol, and rearrangement accompanied by elimination of nitrile (see Scheme).

Although the endoperoxide intermediate (3) was not isolated, the reaction mixture after irradiation of the pyrazin-2(1*H*)-ones (1a—d) gave a positive peroxide test (starch–iodide). Sammes and his co-workers [10] reported that 5-ethoxy-1,3-dimethylpyrazin-2(1*H*)-one (5) reacted with oxygen on exposure to air to give 5-ethoxy-3-hydroxy-1,3-dimethylpyrazine-2,6-(1*H*,3*H*)-dione *via* initial formation of the endoperoxide ‡ followed by rearrangement. However, the pyrazin-2(1*H*)-one (1a) did not react with oxygen on exposure to air and (1a) was recovered quantitatively. On the other hand, irradiation, with visible light, of an oxygenated solution of the pyrazin-2(1*H*)-one (1a) in dichloromethane, with Methylene Blue as a sensitizer, afforded a stable endoperoxide (3a) in 60% yield. Irradiation of an oxygenated solution of (1a) in dichloromethane with visible light in the absence of a sensitizer gave also the endoperoxide (3a) but in low yield, suggesting that the pyrazin-2(1*H*)-one (1a) can act as its own sensitizer. On the other hand, irradiation of the pyrazin-2(1*H*)-one (1a) in the presence of DABCO (1,4-diazabicyclo[2.2.2]octane) as a singlet quencher under an oxygen-containing atmosphere did not give the acetamide derivative (2a). Irradiation of the endoperoxide (3a) thus obtained in methanol in a Pyrex vessel with a high-pressure mercury lamp under argon for 2 h at room temperature gave the acetamide derivative (2a) in quantitative yield. Furthermore, evidence for the formation of the intermediate, *N*-benzoyl-*N*-oxalylmethylamine (4a; R^1 = Me, R^2 = Ph), was obtained from the n.m.r. spectrum. The photolysis of the endoperoxide (3a) in $CDCl_3$ for 5 min

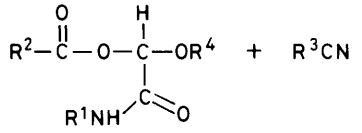
† In his work on the photochemistry of the pyrazin-2(1*H*)-ones, Furrer reported that 1,3,5,6-tetramethylpyrazin-2(1*H*)-one gave an unstable photoisomer, 1,2,4,6-tetramethyl-3-oxo-2,5-diazabicyclo-[2.2.0]hex-5-ene, which could not be isolated and was identified as its dehydro derivative by hydrogenation of the photoisomer (H. Furrer, *Chem. Ber.*, 1972, **105**, 2780).

‡ The endoperoxide intermediate was not isolated; however, the formation of the endoperoxide was observed in the n.m.r. spectrum.[10]



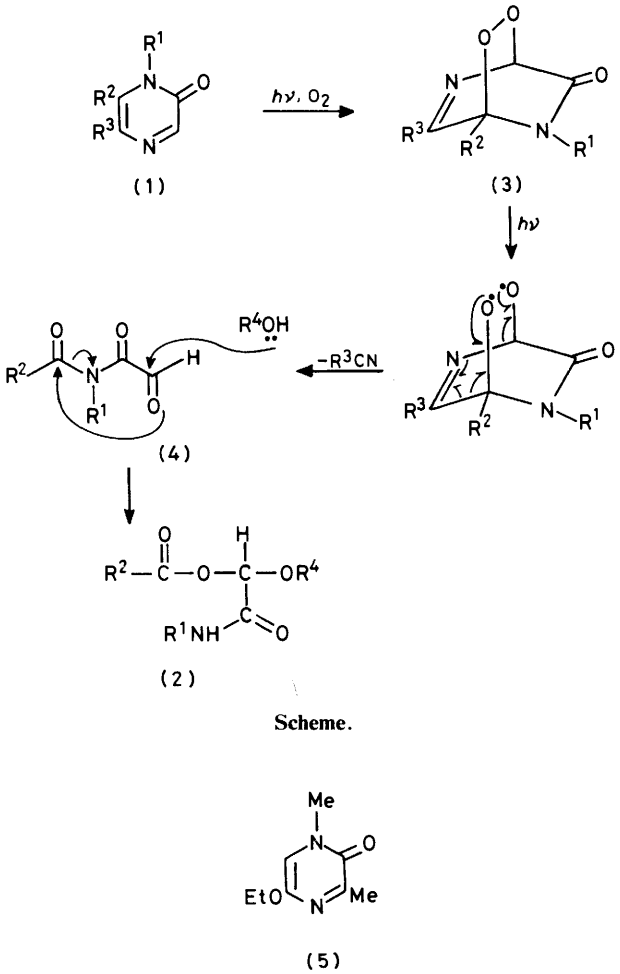
(1)

a; R^1 = Me, R^2 = R^3 = Ph
b; R^1 = Et, R^2 = R^3 = Ph
c; R^1 = Me, R^2 = R^3 = p-MeC_6H_4
d; R^1 = Me, R^2 = H, R^3 = Ph



(2)

a; R^1 = Me, R^2 = Ph, R^4 = Me (60%)
b; R^1 = Et, R^2 = Ph, R^4 = Me (39%)
c; R^1 = Me, R^2 = Ph, R^4 = Et (21%)
d; R^1 = Et, R^2 = Ph, R^4 = Et (40%)
e; R^1 = Me, R^2 = p-MeC_6H_4, R^4 = Me (69%)



Scheme.

(5)

at room temperature also gave compound (4a) (>90%), whose n.m.r. spectrum showed two singlets at δ 3.30 and 9.35 in the ratio of 3 : 1, assignable to methyl and aldehyde protons, respectively, in addition to the aromatic proton signals. These results indicated that the formation of the acetamide products (2) arises *via* the endoperoxide intermediates (3) initially produced by the reaction of the pyrazin-2(1*H*)-one (1) with singlet oxygen followed by O–O bond fission, addition of alcohol, and rearrangement accompanied by elimination of nitrile. When 1-methyl-5-phenylpyrazin-2(1*H*)-one (1d) was irradiated in methanol under the same conditions as described above, the reaction mixture also gave a positive peroxide test; however, no photoproducts could be isolated since the reaction products decomposed explosively after evaporation of the solvent.

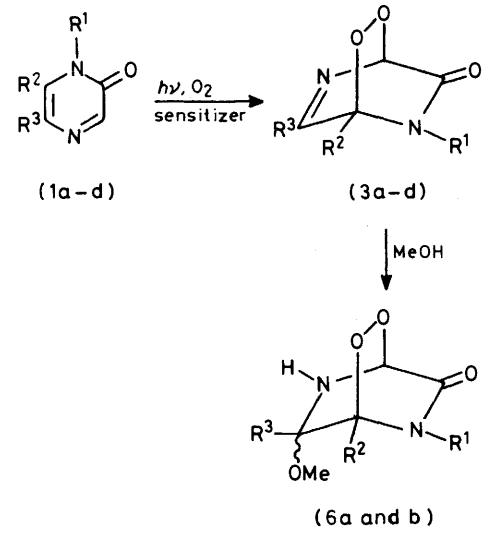
Table 1. Yield of the endoperoxide (3) obtained by reaction of the pyrazin-2(1*H*)-one (1) with singlet oxygen

Compd.	Solvent	Sensitizer	Yield of (3) (%)
(1a)	CH_2Cl_2	MB [a]	60
(1a)	CH_2Cl_2	Eosin	18
(1a)	CH_2Cl_2	TPP [b]	67
(1a)	CH_2Cl_2	RB [c]	28 [PhCOCOPh (15)]
(1a) [d]	CH_2Cl_2	RB	52
(1a)	MeOH	MB	— (49) [e]
(1a)	MeOH	RB	76
(1a)	Acetone	MB	40
(1a)	Acetone	RB	68
(1b)	CH_2Cl_2	MB	22
(1b)	MeOH	RB	— (17) [e]
(1c)	CH_2Cl_2	MB	61

[a] Methylene Blue. [b] Tetraphenylporphine. [c] Rose Bengal. [d] At −50 °C. [e] The yield of the 1 : 1 adduct (4).

Reactions of the Pyrazin-2(1H)-ones (1a—d) *with Singlet Oxygen.*[11]—As the photochemical formation of the acetamides (2) suggested that the pyrazin-2(1*H*)-ones (1) reacted with singlet oxygen to give the endoperoxides (3), we investigated the reaction of (1) with singlet oxygen. Markham and Sammes [12] recently reported that six-membered heterocycles containing nitrogen, such as pyrazines and pyrimidines, reacted with singlet oxygen to form endoperoxides; however, the reactions of singlet oxygen with heterocycles containing nitrogen are largely limited to five-membered-ring systems such as pyrroles and indoles.[13] Irradiation of the pyrazin-2(1*H*)-ones (1a—c) in various solvents in the presence of a sensitizer with visible light at room temperature under oxygen gave the endoperoxides (3a—c) in 18—76% yield. The results are shown in Table 1.

Irradiation of the pyrazin-2(1*H*)-ones (1a and b) in methanol in the presence of Methylene Blue as a sensitizer under the same conditions as described above afforded the 1 : 1 adducts, (6a and b), of the endoperoxide and methanol, formed when the endoperoxide reacted further with methanol. The 1 : 1 adduct (6a) was also obtained in *ca.* quantitative yield when the endoperoxide (3a) was stirred in methanol in the dark at room temperature. On the other hand, irradiation of an oxygenated solution of the pyrazin-2(1*H*)-one (1a) in dichloromethane in the presence of Rose Bengal as a sensitizer at room temperature gave the endoperoxide (3a) and benzil (7) in 28 and 15% yield, respectively, while at −50 °C (1a) gave the



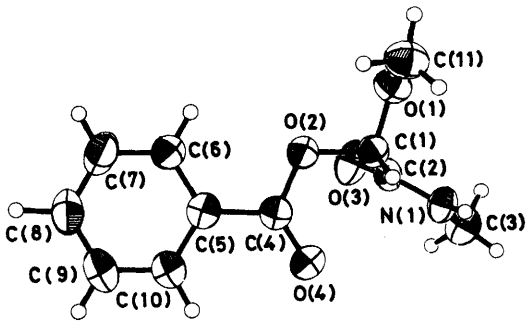
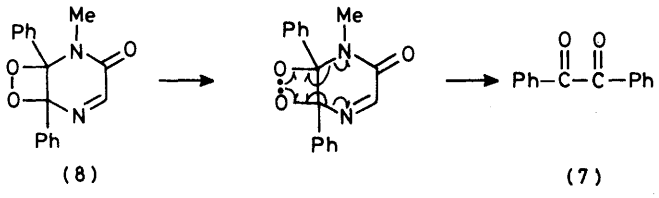


Figure 1. A perspective drawing of (2a)

sole product, the endoperoxide (3a), in 52% yield. The formation of benzil (7) is presumed to arise by radical fragmentation of the dioxetane intermediate (8).



The formation of α-diketones by photo-oxygenation of tetrathioethylene [14] and enamines [15] has been reported. 1-Methyl-5-phenylpyrazin-2(1*H*)-one (1d) also reacted rapidly with singlet oxygen and gave a positive peroxide test; however, the reaction products decomposed explosively after evaporation of the solvent. Although the endoperoxide (3d) was not isolated, evidence for its formation was obtained by n.m.r. spectroscopy. Photo-oxygenation of (1d) in CD_2Cl_2 using Methylene Blue as a sensitizer for 20 min at −50 °C gave a new product (3d), whose n.m.r. spectrum showed a singlet at δ 3.11, two doublets at δ 5.91 (*J* 1.4 Hz) and 6.23 (*J* 1.4 Hz), and a multiplet at δ 7.3—8.1, these in the proportions 3 : 1 : 1 : 5, assignable to methyl, bridgehead methines, and aromatic protons, respectively, in addition to the peaks of the starting pyrazin-2(1*H*)-one (1d).

Molecular and Crystal Structure of the Acetamide (2a).—A perspective drawing of the acetamide (2a) is shown in

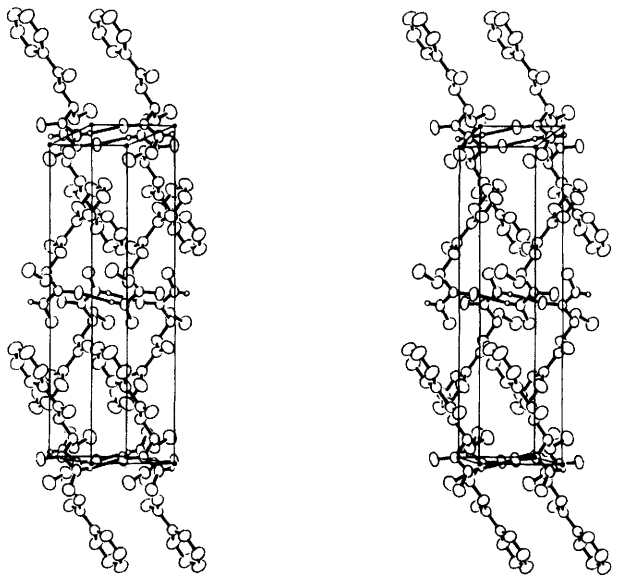


Figure 2. Packing of molecules of (2a) in the unit cell

Table 2. Positional parameters for non-hydrogen atoms (× 10^4) and for hydrogen atoms (× 10^3), with estimated standard deviations in parentheses (U_{eq} = 1/3 trace **u**)

Atom	*x*	*y*	*z*	U_{eq}
O(1)	3 743(2)	415(1)	9 827(3)	543(11)
O(2)	2 757(2)	1 296(1)	7 572(3)	496(10)
O(3)	1 949(2)	97(1)	4 946(3)	670(14)
O(4)	978(2)	1 517(1)	7 837(4)	630(13)
N(1)	1 384(2)	−237(1)	8 948(4)	485(13)
C(1)	2 686(2)	688(1)	9 244(4)	445(13)
C(2)	1 954(2)	155(1)	7 495(4)	430(14)
C(3)	685(3)	−786(2)	7 668(7)	613(19)
C(4)	1 814(2)	1 666(1)	6 970(4)	452(14)
C(5)	1 935(2)	2 265(2)	5 166(4)	480(14)
C(6)	1 034(3)	2 699(2)	4 455(7)	682(19)
C(7)	1 112(4)	3 275(2)	2 802(7)	793(25)
C(8)	2 078(3)	3 404(2)	1 795(7)	716(21)
C(9)	2 975(3)	2 975(2)	2 508(7)	749(22)
C(10)	2 912(3)	2 411(2)	4 178(6)	566(17)
C(11)	4 424(3)	713(2)	12 247(7)	659(22)
H(N)	142(2)	−17(2)	1 058(6)	
H(1)	243(2)	84(1)	1 092(5)	
H(31)	19(5)	−70(3)	580(12)	
H(32)	28(5)	−95(3)	888(10)	
H(33)	115(4)	−121(3)	738(9)	
H(6)	38(4)	263(2)	525(7)	
H(7)	51(5)	360(3)	252(8)	
H(8)	219(3)	386(2)	67(7)	
H(9)	364(4)	307(2)	189(7)	
H(10)	353(3)	213(2)	468(5)	
H(111)	450(4)	120(3)	1 184(8)	
H(112)	407(3)	70(2)	1 384(7)	
H(113)	513(3)	54(2)	1 237(7)	

Figure 1. The molecular packing in the unit cell is shown in Figure 2. Atomic co-ordinates are given in Table 2, and bond distances and angles are given in Tables 3 and 4. The atoms of the benzoyloxy group, C(1) and O(1), are all coplanar, and the C(11)–O(1) bond to the methyl carbon of the methoxy group is almost perpendicular to that system [torsion angle C(11)–O(1)–C(1)–O(2) is 84.6°]. The methylamide moiety is planar [torsion angle C(3)–N(1)–C(2)–O(3) is 0.3°]. There are two

Table 3. Bond lengths involving non-hydrogen atoms (Å)

O(1)–C(1)	1.381(3)	C(1)–C(2)	1.529(3)
O(1)–C(11)	1.430(3)	C(4)–C(5)	1.481(3)
C(2)–C(1)	1.447(3)	C(5)–C(6)	1.387(4)
O(2)–C(4)	1.350(3)	C(5)–C(10)	1.388(4)
O(3)–C(2)	1.227(2)	C(6)–C(7)	1.392(5)
O(4)–C(4)	1.205(3)	C(7)–C(8)	1.374(6)
N(1)–C(2)	1.315(3)	C(8)–C(9)	1.375(5)
N(1)–C(3)	1.443(4)	C(9)–C(10)	1.376(4)

Table 4. Bond angles involving non-hydrogen atoms (°)

C(1)–O(1)–C(11)	113.4(2)	O(2)–C(4)–C(5)	112.6(2)
C(1)–O(2)–C(4)	115.5(1)	O(4)–C(4)–C(5)	124.8(2)
C(2)–N(1)–C(3)	122.6(2)	C(4)–C(5)–C(6)	118.4(2)
O(1)–C(1)–O(2)	106.7(1)	C(4)–C(5)–C(10)	122.8(2)
O(1)–C(1)–C(2)	106.5(2)	C(6)–C(5)–C(10)	118.9(2)
O(2)–C(1)–C(2)	110.1(1)	C(5)–C(6)–C(7)	120.5(3)
O(3)–C(2)–N(1)	124.3(2)	C(6)–C(7)–C(8)	119.8(3)
O(3)–C(2)–C(1)	120.8(2)	C(7)–C(8)–C(9)	119.8(3)
N(1)–C(2)–C(1)	114.9(1)	C(8)–C(9)–C(10)	120.9(3)
O(2)–C(4)–O(4)	122.6(2)	C(5)–C(10)–C(9)	120.2(3)

types of C=O double bond; the benzoyloxy carbonyl which has a ' normal ' bond length of 1.205 Å and the methylamide carbonyl which is significantly longer (1.227 Å). The lengthening of the latter is attributed to two effects: (i) delocalization of the bonds in the planar amide group, and (ii) hydrogen bonding with the amide group of a neighbouring molecule. The delocalization of the bonds in the amide group is also exhibited in the short N(1)–C(2) bond length (1.315 Å). Dunitz and Winkler [16] showed that there is a correlation between the bond lengths and angles in various amides and the degree of protonation. This correlation is such that as the degree of protonation increases, the C–N bond shortens and C=O bond elongates. We find the same effect in (2a) where hydrogen bonding plays a similar role to that of protonation in Winkler's systems. The molecule possesses three types of formally ' single ' C–O bond, but they differ in their bond lengths. The shorter C–O bond (1.350 Å) is that of the benzoyloxy group [C(4)–O(2)]. This bond length is in good agreement with the values commonly found in similar systems where the oxygen atom is attached to a trigonal carbon, such as in 3,4,6-tri-*O*-acetyl-1,2-*O*-(1-ethoxyethylidene)-α-D-glucopyranose [17] (1.354 and 1.340 Å) and in 1,4,6-tri-*O*-acetyl-2,3-dideoxy-2-diacetamido-α-D-*erythro*-hex-2-enopyranose [18] (1.346, 1.353, and 1.371 Å). The longest C–O bond lengths (1.430, 1.447 Å) are observed wherever the oxygen is bonded to a tetrahedral carbon atom [C(11)–O(1) and C(1)–O(2)]. Similar bond lengths have been observed in (*S*)-1-ethoxycarbonyloxyethyl-6β-[(hexahydro-1*H*-azepin-1-yl)methyleneamino]penicillanate hydrochloride,[19] (1.441 and 1.410 Å), in benzylpenicillin 1'-diethylcarbonate ester (1-ethoxycarbonyloxyethyl benzylpenicillanate) [20] (1.437 and 1.435 Å), and in *p*-chlorobenzaldehyde hydrate diacetate [21] (1.424 and 1.450 Å). Although O(1) is bonded to a tetrahedral carbon atom [C(1)], the bond length is significantly shorter than the latter (1.381 Å). Similar shortenings are observed whenever the tetrahedral carbon is bonded to more than a single oxygen.[22] The molecules are held in the crystal by hydrogen bonds which are formed between the carbonyl O(3) atom of an amide group and N(1) of an amide group of a molecule related by a translation along the short *c* axis. The observed interatomic distances are H(1) · · · O(3) 2.146 Å, N(1) · · · O(3) 2.915 Å, and the angle N(1) · · · H(1) · · · O(3) is 169.4°.

Experimental

M.p.s are uncorrected and were measured with a Yanaco micro-melting-point apparatus (MP-J3). U.v. spectra were determined with a JASCO UVIDEC-505 spectrometer and i.r. spectra were recorded on a Hitachi 260-30 spectrometer. N.m.r. spectra were run on a JEOL FX 100 spectrometer using tetramethylsilane as internal standard. A Ushio 450 W high-pressure mercury lamp and a halogen lamp were used as irradiation sources.

Starting Materials.—The pyrazin-2(1*H*)-ones (1a—d) were prepared by alkylation of the corresponding pyrazin-2-ols which were prepared according to the literature method previously described.[23]

General Procedure for Alkylation of the Pyrazin-2-ols.—To a stirred solution of the pyrazin-2-ol (1 mmol) and sodium methoxide [from sodium (1 mmol) and MeOH (5 ml)] in methanol (15 ml) was added dropwise a dialkyl sulphate (1.1 mmol) at room temperature and then the reaction mixture was refluxed for 1 h. The solution was concentrated under reduced pressure, poured into 10% HCl solution, and extracted with dichloromethane. The extract was washed in turn with 10% $NaHCO_3$ solution and water, and dried over anhydrous magnesium sulphate. After removal of the solvent, the residue was chromatographed on a silica gel column with benzene–ethyl acetate (4 : 1 or 2 : 1) as eluant to give the pyrazin-2(1*H*)-one, together with a small amount of the 2-alkoxypyrazine. Thus prepared were 1-*methyl*-5,6-*diphenylpyrazin*-2(1H)-*one* (1a), m.p. 165—167 °C (Found: C, 78.1; H, 5.35; N, 10.6. $C_{17}H_{14}N_2O$ requires C, 77.85; H, 5.35; N, 10.65%); $\lambda_{max.}$ (EtOH) 266 (ε 12 000) and 347 nm (7 300); $\nu_{max.}$ (KBr) 1 640 cm^{-1} (C=O); δ_H (100 MHz; $CDCl_3$) 3.31 (3 H, s, NCH_3), 7.1—7.45 (10 H, m, ArH), and 8.30 (1 H, s, 3-H).

1-*Ethyl*-5,6-*diphenylpyrazin*-2(1H)-*one* (1b), m.p. 159—161 °C (Found: C, 78.1; H, 5.7; N, 10.2. $C_{18}H_{16}N_2O$ requires C, 78.25; H, 5.85; N, 10.15%); $\lambda_{max.}$ (EtOH) 264 (ε 11 000) and 345 nm (6 400); $\nu_{max.}$ (KBr) 1 650 cm^{-1} (C=O); δ_H (100 MHz; $CDCl_3$) 1.15 (3 H, t, CH_2CH_3), 3.90 (2 H, q, CH_2CH_3), 7.1—7.6 (10 H, m, ArH), and 8.33 (1 H, s, 3-H).

1-*Methyl*-5,6-*di*-p-*tolylpyrazin*-2(1H)-*one* (1c), m.p. 182—184 °C (Found: C, 78.45; H, 6.25; N, 9.6. $C_{19}H_{18}N_2O$ requires C, 78.6; H, 6.25; N, 9.65%); $\lambda_{max.}$ (EtOH) 265 (ε 15 000) and 351 nm (7 800); ν_{max} (KBr) 1 650 cm^{-1} (C=O); δ_H (100 MHz; $CDCl_3$) 2.23 (3 H, s, $CH_3C_6H_4$), 2.37 (3 H, s, $CH_3C_6H_4$), 3.30 (3 H, s, NCH_3), 6.95—7.25 (8 H, m, ArH), and 8.28 (1 H, s, 3-H); δ_C ($CDCl_3$) 21.1 (q, $CH_3C_6H_4$), 21.4 (q, $CH_3C_6H_4$), 33.7 (q, NCH_3), 128.5 (d), 128.9 (d), 129.3 (d), 133.9 (s), 134.7 (s), and 136.6 (s) (aromatic), 138.3 (s, C-5 or -6), 139.6 (s, C-6 or -5), 146.2 (d, C-3), and 156.1 p.p.m. (s, C=O).

1-*Methyl*-5-*phenylpyrazin*-2(1H)-*one* (1d), m.p. 132—133 °C (Found: C, 70.85; H, 5.3; N, 15.1. $C_{11}H_{10}N_2O$ requires C, 70.95; H, 5.5; N, 15.05%); $\lambda_{max.}$ (EtOH) 274 (ε 23 000) and 350 nm (5 000); $\nu_{max.}$ (KBr) 1 665 cm^{-1} (C=O); δ_H (100 MHz; $CDCl_3$) 3.57 (3 H, s, NCH_3), 7.3—7.9 (6 H, m, ArH and =CH–), and 8.27 (1 H, s, =CH–).

General Procedure for the Photochemical Reactions of the Pyrazin-2(1H)-ones (1a—d).—A solution of the pyrazin-2(1*H*)-one (1) (200 mg) in the corresponding alcohol (50 ml) was irradiated in a Pyrex vessel with a high-pressure mercury lamp under oxygen for 5 h at room temperature. After removal of the solvent, the residual oil was chromatographed on a silica gel column with benzene–ethyl acetate (1 : 1—4 : 1) to yield the corresponding acetamide derivative (2) and nitrile compound. Thus prepared were 1-*benzoyloxy*-1-*methoxy*-N-*methylacetamide* (2a), m.p. 84—86 °C (Found: C, 59.2; H, 5.8; N, 6.25. $C_{11}H_{13}NO_4$ requires C, 59.2; H, 5.85; N,

6.25%); $\nu_{max.}$ (KBr) 3 430 (NH), 1 725 (CO_2), 1 690 (NC=O), 1 540 (amide II), and 1 260 cm^{-1} (C–O); δ_H (100 MHz; $CDCl_3$) 2.89 (3 H, d, NCH_3), 3.60 (3 H, s, OCH_3), 6.18 (1 H, s, CH), 6.7 (1 H, br s, exchangeable with D_2O, NH), 7.4—7.7 (3 H, m, ArH), and 8.0—8.2 (2 H, m, ArH).

1-*Benzoyloxy*-N-*ethyl*-1-*methoxyacetamide* (2b), m.p. 98 °C (Found: C, 60.7; H, 6.3; N, 5.9. $C_{12}H_{15}NO_4$ requires C, 60.75; H, 6.35; N, 5.9%); $\nu_{max.}$ ($CDCl_3$) 3 420 (NH), 1 720 (CO_2), 1 680 (NC=O), 1 530 (amide II) and 1 260 cm^{-1} (C–O); δ_H (100 MHz; $CDCl_3$) 1.18 (3 H, t, CH_2CH_3), 3.32 (2 H, q, CH_2CH_3), 3.58 (3 H, s, OCH_3), 6.18 (1 H, s, CH), 6.7 (1 H, br s, exchangeable with D_2O, NH), 7.4—7.6 (3 H, m, ArH), and 8.0—8.2 (2 H, m, ArH).

1-Benzoyloxy-1-ethoxy-*N*-methylacetamide (2c), oil; $\nu_{max.}$ (film) 3 320 (NH), 1 720 (CO_2), 1 680 (NC=O), 1 540 (amide II), and 1 250 cm^{-1} (C–O); δ_H (100 MHz, $CDCl_3$) 1.24 (3 H, t, CH_2CH_3), 2.87 (3 H, d, NCH_3), 3.84 (2 H, q, CH_2CH_3), 6.29 (1 H, s, CH), 7.0 (1 H, br s, exchangeable with D_2O, NH), 7.4—7.6 (3 H, m, ArH), and 8.0—8.2 (2 H, m, ArH).

1-Benzoyloxy-1-ethoxy-*N*-ethylacetamide (2d), oil; $\nu_{max.}$ ($CDCl_3$) 3 430 (NH), 1 725 (CO_2), 1 690 (NC=O), 1 530 (amide II), and 1 270 cm^{-1} (C–O); δ_H (100 MHz; $CDCl_3$) 1.17 (3 H, t, CH_2CH_3), 1.25 (3 H, t, CH_2CH_3), 3.31 (2 H, q, CH_2CH_3), 3.86 (2 H, q, CH_2CH_3), 6.28 (1 H, s, CH), 7.0 (1 H, br s, exchangeable with D_2O, NH), 7.4—7.6 (3 H, m, ArH), and 8.0—8.2 (2 H, m, ArH). The results of elemental analyses of the photoproducts (2c and d) were not in accord with the calculated values since compounds (2c and d) decomposed during distillation (40 °C at 10^{-3} mmHg) to give benzoic acid.

1-*Methoxy*-N-*methyl*-1-*toluoyloxyacetamide* (2e), m.p. 100.5—101.5 °C (Found: C, 60.75; H, 6.4; N, 5.85. $C_{12}H_{15}NO_4$ requires C, 60.75; H, 6.35; N, 5.9%); $\nu_{max.}$ (KBr) 3 285 (NH), 1 715 (CO_2), 1 660 (NC=O), 1 575 (amide II), 1 280, and 1 255 cm^{-1} (C–O); δ_H (100 MHz; $CDCl_3$) 2.39 (3 H, s, $CH_3C_6H_4$), 2.86 (3 H, d, NCH_3), 3.56 (3 H, s, OCH_3), 6.15 (1 H, s, CH), 6.9 (1 H, br s, exchangeable with D_2O, NH), 7.22 (2 H, d, *J* 7.8 Hz, ArH), and 7.96 (2 H, d, *J* 7.8 Hz, ArH); δ_C ($CDCl_3$) 21.5 (q, $CH_3C_6H_4$), 25.8 (q, NCH_3), 57.2 (q, OCH_3), 93.6 (d, CH), 126.0 (s), 128.9 (d), 129.9 (d), and 144.2 (s) (aromatic carbons), 165.6 (s, CO_2), and 166.3 p.p.m. (s, NC=O).

General Procedure for the Reaction of the Pyrazin-2(1H)-*ones* (1) *with Singlet Oxygen*.—An oxygenated solution of the pyrazin-2(1*H*)-one (1) (200 mg) in dry solvent (50 ml) in the presence of a sensitizer (*ca.* 2 mg) was irradiated in a Pyrex tube with a halogen lamp for 2 h at room temperature or at −50 °C. After removal of the solvent, the residue was chromatographed on a silica gel column with benzene–ethyl acetate (4 : 1—9 : 1) as eluant to afford the endoperoxide (3). Thus prepared were the *endoperoxide* (3a), m.p. 103—105 °C (decomp.) (Found: C, 69.5; H, 4.75; N, 9.45. $C_{17}H_{14}N_2O_3$ requires C, 69.35; H, 4.95; N, 9.5%); $\nu_{max.}$ (KBr) 1 705 cm^{-1} (C=O); δ_H (100 MHz; $CDCl_3$) 2.60 (3 H, s, NCH_3), 6.08 (1 H, s, CH), and 7.0—7.5 (10 H, m, Ph); *m/z* 295 (QM^+).

The *endoperoxide* (3b), m.p. 112 °C (decomp.) (Found: C, 70.5; H, 5.25; N, 8.75. $C_{18}H_{16}N_2O_3$ requires C, 70.1; H, 5.25; N, 9.05%); $\nu_{max.}$ (KBr) 1 710 cm^{-1} (C=O); δ_H (100 MHz; $CDCl_3$) 0.88 (3 H, t, CH_2CH_3), 2.88—3.77 (2 H, m, CH_2CH_3), 6.08 (1 H, s, CH), and 6.9—7.7 (10 H, m, Ph); *m/z* 309 (QM^+).

The *endoperoxide* (3c), m.p. 123—124 °C (decomp.) (Found: C, 70.65; H, 5.65; N, 8.7. $C_{19}H_{18}N_2O_3$ requires C, 70.8; H, 5.6; N, 8.7%); $\nu_{max.}$ (KBr) 1 700 cm^{-1} (C=O); δ_H (100 MHz; $CDCl_3$) 2.30 (3 H, s, CH_3), 2.38 (3 H, s, CH_3), 2.60 (3 H, s, NCH_3), 6.04 (1 H, s, CH), and 6.8—7.2 (8 H, m, ArH); δ_C ($CDCl_3$) 21.4 (q, CH_3), 28.5 (q, NCH_3), 82.7 (d, CH), 90.4 (s, *C*Ph), 168.9 (s, C=O), and 178.6 (s, C=N) in addition to the peaks for aromatic carbons; *m/z* 323 (QM^+).

An oxygenated solution of the pyrazin-2(1*H*)-one (1a or b) (200 mg) in methanol (50 ml) in the presence of Methylene Blue (*ca.* 2 mg) was irradiated under the same conditions as described above. Usual work-up gave the 1 : 1 adduct (6a or b) of the endoperoxide (3a or b) and methanol. The 1 : 1 *adduct* (6a), m.p. 117—118 °C (decomp.) (Found: C, 66.4; H, 5.2; N, 8.75. $C_{18}H_{18}N_2O_4$ requires C, 66.25; H, 5.55; N, 8.6%); $\nu_{max.}$ (KBr) 3 320 (NH) and 1 710 cm^{-1} (C=O); δ_H (100 MHz; $CDCl_3$) 2.76 (3 H, s, NCH_3), 3.30 (3 H, s, OCH_3), 3.8 (1 H, br s, exchangeable with D_2O, NH), 5.43 (1 H, d, *J* 3.4 Hz, CH), and 7.05—7.6 (10 H, m, Ph); *m/z* 327 (QM^+).

The 1 : 1 adduct (4b), oil; $\nu_{max.}$ (film) 3 320 (NH) and 1 690 cm^{-1} (C=O); δ_H (100 MHz; $CDCl_3$) 0.92 (3 H, t, CH_2CH_3), 3.30 (3 H, s, OCH_3), 3.41 (2 H, q, CH_2CH_3), 3.7 (1 H, br s, exchangeable with D_2O, NH), 5.40 (1 H, d, *J* 3.6 Hz, CH), and 7.1—7.75 (10 H, m, Ph); *m/z* 341 (QM^+). The result of the elemental analysis of (4b) was not in accord with the calculated value since compound (4b) decomposed on distillation.

Crystal Data on the Acetamide (2a).—$C_{11}H_{13}NO_4$, M = 223.2, monoclinic, a = 12.216(6), b = 19.604(9), c = 4.798(2) Å, β = 99.98(2)°, U = 113.65 Å^3, D_c = 1.158 g cm^{-3}, Z = 4, space group $P2_1/n$, $F(000)$ 4.72. Intensities were measured on a PW 1100 Philips four-circle, computer-controlled diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å) using the ω–θ scanning technique (θ 2.5—25.0°, $\Delta\omega$ 1.4°, scan speed 0.05° s^{-1}, background was measured for 10 s on each side of the reflection). Of 1 501 reflections measured, 1 237 reflections with $F_o > 1.5\sigma(F_o)$ were used for the refinement procedure. The crystal structure was solved by MULTAN 80 [24] and refined by full-matrix least-squares [25] with anisotropic thermal parameters for C, N, and O atoms, and isotropic parameters for H atoms. Scattering factors for C, N, and O were taken from Cromer and Mann,[26] and for H from Stewart *et al.*[27] The final R- and R_w-values are 0.048 and 0.056, respectively {w = 1.1454/$[\sigma^2(F)_o + 0.0018(F_o)^2]$}. The lists of observed and calculated structure factors and thermal parameters are contained in Supplementary Publication No. SUP 23741 (9 pp.).*

* For details of Supplementary Publications, see Instructions for Authors (1984) in *J. Chem. Soc., Perkin Trans. 1*, 1984, Issue 1.

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Received 25*th March* 1983; *Paper* 3/476