

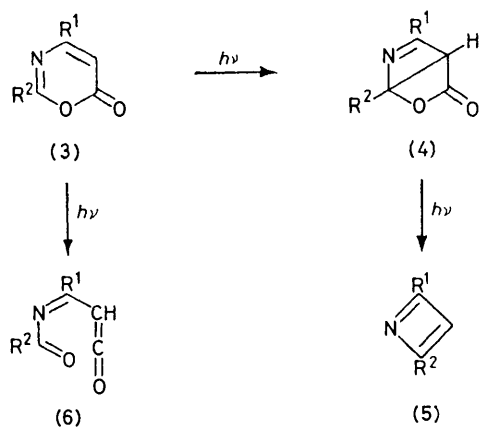
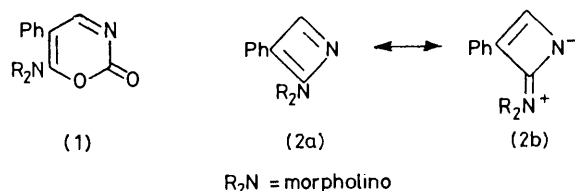
## The Chemistry of 6-Dialkylamino-2*H*-1,3-oxazin-2-ones. Reversible Thermal Ring-opening and Cycloaddition Reactions with *N*-Aryl-maleimides and 1-Diethylaminopropyne. X-Ray Crystal Structures of a 5*H*-2-Pyridone and a 1*H*-2-Pyridone<sup>1</sup>

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Flash-vacuum pyrolysis of the 1,3-oxazin-2-ones (1) and (9) gave the valence-isomeric carbamoylvinylyl isocyanates (8) and (10), respectively, which cyclised to the oxazinones at room temperature. The oxazinones reacted with *N*-arylmaleimides in a Diels–Alder fashion; with 1-diethylaminopropyne, however, the first oxazinone yielded the isomeric pyridones (17) and (21), whose structures were determined by X-ray analysis.

THE chemistry of the novel 1,3-oxazin-2-ones,<sup>2</sup> *e.g.* the morpholino-derivative (1), promises to be versatile, since they possess imine and ester functions and their structure incorporates the 1-azabuta-1,3-diene system. Furthermore, they appeared to be potential precursors of stabilised azetes, such as compound (2), if they could be induced to extrude carbon dioxide. Such fragmentations have been achieved in the case of the isomeric 1,3-oxazin-6-ones (3a)<sup>3</sup> and (3b),<sup>4</sup> which on irradiation at low temperatures gave the valence isomers (4), which in turn decomposed to mixtures of nitriles and acetylenes, probably by way of transient azetes (5).

We did not succeed in bringing about an analogous photolysis of the oxazinone (1) to give (7); the compound



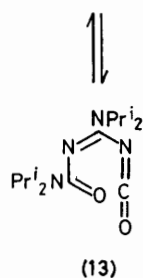
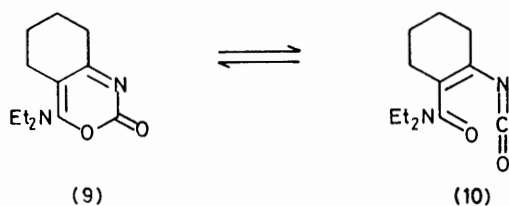
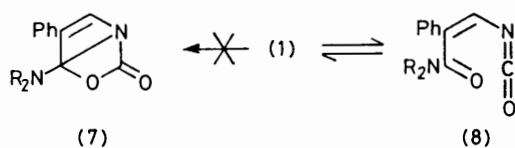
a;  $R^1 = R^2 = H$   
 b;  $R^1 = \text{Me}$ ,  $R^2 = \text{Bu}^t$

was recovered after prolonged exposure to u.v. light in various solvents. We then attempted thermal fragmentation. The oxazinone was stable in boiling benzene but decomposed completely to an intractable tar after two days in refluxing *o*-dichlorobenzene (b.p. 180 °C). Flash-vacuum pyrolysis at 650 °C and 0.007 Torr, however, while not leading to the azete (2), gave an interesting result: the pyrolysate consisted of a mixture of approximately equal amounts of the oxazinone and its precursor, the isocyanate (8).<sup>2</sup> The i.r. and <sup>1</sup>H n.m.r. spectra of the mixture remained unchanged when it was kept below -5 °C, but during 15 h at 35 °C the spectra gradually reverted to those of the oxazinone. The cyclohexeno-oxazinone (9)<sup>2</sup> behaved similarly on flash-vacuum pyrolysis, yielding a mixture which contained more than half of the valence tautomer (10). The latter was stable at -5 °C but changed completely to the cyclic form during 12 h at room temperature.

These results illustrate the use of flash-vacuum pyrolysis to produce mixtures of equilibrating isomers, which are enriched in the less stable form.<sup>5</sup> Also, there are precedents for reversible thermal electrocyclic reactions in the chemistry of 2-pyrones and their aza-analogues. The migration of substituents between positions 3 and 5 on flash-vacuum pyrolysis of 2-pyrones was rationalised by invoking the intermediacy of keten aldehydes (11), in which the aldehydic hydrogen atom underwent a [1,5]sigmatropic shift,<sup>6</sup> and the thermal rearrangement of pyran-2-thiones to thiapyran-2-ones was thought to proceed *via* thioketen aldehydes.<sup>6</sup> 2-Ethoxy-4-methyl-1,3-oxazin-6-one exists in equilibrium with ethyl  $\beta$ -isocyanatocrotonate.<sup>7</sup> In the 1,3,5-oxadiazin-2-one series, there is i.r. spectroscopic evidence for the formation of the unstable isocyanate (13) when compound (12) is thermolysed.<sup>8</sup> Photochemical ring-opening of 2-pyrones to yield transient oxovinylketens is well documented;<sup>9</sup> similarly, irradiation of the 1,3-oxazin-6-ones (3a, b) at low temperatures under certain conditions gave unstable acylimidoalkenes (6a, b).<sup>3,4</sup>

Attempts to carry out cycloaddition reactions with the morpholino-oxazinone (1) were mostly unsuccessful: the compound did not react with the electron-deficient

dienophiles dimethyl acetylenedicarboxylate or diethyl azodicarboxylate nor with the electron-rich 1-pyrrolidino-cyclohexene under mild conditions, and prolonged heating in toluene or xylene led to decomposition. These

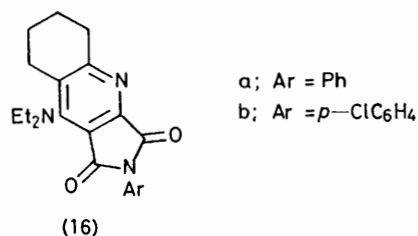
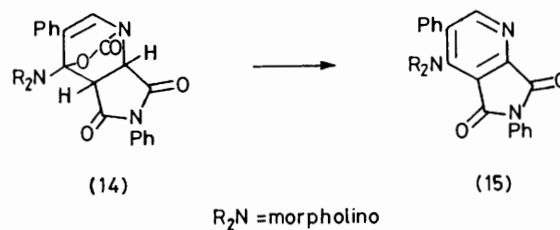


$R_2N = \text{morpholino}$

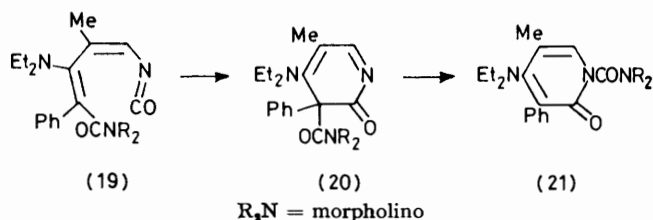
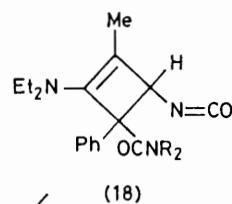
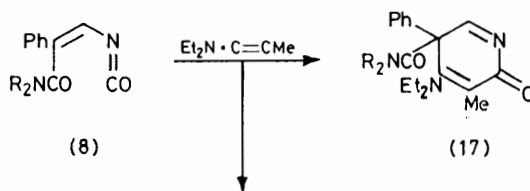
failures were not surprising as Diels-Alder reactions of 1-aza-1,3-dienes are rare.<sup>10</sup> When the oxazinone was refluxed with *N*-phenylmaleimide in *o*-dichlorobenzene for 42 h there was obtained a minute yield of a yellow product, which we formulate as the pyridine derivative (15) on the basis of its mass spectrum and <sup>1</sup>H n.m.r. spectrum, which exhibited a one-proton singlet at low field. The compound is most likely formed by successive loss of carbon dioxide and hydrogen from the initial Diels-Alder adduct (14). Analogous products (16a and b) were obtained in better yields from the reactions of the cyclohexeno-oxazinone (9) with *N*-phenyl- and *N*-*p*-chlorophenyl-maleimide, respectively.

The reaction of the oxazinone (1) with the ynamine 1-diethylaminopropyne took a different course. Heating the components in benzene afforded a yellow and a colourless adduct in 35 and 40% yield, respectively,

which were separated by fractional crystallisation. The i.r. spectrum of the yellow product exhibited carbonyl absorptions at 1 652 and 1 615  $\text{cm}^{-1}$  and its <sup>1</sup>H n.m.r. spectrum showed the presence of methyl, diethylamino, morpholino, and phenyl groups, and of an isolated olefinic proton. The colourless isomer showed carbonyl bands at 1 695 and 1 652  $\text{cm}^{-1}$ ; its <sup>1</sup>H n.m.r. spectrum resembled that of the first compound, except that it exhibited allylic coupling between the olefinic proton



and the protons of the methyl group. The structures of the two adducts were solved by X-ray crystallography (see below), which showed that the yellow compound was



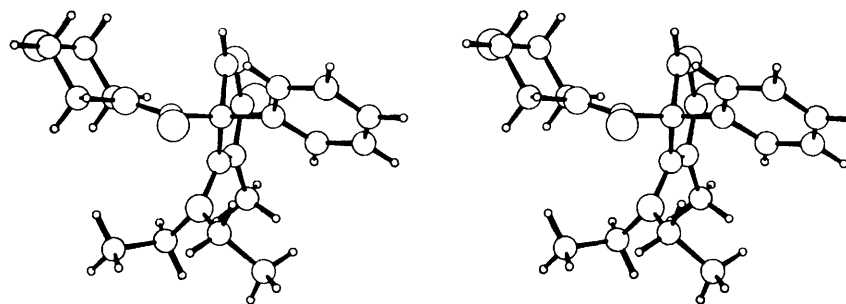


FIGURE 1 A stereo-drawing of compound (17)

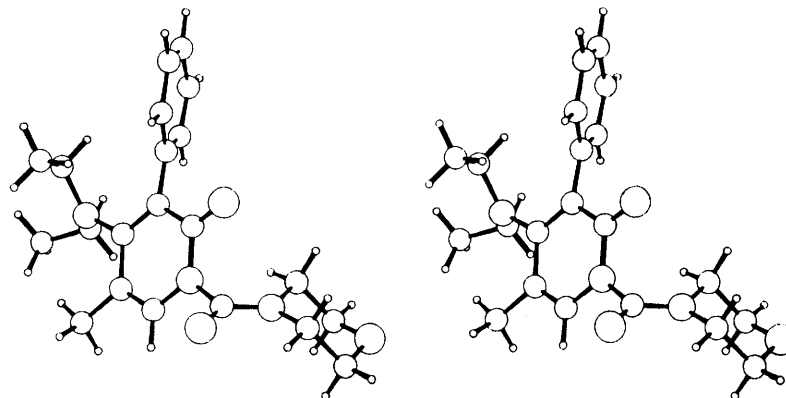


FIGURE 2 A stereo-drawing of compound (21)

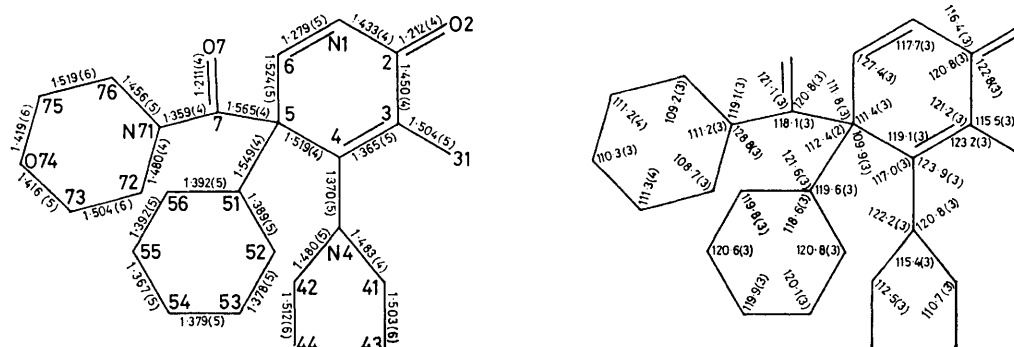


FIGURE 3 Intramolecular bond lengths (Å) and angles (°) for compound (17)

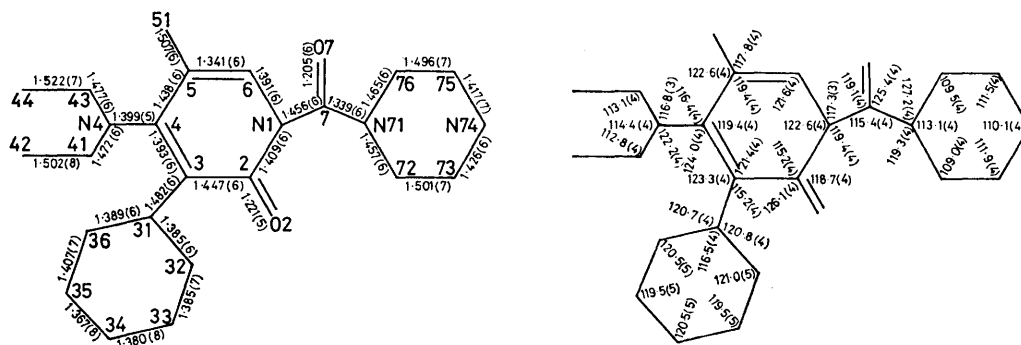


FIGURE 4 Intramolecular bond lengths (Å) and angles (°) for compound (21)

the pyridin-2(5*H*)-one (17) \* and the colourless isomer the pyridin-2(1*H*)-one (21). With hindsight, all the signals in the <sup>13</sup>C n.m.r. spectra of the two adducts could be assigned (see Experimental section).

We suggest that the formation of both products proceeds by initial valence isomerisation to the isocyanate (8). Diels–Alder addition to the ynamine results in the yellow compound (17); similar reactions of styryl isocyanates with ynamines have been reported.<sup>11</sup> A 2π + 2π cycloaddition<sup>12</sup> of the ynamine to the olefinic double bond of the isocyanate produces the cyclobutene (18), which undergoes electrocyclic ring-opening to the azaheptatriene (19). Electrocyclisation of the latter results in the pyridin-2(3*H*)-one (20), which is converted into the more stable, fully conjugated colourless product (21) by a [1,5]sigmatropic shift of the morpholino-carbonyl group.† Compound (17) may not undergo an analogous rearrangement, because the required suprafacial [1,3]shift is forbidden by the rules of orbital symmetry.

*Description of Structures (17) and (21).*—Figures 1 and 2 are stereodrawings of the molecules of compounds (17) and (21) respectively. The atomic labelling in the two structures together with the appropriate intramolecular bond lengths and angles are shown schematically in Figures 3 and 4. Further details of the molecular geometries are given in Table 1.

TABLE 1

Molecular geometry for compounds (17) and (21)

(a) Least-squares planes AX + BY + CZ = D defined by atomic positions and distances of the atoms (Å) from these planes; X, Y, and Z refer to the axes a\*, b, and c

Plane (i): Pyridone ring, N(1), C(2)–C(6) inclusive					
	(17)	(21)	Atom	(17)	(21)
A	0.9611	0.7332	N(1)	–0.046	–0.028
B	–0.0390	–0.6596	C(2)	0.046	0.032
C	0.2733	0.1654	C(3)	0.031	–0.019
D	4.0628	1.3384	C(4)	–0.097	0.000
			C(5)	0.090	0.004
			C(6)	–0.024	0.010
Plane (ii): Phenyl group, C(51)–C(56) and C(31)–C(36) inclusive					
	(17)	(21)	Atom	(17)	(21)
A	0.0459	0.2530	C–1	–0.025	–0.009
B	–0.9664	0.9607	C–2	0.015	0.000
C	0.2529	–0.1140	C–3	0.005	0.008
D	–3.0995	–0.0119	C–4	–0.014	–0.007
			C–5	0.003	–0.002
			C–6	0.017	0.010
Phase (iii): Morpholinocarbonyl group					
	(17)	(21)	Atom	(17)	(21)
A	0.2133	0.4775	C(7)	–0.010	0.012
B	–0.8958	0.0810	O(7)	–0.088	–0.038
C	–0.3900	0.8749	N(71)	0.0634	–0.044
D	–6.9554	3.1311	C(72)	–0.095	–0.022
			C(76)	0.0612	0.052
			C(5)	0.068	
			N(1)		0.041

\* The structure of this compound incidentally provides further proof of the structure of the oxazinone (1) and hence for the orientation of the amic acid produced from morpholine and phenyl-maleic anhydride.<sup>2</sup>

† [1,5] Migrations of acyl groups from carbon to nitrogen occur readily: M. Franck-Neumann and C. Dietrich Buchecker, *Tetrahedron Lett.*, 1976, 2069.

TABLE 1 (continued)

Dihedral angles (°) between planes		
Plane (i) and (ii)	(17)	(21)
(i) and (iii)	81.3	116.7
(ii) and (iii)	83.0	63.8
	39.0	84.3
(b) Torsion angles (°) for morpholino-ring		
	(17)	(21)
N(71)–C(72)–C(73)–O(74)	57.2	56.0
C(72)–C(73)–O(74)–C(75)	–59.6	–59.5
C(73)–O(74)–C(75)–C(76)	60.5	59.8
O(74)–C(75)–C(76)–N(71)	–58.1	–56.0
C(75)–C(76)–N(71)–C(72)	56.2	53.5
C(76)–N(71)–C(72)–C(73)	–55.6	–53.6

The pyridin-2(5*H*)-one ring in (17) and the pyridin-2(1*H*)-one ring in (21) are almost planar, the maximum displacements being –0.097 Å for C(4) in (17) and 0.032 Å for C(2) in (21) respectively. The endocyclic bond lengths in the compounds are consistent with the formulations shown.

The phenyl rings, at C(5) in (17) and C(3) in (21) are planar and make dihedral angles of 81.3° and 116.7° with the least-squares planes defined by the respective pyridone rings.

The morpholino-rings in both compounds adopt the chair conformation with asymmetry parameters,<sup>13</sup> ΔC<sub>s</sub>[N(1)] = 0.81°, ΔC<sub>2</sub>[N(1)–C(72)] = 1.27°, C<sub>2</sub>[C(72)–C(73)] = 4.15° in (17) and C<sub>s</sub>[N(1)] = 0.18°, C<sub>2</sub>[N(1)–C(72)] = 3.04°, C<sub>s</sub>[C(72)–C(73)] = 6.10° in (21). In both compounds the geometry in the vicinity of C(7) and N(71) is approximately planar due to the considerable double-bond character of the C(7)–N(71) linkage; 1.36 Å in (17) and 1.33 Å in (21) [compare with the value of 1.45 Å for the N(1)–C(7) bond in (21)].

There are no intermolecular contacts that are significantly shorter than the sum of the corresponding van der Waals' radii.

## EXPERIMENTAL

For general remarks, see the preceding paper. The apparatus used for the flash-vacuum photolyses has been described.<sup>14</sup> The vapour of the oxazinones, obtained by sublimation at ca. 150 °C and 0.007 Torr, was passed through a Pyrex tube encased in an oven at temperatures in the range 400–800 °C and the product was condensed at a concave cold finger at –78 °C. The pyrolysate was dissolved in dry dichloromethane, which was then removed at room temperature under reduced pressure. The pyrolyses were performed over a range of oven temperatures in order to find the optimum conditions.

Flash-vacuum pyrolysis of 6-morpholino-5-phenyl-1,3-oxazin-2-one (1) (0.516 g) at 650–675 °C gave a pyrolysate (0.456 g), whose i.r. spectrum had ν<sub>max</sub> 2 250 (NCO), 1 740 (CO of oxazinone), and 1 640 cm<sup>–1</sup> (amide CO). There was no change during 15 h at room temperature. <sup>1</sup>H n.m.r.: δ 7.7 (s, 1 H, CH of oxazinone), 7.2 (br s, 10 H, 2 × Ph, due to oxazinone and isocyanate), 6.58 (s, 1 H, CH of isocyanate), 3.7 (br s, 8 H, morpholino-group of oxazinone), and 3.65–3.2 (m, 8 H, morpholino-group of the isocyanate). Integration of the signals due to CH indicated that the mixture contained ca. 50% of the isocyanate (8). The n.m.r. spectrum changed to that of the oxazinone after 16 h at 35 °C.

The best yield of the isocyanate (10) was obtained when

4-diethylamino-5,6,7,8-tetrahydro-3,1-benzoxazin-2-one (9) (0.172 g) was pyrolysed at 475–500 °C. The pyrolysate (0.160 g) showed  $\nu_{\max}$  2 265 (NCO), 1 745 (w, CO of oxazinone), and 1 640  $\text{cm}^{-1}$  (CO of amide). The spectrum did not change when the sample was kept at 0 °C, but it reverted completely to that of the oxazinone (9) after 12 h at room temperature.

**Reactions with N-Arylmaleimides.**—(a) *4-Morpholino-5-phenylpyridine-2,3-dicarboxylic acid N-phenylimide* (15). A mixture of the oxazinone (1) (0.258 g, 1 mmol), *N*-phenylmaleimide (0.173 g, 1 mol equiv.), and *o*-dichlorobenzene (10 ml) was boiled under reflux for 42 h. The solvent was removed and the residue was chromatographed on silica gel, using light petroleum containing increasing amounts of ethyl acetate as eluant. The pale-yellow product (0.012 g, 3%) had m.p. 149 °C,  $\nu_{\max}$  1 720, 1 610, 1 555, and 1 118  $\text{cm}^{-1}$  (morpholine ether);  $\delta$  8.59 (s, CH), 7.6–7.3 (m, 2 × Ph), and 3.86 (s, 8 H, morpholine) [Found: *m/e* 385.14 ( $M^+$ ).  $\text{C}_{23}\text{H}_{19}\text{N}_3\text{O}_3$  requires 385.14].

(b) *4-Diethylamino-5,6,7,8-tetrahydroquinoline-2,3-dicarboxylic acid N-phenylimide* (16a). A solution of the oxazinone (9) (0.222 g, 1.0 mmol) and *N*-phenylmaleimide (0.173 g, 1 mol equiv.) in *o*-dichlorobenzene (10 ml) was refluxed for 15 h. The solvent was removed *in vacuo* and the product (0.172 g, 49%) was isolated by thick-layer chromatography [ $R_F$  0.72 in light petroleum–ethyl acetate (3 : 2)]. It crystallised from benzene as fluffy yellow needles, m.p. 154–155 °C,  $\nu_{\max}$  1 765, 1 702, 1 615, and 1 565  $\text{cm}^{-1}$ ;  $\delta$  7.4 (br s, Ph), 3.74 (q, 2 ×  $\text{CH}_2$ ), 3.2–2.7 (m, 4 H) and 2.0–1.8 (m, 4 H) (cyclohexeno), and 1.24 (t, 2 × Me); *m/e* 349 ( $M^+$ ) (Found: C, 72.5; H, 6.7; N, 11.7.  $\text{C}_{21}\text{H}_{23}\text{N}_3\text{O}_2$  requires C, 72.2; H, 6.65; N, 12.0%).

(c) *4-Diethylamino-5,6,7,8-tetrahydroquinoline-2,3-dicarboxylic acid N-p-chlorophenylimide* (16b). A solution of the oxazinone (9) (0.666 g, 3 mmol) and *N-p*-chlorophenylmaleimide (0.622 g, 1 mol equiv.) in *o*-dichlorobenzene (20 ml) was refluxed for 10 h. The solvent was removed *in vacuo* and the product (0.438 g, 38%) was isolated by thick-layer chromatography [ $R_F$  0.7 in benzene–light petroleum (1 : 1), as yellow needles (from benzene–light petroleum),  $\nu_{\max}$  1 764, 1 730, 1 710, 1 615, and 1 570  $\text{cm}^{-1}$ ;  $\delta$  7.44 (d, 2 H) and 7.29 (d, 2 H) ( $J$  9 Hz) (Ar), 3.73 (q, 2 ×  $\text{CH}_2$ ), 3.2–2.7 (m, 4 H) and 2.05–1.6 (m, 4 H) (cyclohexeno), and 1.23 (t, 2 × Me); *m/e* 385, 383 ( $M^+$ ) (Found: C, 65.6; H, 5.9; N, 10.6.  $\text{C}_{21}\text{H}_{22}\text{ClN}_3\text{O}_2$  requires C, 65.7; H, 5.8; N, 10.95%).

**Reaction of the Oxazinone (1) with 1-Diethylaminopyrpyne.**—A solution of the oxazinone (1.29 g, 5 mmol) and the ynamine (0.555 g, 1 mol equiv.) in benzene (20 ml) was refluxed for 14 h and then cooled. Light petroleum (b.p. 60–80 °C) was added to incipient cloudiness, whereupon *4-diethylamino-3-methyl-5-morpholinocarbonyl-5-phenylpyridin-2(5H)-one* (17) (0.65 g, 35%) crystallised as yellow needles, m.p. 179–181 °C (from benzene–light petroleum),  $\nu_{\max}$  1 652 (pyridone CO), 1 620 (amide CO), 1 595, 1 570, and 1 118  $\text{cm}^{-1}$ ;  $\lambda_{\max}$  (EtOH) 242, 266, 385, and 400–450 nm;  $\delta$  8.42 (s, CH), 7.27 (s, Ph), 4.1–3.3 (m, 8 H, morpholine), 3.2 (q, 2 ×  $\text{CH}_2$ ) and 1.01 (t, 2 × Me) ( $J$  7 Hz) (2 × Et) and 2.09 (s, Me);  $^{13}\text{C}$  n.m.r. (see Figure 3 for numbering):  $\delta$  172.98 (2), 169.40 (7), 165.53 (4), 160.72 (5), 135.33 (6), 128.88 and 128.65 (51–56), 107.36 (3), 66.61 (73 and 75), 62.39 (41), 45.73 (42), 43.68 (72 and 76), 14.60 (31), and 13.25 (43 and 44); *m/e* 369 ( $M^+$ ) (Found: C, 68.3; H, 7.6; N, 11.3.  $\text{C}_{21}\text{H}_{27}\text{N}_3\text{O}_3$  requires C, 68.3; H, 7.4; N, 11.4%). The filtrate was concentrated to half its

volume and again treated with light petroleum until turbid.

*4-Diethylamino-5-methyl-1-morpholinocarbonyl-3-phenylpyridin-2-(1H)-one* (21) (0.75 g, 40%) crystallised as colourless needles, m.p. 158–160 °C,  $\nu_{\max}$  1 695 (pyridone CO), 1 650 (amide CO), 1 615, 1 598, and 1 115  $\text{cm}^{-1}$ ;  $\lambda_{\max}$  (EtOH) 230, 255, and 315 nm;  $\delta$  7.4–7.1 (m, Ph), 7.03 (d, CH) and 2.04 (d, Me) ( $J$  1 Hz) (the doublet at 7.03 collapsed to a singlet on irradiation at  $\delta$  2.04), 3.4–3.1 (m, 8 H, morpholino), 2.69 (q, 2 ×  $\text{CH}_2$ ) and 0.93 (t, 2 × Me) ( $J$  7 Hz) (2 × Et);  $^{13}\text{C}$  n.m.r. (see Figure 4):  $\delta$  160.72 (2), 158.85 (7), 153.28 (4), 136.15 (31), 130.47 and 127.88 (32–36), 126.89 (6), 122.55 (3), 116.57 (5), 66.43 and 66.14 (73 and 75), 47.14 (41), 45.33 (72 and 76), 44.5 (43), 17.06 (51), and 13.48 (42 and 44); *m/e* 369 ( $M^+$ ) (Found: C, 68.4; H, 7.4; N, 11.2%).

**Crystal Data.**—Compound (17),  $\text{C}_{21}\text{H}_{27}\text{N}_3\text{O}_3$ ,  $M = 369.2$ , monoclinic,  $a = 11.105(8)$ ,  $b = 8.671(6)$ ,  $c = 20.625(15)$  Å,  $\beta = 97.67(1)^\circ$ ,  $U = 1 968.2$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.25$  g  $\text{cm}^{-3}$ ,  $D_m = 1.27$  g  $\text{cm}^{-3}$  (by flotation in a mixture of carbon tetrachloride and benzene),  $F(000) = 792$ . Space group  $P2_1/n$  (alternative orientation of  $P2_1/c$ , No. 14),  $\mu(\text{Cu-K}\alpha) = 8.03$   $\text{cm}^{-1}$ .

Compound (21),  $\text{C}_{21}\text{H}_{27}\text{N}_3\text{O}_3$ , monoclinic,  $a = 6.354(2)$ ,  $b = 14.100(5)$ ,  $c = 21.445(8)$  Å,  $\beta = 93.25(2)^\circ$ ,  $U = 1 918.1$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.28$ ,  $D_m = 1.28$  g  $\text{cm}^{-3}$  (by flotation in a mixture of carbon tetrachloride and benzene). Space group  $P2_1/c$ , No. 14.

Compound (17) forms yellow prismatic crystals, whereas those of compound (21) are colourless. Preliminary unit-cell dimensions and space-group information were obtained from precession photographs in both cases; Ni-filtered copper radiation was used throughout the data collection. Accurate cell dimensions were obtained by least-squares refinement of the  $\theta$  values of the  $\text{Cu-K}\alpha_1$  components ( $\lambda = 1.5405$  Å) of 20 reflections measured on a Hilger and Watts Y290 automated four-circle diffractometer.

Intensity data were also measured on this instrument over the ranges  $1^\circ \leq \theta \leq 70^\circ$  for (17) and  $1^\circ \leq \theta \leq 60^\circ$  for (21) by use of the  $\omega/2\theta$  step scanning technique. In the case of (17) steps of  $0.01^\circ$  in  $\omega$  were used with a count time of 1 s  $\text{step}^{-1}$  and a peak width of 90 steps plus a dispersion correction. Stationary background counts were measured at either end of each scan for one-tenth of the total scan time. For compound (21) steps of  $0.02^\circ$  in  $\omega$  were used but the net integrated intensity was obtained with a 'moving window' technique.<sup>15</sup> For both data sets gradual variations in the experimental conditions were monitored throughout the data collection by measuring reference reflections after every 50 measurements and the intensity sums of these reference reflections were used to scale the observed intensities by interpolation between groups of references. 3 172 Independent reflections were obtained for compound (17) of which 2 855 were considered significant, having  $I \geq 3\sigma(I)$ ; values for (21) are 3 177 and 2 656. Symmetry related reflections were collected for both data sets to check for internal consistency and weighed averages for these reflections were incorporated in the sets of independent reflections; agreement residuals were 2.46% for (17) and 3.48% for (21). Lorentz and polarisation corrections were applied to all reflections but no corrections were made for absorption.

**Structure Solution and Refinement.**—Both compounds were solved without difficulty using 'MULTAN'<sup>16</sup> to determine an initial set of phases from which the complete structure was determined using Fourier synthesis.

Refinement of both structures was carried out using a full-matrix least-squares technique and initially all non-hydrogen atoms were treated isotropically. Most of the hydrogen atoms were located from difference Fourier syntheses as diffuse electron density maxima. In subsequent computations the hydrogen atoms were placed in calculated positions assuming a C-H bond length of 1.0 Å; no attempts were made to refine the positional or thermal parameters of the hydrogen atoms. Further refinement with the non-hydrogen atoms treated anisotropically and using only the significant reflections gave conventional  $R$  values of 0.083 for (17) and 0.095 for (21). A weighting scheme  $w = a_3$  for  $|F_o| < F_{\min}$ , else  $w = [1 - \exp(-a_0 \sin^2\theta/\lambda^2)] / (a_1 + |F_o| + a_2|F_o|^2)$  was used to make the average values of  $w\Delta^2$  uniform when analysed in batches of increasing  $|F_o|$  and  $\sin\theta/\lambda$ .

Difference Fourier syntheses computed after the final refinement cycles showed no significant details and structure factor calculations for the insignificant reflections showed no outstanding discrepancies. Throughout the structure factor calculations the atomic scattering factors listed in reference 17 were used. Computations were carried out on an IBM360 computer at University College, London, and on the CDC6600 computer at the University of London Computer Centre, using the Birkbeck College crystallographic program library. The least-squares refinement program is a modified version of that originally written by D. W. J. Cruickshank and J. G. F. Smith. Final atomic coordinates for (17) and (21) are given in Tables 2 and 3.

TABLE 2

Positional parameters for the non-hydrogen atoms in (17) with estimated standard deviations in parentheses

Atom	$x$	$y$	$z$
N(1)	0.174 0(3)	0.359 5(4)	0.420 2(2)
C(2)	0.155 7(3)	0.453 4(5)	0.475 2(2)
C(3)	0.161 7(3)	0.620 1(4)	0.471 5(2)
C(4)	0.182 7(3)	0.692 5(4)	0.415 3(2)
C(5)	0.278 0(3)	0.598 5(4)	0.361 3(1)
C(6)	0.206 2(3)	0.426 7(4)	0.370 0(2)
O(2)	0.134 8(2)	0.385 7(4)	0.523 9(1)
C(31)	0.150 2(4)	0.704 5(5)	0.534 0(2)
N(4)	0.162 9(3)	0.846 4(3)	0.403 4(1)
C(41)	0.056 5(4)	0.925 4(5)	0.424 9(2)
C(42)	0.256 0(4)	0.947 9(4)	0.380 8(2)
C(43)	-0.021 1(4)	0.997 5(6)	0.367 7(2)
C(44)	0.337 1(4)	1.022 3(5)	0.436 9(2)
C(51)	0.368 1(3)	0.605 7(4)	0.364 8(2)
C(52)	0.438 5(3)	0.638 9(5)	0.424 0(2)
C(53)	0.563 5(3)	0.644 9(5)	0.428 7(2)
C(54)	0.620 3(3)	0.614 4(5)	0.374 6(2)
C(55)	0.552 8(3)	0.575 3(5)	0.316 7(2)
C(56)	0.426 5(3)	0.568 3(4)	0.311 3(2)
C(7)	0.161 4(3)	0.653 6(4)	0.293 5(1)
O(7)	0.215 7(2)	0.723 4(3)	0.255 7(1)
N(71)	0.042 3(3)	0.615 9(4)	0.277 5(1)
C(72)	-0.044 7(3)	0.558 9(5)	0.320 5(2)
C(73)	-0.115 3(4)	0.426 6(6)	0.287 0(2)
O(74)	-0.177 6(3)	0.471 6(4)	0.225 5(1)
C(75)	-0.093 6(4)	0.522 6(6)	0.183 9(2)
C(76)	-0.020 0(4)	0.659 0(5)	0.213 5(2)

Satisfactory tensor analyses of the anisotropic thermal vibration parameters were obtained in all cases.

Observed and calculated structure factors, anisotropic thermal parameters, and calculated hydrogen atom coordinates are contained in a Supplementary Publication [SUP No. 23127 (33 pages)]\*

\* For details of the Supplementary Publications scheme, see Notice to Authors No. 7, *J. Chem. Soc., Perkin Trans. 1*, 1980, Index issue.

TABLE 3

Positional parameters for the non-hydrogen atoms of (21). Estimated standard deviations are given in parentheses

Atom	$x$	$y$	$z$
N(1)	0.341 5(6)	0.071 7(3)	0.115 3(2)
C(2)	0.318 2(7)	0.078 4(3)	0.180 0(2)
C(3)	0.162 1(7)	0.015 9(3)	0.204 3(2)
C(4)	0.058 3(7)	-0.051 8(3)	0.166 6(2)
C(5)	0.099 2(7)	-0.056 7(3)	0.101 4(2)
C(6)	0.239 2(7)	0.003 0(3)	0.078 3(2)
O(2)	0.424 3(5)	0.136 5(2)	0.210 1(2)
C(31)	0.113 6(7)	0.033 4(3)	0.270 1(2)
C(32)	-0.086 4(8)	0.061 1(3)	0.285 2(2)
C(33)	-0.131 7(9)	0.078 3(4)	0.346 6(3)
C(34)	0.023 1(10)	0.067 0(4)	0.393 7(2)
C(35)	0.222 3(9)	0.040 5(4)	0.380 3(2)
C(36)	0.269 2(8)	0.024 6(3)	0.317 9(2)
N(4)	-0.076 4(6)	-0.120 9(2)	0.188 8(2)
C(41)	-0.038 2(8)	-0.165 8(3)	0.250 4(2)
C(42)	0.182 1(9)	-0.203 6(4)	0.260 6(2)
C(43)	-0.300 8(7)	-0.114 6(3)	0.167 3(2)
C(44)	-0.397 1(9)	-0.210 3(4)	0.149 7(3)
C(51)	0.006 2(9)	-0.132 5(4)	0.058 7(2)
C(7)	0.503 2(8)	0.127 7(3)	0.087 0(2)
O(7)	0.650 0(6)	0.087 6(3)	0.065 5(2)
N(71)	0.465 9(6)	0.221 0(3)	0.083 7(2)
C(72)	0.288 0(8)	0.271 8(3)	0.107 6(3)
C(73)	0.204 5(9)	0.340 6(4)	0.058 9(3)
O(74)	0.364 1(6)	0.403 9(2)	0.040 1(2)
C(75)	0.530 5(9)	0.352 3(4)	0.014 9(2)
C(76)	0.628 5(8)	0.284 1(4)	0.061 4(2)

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