Oxazol-5(4*H*)-ones. Part 7.[1] New Synthesis of Oxazolo[5,4-*b*]pyridines

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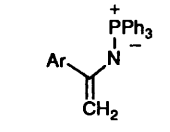
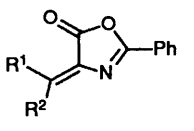
Oxazolo[5,4-*b*]pyridines **4** are synthesized by heating the iminophosphoranes **1** and alkylideneoxazol-5(4*H*)-ones **2**. At room temperature the reaction of 4-ethoxymethyleneoxazol-5(4*H*)-one **2f** with iminophosphorane **1a** yields the enamino lactone **6**, which is, in turn, transformed by heating in acetic acid into the 2(1*H*)-pyridone **7**.

The reactivity of oxazol-5(4*H*)-ones with phosphorus ylides has been under study by our research group over the last few years. One finding is that 4-alkyl- and 4-aryloxazol-5(4*H*)-ones react with phosphoranes at the carbonyl group: two competing reaction paths were observed affording substituted oxazole derivatives and stabilized phosphoranes respectively.[2] Again, the reaction of 4-alkylideneoxazol-5(4*H*)-ones and ethyl 3-oxo-4-triphenylphosphoranylidenebutyrate afforded two different products, *i.e.* substituted benzoxazole derivatives and cyclohexane-1,3-dione ylides.[1]

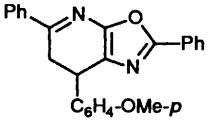
We now report a new synthesis of oxazolo[5,4-*b*]pyridines based on the easy reaction of *N*-arylvinyliminophosphoranes with 4-alkylideneoxazol-5(4*H*)-ones. Oxazolo[5,4-*b*]pyridines are heterocyclic compounds of general interest since many derivatives are known to have antiinflammatory[3] and antibacterial properties[4] and to be active on the central nervous system.[5] Accordingly, several synthetic approaches to these compounds have already been reported.[3,4,6] A common feature of these methods is to start from pyridine derivatives, which are not, as a rule, readily available, particularly when a specific substitution pattern is needed. In many cases our synthesis starting from 4-alkylideneoxazol-5(4*H*)-ones overcomes this drawback. Another route to oxazolo[5,4-*b*]pyridines was recently reported[7] but our results cast some doubts on the validity of this synthesis (see later).



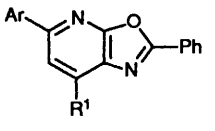
1a Ar = Ph
1b Ar = *p*-MeC$_6$H$_4$



2a R^1 = *p*-MeOC$_6$H$_4$, R^2 = H
2b R^1 = *p*-ClC$_6$H$_4$, R^2 = H
2c R^1 = Ph, R^2 = H
2d R^1 = Me, R^2 = H
2e R^1 = Me, R^2 = OEt
2f R^1 = H, R^2 = OEt



3a



4a R^1 = *p*-MeOC$_6$H$_4$, Ar = Ph
4b R^1 = *p*-ClC$_6$H$_4$, R^2 = Ph
4c R^1 = Ph, R^2 = Ph
4d R^1 = Me, Ar = *p*-MeC$_6$H$_4$
4e R^1 = *p*-MeOC$_6$H$_4$, Ar = *p*-MeC$_6$H$_4$
4f R^1 = Me, Ar = Ph
4g R^1 = H, Ar = Ph

Results and Discussion

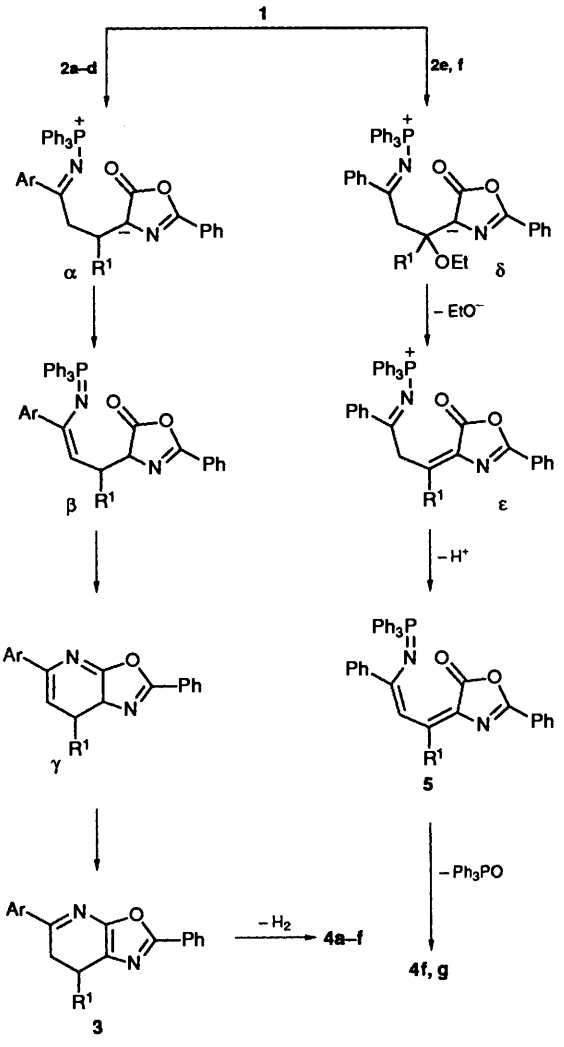
Phosphoranes **1** and oxazolones **2** react smoothly in refluxing benzene or anisole within 2–48 hours. Starting from **1a** and **2a** a reaction mixture was obtained from which the 6,7-dihydrooxazolo[5,4-*b*]pyridine **3a** was isolated by chromatography, together with a major amount of the corresponding fully aromatic compound **4a**. In fact we were never able to obtain **3a** in a completely pure form since it underwent a slow spontaneous oxidation to **4a** even during the chromatographic process. Thus **3a** was characterized only by ^{1}H and ^{13}C NMR spectra. In the former spectra a clear ABX pattern (δ_A 3.39, δ_B 3.47, δ_X 4.38; J_{AX} 10.7, J_{BX} 5.9, J_{AB} 17.2 Hz) is associated with the hydrogen atoms on C-6 and C-7. These two carbon atoms respectively correspond to signals at δ 30.2 and 36.9 in the ^{13}C NMR spectrum. Due to the lability of the primary reaction products it was decided to perform later experiments by adding an oxidizing agent directly to the crude reaction mixture. Dichlorodicyanoquinone was found satisfactory and, using this technique, products **4b–f** were obtained in good yields from the corresponding reactants (Table 1).

Scheme 1 depicts a rationalization of our results. Vinyliminophosphoranes are ambident nucleophiles and there is ample literature which shows that in most cases they react as carbon nucleophiles rather than nitrogen nucleophiles.[8] In our case too, the first step of the reaction can be envisaged as an addition to the exocyclic double bond of oxazolone **2**. The dipolar intermediate α thus produced is transformed into β by hydrogen shift and then into γ by an aza-Wittig reaction. Tautomerization of γ affords the dihydro-derivatives **3**. As expected, and in good agreement with the above picture, treatment of the 4-ethoxymethyleneoxazol-5(4*H*)-ones **2e–f** with **1a** under the usual conditions (refluxing anisole) directly

Table 1 Reaction conditions

Reagents		Conditions		Product **4**	Column chromatography[a]
1	**2**	Solvent	Time/h	[Yields (%)]	eluent (ratio)
a	**a**	anisole	6	**a** (48)	a (2:3)
a	**b**	benzene	48	**b** (74)	a (1:4)
a	**c**	benzene	6	**c** (78)	a (2:3)
b	**d**	benzene	4	**d** (49)	a (1:4)
b	**a**	anisole	48	**e** (64)	b
a	**d**	benzene	2	**f** (75)	a (2:3)
a	**e**	anisole	24	**f** (70)	b
a	**f**	anisole	24	**g** (77)	a (2:3)

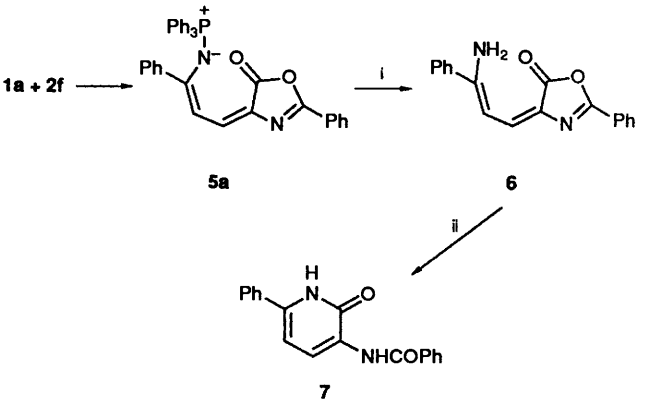
[a] a: AcOEt–C$_6$H$_{12}$; b: C$_6$H$_{14}$–CH$_2$Cl$_2$ (1:0–0:1 v/v).



Scheme 1

affords the corresponding oxazolopyridines **4f–g**. In this case after the nucleophilic addition of the iminophosphorane (intermediate δ) ethoxide was eliminated producing ε from which products **5** are formed on deprotonation of the CH_2 group. The aza-Wittig reaction of compounds **5** affords **4f–g**. This reaction path is further confirmed by an experiment involving treatment of **1a** with **2f** at room temperature. Under these mild conditions product **5a** (Scheme 2) did not cyclize further and could be isolated, although in impure form, and characterized by ^{1}H NMR spectroscopy and mass spectrometry (see Experimental section). As expected, **4g** formed readily when **5a** was heated in refluxing anisole. Compound **5a** tended to hydrolyse easily and, in fact, hydrolysis occurred spontaneously, resulting in the stable enaminolactone **6** during an attempt to perform a chromatographic purification. The structure of **6** was confirmed by IR (ν_{CO} 1740 cm^{-1}) and ^{1}H NMR spectroscopy; this latter showed evidence that a mixture of two main stereoisomers was formed (AX system at δ 6.42, 7.08; *J* 12.6 and AB system centred at δ 7.15). On heating in refluxing acetic acid, **6** was transformed into the 2(1*H*)-pyridone **7**.

The structure of the substituted oxazolo[5,4-*b*]pyridines **4** is clearly demonstrated by their ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR spectra of **4a, b, c, e** show, besides the expected signals for the aryl substituents, a singlet in the δ 7.90–8.00 range associated with the H-atom on the pyridine nucleus. In the case of **4a** the 2,2′-hydrogens on the *p*-methoxyphenyl ring and on the 5-phenyl group are clearly detectable. A NOESY experiment



Scheme 2 *Reagents and conditions:* i, SiO_2(AcOEt); ii, AcOH, heat

evidenced the expected interaction of these H-atoms with 6-H. The ^{1}H NMR spectra of **4d** and **4f** show a further singlet at δ 2.7, corresponding to the methyl group in position 7. Finally in the case of **4g** an AB pattern is present with the lowerfield (7-H) partially overlapped by the aryl hydrogens (δ 7.83, *J* 9.1 Hz, 6-H; δ *ca.* 8.1, 7-H). The ^{13}C NMR spectrum of **4a** shows signals in the expected ranges, in good agreement with the published data of an extensive study of NMR spectroscopic features of the azolopyridine heterocycles.[9] The above analytical and spectroscopic evidence (Table 2) can be deemed to be conclusive of the structure of products **4**. However a recent publication[7] claims, among other things, that the synthesis of compound **4a–c** has been brought about by the general reaction of the corresponding alkylideneoxazolones **2a–c** and *N*-phenacylpyridinium salts in the presence of ammonium acetate, according to an extension of the synthesis of substituted pyridines;[10] however the physical and spectroscopic data reported for compounds **4a–c** do not correspond to our results. Moreover, in our hands the described reaction failed to give the claimed outcome. To rule out any possible doubt concerning our data the structure of compound **4f**, which gave particularly nice crystals, was confirmed by single crystal X-ray analysis. Positional parameters for all 36 atoms of **4f** are given in Table 3; the corresponding atomic displacement parameters (thermal parameters) have been deposited at the Cambridge Crystallographic Data Centre.* A portion of the derived molecular geometry is reported in Table 4, and the configuration of the molecule, as observed in the crystal, is shown in Fig. 1 where the atoms are numbered according to the scheme adopted for the X-ray analysis. Compared with the values listed by Allen *et al.* in their extensive report[12] on bond lengths in organic compounds, most of those given in Table 4, fall within the expected ranges. The 9 non-H atoms of the two fused rings are coplanar within 0.03 Å; the least-squares plane through them makes dihedral angles of only *ca.* 4° with the average plane of the phenyl ring at C(2), and *ca.* 22° with that of the phenyl ring at C(5).

Experimental

M.p.s were determined using a Büchi 510 (capillary) apparatus. IR spectra were measured using a SP Pye Unicam SP3-2005 Philips spectrophotometer. NMR spectra were obtained with Bruker AC 200 and EM-390 Varian instruments. *J*-Values are given in Hz. Mass spectra data were performed on a Varian MAT IH COS 50 instrument using electron-impact ionization techniques. Column chromatography was performed on silica gel using Kieselgel 60 (Merk).

* For details of the CCDC deposition scheme see 'Instructions for Authors (1992)', *J. Chem. Soc., Perkin Trans. 1*, 1992, Issue 1.

Table 2 Analytical and spectroscopic data *

Compound (Formula)	M.p./°C (Solvent)	Found % (Required) C	H	N	δ_H [a] 6-H	Aromatic protons	Other protons
4a ($C_{25}H_{18}N_2O_2$)	182–183 (CH_2Cl_2–Pr^i_2O)	79.10 (79.36	4.90 4.76	7.24 7.41)	7.96	7.08–7.13, 7.43–7.58 8.09–8.37	3.90 (3 H, s, OMe)
4b ($C_{24}H_{15}ClN_2O$)	217 (CH_2Cl_2–Et_2O)	75.10 (75.30	3.99 3.90	7.07 7.30)	7.97	7.45–7.59, 8.11–8.38	
4c ($C_{24}H_{16}N_2O$)	146 (CH_2Cl_2–Pr^i_2O)	82.30 (82.76	4.70 4.60	8.33 8.05)	8.01	7.46–7.64	
4d ($C_{20}H_{16}N_2O_2$)	168–169 (CH_2Cl_2–Pr^i_2O)	79.80 (80.00	5.29 5.33	9.32 9.33)	7.61	7.26–7.32, 7.51–7.58 7.94–7.99, 8.28–8.33	2.74 (3 H, s, 7-Me), 2.42 (3 H, s, *p*-MePh)
4e ($C_{26}H_{20}N_2O_2$)	177 (CH_2Cl_2–Pr^i_2O)	79.32 (79.59	5.22 5.10	6.90 7.14)	7.94	7.09–7.34, 7.52–7.59, 8.01–8.38	3.92 (3 H, s, OMe) 2.44 (3 H, s, *p*-MePh)
4f ($C_{19}H_{14}N_2O$)	141–142 (CH_2Cl_2–Pr^i_2O)	79.71 (79.72	5.05 4.89	9.93 9.79)	7.62	7.26–7.62, 8.05–8.34	2.74 (3 H, s, 7-Me)
4g ($C_{18}H_{12}N_2O$)	135–137 (CH_2Cl_2–Pr^i_2O)	79.20 (79.41	4.63 4.41	10.08 10.29)	7.83 [b]	7.26–7.63, 8.07–8.34	*ca.* 8.1 (7-H)

[a] $CDCl_3$, *J* values are given in Hz. [b] d, *J* 9.1.
* *Appendix*: $\delta_C(CDCl_3)$ **4a**: 55.9 (OMe), 114.8, 115.6 (C arom), 127.3–132.4 (C arom. and C-6), 130.5 (C-7), 139.3, 140.9 (C arom. and C-7a), 153.7 (C-5), 161.3, 161.4, 162.9 (C-2, C-3a and C-OMe); *m/z* **4a**: 378 (M^+, 100) and 189 (64).

Table 3 Final atomic coordinates with esds in parentheses for compound **4f**

Atom	*x*	*y*	*z*
N(1)	0.481 4(2)	0.125 27(6)	0.376 2(1)
C(2)	0.456 8(2)	0.098 53(8)	0.250 3(2)
O(3)	0.552 8(1)	0.039 36(5)	0.251 8(1)
N(4)	0.753 2(2)	−0.023 65(7)	0.444 4(1)
C(5)	0.828 8(2)	−0.025 00(8)	0.590 7(2)
C(6)	0.792 2(2)	0.024 55(9)	0.678 0(2)
C(7)	0.677 0(2)	0.079 34(8)	0.622 6(2)
C(8)	0.603 4(2)	0.081 31(8)	0.473 0(2)
C(9)	0.647 5(2)	0.029 10(8)	0.397 0(1)
C(10)	0.628 6(2)	0.130 59(9)	0.715 8(2)
C(11)	0.338 4(2)	0.122 39(8)	0.110 0(2)
C(12)	0.231 1(2)	0.178 69(9)	0.103 0(2)
C(13)	0.116 0(2)	0.201 31(9)	−0.028 5(2)
C(14)	0.105 0(2)	0.167 87(9)	−0.154 1(2)
C(15)	0.209 5(2)	0.111 59(9)	−0.148 5(2)
C(16)	0.326 1(2)	0.089 16(9)	−0.017 1(2)
C(17)	0.947 4(2)	−0.084 54(9)	0.652 3(2)
C(18)	0.934 4(3)	−0.144 7(1)	0.573 2(2)
C(19)	1.042 3(3)	−0.200 7(1)	0.628 7(2)
C(20)	1.165 4(2)	−0.197 8(1)	0.765 3(2)
C(21)	1.181 1(2)	−0.138 8(1)	0.845 5(2)
C(22)	1.072 9(2)	−0.082 4(1)	0.789 9(2)

Table 4 Selected bond lengths (Å) and angles (°), with their estimated standard deviations in parentheses, for compound **4f**

Bond lengths			
N(1)–C(2)	1.296(2)	N(1)–C(8)	1.395(2)
C(2)–O(3)	1.384(2)	C(2)–C(11)	1.453(2)
O(3)–C(9)	1.379(1)	N(4)–C(5)	1.355(2)
N(4)–C(9)	1.308(2)	C(5)–C(6)	1.393(3)
C(5)–C(17)	1.485(2)	C(6)–C(7)	1.391(2)
C(7)–C(8)	1.384(3)	C(7)–C(10)	1.502(3)
C(8)–C(9)	1.382(2)		
Bond angles			
C(2)–N(1)–C(8)	104.1(1)	N(1)–C(2)–C(11)	127.7(2)
N(1)–C(2)–O(3)	115.3(2)	O(3)–C(2)–C(11)	116.9(2)
C(2)–O(3)–C(9)	103.5(1)	C(5)–N(4)–C(9)	112.7(1)
N(4)–C(5)–C(17)	115.6(2)	N(4)–C(5)–C(6)	122.2(2)
C(6)–C(5)–C(17)	122.1(2)	C(5)–C(6)–C(7)	123.0(2)
C(6)–C(7)–C(10)	123.5(2)	C(6)–C(7)–C(8)	114.4(2)
C(8)–C(7)–C(10)	122.1(2)	N(1)–C(8)–C(7)	132.8(2)
C(7)–C(8)–C(9)	117.7(2)	N(1)–C(8)–C(9)	109.4(1)
N(4)–C(9)–C(8)	129.9(1)	O(3)–C(9)–C(8)	107.7(1)
O(3)–C(9)–N(4)	122.4(1)		

5(4*H*)-Oxazolones **2a–c**,[13] **2d**,[14] **2e**,[15] **2f**[16] and *N*-(1-phenylvinyl)iminotriphenylphosphorane **1a**[8] are known.

N-[1-(p-*Tolyl*)*vinyl*]*iminotriphenylphosphorane* **1b**.—Compound **1b** was prepared as described for **1a**:[8] yield 52%; m.p. 112 °C (Found: C, 82.1; H, 5.95; N, 3.45. $C_{27}H_{24}NP$ requires C, 82.40; H, 6.15; N, 3.58%); $\delta_H(CDCl_3)$ 2.4 (3 H, s, Me), 3.8, 4.5 (2 H, AB system, *J* 2.1, CH_2) and 7.0–7.9 (19 H, m, H arom.).

7-(p-*Methoxyphenyl*)-2,5-*diphenyl*-6,7-*dihydrooxazolo*[5,4-b]*pyridine* **3a** *and* 7-(p-*Methoxyphenyl*)-2,5-*diphenyloxazolo*-[5,4-b]*pyridine* **4a**.—Oxazolone **2a** (360 mg, 1.3 mmol) and iminophosphorane **1a** (500 mg, 1.3 mmol) were refluxed in benzene (30 cm^3) under nitrogen for 3 h. After solvent elimination the crude mixture was chromatographed on silica gel column with C_6H_{14}–CH_2Cl_2 (1:0–0:1 v/v). Two main fractions were obtained: the first after crystallization, yielded pure **4a** (80 mg, 16%); the second contained a mixture of **4a** and **3a** (150 mg). **3a**: $\delta_H(CDCl_3)$ 3.39, 3.47, 4.38 (3 H, ABX system J_{AB} 10.7, J_{BX} 5.9, J_{AB} 17.2, 6-CH_2 and 7-H), 3.9 (3 H, s, OMe) and 6.8–8.2 (14 H, m, H arom.); $\delta_C(CDCl_3)$ 30.2 (C-6), 36.9 (C-7), 55.7 (OMe), 114.5, 114.6, 128.0–126.8 (C arom.), 134.7, 137.9 (C arom. and C-7a), 154.0 (C-5) and 159.2, 159.3 and 164.0 (C-2, C-3a and OMe-C); *m/z* 380 (M^+, 31%), 174 (19) and 105 (100). Physical and spectroscopic data for **4a** are given in Table 2.

General Procedure for the Preparation of Oxazolo[5,4-b]-*pyridines* **4**.—Vinyliminophosphorane **1** (2 mmol) and oxazolone **2** (2 mmol) were refluxed in dry benzene or anisole (50 cm^3) under nitrogen. After the period indicated in Table 1 DDQ

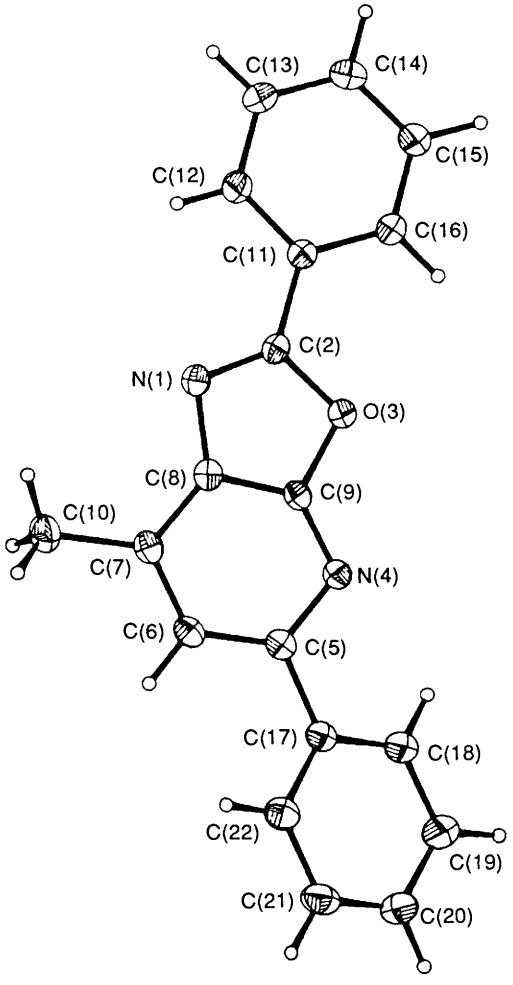


Fig. 1 Perspective view of **4f** with the numbering scheme adopted for the X-ray analysis. The non-hydrogen atoms are represented by ellipsoids drawn[11] at a probability level of 0.20. Hydrogen atoms, represented by circles on an arbitrary scale, were numbered according to the carbon atom to which they are bonded.

(2 mmol) was added and the heating was continued for 1 h. The solvent was eliminated and the crude mixture was chromatographed with the solvent indicated. The pure compound **4** was isolated after crystallization. Reaction conditions are given in Table 1, analytical and spectroscopic data are given in Table 2.

Reaction of N-(1-*Phenylvinyl*)*iminotriphenylphosphorane* **1a** *with* 4-(*Ethoxymethylene*)-2-*phenyloxazol*-5(4H)-*one* **2f**.—A mixture of **1a** (1.0 g, 2.64 mmol) and **2f** (573 mg, 2.64 mmol) in CH_2Cl_2 (30 cm^3) was stirred at room temp. under nitrogen. The colour of the solution became red. After 1 h the starting materials had disappeared and the resulting mixture was worked up in three different ways: (a) After solvent elimination the red compound **5a** was characterized in the impure form because of its lability. ν_{max}(Nujol)/cm^{-1} 1740 (CO); δ_H-($CDCl_3$) 6.4–8.2 (H arom. and H vinylic); *m/z* 550 (M^+, 14%), 417 (61), 278 (24), 277 (50), 262 (42), 183 (96) and 77 (100); (b) the solvent was evaporated and the residue chromatographed on silica gel column (1 m high, 3 cm diameter) eluting slowly (about 24 h) with ethyl acetate. Orange compound **6** (550 mg, 69%) was isolated after crystallization from hot benzene; m.p. 165–167 °C; (Found: C, 74.6; H, 5.05; N, 9.9. $C_{18}H_{14}N_2O_2$ requires C, 74.48; H, 4.82; N, 9.65%); ν_{max}(Nujol)/cm^{-1} 3300–3500 (NH_2) and 1740 (C=O); δ_H($CDCl_3$) (mixture of two stereoisomers) 5.0–5.2 and 5.5–5.8 (2 H, two br, NH_2 D_2O-exchangeable), 6.42, 7.08 and *ca.* 7.15 (2 H, AX system, *J* 12.6 and AB system, vinylic H); (c) CH_2Cl_2 was eliminated and replaced with anisole (30 cm^3). The solution was refluxed for 24 h. The solvent was evaporated and the crude mixture chromatographed, after crystallization pure **4g** (546 mg, 76%) was isolated.

3-*Benzoylamino*-6-*phenyl*-2(1H)-*pyridone* **7**.—Compound **6** (550 mg, 1.8 mmol) was refluxed in acetic acid (30 cm^3) for 1 h. After solvent elimination the crude mixture was crystallized from CH_2Cl_2–Et_2O yielding the title compound **7** (350 mg, 67%); m.p. 285 °C (Found: C, 74.1; H, 5.0; N, 9.6. $C_{18}H_{14}N_2O_2$ requires C, 74.48; H, 4.82; N, 9.65%); ν_{max}(Nujol)/cm^{-1} 3320 (NH) and 1690, 1620 (C=O); δ_H(DMSO) 6.7, 8.4 (2 H, AX system, *J* 7.7, 5-H, 4-H), 7.7–8.0 (10 H, m, H arom.), 9.4, 12.4 (2 H, two s, NH D_2O-exchangeable).

X-Ray Crystallographic Analysis of **4f**.—*Crystal data.* $C_{19}H_{14}N_2O$, M = 286.34. Monoclinic, a = 8.301(1), b = 19.178(4), c = 9.928(2) Å, β = 111.54(1)°, V = 1470.1(5) $Å^3$ (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.710 73 Å), space group $P2_1/n$ (alt. $P2_1/c$ No. 14), Z = 4, D_x = 1.29 g cm^{-3}. Colourless, transparent prisms. Approximate crystal dimensions: 0.20 × 0.30 × 0.35 mm. μ(Mo-Kα) = 0.76 cm^{-1}.

Data collection and processing.[17] Crystal quality checked by film techniques. CAD4 diffractometer, ω mode with ω scan width = 1.4 + 0.35 tan θ, ω scan speed 2.3–8.2 deg min^{-1}, graphite-monochromated Mo-Kα radiation; 5826 reflections measured ($1.0 \leq \theta \leq 26.0$, full hemisphere), 2888 unique (merging R = 0.017), 2735 with $I > 0$ classed as observed. Data were corrected for Lorentz and polarisation effects but not for absorption.

Structure analysis and refinement. An E-map, computed from 238 $E \geq 1.66$, distinctly revealed 22 peaks, corresponding to the skeleton of the molecule, with very little extraneous detail. Proof of atom identity was obtained as follows: first all 22 peaks of the E-map, irrespective of their heights, were assumed to correspond to carbon atoms, and isotropic least-squares refinement was carried out on 1503 data with $F^2 > 3\sigma(F^2)$. Convergence (max. Δ/σ = 0.02 for the 89 refined parameters) was reached after 5 cycles, with an R index ($= \Sigma||F_o| - |F_o||/\Sigma|F_o|$) of 0.125. Anomalously small B values for three atoms of the two fused rings were clearly evident: compared with an average B of 3.6 $Å^2$ for this molecular fragment, two atoms of the five-membered ring showed isotropic 'temperature' factors of 1.10(9) and 2.6(1), respectively, and the latter value was also found for one atom of the other ring. Accordingly, the first two atoms were identified as oxygen and nitrogen, respectively, in agreement also with the resulting bond distances (two C–O bonds of 1.36 and 1.34 Å, a C=N bond 1.28 Å long, and a C–N bond of 1.39 Å). Rather than immediately identifying also the third anomalous 'carbon' atom as nitrogen, as strongly suggested by its B value and by the two bond distances (of 1.32 and 1.33 Å) in which it was involved, a further test was made, by keeping its original assignment as carbon atom, and assuming that another atom of the six-membered ring [atom C(6) of Fig. 1) was a nitrogen atom. Four least-squares refinement cycles of this model converged to an R index of 0.107, but again two anomalous B values were apparent: that of the previously strongly-suspicious 'carbon' atom had decreased from 2.6(1) to 2.0(1) $Å^2$, and the 'temperature' factor of the assumed nitrogen atom had increased from 4.6(2) to 6.3(2) $Å^2$, the average B value for the nine atoms of the two fused rings still being 3.6 $Å^2$. Clearly, this suggested to interchange the identity of the two atoms, thus confirming the interpretation of the results of the first least-squares cycles. Isotropic refinement of the corresponding final model for the

22 non-H atoms reduced R to 0.095 after three cycles (max. $\Delta/\sigma = 0.02$). A subsequent difference map clearly indicated the positions of all 14 hydrogen atoms, and the model was complete.

The final least-squares refinement was carried out on all 2735 observed data and included, in single matrix, 256 parameters: coordinates and anisotropic 'temperature' coefficients B_{ij} for the 22 heavy atoms, coordinates and isotropic B's for the 14 atoms, a scale factor, and a secondary extinction parameter [final value = $4.5(4) \times 10^{-7}$]. Weighting scheme: $w = 4F_o^2/\sigma(F_o^2)$ with $\sigma^2(F_o^2)$ including, besides counting statistics, a term $(0.02S)^2$, where S is the scan count. For the 1698 reflections with $I > 2\sigma(I)$ final $R(F)$ and $wR(F)$ values are 0.038 and 0.035, with goodness-of-fit = 1.360. Programs and computers used and sources of scattering factors are given in ref. 17.

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17 For full details of experimental techniques used see R. Destro, A. Maghini and F. Merati, *Acta Crystallogr., Sect. C*, 1987, **43**, 949.

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