N-Oxides and Related Compounds. Part 60.[1] Novel Thermal and Photochemical Rearrangements of *N*-Substituted 2-Pyridones [2]

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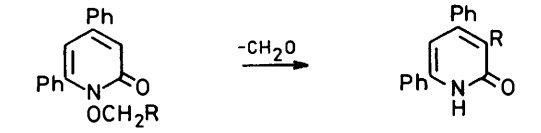
Examples of four novel rearrangements of derivatives of 1-hydroxy-4,6-diphenyl-2-pyridone are reported: all involve N–O fission and formation of 3-substituted or both 3- and 5-substituted-4,6-diphenyl-2-pyridones. (*a*) 1-OCH_2CH_2R (R = vinyl or phenyl) compounds give 3-CH_2R (R = vinyl or phenyl) derivatives with elimination of CH_2O. (*b*) The 1-octyloxy-compound gives the 3-octyloxy-derivative by simple transposition. (*c*) 1-Acyloxy-compounds form the corresponding 3- and 5-acyloxy-2-pyridones. (*d*) 1-Imidoyloxy-compounds yield the rearranged 3- and 5-amido-2-pyridones. The mechanisms probably all involve homolytic N–O fission.

OUR studies [3] on the thermolysis and photolysis of 1-alkoxy-4,6-diphenyl-2-pyridones to give aldehydes have shown that, whereas benzaldehydes are formed without appreciable amounts of side products, the aliphatic aldehydes obtained from this route are accompanied not only by alcohols but also by by-products derived from rearrangements. We have now elucidated the structures of these by-products and the courses of these and related rearrangements (which increase significantly the range of those known for heteroaromatic *N*-oxides [4,5]).

Rearrangements with Loss of Formaldehyde.—Thermolysis of the phenethoxypyridone (1) at 220 °C yields [in addition to phenylacetaldehyde (49%) and 4,6-diphenyl-2-pyridone [3b]] 26% of 3-benzyl-4,6-diphenyl-2-pyridone (3). The i.r. [amide ν(C=O) 1 630; ν(NH) 2 800—3 100 cm^{-1}] and ^1H n.m.r. spectra (2 H, s at δ 3.7; 1 H, s at δ 6.4; 15 H, m at δ 6.8—7.7; and 1 H, broad s at δ 12.0) were similar to those of 4,6-diphenyl-2-pyridone. These, together with ^{13}C n.m.r. and mass spectra and analytical data, indicated the structure (3) or the isomeric 5-benzyl compound (5): distinction was achieved by elimination of the oxygen atom. In model reactions, 4,6-diphenyl-2-pyridone was converted by $POCl_3$ at 200 °C into the 2-chloropyridine (6) (84%) which on hydrogenation at 20 °C and 760 mmHg gave 2,4-diphenylpyridine (7) (80%), for which 6-H displayed a clear doublet at δ 8.75 (*J* 10 Hz) in the ^1H n.m.r. spectrum. Under the same reaction conditions we converted the benzyl derivative (3) successively into the chloro-compound (8) (96%) and 2,4-diphenyl-5-benzylpyridine (9) in which the 2-proton signal was a *singlet* at δ 8.8. This eliminates structure (5) and strongly supports (3) for the original benzyl derivative.

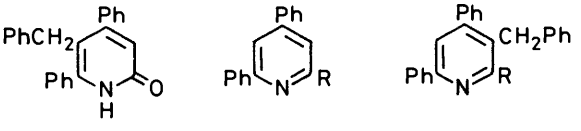
Similar thermal rearrangements with loss of formaldehyde occur in the but-3-enyloxy series. Thermolysis at 230 °C of 1-(but-3-enyloxy)-4,6-diphenyl-2-pyridone (2) gave [in addition to crotonaldehyde (50%) [3]] 3-allyl-4,6-diphenyl-2-pyridone (4) (33%). The i.r. [amide ν(C=O), 1 610; ν(NH), 2 800—3 200 cm^{-1}] and ^1H n.m.r. data (see Experimental section) together with analytical data narrowed the structure to the 3- and 5-allyl isomers; the former is considered more likely particularly by analogy with the benzyl analogue.

We also converted 1-phenethyloxy-4,6-diphenyl-2-pyridone into phenylacetaldehyde (30%) by photolysis, details of which are given elsewhere [3b]: now, using chromatographic separation of the products we find



(1) R = CH_2Ph (3) R = CH_2Ph

(2) R = $CH_2CH{:}CH_2$ (4) R = $CH_2CH{:}CH_2$



(5) (6) R = Cl (8) R = Cl

(7) R = H (9) R = H

rearrangement with elimination of formaldehyde also occurred to give (3) (14%).

Rearrangement to Ring-substituted Isomeric Products.—We have reported [3b] that 1-n-octyloxy-4,6-diphenyl-2-pyridone (11) on thermolysis gives n-octaldehyde (37%) and n-octanol (13%); photolysis gives the same products in yields of 47% and 23%, respectively. We have now

(10) R = Na (13) R = $[CH_2]_7Me$

(11) R = $[CH_2]_7Me$ (14) R = 5-nitro-2-pyridyl

(12) R = 5-nitro-2-pyridyl

found that preparative t.l.c. of the pyrolysis residue gives a third product in 5% yield, shown analytically to be an isomer of the starting material: the component was also isolated from the photolysis residue in 2% yield. The i.r. [amide ν(C=O), 1 600—1 625; ν(NH)

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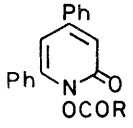
2 700—3 100; ν(C–O–C) 1 230 and 1 040 cm^{-1}] and ^{1}H n.m.r. spectra [δ 1.6 (15 H, m), 4.0 (2 H, t), 6.5; (1 H, s), 7.3—7.9 (10 H, m), 12.7 (1 H, br s)] indicate either 3- (13) or 5-n-octyloxy-4,6-diphenyl-2-pyridone as the structure: the former is more likely.

Photolysis of 1-(5-nitro-2-pyridyl)-4,6-diphenyl-2-pyridone (12) in dry benzene gave the 3-pyridylpyridone (14) (50%) as a brown crystalline solid, insufficiently stable to permit isolation as the pure material. Assignment was based on i.r. [amide ν(C=O) 1 640, ν(N–H) 2 500—3 500, ν(NO_2) 1 350, ν(C–O) 1 250 cm^{-1}] and ^{1}H n.m.r. spectral data: in particular the latter showed absorptions characteristic of a 2,5-disubstituted pyridine and a trisubstituted 2-pyridone. Again the 3-isomer is considered more likely than the 5-isomer by analogy with the preceding rearrangements.

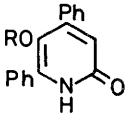
Photochemical Rearrangements of 1-Aroyloxy- and 1-Acyloxy-4,6-diphenyl-2-pyridones.— 1-Acyloxy-2-quinolones were reported some years ago.[6] Paquette [7,8] prepared 1-acyloxy-2-pyridones by reaction of acyl chlorides with 2-ethoxypyridine 1-oxide and utilised them as acylating agents.[8,9] They have also been prepared using thallium salts.[10]

We prepared the 1-acyloxy-4,6-diphenyl-2-pyridones (15a—e) from the sodium salt (10) and the corresponding acid chlorides: the structures are supported by spectral data (see Experimental section), particularly the ester ν(C=O) absorption at 1 780—1 815 cm^{-1} and the amide ν(C=O) absorption at *ca.* 1 670 cm^{-1}. The 1-acyloxy-compounds are sensitive to water, especially the 1-acetoxy (15a) and 1-phenylacetoxy (15b) derivatives.

Pyrolysis of the 1-acyloxy-derivatives (15a, b, d, and e) gave merely tar and some of the corresponding acid. We photolysed our compounds (15d and e) in acetonitrile to minimise solvent participation. At 253.7 nm, (15e), which shows u.v. $\lambda_{max.}$ at 250 and 330 nm, gave a mixture of products from which only 4,6-diphenyl-2-pyridone was isolated, but irradiation at 350



(15) a; R = Me
b; R = CH_2Ph
c; R = C_6H_4Me–*o*
d; R = C_6H_4Me–*p*
e; R = Ph



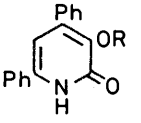
(16) R = COPh
(17) R = H
(18) R = COC_6H_4Me–*p*

nm gave, after 36 h, rearranged ester (16) (12%) together with 4,6-diphenyl-2-pyridone (15%) and benzoic acid (2%).

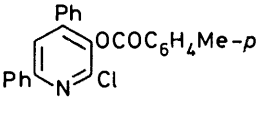
Structure (16) was supported by ester ν(C=O) 1 740, pyridone ν(C=O) 1 650, and pyridone ν(N–H) 2 600—3 000 cm^{-1} absorptions. In the ^{1}H n.m.r. spectrum the AB quartet of the starting material, for the 3-H and 5-H protons, had collapsed to a one-proton singlet at δ 6.6, but the signal for the *ortho* protons of the benzoyl group remained as a doublet of δ 7.8. The mass spectrum disclosed a molecular ion peak at *m/e* 369, and a base peak at *m/e* 105 for $PhCO^+$. Hydrolysis of (16) in 20% aqueous sodium hydroxide gave benzoic acid and the hydroxypyridone (17) [ν(OH) 2 500—3 500, pyridone ν(C=O) 1 640 cm^{-1}; 3-H singlet at δ 7.25 with other aromatic protons near δ 7.65].

Irradiation at 350 nm of 4,6-diphenyl-1-(*p*-toluoyloxy)-2-pyridone (15d) in dry acetonitrile for 38 h and separation by column chromatography gave both the rearranged 5- (18) (10%) and 3-*p*-toluoyloxy-isomers (19) (16%). *p*-Toluic acid (12%), 4,6-diphenyl-2-pyridone (35%), and other minor unidentified products were also obtained.

The rearranged esters (18, 19) had similar physical and spectral properties to those of (16) obtained earlier: ν(NH) 2 500—3 100, ν(C=O) 1 740 and 1 650—1 660 cm^{-1}. The ^{1}H n.m.r. spectrum showed the characteristic AB pattern and the Me singlet of the *p*-toluoyl group, with a 3-H singlet at δ 6.6 ($CDCl_3$) for the 5-*p*-toluoyloxy-isomer (18) and a 5-H absorption for the 3-*p*-toluoyloxy-isomer (19) ($CDCl_3$) at δ 6.4 (obscured by the aromatic peaks in CF_3CO_2H). Mass spectra did not distinguish the two isomers but provided further evidence for the proposed structures [molecular ion *m/e* 381; base peaks *m/e* 119 ($MeC_6H_4CO^+$) and 104, ($PhC{\equiv}NH^+$)].



(19) R = COC_6H_4Me–*p*
(20) R = H



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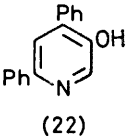


(22)

The two toluoyloxy-isomers (18) and (19) were separately hydrolysed by sodium hydroxide into *p*-toluic acid and the corresponding hydroxypyridones (17) and (20), the first identical to that obtained from ester (16). The other hydroxypyridone (20) was characterised by elemental analysis and i.r. [$\nu_{max.}$ 3 350 (OH), 3 060 (NH), and 1 630 cm^{-1} (C=O)] and ^{1}H n.m.r. spectroscopy [δ 6.6 (1 H, s, 5-H), 7.2—7.8 (10 H, m), and 12.5 (exchanged by D_2O)]. Mass spectral fragmentation patterns are characterised by loss of H (*m/e* 262) followed by sequential loss of two CO units (*m/e* 234 and 206). For (17) a competing fragmentation involves loss of CO from the parent ion. Both spectra exhibit *m/e* 104 assigned to $PhC{\equiv}\overset{+}{N}H$. Compared with the ^{13}C n.m.r. spectrum for 4,6-diphenyl-2-pyridone, those for (17) and (20) each showed one ring peak (C-3 or C-5) shifted downfield by the attached hydroxy-group and a singlet in the off-

resonance-decoupled spectrum; the other peak remained approximately at the same chemical shift, remaining as a doublet on off-resonance decoupling. However, due to the similar chemical shifts of carbon atoms C-3 and C-5 (113.7 and 104.2 p.p.m.) in 4,6-diphenyl-2-pyridone, it was not possible to determine unambiguously which peak had shifted, and thus to identify (17) and (20).

To differentiate the 3- and 5-substituted series, pyridone (19) was reduced to the pyridine (22). Phosphoryl chloride at 200 °C gave 2-chloro-4,6-diphenyl-3-(*p*-toluoyloxy)pyridine (21) (28%) and *p*-toluamide (47%) (after aqueous ammonia work-up) indicating appreciable ester cleavage. Hydrogenation of the chloropyridine (21) both removed the chlorine and cleaved the ester to give 3-hydroxy-4,6-diphenylpyridine (22) (89%) with the 2-H singlet absorbing at δ 8.5. This enabled structural assignment of the pyridone (19) and by extension those of (16), (17), (18), and (20).

The 5-toluoyloxy-isomer (18) has a lower u.v. absorption maximum (327 nm) than the 3-toluoyloxy-isomer (19) (333 nm), consistent with the structural assignments; the decrease in $\lambda_{max.}$ is attributed to the greater steric hindrance in the 5-toluoyloxy-isomer (18).

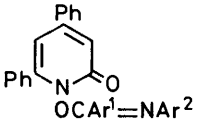
Photochemical Rearrangements of 1-*Benzimidoyloxy*-4,6-*diphenyl*-2-*pyridones*.— 4,6-Diphenyl-1-(*N*-phenylbenzimidoyloxy)-2-pyridone (24a) (88%) was prepared from *N*-phenylbenzimidoyl chloride (23a) [11] and the salt (10) in dry acetonitrile at 20 °C. Similarly the 1-[*N*-(*p*-methoxyphenyl)-*o*-toluimidoyloxy]- (24b) (93%) and 1-[*N*-(*p*-tolylbenzimidoyloxy)]-4,6-diphenyl-2-pyridones (24c) (95%) were prepared from *N*-(*p*-methoxyphenyl)-*o*-toluimidoyl chloride (23b) and *N*-(*p*-toluoyl)benzimidoyl chloride (23c),[12] themselves obtained from the corresponding amides and thionyl chloride.

$$Ar^1CCl{=}NAr^2$$

(23) a; $Ar^1 = Ph, Ar^2 = Ph$

b; $Ar^1 = C_6H_4Me\text{-}o$, $Ar^2 = C_6H_4OMe\text{-}p$

c; $Ar^1 = Ph, Ar^2 = C_6H_4Me\text{-}p$



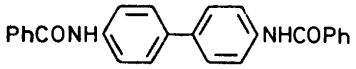
(24) a; $Ar^1 = Ph, Ar^2 = Ph$

b; $Ar^1 = C_6H_4Me\text{-}o, Ar^2 = C_6H_4OMe\text{-}p$

c; $Ar^1 = Ph, Ar^2 = C_6H_4Me\text{-}p$

Each 1-benzimidoyloxypyridone (24a, b, and c) showed in the ^{1}H n.m.r. spectrum protons 3-H and 5-H as a pair of doublets near δ 6.45 and δ 6.95 (*J* 2.5 Hz) and the two protons *ortho* to the benzimidoyl group near δ 6.5 (upfield from the remaining aromatic protons) as a doublet (*J* 8 Hz) or in the case of the *p*-methoxyphenyl derivative (24b) contributing to a four-proton singlet, coinciding with the adjacent *meta* protons. The i.r. spectra all showed the pyridone ν(C=O) 1 660 and ν(C=N) 1 600 cm^{-1} absorptions.

Pyrolysis of the 1-(*N*-phenylbenzimidoyloxy)-2-pyridone (24a) at 130 °C and 0.5 mmHg gave a mixture from which only benzanilide was identified. The u.v. spectra show that the benzimidoyloxy-derivatives absorb strongly near 250 nm and more weakly near 350 nm. Photolysis of (24a) in dry acetonitrile at 253.7 nm gave only a little rearranged product (26). Irradiation for 46 h at 350 nm in dry acetonitrile was more successful. 4,4′-Dibenzamidobiphenyl (25) (1.7%) precipitated from the photolysis mixture; the structure follows from elemental analysis, i.r. [amide ν(NH) 3 240 and amide ν(C=O) 1 645 cm^{-1}] and ^{1}H n.m.r. spectra (18 aromatic protons, 2 NH protons), m.p. comparison [m.p. >335 °C (lit.,[13] 352 °C)], mass spectral data [molecular ion peak, *m/e* 392; base peak, 105 ($PhCO^+$); 77 (Ph^+); 287 ($PhCO\overset{+}{N}H{=}C_6H_4{=}C_6H_4{=}NH$)], and its insolubility in most solvents.[13,*]



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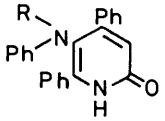
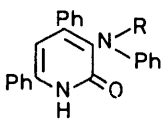


(26) R = COPh

(27) R = H



(28) R = COPh

(29) R = H

Column chromatography and fractional crystallisation gave additional compounds from the 350 nm photolysis, *viz.* two rearranged benzanilidopyridones (26) (13.5%) and (28) (4%), 4,6-diphenyl-2-pyridone (18.5%), benzanilide (4%), two unknowns in moderate quantities (*ca.* 10% by weight), and several unidentified minor components.

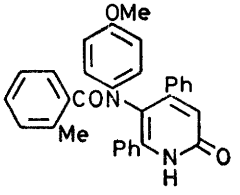
The ^{1}H n.m.r. and i.r. spectra of the rearranged pyridones (see Experimental section) support the proposed structures. Satisfactory elemental analysis and mass spectrum [base and molecular ion peak, *m/e* 442; *m/e* 337, loss of PhCO; 309, further loss of CO; 105, $PhCO^+$; 104, $PhC{\equiv}NH^+$; 77, Ph^+] were obtained for the 3-substituted isomer (28). After eight recrystallisations a 2% error in carbon analysis was still found for isomer (26); a mass spectrum was unobtainable because of non-volatility (10^{-6} mmHg at 350 °C). However, hydrolysis of this isomer (26) in 70% sulphuric acid gave benzoic acid and 5-anilino-4,6-diphenyl-2-pyridone (27) [ν(NH) 3 440 and 3 330, ν(NC=O) 1 640 cm^{-1}], for

* The m.p. evidence for (27), though equivocal, precludes the 2,2′-, 2,4′-, and 3,4′-isomers which have lower m.p.s (ref. 13; R. B. Carlin and E. A. Swakon, *J. Amer. Chem. Soc.*, 1955, **77**, 966; R. B. Carlin and W. O. Forshey jun., *J. Amer. Chem. Soc.*, 1950, **72**, 793). The unknown 2,3′- and 3,3′-isomers cannot be excluded but are considered less likely.

which ^{13}C n.m.r. shows a similar C-3 signal to that observed for 4,6-diphenyl-2-pyridone but a lack from the usual position of a signal for C-5. The 3-anilidopyridone (28) was hydrolysed by sulphuric acid to benzoic acid, the expected 3-anilino-2-pyridone (29) not being obtained pure.

To obtain rearrangement products with more informative ^1H n.m.r. spectra, 1-[*N*-(*p*-methoxyphenyl)-*o*-toluimidoyloxy]-4,6-diphenyl-2-pyridone (24b) was irradiated at 350 nm in dry acetonitrile for 48 h. Column chromatography, fractional crystallisation, and preparative t.l.c. separated 4,6-diphenyl-2-pyridone (25%) and the amide (31) (40%) (both identified by comparison with authentic samples), and a rearranged pyridone (30) (15%).

The ^1H n.m.r. spectrum of (30) displayed methoxy, methyl, phenyl, and tolyl peaks as expected; the AB quartet for the *p*-methoxyphenyl ring appeared near δ 6.0, and the 3-H singlet at δ 6.5. Mass spectral fragmentations include initial loss of 2-MeC_6H_4CO (*m/e* 367) followed by loss of CO (*m/e* 339). A peak for *m/e* 104, $PhC{\equiv}NH^+$ is also present.



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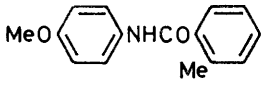

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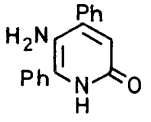

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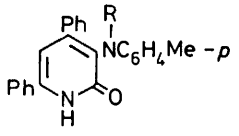
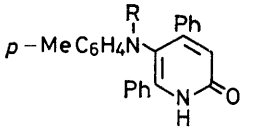
Attempted hydrolysis of (30) in 70% sulphuric acid gave *o*-toluic acid with intractable tar: lower concentrations of sulphuric acid or refluxing aqueous sodium hydroxide or hydrochloric acid gave recovered starting material. Mixed hydrochloric acid and acetic acid in a sealed tube yielded the 5-aminopyridone (32), an assignment supported by mass spectrometry [molecular ion peak, *m/e* 262; *m/e* 261 ($M^+ - H$), 104, ($PhC{\equiv}NH^+$), 77 (Ph^+)], i.r. [$\nu_{max.}$ 3 430 (NH_2), 3 300 (NH_2), and 1 655 cm^{-1} (C=O)], and ^1H n.m.r. spectral data [δ 2.2 (NH_2), 6.5 (3-H), 7.5 (2 × Ph)] although it was obtained in insufficient quantity to purify for elemental analysis.

To obtain rearrangement products which would undergo hydrolysis more smoothly, 4,6-diphenyl-1-[*N*-(*p*-tolyl)benzimidoyloxy]-2-pyridone (24c) was photolysed at 350 nm. Differential solubility and column chromatography afforded 4,6-diphenyl-2-pyridone (12%) and benzo-*p*-toluidide (14%) (both identified by comparison with authentic samples), two rearranged pyridones (33) (16%) and (35) (18%), and a compound (14%) which analysed as $C_{21}H_{19}O_2$. Two alternative possible structures (39) and (40) are proposed for the compound ($C_{21}H_{19}O_2$) on the basis of i.r. [ν(C=O) 1 655 cm^{-1}], ^1H n.m.r. [δ 1.6 (3 H, s, Me), 2.2 (3 H, s, Me), 6.2 (2 H, d, *J* 10 Hz), and 7.8—8.4 (11 H, m)], and mass spectral data [molecular ion peak, *m/e* 317; *m/e* 211 (loss of MeC_6H_4O); base peak, *m/e* 107, ($MeC_6H_4O^+$); *m/e* 105, ($PhCO^+$); and 77, (Ph^+)].



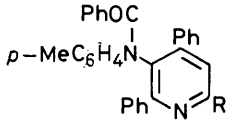
(33) R = COPh

(34) R = H



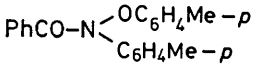
(35) R = COPh

(36) R = H

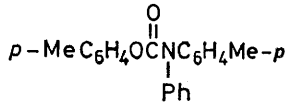


(37) R = Cl

(38) R = H



(39)



(40)

The two benzotoluidinopyridones (33) and (35) gave satisfactory elemental analyses and showed the expected i.r. spectra (see Experimental section). The ^1H n.m.r. spectra both had methyl singlets near δ 2.1. The 3-substituted isomer (33) showed singlets for 5-H at δ 6.5 (in $CDCl_3$) and NH at δ 9.4, while the 5-substituted isomer (35) showed a singlet for 3-H at δ 6.6 (in $CDCl_3$; poor solubility) or at δ 6.9 (in CF_3CO_2H). The mass spectra of both isomers had the expected molecular ion (*m/e* 456) and base (*m/e* 105, $PhCO^+$) peaks.

The two rearranged pyridones were each hydrolysed by 70% sulphuric acid to benzoic acid and the corresponding toluidinopyridones (34) and (36). The proposed structures were supported by analyses and spectra: ν(NH) 3 330 and 3 400 cm^{-1} (34), or 3 320 and 3 440 cm^{-1} (36); pyridone ν(C=O) 1 625 cm^{-1} (34) or 1 650 cm^{-1} (36). The pyridone ring ^1H n.m.r. peaks overlapped with the *p*-toluidino-absorption but 3-H was distinguished as a singlet at δ 6.3 for (36) [in $(CD_3)_2SO$] and 5-H as a singlet at δ 6.5 for (34) (in $CDCl_3$). The mass spectral fragmentation patterns both include loss of H (*m/e* 351). This precedes loss of CO for (36) but competes with it for (34). Both spectra include *m/e* 104 found elsewhere in this series. Comparison of the ^{13}C n.m.r. spectra with that of 4,6-diphenyl-2-pyridone is complicated by the presence of the toluidino-group; however the C-5 doublet occurs at 108.5 p.p.m. in the off-resonance decoupled spectrum of the 3-substituted isomer (34) (in $CDCl_3$), another doublet at 118.5 p.p.m.

being assigned to the *ortho* carbons of the toluidino-group. The 5-substituted isomer (36) (in trifluoroacetic acid–$CDCl_3$) showed the C-3 signal near the aryl carbon absorptions.

Again physical methods failed to differentiate clearly between the 3- and 5-substituted pyridones (33) and (35). The appearance of C-3 downfield from C-5 in the ^{13}C n.m.r. spectra supports the suggested structural assignment; however, changes in chemical shift with solvent render this evidence uncertain. The problem was resolved chemically. The pyridone (35) was reduced to the corresponding pyridine (38) *via* initial reaction with phosphoryl chloride to give the 2-chloropyridine (37) (32%), characterised by analysis and spectra (see Experimental section). The pyridine (38) was identified by analysis and spectra: in the ^1H n.m.r. spectrum the 2-H proton appeared as a doublet (J 6 Hz) at δ 8.8, showing that the rearrangement had located the benzoyltoluidino-group at the 5-position and confirming all the structural assignments in this series.

U.v. spectra of the amido- and amino-pyridones (26)—(30) and (33)—(36) support the structures assigned above (see Table). The 5-substituted compounds have a lower and weaker absorption maximum than the corresponding 3-substituted isomers, attributed to the greater steric hindrance in the 5-isomers. The differences in wavelength between the maxima of the toluidino- and *N*-benzoyltoluidino-isomers are greater than the corresponding differences between the maxima of the anilino- and benzanilido-isomers, due to the greater bulk of the toluidino- and *N*-benzoyltoluidino-substituents.

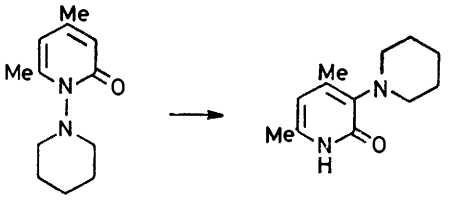
U.v. spectral data of amino- and amido-pyridones (in $CHCl_3$)

	3-Isomer			5-Isomer		
Substituent	Cmpd. no.	$\lambda_{max.}$ (nm)	$10^{-3}\varepsilon$	Cmpd. no.	$\lambda_{max.}$ (nm)	$10^{-3}\varepsilon$
Benzanilido	(28)	354	19.9	(26)	<340 [a]	
Anilino	(29)	355	*b*	(27)	348	*b*
N-(*o*-Toluoyl)-*p*-anisidino				(30)	327	7.7
N-Benzoyl-*p*-toluidino	(33)	351	15.0	(35)	332	9.0
Toluidino	(34)	347	12.7	(36)	318	9.0

[a] Overlapped by absorption at $\lambda_{max.}$ 293 nm. [b] Not completely dissolved.

Pyridone Rearrangement Mechanisms.—There are few close analogies in pyridine 1-oxide chemistry to the rearrangements presented above. The photochemistry of derivatives of 1-hydroxy-2-pyridones has received little previous attention. Furrer [14] photolysed 1-alkoxy-4,6-dimethyl-2-pyridones, but found only cleavage to give aldehydes, and in one instance the alcohol. No rearrangement products were observed although the *N*-piperidino-derivative (41) gave the 3-substituted pyridone (42) (10%) together with 4,6-dimethyl-2-pyridone (56%). Taylor *et al.*[15] photolysed 1-aroyloxy-2-pyridones into arylcarboxylic acids and arylbenzenes (on trapping with benzene); no rearrangement was observed.

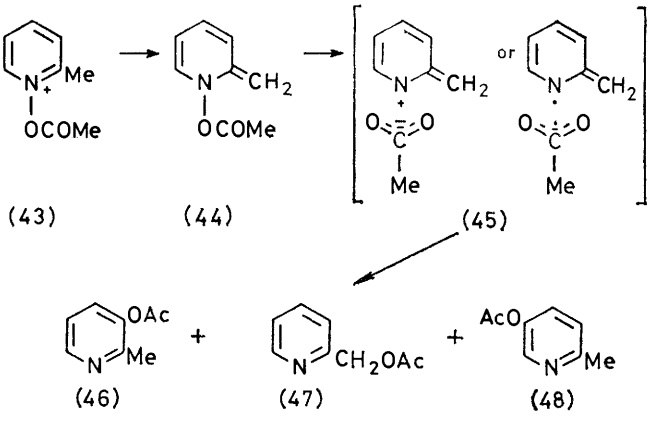
2-Picoline 1-oxide and acetic anhydride give an initial *N*-acetoxypicolinium salt (43). This loses a proton to produce the anhydro-base (44) which undergoes intramolecular N–O bond cleavage and recombination to give (46)—(48): evidence for both heterolytic cleavage to give ion pairs [16] and homolytic cleavage to give radical pairs [17,18] has been presented. The anhydro-base (44) is a methylene analogue of a 1-acyloxy-2-pyridone: rearrangement of (44) in part to 3- and 5-acetoxypicoline (46, 48) is analogous to the rearrangements outlined above to 3- and 5-acyloxypyridones.



(41) (42)

Such rearrangements of *N*-acyloxy-groups to the side chain or to a β-position occurs with many heterocyclic *N*-oxides: those of 1-methylisoquinoline,[19] 4-lepidine,[19,20] and 4-picoline [21,22] give higher yields of β-ring-substituted products. Participation of intermolecular processes in the rearrangement of the anhydro-bases of 4-picoline [18,22,23] and lepidine [20] has been suggested by Oae and his co-workers.

Abramovitch and his co-workers found rearrangements of heteroaromatic *N*-oxides on treatment with aryl isocyanates, imidoyl chlorides, nitrilium salts, activated acetylenes, and benzyne.[5] Thus, an *N*-oxide blocked at the α-positions, such as lutidine 1-oxide, reacts with *N*-phenylbenzimidoyl chloride to give, among other products, the 3-imidate (51).[24] Initial nucleophilic attack by the *N*-oxide oxygen is followed by intramolecular addition, the 1,2-dihydropyridine intermediate (49) undergoing a [1,5] sigmatropic shift to the



(43) (44) (45) (46) (47) (48)

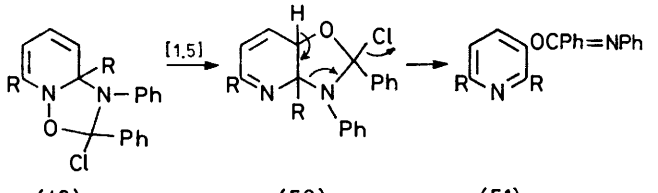
2,3-dihydro-isomer (50) which then aromatises into the 3-imidate (51). Aryloxypyridinium salts such as (52) rearrange in the presence of nucleophiles to 3-(*o*-hydroxyphenyl)pyridines (53); [25] the isolation of small amounts of pyridine and *p*-nitrophenol suggests the involvement of radicals.

Homolytic cleavage of N–O bonds has been observed by e.s.r. in the homolytic cleavage of the acetoxyimine

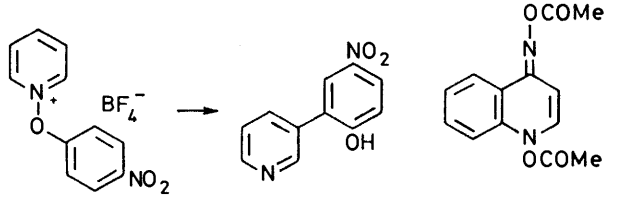
(54) [26] and in the rearrangement of the 1-(4-pyridyloxy)-4-pyridone.[27]

Oae *et al.*[28] rearranged the arenesulphonoxy-groups from the 2- to the 4-position in 1-isoquinolone: the main pathway was *via* solvent-separated ion pairs, with some participation by an oxygen-bridged ion pair.

The thermal decomposition of 1-alkoxy-4,6-diphenyl-2-pyridones leading to aldehydes, alcohols, and 3-substituted pyridones is, we believe, the result of two competing pathways. Aldehyde formation is rationalised in terms of a six-centre transition state involving proton abstraction by the amide carbonyl whereas the other products result from homolytic cleavage of the N–O bond to give an alkoxy-radical. The latter either abstracts a hydrogen atom or fragments to an alkyl



(49) (50) (51)



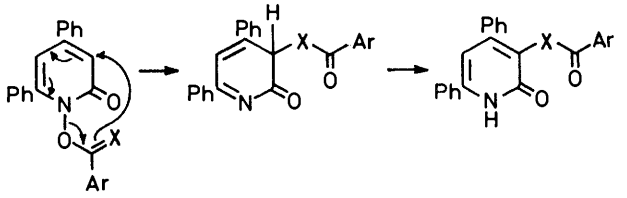
(52) (53) (54)

radical and a carbonyl compound, the relative importance of the two modes being a function of the alkyl radical stability.[29]

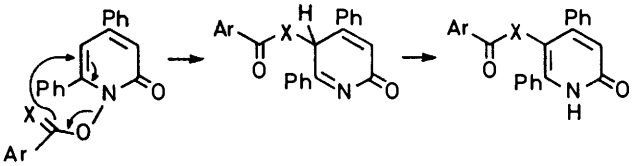
1-Benzyloxypyridones give high yields of aldehydes consistent with the ease of abstraction of the benzylic proton. For other 1-alkoxy-derivatives the radical pathway competes. The primary n-octyloxy-radical recombines intact at the 3-position of the pyridone nucleus but in contrast the phenethyloxy- and but-3-enyloxy-radicals first fragment with loss of formaldehyde. The resultant conjugated radical subsequently reacts with the pyridonyl radical, again at the 3-position.*

In the analogous photochemical reactions we propose excitation of the pyridone carbonyl function. Aldehyde formation arises from abstraction of a benzylic proton and the rearrangement products again arise from the alternative N–O cleavage pathway. The rearrangement of the pyridyloxy-pyridone (12) may involve a similar homolytic cleavage or a [1,5]sigmatropic shift.

The rearrangement of the 1-imidoyloxy-compounds with cleavage of an N–O bond and formation of a C–N rather than C–O bond demonstrates that the process does not follow a sequence of the type (49)—(51). Direct [1,5] and [1,3] sigmatropic shifts (to give the 3- and 5-substituted products respectively) are precluded for the same reason. Concerted rearrangements (55) to (56) and (57) to (58), though attractive, seem unlikely



(55) (56)



(57) (58)

on steric grounds and do not account for the observed by-products, *e.g.* (25). We therefore favour N–O cleavage followed by recombination [*i.e.* mechanisms analogous to those indicated by the conversion (44) into (46)—(48)] of which the free-radical pathway is preferred over the ion-pair mechanism, bearing in mind the reaction conditions and instability of a pyridone cation. The rearrangements of the 1-acyloxy-pyridones appear to be analogous.

EXPERIMENTAL

All melting points were determined using a Reichert hot stage microscope. I.r. spectra were recorded on Perkin-Elmer 237, 257, or 297 spectrophotometers. ^{1}H N.m.r. spectra were recorded either on a Varian HA 100 spectrometer at 100 MHz or on a Perkin-Elmer R12 spectrometer at 60 MHz. Mass spectra were obtained either on a Hitachi–Perkin-Elmer RMU-6E or A.E.I. MS9 mass spectrometers. ^{13}C N.m.r. spectra were recorded on a JEOL FX 100 spectrometer. Preparative thick layer chromatography was carried out on Kieselgel 60PF_{254} silica gel. Except where stated, column chromatography was carried out on alumina (UG 01). Dry or purified acetonitrile refers to drying over $MgSO_4$, followed by reflux over P_2O_5, distillation, and storage over molecular sieves. Dry diethyl ether and dry light petroleum refer to material dried over sodium wire. Dry ethyl acetate refers to material washed with aqueous sodium hydrogencarbonate (5%), and saturated aqueous sodium chloride, dried over $MgSO_4$, distilled, and stored over molecular sieves.

Except where stated, photochemical reactions were performed in a quartz glass vessel using a Rayonet photochemical reactor of sixteen tubular u.v. sources mounted around the inner surface of a polished cylindrical reflector.

* In response to a referee's comment we note that, in principle, aldehyde formation could derive from decomposition of alkoxy-radicals implying that all products originate from initial homolytic cleavage of the N–O bond. However if this were the case we might expect formation of some 3-benzyloxy-4,6-diphenyl-2-pyridone from the decomposition of the 1-benzyloxy-isomer; at the present time we have no evidence for this product in the reaction mixture. We believe a detailed mechanistic study of the whole series of rearrangements is warranted and indeed this is being considered by Dr. I. Shinkai.

Irradiation at 253.7 nm refers to the use of low-pressure mercury lamps (No. RPR-2537A), with 84% of emission at 253.7 nm. Irradiation at 350 nm refers to the use of black-light lamps (No. RPR-3500A) with 90% of emission in the 310 to 410 nm region (maximum at 350 nm). All photolyses were carried out in purified MeCN. Prior to irradiation, the reaction mixture was thoroughly flushed with a stream of dry nitrogen (for at least 1 h) to remove oxygen. During photolysis the reaction solution was kept free of oxygen and dry by the passage of a slow stream of dry nitrogen and the connection of a drying tube.

The following compounds were prepared according to literature procedures: the sodium salt (10) of 1-hydroxy-4,6-diphenyl-2-pyridone (pyridona), m.p. 299—301 °C (lit.,[3] 299—301 °C); phenylacetyl chloride, b.p. 47—51 °C at 1.0 mmHg (lit.,[30] 104—105 °C at 24 mmHg); *o*-toluoyl chloride, b.p. 73.5—74.5 °C at 5 mmHg (lit.,[31] 213 °C at 760 mmHg); *p*-toluoyl chloride, b.p. 42—45 °C at 0.4 mmHg (lit.,[32] 102 °C at 15 mmHg); *N*-phenylbenzimidoyl chloride (23a), b.p. 104—106 °C at 0.25 mmHg (lit.,[11] b.p. 174—176 °C at 12 mmHg); *N*-(*p*-tolyl)benzimidoyl chloride (23c), b.p. 138—140 °C at 0.1 mmHg (lit.,[12] b.p. 104 °C at 0.005 mmHg).

Pyrolysis of 1-*Phenethyloxy*-4,6-*diphenyl*-2-*pyridone* (1).—1-Phenethyloxy-4,6-diphenyl-2-pyridone [3] (0.96 g, 2.6 mmol) was heated in an evacuated Claisen distillation flask at 180—220 °C and 1.0 mmHg for 4 h. The cooled receiver contained phenylacetaldehyde (0.15 g, 49%). 3-*Benzyl*-4,6-*diphenyl*-2-*pyridone* (3) (0.023 g, 26%) was separated from 4,6-diphenyl-2-pyridone [3b] by extracting the residue with hot Me_2CO (20 ml); the former was collected by filtration. Crystallisation from cyclohexane gave *prisms*, m.p. 165—167 °C (Found: C, 85.1; H, 6.0; N, 4.4 $C_{24}H_{19}NO$ requires C, 85.4; H, 5.7; N, 4.2%); $\nu_{max.}$ ($CHBr_3$) 2 800—3 100 (N–H) and 1 630 cm^{-1} (C=O); δ[$(CD_3)_2SO$] 3.7 (2 H, s), 6.4 (1 H, s), 6.8—7.7 (15 H, m), and 12.0 (1 H, br s); *m/e* 337 (M^+).

Photolysis of 1-*Phenethyloxy*-4,6-*diphenyl*-2-*pyridone* (1).—A solution of the 1-phenethoxypyridone (1.10 g, 3.0 mmol) in EtOAc (100 ml) was deoxygenated and irradiated for 4.5 h in a Pyrex photolysis reactor equipped with a Hanovia 100-W medium-pressure mercury lamp. The solvent was evaporated off and the residue steam-distilled. The residue of the steam distillation was eluted on a silica-gel column (Kieselgel 60PF254). The silica was first heated under reflux in MeOH to remove the indicator. The eluant was first Et_2O (100 ml), then Et_2O–EtOAc (100 ml, 1 : 1), then EtOAc (200 ml). The third fraction to be eluted (under pressure) was the above-mentioned 3-benzyl-4,6-diphenyl-2-pyridone (0.14 g, 14%), which crystallised from cyclohexane as prisms, m.p. 165—167 °C.

2-*Chloro*-4,6-*diphenylpyridine* (6).—4,6-Diphenyl-2-pyridone (2.00 g, 8.1 mmol) and $POCl_3$ (5 ml) were heated in a Carius tube at 200 °C for 4.5 h. The black solution was poured onto ice–water (500 g, 100 ml) maintained basic with NH_4OH (to phenolphthalein). The precipitate was crystallised from EtOH to give the *chloropyridine* (6) (1.82 g, 84%) as pale tan prisms, m.p. 63—65 °C (Found C, 76.5; H, 4.6; N, 5.2; Cl, 13.4. $C_{17}H_{12}ClN$ requires C, 76.8; H, 4.5; H, 5.3; Cl, 13.3%); $\nu_{max.}$ 1 600 cm^{-1} (C=N, C=C); δ($CDCl_3$) 7.5—8.4 (11 H, m) and 8.4 (1 H, s).

2,4-*Diphenylpyridine*.— 2-Chloro-4,6-diphenylpyridine (0.53 g, 2 mmol), KOH (0.16 g), Pd–C (5%, 0.20 g), and MeOH (50 ml) were stirred under H_2 at 18 °C and 760 mmHg for 18 h. The mixture was filtered and evaporated. The residue was dissolved in H_2O (100 ml) and extracted with $CHCl_3$ (3 × 75 ml). The combined dried ($MgSO_4$) extracts were evaporated, leaving 2,4-diphenylpyridine as an intractible oil; $\nu_{max.}$ (liquid film) 1 600 cm^{-1} (C=N, C=C); δ($CDCl_3$) 7.4—8.4 (12 H, m) and 8.7 (1 H, d, *J* 10 Hz). The oil was converted into the picrate (0.74 g, 80%) which crystallised from aqueous EtOH (95%), m.p. 190.5—192.5 °C [lit.,[33] m.p. 187 °C].

3-*Benzyl*-2-*chloro*-4,6-*diphenylpyridine* (8).—3-Benzyl-4,6-diphenyl pyridone (9) (0.66 g, 1.95 mmol) and $POCl_3$ (2.0 ml) were heated at 200 °C for 4 h in a Carius tube. The cooled $POCl_3$ solution was poured into ice–water (100 g, 25 ml) maintained basic with NH_4OH (to phenolphthalein). The aqueous suspension was extracted with $CHCl_3$ (3 × 50 ml) and the combined organic layers were washed with H_2O (3 × 50 ml). After drying ($MgSO_4$), the solvent was evaporated off, leaving the 3-*benzyl*-2-*chloro*-4,6-*diphenylpyridine* (8) which crystallised from $CHCl_3$–MeOH as prisms (0.67 g, 96%), m.p. 148.5—150.5 °C (Found: C, 80.6; H, 5.2; N, 3.9; Cl, 10.1. $C_{24}H_{18}ClN$, requires C, 81.0; H, 5.1; N, 3.9; Cl, 10.0%); $\nu_{max.}$ ($CHBr_3$) 1 600 (C=N), 1 590 (C=C), and 1 150 cm^{-1} (CCl); δ($CDCl_3$) 4.15 (2 H, s), 6.9—7.5 (13 H, m), 7.6 (1 H, s), and 8.0—8.2 (2 H, m).

5-*Benzyl*-2,4-*diphenylpyridine* (9).—3-Benzyl-2-chloro-4,6-diphenylpyridine (8) (0.46 g, 1.3 mmol), KOH (0.20 g), Pd–C (5%, 0.40 g), and EtOH (50 ml) were shaken under H_2 at 15 °C and 2 atm for 18 h. The mixture was filtered, the filtrate was evaporated, and the residue was dissolved in H_2O (60 ml) and extracted with $CHCl_3$ (3 × 60 ml). The extracts were combined, dried ($MgSO_4$), and evaporated, leaving a clear oil (0.41 g, 98%) which did not crystallise; $\nu_{max.}$ ($CHBr_3$) 1 600 (C=N) and 1 590 cm^{-1} (C=C); δ($CDCl_3$) 4.0 (2 H, s), 6.9—7.6 (13 H, m), 7.8 (1 H, s), 8.1—8.3 (2 H, m), and 8.7 (1 H, s). The crude *pyridine* (9) was converted into the *hydrochloride salt*, which crystallised from EtOH as needles, m.p. 196—198 °C (Found: C, 80.3; H, 5.7; N, 3.9; Cl, 10.0. $C_{24}H_{20}ClN$ requires C, 80.5; H, 5.6; N, 3.9; Cl, 9.9%); $\nu_{max.}$ ($CHBr_3$) 2 300 (broad, $\overset{+}{N}H$) and 1 600 cm^{-1} (C=C, C=N); δ[$(CD_3)_2SO$] 4.2 (2 H, s), 6.9—7.7 (13 H, m), 8.2 (1 H, s), 8.3—8.4 (2 H, m), and 8.8 (1 H, s).

Pyrolysis of 1-(*But*-3-*enyloxy*)-4,6-*diphenyl*-2-*pyridone*.—1-(But-3-enyloxy)-4,6-diphenyl-2-pyridone [3] (0.50 g, 1.6 mmol) was distilled at 200—230 °C and 15 mmHg over 3 h. After this period, the cooled receiver (−78 °C) held an oil (0.055 g, 50%) which was shown to be crotonaldehyde; $\nu_{max.}$ (liquid film) 1 700 cm^{-1} (C=O); δ(CCl_4) 2.0 (3 H, d, *J* 11 Hz), 6.1 (1 H, m), 6.7 (1 H, m), and 9.5 (1 H, d, *J* 11 Hz). The pyrolysis residue was eluted on an alumina column (EtOAc), and the second fraction was 3-*allyl*-4,6-*diphenyl*-2-*pyridone* (0.15 g, 33%), which, after sublimation (185 °C at 15 mmHg) was obtained as needles, m.p. 187—189 °C (Found: N, 4.6. $C_{20}H_{17}NO$ requires B, 4.9%); $\nu_{max.}$ ($CHBr_3$) 2 800—3 200 (NH) and 1 610 cm^{-1} (C=O); δ($CDCl_3$) 3.2 (2 H, d), 4.9 (2 H, m), 5.9 (1 H, m), 6.3 (1 H, s), 7.3 (10 H, m), and 12.5 (1 H, br s).

Pyrolysis of 1-*Octyloxy*-4,6-*diphenyl*-2-*pyridone* (11).—1-Octyloxy-2,4-diphenyl-2-pyridone (0.75 g, 2 mmol) was slowly distilled at 200—240 °C and 15 mmHg. After 4 h, the cooled receiver (−78 °C) held a mixture (0.13 g) of octanal (37%) and octan-1-ol (13%). The residue (0.60 g) was separated by preparative t.l.c. (silica; $CHCl_3$, 4 developments). The third band from the baseline was 3-*octyloxy*-4,6-*diphenyl*-2-*pyridone* (13) (0.04 g, 5%) which

crystallised from $CHCl_3$–light petroleum (b.p. 60—80 °C) as needles, m.p. 133—136 °C (Found: C, 79.6; H, 7.6; N, 3.6. $C_{25}H_{29}NO_2$ requires C, 80.0; H, 7.8; N, 3.7%); $\nu_{max.}$ ($CHBr_3$) 2 700—3 100 (NH), 1 600—1 650 (C=O), and 1 040 cm^{-1} (C–O); δ($CDCl_3$) 1.6 (15 H, m), 4.0 (3 H, t, *J* 8 Hz), 6.5 (1 H, s), 7.3—7.9 (10 H, m), and 12.7 (1 H, br s).

Photolysis of 1-*Octyloxy*-4,6-*diphenyl*-2-*pyridone* (11).—A solution of 1-octyloxy-4,6-diphenyl-2-pyridone (11) (1.13 g, 3.0 mmol) in dry, deoxygenated EtOAc (100 ml) was irradiated for 4 h in a pyrex photolysis reactor equipped with a Hanovia 100-W medium-pressure mercury lamp. The solvent was evaporated off and the residue steam-distilled, giving octanal (47%) and octanol (23%). On preparative t.l.c. (silica; toluene-EtOAc, 2 : 1) the distillation residue gave the above-mentioned 3-octyloxypyridone (0.02 g, 2%).

1-(5-*Nitro*-2-*pyridyloxy*)-4,6-*diphenyl*-2-*pyridone* (12).—Sodium 1-oxido-4,6-diphenyl-2-pyridone (10) (0.95 g, 3.3 mmol), 2-chloro-5-nitropyridine (0.48 g, 3.0 mmol), and absolute EtOH (40 ml) were heated under reflux for 7 h. The solution was cooled and filtered to give the *pyridyloxypyridone* (12) (1.11 g, 96%) as prisms which crystallised from EtOH, m.p. 190—192 °C (Found: C, 68.4; H, 4.1; N, 10.7. $C_{22}H_{15}N_3O_4$ requires C, 68.6; H, 3.9; N, 10.9%); $\nu_{max.}$ ($CHBr_3$) 1 670 (C=O) and 1 360 cm^{-1} (NO_2); δ($CDCl_3$) 6.5 (1 H, d, *J* 2 Hz), 6.9 (1 H, d, *J* 2 Hz), 7.0 (1 H, d, *J* 9 Hz), 7.3—7.7 (10 H, m), 8.4 (1 H, dd, *J* 9 Hz, *J* 3 Hz), and 9.0 (1 H, d, *J* 3 Hz).

Photolysis of 1-(5-*Nitro*-2-*pyridyloxy*)-4,6-*diphenyl*-2-*pyridone* (12).—A dry, deoxygenated solution of 1-(5-nitro-2-pyridyloxy)-4,6-diphenyl-2-pyridone (0.93 g, 2.4 mmol) in benzene (100 ml) was irradiated for 3 h in a Pyrex photolysis reactor equipped with a Hanovia 100-W medium-pressure mercury lamp. The benzene was evaporated off and the residue taken up in acetone. Filtration gave a dark brown microcrystalline solid, 3-(5-nitro-2-pyridyloxy)-4,6-diphenyl-2-pyridone (14) (0.46 g, 50%) which resisted purification; $\nu_{max.}$ ($CHBr_3$) 3 200—2 800 (N–H), 1 670—1 620 (C=O), 1 350 (NO_2), and 1 260 cm^{-1} (C–O); δ($CDCl_3$), 6.5 (1 H, d, *J* 10 Hz), 6.7 (1 H, s), 7.4 (10 H, m), 8.1 (1 H, dd, *J* 10, 2 Hz), and 8.4 (1 H, d, *J* 2 Hz).

1-*Benzoyloxy*-4,6-*diphenyl*-2-*pyridone* (15e).—Benzoyl chloride (1.12 g, 0.008 mol), the salt (10) (1.14 g, 0.004 mol), and MeCN (25 ml) were stirred for 2.5 h at 20 °C. Solid was filtered off and the filtrate was reduced to 5 ml and again filtered. The combined precipitates were recrystallised from EtOAc to give colourless needles of 1-*benzoyloxy*-4,6-*diphenyl*-2-*pyridone* (15e) (1.35 g, 92%), m.p. 215—216 °C (Found: C, 78.2; H, 4.6; N, 4.0. $C_{24}H_{17}NO_3$ requires C, 78.5; H, 4.7; N, 3.8%); $\nu_{max.}$ (Nujol) 1 780 (O–C=O) and 1 670 cm^{-1} (N–C=O); $\lambda_{max.}$ (EtOH) 341 and 244 nm; δ($CDCl_3$) 6.44 (1 H, d, *J* 3 Hz), 6.90 (1 H, d, *J* 3 Hz), 7.2—7.7 (13 H, m), and 7.95 (2 H, d of d, *J* 9 and 1.5 Hz).

The following were prepared similarly: 1-*acetoxy*-4,6-*diphenyl*-2-*pyridone* (15a) (76%), needles from *dry* EtOAc–*dry* light petroleum (b.p. 60—80 °C), m.p. 123—124 °C (Found: C, 74.6; H, 5.0; N, 4.6. $C_{19}H_{15}NO_3$ requires C, 74.7; H, 5.0; N, 4.6%); $\nu_{max.}$ (Nujol) 1 815 (O–C=O) and 1 670 cm^{-1} (N–C=O); δ($CDCl_3$) 2.10 (3 H, s, Me), 6.44 (1 H, d, *J* 2.5 Hz), 6.82 (1 H, d, *J* 2.5 Hz), and 7.50 (10 H, s, 2Ph); 4,6-*diphenyl*-1-*phenylacetoxy*-2-*pyridone* (15b) (68%) not purified; $\nu_{max.}$ (Nujol) 1 810 (O–C=O) and 1 670 cm^{-1} (N–C=O); δ($CDCl_3$) 3.72 (2 H, s, CH_2), 6.40 (1 H, d, *J* 2.5 Hz), 6.70 (1 H, d, *J* 2.5 Hz), and 7.0—7.7 (17 H, m); 4,6-*diphenyl*-1-(o-*toluoyloxy*)-2-*pyridone* (15c) (66%), prisms from *dry* EtOAc–*dry* light petroleum (b.p. 60—80 °C), m.p. 133.5—135 °C (Found: C, 78.7; H, 5.2; N, 3.6. $C_{25}H_{19}NO_3$ requires C, 78.7; H, 5.0; N, 3.7%); $\nu_{max.}$ (Nujol) 1 780 (O–C=O) and 1 660 cm^{-1} (N–C=O); δ($CDCl_3$) 2.44 (3 H, s, Me), 6.50 (1 H, d, *J* 2.5 Hz), 6.98 (1 H, d, *J* 2.5 Hz), and 7.5 (14 H, m); 4,6-*diphenyl*-1-(p-*toluoyloxy*)-2-*pyridone* (15d) (95%), needles from *dry* EtOAc, m.p. 213—214 °C (Found: C, 78.8; H, 5.0; N, 3.7. $C_{25}H_{19}NO_3$ requires C, 78.7; H, 5.0; N, 3.7%); $\nu_{max.}$ (Nujol) 1 780 (O–C=O) and 1 660 (N–C=O), δ($CDCl_3$) 2.45 (3 H, s, Me), 6.56 (1 H, d, *J* 2.5 Hz), 6.96 (1 H, d, *J* 2.5 Hz), 7.23 (2 H, d, *J* 8 Hz), 7.5 (10 H, m), and 7.90 (2 H, d, *J* 8 Hz).

Photolysis of 1-*Benzoyloxy*-4,6-*diphenyl*-2-*pyridone* (15e).—1-Benzoyloxy-4,6-diphenyl-2-pyridone (1.14 g, 3.1 mmol) in *dry* MeCN (250 ml) was degassed and irradiated at 350 nm for 36 h. The solution was reduced to 25 ml, cooled overnight at 0 °C, and filtered. The precipitate crystallised from *dry* MeCN to give 5-*benzoyloxy*-4,6-*diphenyl*-2-*pyridone* (16) (140 mg, 12%) as needles, m.p. 249—252 °C (Found: C, 78.1; H, 4.5; N, 3.8. $C_{24}H_{17}NO_3$ requires C, 78.5; H, 4.7; N, 3.8%); $\nu_{max.}$ (Nujol) 3 000—2 500 (NH), 1 740 (O–C=O), and 1 650 cm^{-1} (N–C=O); δ($CDCl_3$) 6.6 (1 H, s, 3-H), 7.2—7.7 (13 H, m), and 7.8 (2 H, d, *J* 9 Hz); *m/e* (70 eV) 368 (8.2%), 367 (26), 262 (4.1), 247 (1.5), 234 (2.4), 206 (3.6), 128 (1.6), 122 (33), 105 (100), 83 (11), 77 (60), 66 (9.3), 57 (5.7), 51 (10), and 45 (9.8); $\lambda_{max.}$ ($CHCl_3$) 335 nm.

The filtrate was evaporated and the residue separated by preparative t.l.c. (silica), eluting with EtOAc, to give 4,6-diphenyl-2-pyridone [4th fraction, R_F 0.30 (EtOAc, silica)]; recrystallised from Me_2CO (80 mg, 10%), m.p. 212—215 °C, mixed m.p. 210—213 °C, m.p. (authentic sample) 210—213 °C (lit.,[34] 208 °C), identical (i.r. and ^1H n.m.r. spectra) with an authentic sample, benzoic acid [2nd fraction, R_F 0.80 (EtOAc, silica)]; isolated by dissolving in $CHCl_3$, extraction with aqueous Na_2CO_3, acidification, re-extraction with $CHCl_3$, drying, and removal of solvent (9 mg, 2%), m.p. 120—122 °C (lit.,[35] m.p. 122 °C), identical (i.r. spectrum) with an authentic sample].

Hydrolysis of 5-*Benzoyloxy*-4,6-*diphenyl*-2-*pyridone* (16).—5-Benzoyloxy-4,6-diphenyl-2-pyridone (16) (60 mg, 16 mmol) was refluxed in aqueous NaOH (20%, 5 g) with stirring for 3.5 h. On cooling, water (45 ml) was added and the mixture acidified with concentrated HCl and then basified to pH 8.5 with Na_2CO_3. The precipitate was washed with water (10 ml), and recrystallised from aqueous HOAc to give 5-*hydroxy*-4,6-*diphenyl*-2-*pyridone* (17) (31 mg, 71%) as needles, m.p. 273—276 °C (Found: C, 77.4; H, 4.9; N, 5.2. $C_{17}H_{13}NO_2$ requires C, 77.5; H, 5.0; N, 5.3%); $\nu_{max.}$ (Nujol) 3 500—2 500 (OH) and 1 640 cm^{-1} (N–C=O); δ(CF_3CO_2H) 7.25 (1 H, s, 3-H) and 7.65 (10 H, m); *m/e* 264 (19%), 263 (100), 262 (31), 247 (8.1), 244 (4.1), 235 (9.0), 234 (4.3), 206 (18), 191 (2.1), 130 (5.3), 105 (17), 104 (17), 102 (6.9), and 77 (12); $\lambda_{max.}$ ($CHCl_3$) 333 nm (11 300).

The aqueous filtrate was acidified with concentrated HCl and extracted with $CHCl_3$ (3 × 20 ml). The $CHCl_3$ extracts were combined, dried ($MgSO_4$), and evaporated. The residue was recrystallised from light petroleum (b.p. 60—80 °C) to give benzoic acid, (19 mg, 68%), m.p. 121—122 °C, mixed m.p. 121—122 °C, identical (i.r. spectrum) with an authentic sample.

Photolysis of 4,6-*Diphenyl*-1-(p-*toluoyloxy*)-2-*pyridone*

(15d).—4,6-Diphenyl-1-(*p*-toluoyloxy)-2-pyridone (3.0 g, 7.9 mmol) in dry MeCN (500 ml) was degassed and irradiated at 350 nm for 38 h. The photolysis mixture on filtration yielded a precipitate (a). The filtrate was reduced to 30 ml and filtered again to afford a further precipitate (b). $CHCl_3$ (25 ml) was added to the precipitate (a) and the suspension was boiled for 5 min, cooled and filtered to give a precipitate (c) (405 mg). The filtrate was added to the precipitate (b) and the suspension boiled for 5 min, cooled, and filtered to give another precipitate (d) (52 mg). The filtrate was eluted down an alumina column with $CHCl_3$–EtOH (9 : 1 v/v). The first fraction (35 mg), identical to precipitates (c) and (d), was 4,6-*diphenyl*-3-(p-*toluoyloxy*)-2-*pyridone* (19) (total yield 492 mg, 16%), which crystallised from *dry* MeCN as needles, m.p. 290—295 °C (Found: C, 78.6; H, 5.0; N, 3.7. $C_{25}H_{19}NO_3$ requires C, 78.7; H, 5.0; N, 3.7%); $\nu_{max.}$ (Nujol) 3 100—2 500 (NH), 1 740 (O–C=O), and 1 660 cm^{-1} (N–C=O); δ(CF_3CO_2H) 2.4 (3 H, s, Me), 7.2—7.9 (13 H, m) and 8.0 (2 H, half of an ABq, *J* 8 Hz); δ($CDCl_3$) 2.4 (3 H, s, Me), 6.4 (1 H, s, 5-H), and 7.0—7.4 (14 H, m); $\lambda_{max.}$ (EtOH) 333 nm (ε 14 000); ($CHCl_3$) 335 nm (15 800); *m/e* (70 e.v.) 381 (12%), 263 (6.0), 262 (4.3), 243 (3.1), 119 (100), 104 (8.9), 91 (25), 77 (4.7), and 65 (5.9). The second fraction from the column crystallised from dry MeCN to give 4,6-*diphenyl*-5-(p-*toluoyloxy*)-2-*pyridone* (18) (295 mg, 10%) as needles, m.p. 246—252 °C (Found: C, 79.1; H, 5.0; N, 3.7. $C_{25}H_{19}NO_3$ requires C, 78.7; H, 5.0; N, 3.7%); $\nu_{max.}$ (Nujol) 3 100—2 500 (NH), 1 740 (O–C=O), and 1 650 cm^{-1} (N–C=O); δ($CDCl_3$) 2.3 (3 H, s, Me), 6.6 (1 H, s, 3-H), 7.1 (2 H, half of an ABq, *J* 8 Hz), 7.1—7.7 (10 H, m), and 7.7 (2 H, half of an ABq, Y 8 Hz); $\lambda_{max.}$ (EtOH) 327 nm; *m/e* (70 eV) 381 (22%), 262 (4.3), 247 (4.8), 206 (4.1), 119 (100), 104 (15), 102 (9.6), 91 (27), 77 (15), and 65 (13).

Filtrate (b) was evaporated and the residue separated on an alumina column eluting successively with $CHCl_3$–EtOAc (4 : 1 v/v), EtOAc, EtOAc–MeOH, and MeOH. The second fraction [R_F 0.80 (EtOAc, silica), 0.55 (EtOAc–$CHCl_3$, 4 : 1 v/v; silica)] was *p*-toluic acid (128 mg, 12%), m.p. 179—181 °C (lit.,[36] m.p. 181 °C), identical (i.r. spectrum and t.l.c.) with an authentic sample. Also collected was 4,6-diphenyl-2-pyridone (680 mg, 35%) [R_F 0.30 (EtOAc, silica); m.p. 209—213 °C (from Me_2CO) (lit.,[34] m.p. 208 °C); identical (i.r. spectrum and t.l.c.) with an authentic sample], and several minor unidentified products.

Hydrolysis of 4,6-*Diphenyl*-5-(p-*toluoyloxy*)-2-*pyridone* (18).—4,6-Diphenyl-5-*p*-toluoyloxy-2-pyridone (18) (800 mg, 2.1 mmol) was refluxed with aqueous NaOH (20%, 20 g) for 75 min with stirring. On cooling, water (40 ml) was added and the mixture was acidified with concentrated HCl and then re-basified to pH 8.5 with Na_2CO_3. The precipitate was filtered off, washed with water (25 ml), and recrystallised from aqueous HOAc to give 5-hydroxy-4,6-diphenyl-2-pyridone (354 mg, 64%) as needles, identical to compound (17) obtained from hydrolysis of 5-benzoyloxy-4,6-diphenyl-2-pyridone (16). The aqueous filtrate was acidified with concentrated HCl. The precipitate was filtered off, washed with water (10 ml), and recrystallised from water to give *p*-toluic acid (189 mg, 66%), m.p. 180—182 °C, identical (i.r. spectrum, m.p.) with an authentic sample.

4,6-*Diphenyl*-3-(p-*toluoyloxy*)-2-*pyridone* (19) was hydrolysed similarly to give *p*-toluic acid (69%), m.p. 180—182 °C, and 3-*hydroxy*-4,6-*diphenyl*-2-*pyridone* (20) (70%) as needles (from Me_2CO), m.p. 204—205 °C (Found: C, 77.3; H, 4.9; N, 5.3. $C_{17}H_{13}NO_2$ requires C, 77.5; H, 5.0; N, 5.3%); $\nu_{max.}$ (Nujol) 3 350, 3 060, and 1 630 cm^{-1} (N–C=O); δ($CDCl_3$) 6.6 (1 H, s, 5-H), 7.2—7.8 (10 H, m), and 12.5 (1 H, disappears on shaking with D_2O); $\lambda_{max.}$ ($CHCl_3$) 335 nm (ε 11 300); *m/e* (70 eV) 263 (100%), 262 (66), 244 (5.9), 234 (2.9), 217 (7.8), 216 (8.5), 206 (5.3), 191 (3.0), 189 (6.3), 128 (1.9), 104 (10), and 77 (8.3).

2-*Chloro*-4,6-*diphenyl*-3-(p-*toluoyloxy*)*pyridine* (21).—4,6-Diphenyl-3-(*p*-toluoyloxy)-2-pyridone (19) (570 mg, 1.5 mmol) in PCl_3 (15 ml) was heated in a Carius tube at 200 °C for 2 h. The resultant yellow liquid was poured into ice-water (600 g: 150 ml) containing sufficient aqueous NH_4OH to maintain the solution basic (to phenolphthalein). The precipitate was filtered off, washed with water (250 ml), and dried to give the crude 2-*chloro*-3-(p-*toluoyloxy*)*pyridine* (21) (164 mg, 28%). Recrystallisation from aqueous EtOH (95%) afforded needles, m.p. 198—199 °C (Found: C, 74.7; H, 4.4; N, 3.4. $C_{25}H_{18}ClNO_2$ requires C, 75.1; H, 4.5; N, 3.5%); $\nu_{max.}$ (Nujol) 1 745 cm^{-1} (C=O); δ($CDCl_3$) 2.4 (3 H, s, Me) and 7.1—8.2 (15 H, m).

The aqueous filtrate and washings were extracted with $CHCl_3$ (2 × 150 ml). The $CHCl_3$ extracts were combined, washed with water (2 × 50 ml), and dried ($MgSO_4$), and the solvent removed. The solid residue was crystallised from $CHCl_3$ to give *p*-toluamide (92 mg, 47%) as needles, m.p. 159—160 °C (lit.[37] m.p. 165 °C).

2,4-*Diphenylpyridin*-5-*ol* (22).—Pd–C (5%, 100 mg), 2-chloro-4,6-diphenyl-3-(*p*-toluoyloxy)pyridine (98 mg, 0.245 mmol), KOH (35 mg), and MeOH (50 ml) were stirred under H_2 at 20 °C and 760 mmHg for 69 h. The mixture was filtered and the filtrate evaporated. Water (50 ml) was added to the residue and this solution was extracted with $CHCl_3$ (3 × 25 ml). The combined dried ($MgSO_4$) extracts were evaporated to leave the 3-*hydroxypyridine* (22) (54 mg, 89%) which was recrystallised from $CHCl_3$ as needles (38 mg, 63%), m.p. 184—185 °C with some sublimation at *ca.* 180 °C (Found: C, 82.2; H, 5.1; N, 5.6. $C_{17}H_{13}NO$ requires C, 82.6; H, 5.3; N, 5.7%); $\nu_{max.}$ (Nujol) 2 800—2 500 cm^{-1} (broad, OH); δ[$(CD_3)_2SO$] 7.2—7.6 (6 H, m, *m*-H, *m'*-H, *p*-H, *p'*-H), 7.6—7.9 (3 H, m, *o'*-H, 3-H), 7.9—8.2 (2 H, m, *o*-H), and 8.5 (s, 6-H).

α-(p-*Anisidino*)-o-*tolualdehyde* (31).—*o*-Toluoyl chloride (7.87 g, 0.05 mol) was shaken with *p*-anisidine (5.53 g, 0.045 mol) in aqueous NaOH (10%, 37 ml) for 15 min. After dilution with water (50 ml), the precipitate was filtered off, washed with water (50 ml), and recrystallised from EtOH to give the *tolualdehyde* (31) as needles (5.8 g, 55%), m.p. 143—144.5 °C (Found: C, 74.9; H, 6.3; N, 5.8. $C_{15}H_{15}NO_2$ requires C, 74.7; H, 6.3; N, 5.8%); $\nu_{max.}$ (Nujol) 3 290 (NH) and 1 650 cm^{-1} (C=O); δ($CDCl_3$) 2.44 (3 H, s), 3.78 (3 H, s), 6.93 (2 H, d, *J* 9 Hz), 7.3 (4 H, m), and 7.76 (2 H, d, *J* 9 Hz).

N-(p-*Methoxyphenyl*)-o-*toluimidoyl Chloride* (23b).—Thionyl chloride (7 g) and α-(*p*-anisidino)-*o*-tolualdehyde (8.7 g, 0.036 mol) were refluxed for 1.5 h. The excess of thionyl chloride was removed and the product was distilled to give the *imidoyl chloride* (23b) (8.1 g, 86%) as a pale yellow oil, b.p. 152—155 °C at 0.05 mmHg, which solidified to needles (Found: C, 69.5; H, 5.8; N, 5.3. $C_{15}H_{14}ClNO$ requires C, 69.4; H, 5.4; N, 5.4%); $\nu_{max.}$ (Nujol) 1 645 (C=N) cm^{-1}; δ($CDCl_3$) 2.50 (3 H, s), 3.82 (3 H, s), 7.05 (2 H, d, *J* 4 Hz), 7.3 (4 H, m), and 7.70 (2 H, d, *J* 4 Hz).

4,6-*Diphenyl*-1-(N-*phenylbenzimidoyloxy*)-2-*pyridone* (24a).—*N*-Phenylbenzimidoyl chloride (23a) (0.22 g, 1 mmol), sodium 1-oxido-4,6-diphenyl-2-pyridone (10) (0.29 g,

1 mmol), and *dry* MeCN (10 ml) were stirred for 6 h at 20 °C with exclusion of light and water vapour. The reaction mixture was filtered through Kieselguhr. The solvent was removed from the filtrate and the residue recrystallised from *dry* Et_2O to give the 1-*benzimidoyloxypyridone* (24a) (0.39 g, 88%) as needles, m.p. 147—148 °C (Found: C, 81.0; H, 5.2; N, 6.4. $C_{30}H_{22}N_2O_2$ requires C, 81.4; H, 5.0; N, 6.3%); $\nu_{max.}$ (Nujol) 1 660 cm^{-1} (C=O); δ($CDCl_3$) 6.44 (1 H, d, *J* 2.5 Hz), 6.56 (2 H, d, *J* 8 Hz), 6.94 (1 H, d, *J* 2.5 Hz), and 6.9—7.8 (20 H, m).

The following were prepared similarly: 1-[N-(p-*methoxyphenyl*)-o-*toluimidoyloxy*)-4,6-*diphenyl*-2-*pyridone* (24b) (93%) as needles from *dry* Et_2O, m.p. 143—145 °C (Found: C, 78.6; H, 5.4; N, 5.7. $C_{32}H_{26}N_2O_3$ requires C, 79.0; H, 5.4; N, 5.8%); $\nu_{max.}$ (Nujol) 1 660 cm^{-1} (C=O); δ($CDCl_3$) 1.8 (3 H, s), 3.64 (3 H, s), 6.5 (4 H, s), 6.54 (1 H, d, *J* 2.5 Hz), 6.95 (1 H, d, *J* 2.5 Hz), and 7.0—7.8 (14 H, m); 4,6-*diphenyl*-1-[N-(p-*toluoyl*)*benzimidoyloxy*]-2-*pyridone* (24c) (95%) as needles (from dry EtOAc), m.p. 147—149 °C (Found: C, 81.3; H, 5.2; N, 6.1. $C_{31}H_{24}N_2O_2$ requires C, 81.6; H, 5.3; N, 6.1%); $\nu_{max.}$ (Nujol) 1 660 cm^{-1} (C=O); δ($CDCl_3$) 2.19 (3 H, s, Me), 6.45 (1 H, d, *J* 2.5 Hz), 6.5 (2 H, d, *J* 8 Hz), 6.95 (2 H, d, *J* 8 Hz), 7.0 (1 H, d, *J* 2 Hz), and 7.1—7.8 (15 H, m).

Photolysis of 4,6-*Diphenyl*-1-(*N*-*phenylbenzimidoyloxy*)-2-*pyridone* (24a).—The benzimidoyloxypyridone (24a) (7.78 g, 17.6 mmol) in dry MeCN (500 ml) was degassed and irradiated at 350 nm for 40 h. The precipitate was filtered off and recrystallised from CF_3CO_2H to give needles of 4,4′-dibenzamidobiphenyl (25) (60 mg, 1.7%), m.p. >335 °C [lit.,[13] m.p. 352 °C] (Found: C, 79.6; H, 5.2; N, 7.1. $C_{26}H_{20}N_2O_2$ requires C, 79.6; H, 5.1; N, 7.1%); $\nu_{max.}$ (Nujol) 3 240 (NH) and 1 645 cm^{-1} (N–C=O); δ($CDCl_3$) 7.7 (18 H, m), and 9.4 (2 H, s, NH); *m/e* (70 eV) 392 (63%), 391 (2.1), 289 (5.8), 287 (3.7), 105 (100), 77 (63), and 44 (6.6).

Removal of solvent from the filtrate, addition of $CHCl_3$ (30 ml) to the residue and cooling overnight at 0 °C gave crystalline 5-*benzanilido*-4,6-*diphenyl*-2-*pyridone* (26) (980 mg, 12.5%), which recrystallised from $CHCl_3$ as needles, m.p. 306—308 °C (Found: N, 6.1. $C_{30}H_{22}N_2O_2$ requires N, 6.3%); $\nu_{max.}$ (Nujol) 1 645 cm^{-1}; δ(CF_3CO_2H) 7.0—8.0 (m); $\lambda_{max.}$ ($CHCl_3$) 293 (22 300) and 340 nm (shoulder).

The filtrate was eluted from an alumina column successively with $CHCl_3$ and $CHCl_3$–MeOH (19 : 1 v/v). The 3rd fraction collected was benzanilide (140 mg, 4%), m.p. 160—163 °C (lit.,[38] m.p. 162 °C), identical with authentic sample (i.r. spectrum). The 10th fraction crystallised from *dry* MeCN to give 3-*benzanilido*-4,6-*diphenyl*-2-*pyridone* (28) (362 mg, 4%) as needles, m.p. 330—333 °C (Found: C, 81.2; H, 5.2; N, 6.6. $C_{30}H_{22}N_2O_2$ requires C, 81.4; H, 5.0; N, 6.3%); $\nu_{max.}$ (Nujol) 1 670 and 1 630 cm^{-1}; δ(CF_3CO_2H) 7.2—8.1 (m); $\lambda_{max.}$ ($CHCl_3$) 354 nm (19 900); *m/e* (70 eV) 442 (100%), 441 (98). 423 (5.0), 337 (22), 309 (12), 291 (5.0), 280 (6.2), 265 (5.0), 230 (6.2), 203 (6.7), 178 (5.9), 105 (86), 104 (8.4), and 77 (70). The 12th fraction was a mixture of 4,6-diphenyl-2-pyridone and 5-benzanilido-4,6-diphenyl-2-pyridone (26). Recrystallisation from Me_2CO afforded solely 4,6-diphenyl-2-pyridone (540 mg, 12.5%), m.p. 210—214 °C (lit.,[34] 208 °C), identical (i.r. spectrum) with an authentic sample. Removal of solvent from the mother-liquor and recrystallisation of the residue from $CHCl_3$ afforded solely the 5-benzanilidopyridone (26) (80 mg, 1%; total yield 1.06 g, 13.5%). Removal of solvent from the mother-liquor and recrystallisation from Me_2CO afforded further 4,6-diphenyl-2-pyridone (270 mg, 6%, total yield 810 mg, 18.5%). Also obtained from the column in moderate quantities were two unidentified products (680 mg and 930 mg).

Hydrolysis of 5-*Benzanilido*-4,6-*diphenyl*-2-*pyridone* (26).—Aqueous H_2SO_4 (70%, 5 g) was added to the 5-benzanilidopyridone (26) (216 mg, 0.49 mmol) and the mixture heated at 140 °C for 4 h with stirring. A small quantity of benzoic acid sublimed from the reaction mixture as needles, m.p. 116—122 °C, identical with an authentic sample (i.r., m.p.). After cooling, the reaction mixture was diluted with water (45 ml) and neutralised to pH 8.5 (Na_2CO_3). The precipitate was filtered off, washed with water (50 ml), dried, and recrystallised from EtOH to give 5-*anilino*-4,6-*diphenyl*-2-*pyridone* (27) (132 mg, 80%) as needles, m.p. 334—337 °C (Found: C, 81.5; H, 5.3; N, 8.1. $C_{23}H_{18}N_2O$ requires C, 81.6; H, 5.4; N, 8.3%); $\nu_{max.}$ (Nujol) 3 440, 3 330, and 1 640 cm^{-1}; δ(CF_3CO_2H–$CDCl_3$) 7.3 (m); $\lambda_{max.}$ ($CHCl_3$) 348 nm.

The filtrate from above after removal of the precipitate of (27) and washings were combined, acidified (concentrated HCl), and extracted with $CHCl_3$ (3 × 30 ml). The extracts were combined and dried ($MgSO_4$) and the solvent was removed. The solid residue was recrystallised from light petroleum (b.p. 60—80 °C) to give benzoic acid (39 mg, 66%), m.p. 120—123 °C.

Hydrolysis of 3-*Benzanilido*-4,6-*diphenyl*-2-*pyridone* (28).—Aqueous H_2SO_4 (70%, 5 g) and 3-benzanilidopyridone (28) (159 mg) were stirred at 150 °C for 105 min. Benzoic acid partially sublimed from the reaction mixture. On cooling, the reaction mixture was diluted with water (45 ml), and neutralised to pH 8.5 (Na_2CO_3). A dark green precipitate of crude 3-anilino-4,6-diphenyl-2-pyridone (29) (116 mg, 95%) was filtered off, washed with water (50 ml), and dried; $\lambda_{max.}$ ($CHCl_3$) 355 nm. The filtrate and washings were combined, acidified (concentrated HCl), and extracted with $CHCl_3$ (3 × 30 ml) to give benzoic acid (36 mg, 81%).

Photolysis of 1- N-(p-*Methoxyphenyl*)-o-*toluimidoyloxy*]-4,6-*diphenyl*-2-*pyridone* (24b).—The 1-toluimidoyloxypyridone (7.06 g, 14.5 mmol) in *dry* MeCN (250 ml) was degassed and irradiated for 48 h at 350 nm. The precipitate was filtered off. Solvent was evaporated off from the filtrate and the residue in EtOAc (25 ml) was cooled overnight. Solid was filtered off, combined with the first precipitate, and recrystallised from *dry* MeCN to give 4,6-*diphenyl*-5-[N-o-*toluoyl*)-p-*anisidino*]-2-*pyridone* (30) (820 mg, 11.5%) as needles, m.p. 296—300 °C (Found: C, 79.0; H, 5.5; N, 5.8. $C_{32}H_{26}N_2O_3$ requires C, 79.0; H, 5.4; N, 5.8%); $\nu_{max.}$ (Nujol) 1 650 cm^{-1}; δ($CDCl_3$) 2.3 (3 H, s, Me), 2.5 (3 H, s, OMe), 6.0 (4 H, AB q, *J* 9 Hz), 6.5 (1 H, d, 3-H), 7.0 (2 H, d, *J* 4 Hz), and 7.4 (12 H, m); $\lambda_{max.}$ ($CHCl_3$) 327 nm (ε 7 700); *m/e* (70 eV) 486 (32%), 367 (16), 224 (16), 119 (100), 104 (6.7), 91 (31), 77 (8.9), 65 (5.3), and 44 (11.6).

Removal of solvent from the EtOAc filtrate left a residue which was eluted on alumina with $CHCl_3$–EtOAc (4 : 1 v/v) followed by $CHCl_3$–MeOH (10 : 1 v/v), to afford *N*-(*o*-toluoyl)-*p*-anisidine (31) (1.40 g, 40%), m.p. 143—145 °C (from ether), identical with an authentic sample (t.l.c., m.p., ^1H n.m.r. and i.r.). A further component, on recrystallisation from tetrahydrofuran (THF), gave 4,6-diphenyl-2-pyridone (720 mg, 20%), which after recrystallisation from Me_2CO had m.p. 210—214 °C (lit.,[34] m.p. 208 °C), identical with an authentic sample (m.p., i.r., and t.l.c.). The 5-toluoylanisidinopyridone (30) (120 mg, 1.7%) precipitated

from the THF mother-liquor on standing. The residual mixture was separated by preparative t.l.c. eluting twice with $CHCl_3$–MeCN (1 : 1 v/v) to give 4,6-diphenyl-2-pyridone (R_F 0.25; 180 mg, 5%; total yield 900 mg, 25%) and the 5-toluoylanisidinopyridone (30) (R_F 0.30; 140 mg, 2%; total yield 980 mg, 15%).

Hydrolysis of 4,6-*Diphenyl*-5-[N-(o-*toluoyl*)-p-*anisidino*)-2-*pyridone* (30).—Compound (30) (100 mg, 0.2 mmol) in glacial HOAc (2 ml) and concentrated HCl (13 ml) was heated (sealed tube) at 150 °C for 2.5 h. The reaction mixture was diluted with water to 70 ml, neutralised to pH 8 (Na_2CO_3), and extracted with $CHCl_3$ (3 × 30 ml). The extracts were combined and dried ($MgSO_4$) and the solvent removed. Trituration with Me_2CO and recrystallisation from Me_2CO gave 5-*amino*-4,6-*diphenyl*-2-*pyridone* (32) (18 mg, 33%) as a brown powder, m.p. 228—233 °C; $\nu_{max.}$ (Nujol) 3 430 (NH_2), 3 300 (NH_2), and 1 655 cm^{-1} (C=O); δ($CDCl_3$) 2.2 (2 H, s, NH_2), 6.5 (1 H, s, 3-H), and 7.5 (10 H, m); *m/e* (70 eV) 262 (100%), 261 (34), 243 (7.5), 234 (19), 216 (8.9), 206 (8.5), 130 (20), 104 (17), 102 (11), and 77 (17).

Photolysis of 4,6-*Diphenyl*-1-[N-(p-*tolyl*)*benzimidoyloxy*]-2-*pyridone* (24c).—The 1-benzimidoyloxypyridone (24c) (7.8 g, 17.1 mmol) in dry MeCN (500 ml) was degassed and irradiated for 36 h at 350 nm. After filtration, the filtrate was reduced to 30 ml, cooled overnight at 0 °C, and filtered again. The precipitates were combined and recrystallised from dry MeCN to yield 5-(N-*benzoyl*-p-*toluidino*)-4,6-*diphenyl*-2-*pyridone* (35) (810 mg, 10%) as needles, m.p. 259—261.5 °C (Found: C, 81.2; H, 5.2; N, 6.0. $C_{31}H_{24}N_2O_2$ requires C, 81.6; H, 5.3; N, 6.1%); $\nu_{max.}$ (Nujol) 1 645 cm^{-1} (C=O); δ(CF_3CO_2H) 2.28 (3 H, s, Me), 6.9 (1 H, s, 3-H), and 7.5 (19 H, m); δ($CDCl_3$) 2.1 (3 H, s, Me), 6.6 (1 H, s, 3-H), and 7.3 (19 H, m); $\lambda_{max.}$ ($CHCl_3$) 332 (9 000); *m/e* (70 eV) 456 (51%), 381 (24), 352 (7.4), 335 (22), 323 (5.9), 307 (23), 274 (6.9), 105 (100), and 77 (33). On standing, a precipitate formed in the filtrate. This was recrystallised from *dry* MeCN to yield 3-(N-*benzoyl*-p-*toluidino*)-4,6-*diphenyl*-2-*pyridone* (33) (270 mg, 3.5%) as needles, m.p. 305—308 °C (Found: C, 81.2; H, 5.2; N, 6.5. $C_{31}H_{24}N_2O_2$ requires C, 81.6; H, 5.3; N, 6.1%); $\nu_{max.}$ (Nujol) 1 670 cm^{-1} (C=O); $\lambda_{max.}$ ($CHCl_3$) 351 nm (ε 15 000); *m/e* (70 eV) 456 (44%), 439 (35), 379 (15), 351 (9.0), 335 (94), 293 (5.5), 105 (100), and 77 (44). The solvent was removed from the filtrate and the residue separated on an alumina column eluting successively with $CHCl_3$, $CHCl_3$–EtOAc (4 : 1 v/v) and $CHCl_3$–MeOH (4 : 1 v/v). The 3rd fraction was recrystallised from EtOH to afford *N*-benzyl-*p*-toluidide (500 mg, 14%), m.p. 159—161 °C (lit.,[39] m.p. 156—158 °C), identical with an authentic sample (i.r., t.l.c.). A further fraction was recrystallised from Et_2O to give compound (39) or (40) (460 mg, 17%) as plates, m.p. 158—159 °C (Found: C, 79.4; H, 6.0; N, 4.3. $C_{21}H_{19}NO_2$ requires C, 79.5; H, 6.0; N, 4.4%); $\nu_{max.}$ (Nujol) 1 660, 1 640, 1 625, 1 600, 1 575, 1 510, 1 345, 855, and 700 cm^{-1}; δ($CDCl_3$) 1.6 (3 H, s, Me), 2.2 (3 H, s, Me), 6.2 (2 H, d, *J* 10 Hz), and 7.8—8.4 (11 H, m); *m/e* (70 eV) 317 (4.15%), 211 (31), 107 (100), 105 (94), 90 (13), 77 (75), 51 (23), and 39 (15). Subsequent fractions contained more 3-benzoyltoluidinopyridone (33) (total yield 1.25 g, 16%), and a mixture of 4,6-diphenyl-2-pyridone (500 mg, 12%) and more 5-benzoyltoluidinopyridone (35) (total yield 1.40 g, 18%); the ratio was determined from integration of the ^1H n.m.r. signals.

Hydrolysis of 3-(N-*Benzoyl*-p-*toluidino*)-4,6-*diphenyl*-2-*pyridone* (33).—Aqueous H_2SO_4 (70%, 10 g) and the 3-benzoyltoluidinopyridone (33) (473 mg, 1.04 mmol) were heated at 140 °C for 1.5 h with stirring. Some benzoic acid sublimed. On cooling, the mixture was diluted with water (40 ml) and basified to pH 8 (Na_2CO_3). The yellow precipitate was filtered off, washed with water (50 ml), dried, and recrystallised from aqueous EtOH (charcoal) to give the 4,6-*diphenyl*-3-*toluidino*-2-*pyridone* (34) (261 mg, 80%) as yellow needles, m.p. 260.5—262.5 °C (Found: C, 81.8; H, 5.7; N, 7.7. $C_{24}H_{20}N_2O$ requires C, 81.8; H, 5.7; N, 7.9%); $\nu_{max.}$ (Nujol) 3 400 (NH), 3 330, and 1 625 cm^{-1} (C=O); δ($CDCl_3$) 2.0 (3 H, s, Me), 6.5 (1 H, s, 5-H), and 6.5—8.0 (15 H, m); $\lambda_{max.}$ ($CHCl_3$) 347 nm (ε 12 700); *m/e* (70 eV) 352 (72%), 351 (12), 335 (100), 324 (2.7), 319 (6.0), 275 (46), 220 (2.2), 217 (2.3), 204 (5.6), 191 (5.4), 176 (11), 168.5 (9.0), 104 (6.8), and 77 (9.5).

The aqueous filtrate from above was combined with the washings, and the whole acidified (concentrated HCl) and extracted with $CHCl_3$ (3 × 40 ml). The extracts were combined and dried ($MgSO_4$) and the solvent was removed. The residue and sublimate were recrystallised from light petroleum (b.p. 60—80 °C) to give benzoic acid (113 mg, 55%), m.p. 120—123 °C.

Hydrolysis of 5-(N-*Benzoyl*-p-*toluidino*)-4,6-*diphenyl*-2-*pyridone* (35).—Aqueous H_2SO_4 (70%, 10 g) and the 5-benzoyltoluidinopyridone (35) (350 mg, 0.77 mmol) were heated to 150 °C for 5 h with stirring, during which time some benzoic acid sublimed. The cooled mixture was diluted with water (40 ml) and basified to pH 8 (Na_2CO_3). The precipitate was filtered off, washed with water (25 ml), dried, and recrystallised from EtOH to give 4,6-*diphenyl*-5-*toluidino*-2-*pyridone* (36) (183 mg, 68%) as prisms, m.p. 296—299 °C (Found: C, 81.6; H, 5.5; N, 7.9. $C_{24}H_{20}N_2O$ requires C, 81.8; H, 5.7; N, 7.9%); $\nu_{max.}$ (Nujol) 3 440, 3 320, 1 650 cm^{-1} (C=O); δ($CDCl_3$) 2.0 (3 H, s, Me), 3.2 (2 H, broad, NH_2), 6.5 (5 H, m), and 7.2 (10 H, m); δ[$(CD_3)_2SO$] 1.9 (3 H, s, Me), 3.6 (2 H, broad, NH_2), 6.4 [5 H, AB q, (*J* 10 Hz) and s], and 7.2 (10 H, m); $\lambda_{max.}$ ($CHCl_3$) 318 nm (ε 9 000); *m/e* (70 eV) 352 (100%), 351 (5.6), 323 (2.2), 311 (3.8), 308 (21), 307 (35), 275 (13), 221 (1.9), 206 (3.2), 104 (3.0), and 77 (3.3).

The aqueous filtrate from above and washings were combined, acidified (concentrated HCl), and extracted with $CHCl_3$ (3 × 40 ml). The extracts were combined and dried ($MgSO_4$), and the solvent removed. The residue and sublimate were recrystallised from light petroleum (b.p. 60—80 °C) to give benzoic acid (85 mg, 91%), m.p. 120—123 °C.

5-(N-*Benzoyl*-p-*toluidino*)-2-*chloro*-4,6-*diphenylpyridine* (37).— 5-(*N*-Benzoyl-*p*-toluidino-4,6-diphenyl-2-pyridone (35) (0.36 g, 0.79 mmol) in phosphoryl chloride (3 ml) was heated in a sealed Carius tube for 4 h at 195 °C and poured slowly into ice–water (150 g, 50 ml) containing sufficient aqueous NH_4OH to maintain basicity (phenolphthalein). The precipitate was filtered off, washed with water (50 ml), dried, and recrystallised from aqueous EtOH (charcoal) to give the 5-*benzoyltoluidino*-2-*chloropyridine* (37) (118 mg, 32%) as yellow needles, m.p. 172—176 °C (Found: C, 78.4; H, 4.8; N, 6.0. $C_{31}H_{23}ClN_2O$ requires C, 78.4; H, 4.9; N, 5.9%); $\nu_{max.}$ (Nujol) 1 670 cm^{-1} (C=O); δ($CDCl_3$) 2.1 (3 H, s, Me), 6.8 (1 H, s), and 7.0—7.8 (19 H, m).

3-(*N*-*Benzoyl*-p-*toluidino*)-2,4-*diphenylpyridine* (38).—Pd–C (5%, 86 mg), 5-(*N*-benzoyl-*p*-toluidino)-2-chloro-4,6-diphenylpyridine (37) (110 mg, 0.28 mmol), KOH (39 mg), and MeOH (AnalaR, 25 ml) were stirred under hydrogen at 20 °C and 760 mmHg for 18 h. The reaction mixture

was filtered and the solvent removed from the filtrate. Water (40 ml) was added to the residue and this was extracted with $CHCl_3$ (3 × 25 ml). The extracts were combined and dried ($MgSO_4$) and the solvent was removed to leave a yellow solid (92 mg, 90%), m.p. 170—180 °C. Recrystallisation from EtOH afforded the *3-benzoyltoluidino-pyridine* (38) (67 mg, 66%) as pale yellow needles, m.p. 191—192 °C (Found: C, 84.6; H, 5.5; N, 6.2. $C_{31}H_{24}N_2O$ requires C, 84.5; H, 5.5; N, 6.4%); $\nu_{max.}$ (Nujol) 1 670 cm^{-1} (C=O); $\delta(CDCl_3)$ 2.1 (3 H, s, Me), 6.9—7.5 (19 H, m), 7.7 (1 H, d, *J* 9 Hz), and 8.8 (1 H, d, *J* 5.5 Hz, 6-H).

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