Fused Mesoionic Heterocycles: Synthesis of 1,3,4-Oxadiazolo[3,2-*a*]-pyridine and 1,3,4-Thiadiazolo[3,2-*a*]pyridine Derivatives [1]

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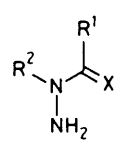
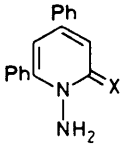
Two general methods are reported for the preparation of mesoionic derivatives of 1,3,4-oxadiazolo[3,2-*a*]pyridine and 1,3,4-thiadiazolo[3,2-*a*]pyridine from 1-amino-4,6-diphenyl-2-pyridone (3) and 1-amino-4,6-diphenylpyridine-2-thione (4), respectively. The first involves the initial formation of *N,N'*-disubstituted ureas or thioureas (7)—(11), which undergo cyclization either by thermal treatment [to give (14) and (15)] or by the action of Ph_3P–CCl_4 [to give (16)—(20)]. The second is based in the reaction of the iminophosphoranes (12) and (13) with carbon dioxide or carbon disulphide and isocyanates or isothiocyanates to give 2-olates [(14) and (15)], 2-thiolates [(21) and (22)], or 2-aminides [(16)—(20)]. The reactions of the *N*-amino-heterocycle (4) with phenyl isothiocyanate and ethoxycarbonyl isothiocyanate led directly to the mesoionic compounds (19) and (20), respectively.

NUMEROUS routes are available for the preparation of monocyclic mesoionic compounds [2] and new methods continue to appear.[3] In contrast, useful methods for the preparation of fused mesoionic compounds, in particular derivatives of 1,3,4-oxadiazolo[3,2-*a*]pyridine and 1,3,4-thiadiazolo[3,2-*a*]pyridine, are rare. The first bicyclic derivative to be prepared was compound (5), formed from 1-amino-2-pyridone and carbonyl chloride,[4] and recently the formation of the derivative (6) by an unusual rearrangement has been reported.[5]

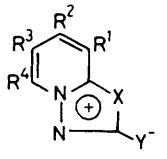
N-Acylhydrazines (1) and *N*-thioacylhydrazines (2) are



(1) X = O
(2) X = S



(3) X = O
(4) X = S



(5) $R^1 = R^2 = R^3 = R^4 = H$, X = Y = O
(6) $R^1 = R^4 = Me$, $R^2 = R^3 = Ph$, X = Y = O

SCHEME 1

useful starting materials for the preparation of the mesoionic 1,3,4-oxadiazolium and 1,3,4-thiadiazolium systems.[6-9] The structural similarity between the hydrazines (1) and (2) and the heterocycles 1-amino-4,6-diphenyl-2-pyridone (3) and 1-amino-4,6-diphenylpyridine-2-thione (4) is such that these *N*-amino-heterocycles might be expected to be suitable starting materials for the preparation of fused mesoionic derivatives of 1,3,4-oxadiazolo[3,2-*a*]pyridine and 1,3,4-thiadiazolo[3,2-*a*]pyridine (Scheme 1). We report here attempts to synthesize such derivatives by two approaches: (*a*) from urea and thiourea derivatives and (*b*) *via* iminophosphoranes.

RESULTS AND DISCUSSION

The *N*-amino-heterocycle (3) reacts with isocyanates and isothiocyanates at room temperature in dimethylformamide giving *N,N'*-disubstituted ureas [(7), (8)] or thioureas [(9), (10)] as crystalline solids in high yields (87—95%) (Table 1). The i.r. spectra of (7) and (8) show absorption at 1 730—1 735 and 1 640—1 660 cm^{-1} for the two carbonyl groups. The ($M^+ - RNH_2$) ion is the base peak in the mass spectra of compounds (7) and (8); the parent peak shows very low intensity. We conclude that this type of compound has a strong tendency to expel RNH_2. The i.r. spectra of the thioureas (9) and (10) show absorption at 1 650—1 655 cm^{-1} for the ring carbonyl group and in addition (10) shows ester carbonyl absorption at 1 730 cm^{-1}. The fragment at *m/z* 247, corresponding to the 2-pyridone ring, provides the base peak in the mass spectra of (9) and (10), which also show a fragment corresponding to $M^+ - SH_2$ (Table 2) (Scheme 2).

Similarly, the *N*-amino-heterocycle (4) reacts with phenyl isocyanate at room temperature in dry acetonitrile to give the urea (11) in 86% yield. The spectral characteristics are very similar to those of (7) and (8).

TABLE 1

N,N'-Disubstituted ureas or thioureas

No.	Crystal form	Yield (%)	M.p. (°C)	Solvent	Found (%) C	H	N	S	Formula	Required (%) C	H	N	S
(7)	Needles	95	200—202	MeOH	75.6	5.0	11.0		$C_{24}H_{19}N_3O_2$	75.55	4.95	11.0	
(8)	Needles	88	210—212	MeOH	77.9	4.8	9.7		$C_{28}H_{21}N_3O_2$	77.95	4.85	9.75	
(9)	Needles	94	172—173	EtOH	72.4	4.7	10.55	8.0	$C_{24}H_{19}N_3OS$	72.55	4.8	10.55	8.05
(10)	Prisms	82	203—204	EtOH	63.95	4.75	10.65	8.15	$C_{21}H_{19}N_3O_3S$	64.1	4.85	10.7	4.15
(11)	Needles	86	205	MeOH	72.6	5.05	10.45	7.95	$C_{24}H_{19}N_3OS$	72.55	4.8	10.55	8.05

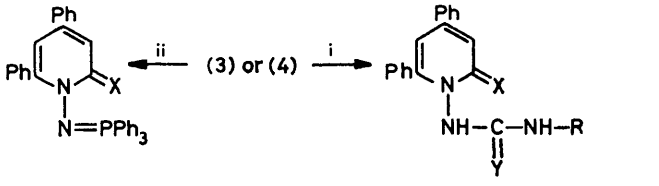
TABLE 2

I.r.[a] and mass spectra of *N,N'*-disubstituted ureas and thioureas

No.	$\nu_{max.}$/cm^{-1}	*m/z* (%)
(7)	3 270br, 3 200br, 1 730s, 1 660s, 1 610s, 1 560s, 1 500s, 1 450w, 1 325s, 1 260s, 1 030w, 970w, 870w, 770s, 750s, 690s	381 (M^+, 5), 288 (100), 261 (25), 247 (45), 218 (75), 203 (40), 202 (40), 191 (10), 115 (20), 103 (35), 77 (20)
(8)	3 260br, 3 060w, 1 735s, 1 640s, 1 550s, 1 350s, 1 260w, 1 200s, 1 175w, 1 000w, 960w, 860w, 800s, 770s, 700s	431 (M^+, 5), 368 (10), 312 (10), 288 (100), 261 (72), 247 (20), 218 (40), 203 (32), 202 (32), 169 (47), 143 (50), 115 (40), 103 (30), 77 (25)
(9)	3 320br, 3 180br, 1 650s, 1 550s, 1 450w, 1 370w, 1 330w, 1 030s, 970w, 870w, 860w, 770s, 700s	397 (M^+, 5), 261 (60), 247 (100), 218 (60), 203 (10), 202 (10), 191 (20), 135 (15), 115 (30), 103 (15), 77 (20)
(10)	3 250br, 3 190br, 1 730vs, 1 665vs, 1 615s, 1 600s, 1 580s, 1 540vs, 1 335w, 1 205s, 1 200s, 1 055w, 1 040s, 860w, 780s, 700s	393 (M^+, 4), 360 (40), 314 (25), 288 (40), 261 (75), 247 (100), 218 (60), 203 (15), 202 (15), 191 (20), 189 (15), 115 (15), 77 (15)
(11)	3 315br, 3 290br, 1 680s, 1 620s, 1 600m, 1 550s, 1 500w, 1 450w, 1 320w, 1 230s, 1 180s, 1 080w, 910w, 860w, 760s, 700s	397 (M^+, 4), 302 (25), 277 (60), 261 (20), 247 (10), 230 (10), 202 (25), 115 (30), 92 (100), 77 (90)

[a] In Nujol.

On pyrolysis, the ureas (7) and (8) are converted into 5,7-diphenyl-1,3,4-oxadiazolo[3,2-*a*]pyridylium-2-olate (14) in 82% yield and the corresponding amine. The reaction can be performed by simply heating the urea at 220—250 °C for 1 h. Compound (14) was prepared in



(12) X = O
(13) X = S

(7) X=Y=O, R = Ph
(8) X=Y=O, R = α-$C_{10}H_7$
(9) X=O, Y=S, R = Ph
(10) X=O, Y=S, R = CO_2Et
(11) X=S, Y=O, R = Ph

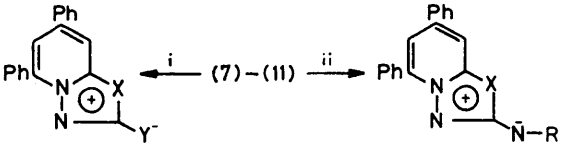
SCHEME 2 Reagents: i, R—N=C=Y; ii, Br_2Ph_3P–Et_3N

37% yield from (3) by reaction with *N,N'*-carbonyldiimidazole in *p*-xylene at reflux temperature for 5 h. *N,N'*-Bis-(1,2-dihydro-2-oxo-4,6-diphenyl-1-pyridyl) urea was a by-product of this reaction.

Similarly, thermal cyclization of the urea (11) leads, in 87% yield, to 5,7-diphenyl-1,3,4-thiadiazolo[3,2-*a*]pyridylium-2-olate (15), as yellow crystals. However, attempted pyrolysis of the thiourea (9) failed to yield the isomeric compound (21) or 5,7-diphenyl-1,3,4-triazolo-[3,2-*a*]pyridylium-2-thiolate in a reaction similar to those reported in the monocyclic series.[10]

Ollis and Ramsden [8] have reported that *N*-thioacylhydrazines (2) and aryl isothiocyanates give 1,3,4-triazolium-2-thiolates directly at room temperature. In our hands, the *N*-amino-heterocycle (4) reacts with phenyl isothiocyanate and ethoxycarbonyl isothiocyanate at room temperature in dry acetonitrile affording 5,7-diphenyl-1,3,4-thiadiazolo[3,2-*a*]pyridylium-2-(phenylaminide) (19) (65%) and the 2-ethoxycarbonylaminide (20) (78%), respectively. This transformation presumably involves the corresponding thiourea as a highly reactive intermediate which easily undergoes cyclodehydrosulphurization.

Our approach to a general synthesis of 1,3,4-oxadiazolo and 1,3,4-thiadiazolo-[3,2-*a*]pyridylium-2-aminides is based on the understanding that the valence tautomeric carbodi-imide could cyclise spontaneously. The problem of synthesis is, therefore, reduced to finding a route to carbodi-imides from ureas or thioureas. Appel *et al.*[11] have described the synthesis of carbodi-imides by the reaction of ureas or thioureas with triphenylphosphine–carbon tetrachloride. Cyclodehydration of the urea (7) could be achieved by refluxing with this reagent in the presence of triethylamine in dichloromethane and the cyclized 5,7-diphenyl-1,3,4-oxadiazolo[3,2-*a*]pyridylium-2-(phenylaminide) (16) was obtained in 78% yield, as orange crystals. Similarly, the urea (11) gives the mesoionic compound (19) in yield higher than that obtained from the reaction of (4) with phenyl isothiocyanate. In a similar manner, the thiourea (10) undergoes cyclodehydrosulphurization to afford 5,7-diphenyl-1,3,4-oxadiazolo[3,2-*a*]pyridylium-2-ethoxycarbonylaminide (18) in 61% yield (Scheme 3).



(14) X=Y=O
(15) X=S, Y=O

(16) X=O, R = Ph
(17) X=O, R = α-$C_{10}H_7$
(18) X=O, R = CO_2Et
(19) X=S, R = Ph
(20) X=S, R = CO_2Et

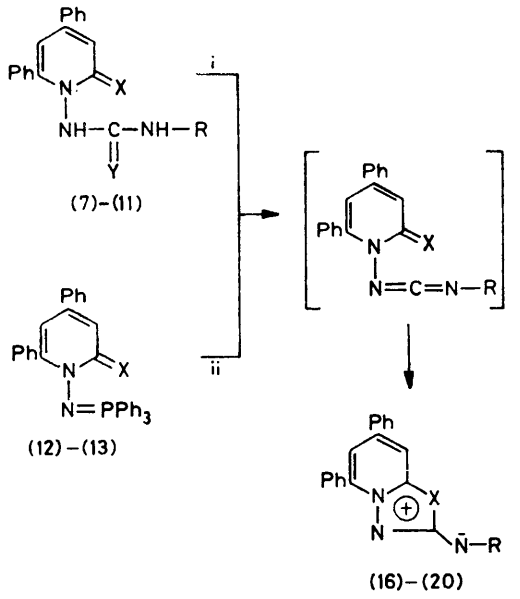
SCHEME 3 Reagents: i, heat; ii, Ph_3P–CCl_4

An alternative route to mesoionic compounds of this type is based on the reaction of the iminophosphoranes (12) and (13) with compounds with cumulated double bonds. The *N*-amino-heterocycles (3) and (4) react with triphenylphosphine dibromide in the presence of triethylamine in dry benzene, under nitrogen, to give the iminophosphoranes (12) and (13), respectively, as crystalline solids in high yields (72—81%). Compound (12) reacts with isocyanates or isothiocyanates at room temperature to give 5,7-diphenyl-1,3,4-oxadiazolo[3,2-*a*]pyridylium-2-aminides (16)—(18) in high yields (72—81%). In the same way the iminophosphorane (13) leads to 5,7-diphenyl-1,3,4-thiadiazolo[3,2-*a*]pyridylium-2-aminides (19) and (20) in 70—80% yields.

The preparation of mesoionic 2-aminides of type (16)—(20) from the iminophosphoranes (12) and (13) supports

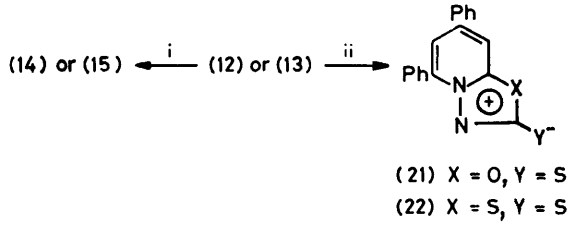
the assumption that the carbodi-imides are intermediates in this reaction (Scheme 4).

In addition, the iminophosphoranes (12) and (13) react with carbon dioxide at room temperature to give (14) and (15), respectively, in 88—93% yields. Similarly,



SCHEME 4 Reagents: i, PPh_3–CCl_4; ii, R–N=C=Y

reaction with carbon disulphide affords 5,7-diphenyl-1,3,4-oxadiazolo[3,2-*a*]pyridylium-2-thiolate (21) (76%) and the thio-analogue (22) (80%), unavailable by thermolysis of the corresponding thioureas (Scheme 5). We believe that the reaction of iminophosphoranes of type (12) and (13) with carbon-centered heterocumulenes



SCHEME 5 Reagents: i, CO_2; ii, CS_2

could be of considerable general utility in the synthesis of mesoionic compounds.

Support for the formulation of 5,7-diphenyl-1,3,4-oxadiazolo[3,2-*a*]pyridylium-2-olate (14) is clearly provided by its i.r. spectrum; this shows a strong band in the carbonyl region (1 770 cm^{-1}) similar in position to the carbonyl band shown by monocyclic isosydnones [6] (1 758—1 770 cm^{-1}). The two mesoionic isomers (15) and (21) show distinct physical properties. The i.r. spectrum of (15) shows strong absorption in the 1 655 cm^{-1} region, which can be attributed to carbonyl stretching.[9] This wavenumber is lower than that of the carbonyl absorption of (14). The i.r. spectrum of (21) shows absorption in the 1 430 cm^{-1} region which can be attributed to thione stretching.[9] The corresponding absorption of 5,7-diphenyl-1,3,4-thiadiazolo[3,2-*a*]pyridylium-2-thiolate (22) occurs at 1 340 cm^{-1}, which is similar to that of C=S stretching in the 1,3,4-thiadiazolium-2-thiolate series.[9]

The spectroscopic properties of the 2-aminides (16)—(20), while not being conclusive, support their formulation as mesoionic compounds. Their i.r. spectra show absorption in the C=N stretching region (1 620—1 650 and 1 550—1 570 cm^{-1}, respectively). These values are in good agreement with those reported for the monocyclic systems.[8] The absence of NH, isocyanate, isothiocyanate, and carbodi-imide bands in the i.r. spectra of (14)—(22) provides support for their formulation as cyclic mesoionic structures rather than the alternative valence tautomers.

Although the u.v. absorption spectra of these compounds have not been interpreted in detail, they are similar to the analogous monocyclic systems,[6,9] and are consistent with a mesoionic structure.

Mass spectrometry has been a useful tool for distinguishing between the isomeric systems (15) and (21). The mass spectrum of (15), in addition to the molecular ion at *m/z* 304 (base peak), shows a fragment at *m/z* 276 (M^+ — CO). The mass spectrum of the isomer (21) also shows the molecular ion, but the base peak occurs at *m/z* 244, corresponding to M^+ — COS. The fragmentation patterns of these two molecules are very similar, but the differences between the fragment ions are characteristic. Compounds (14), (16), and (19) all show the molecular ion as the base peak in their mass spectra, while the 5,7-diphenyl-1,3,4-thiadiazolo[3,2-*a*]pyridylium-2-thiolate (22) in addition to the molecular ion, shows the base peak at *m/z* 288 (M^+ — 32).

The dipole moments of compounds (14) (7.85 D), (21) (9.15 D), (16) (7.61 D), (15) (7.78 D), (22) (9.31 D), and (19) (7.16 D) in benzene solution are in excellent agreement with the mesoionic structures indicated.[6]

EXPERIMENTAL

All m.p.s were determined with a Kofler hot-stage microscope. Spectral characterizations were performed with the following instruments: i.r., Perkin-Elmer Infracord 457; ^1H n.m.r., Varian FT-80 ($SiMe_4$ internal standard), mass spectra (70 eV), Hewlett–Packard 5980 A; u.v., Varian 634 spectrophotometer. Combustion analyses were performed with a Perkin-Elmer 240 instrument.

Reagents.—1-Amino-4,6-diphenyl-2-pyridone (3) was prepared essentially according to El-Kholy's procedure [12] and 1-amino-4,6-diphenylpyridine-2-thione (4) from 4,6-diphenylpyran-2-thione and hydrazine hydrate.[13]

N,N'-*Disubstituted Ureas or Thioureas* (7)—(11). *General Procedure.*—The appropriate isocyanate or isothiocyanate (5 mmol) was added to a solution of the *N*-amino-heterocycle (5 mmol) in dimethylformamide (75 ml). After 24 h stirring at room temperature the mixture was poured into ice–water (150 ml) to give a solid precipitate, which was filtered off and purified by recrystallization from the appropriate solvent. Data for the products are given in Tables 1 and 2.

1-*Triphenylphosphoranylideneamino*-4,6-*diphenyl*-2 (1 H)-*pyridone* (12).—Bromine (4.8 g, 0.03 mol) in dry benzene (30 ml) was added dropwise to a stirred solution of triphenylphosphine (7.86 g, 0.03 mol) in dry benzene (30 ml) at 0—5 °C under nitrogen. The mixture was stirred for 1 h and then allowed to warm to room temperature. A solution of 1-amino-4,6-diphenyl-2 (1 H)-pyridone (3) (7.86 g, 0.03 mol), and triethylamine (6 g) in dry benzene (80 ml) was added, after 3 h heating under reflux, triethylammonium bromide was deposited. The salt was separated by filtration and the filtrate concentrated to dryness to afford a crude product which, recrystallized from hexane, gave the *imine* (12) (12.68 g, 81%), yellow crystals, m.p. 179—182 °C (Found: C, 80.25; H, 5.1; N, 5.35. $C_{35}H_{27}N_2OP$ requires C, 80.45; H, 5.15; N, 5.35%); $\nu_{max.}$ (Nujol) 1 640, 1 565, 1 440, 1 230, 1 145, 1 100, 850, 770, and 700 cm^{-1}; *m/z* 522 (M^+), 445, 247, 203, 183 (base peak), 108, 103, and 77.

By the same procedure 1-amino-4,6-diphenylpyridine-2-thione (4) (8.34 g, 0.03 mol) yielded 1-*triphenylphosphoranylideneamino*-4,6-*diphenylpyridine*-2-*thione* (13) (11.61 g, 72%), yellow crystals, m.p. 218—220 °C (Found: C, 77.85; H, 5.25; N, 5.4; S, 6.05. $C_{35}H_{27}N_2SP$ requires C, 78.05; H, 5.05; N, 5.2; S, 5.95%); $\nu_{max.}$ (Nujol) 1 620, 1 600, 1 530, 1 230, 1 160, and 1 110 cm^{-1}; *m/z* 538 (M^+), 524, 491, 459, 384, 276 (base peak), 262, 230, 203, and 77.

5,7-*Diphenyl*-1,3,4-*oxadiazolo*[3,2-a]*pyridylium*-2-*olate* (14).—(a) *From the urea* (7). The urea (7) (3.81 g, 0.01 mol) was dried for 10 h at 80 °C and 0.5 mmHg. It was then heated in an oil-bath at 220 °C for 1 h in a distillation apparatus. Aniline smoothly distilled out of the flask. The remaining solid was dissolved in hot EtOH (50 ml) and the resultant solution treated with animal charcoal and concentrated to give a solid which, recrystallized from benzene, gave 5,7-*diphenyl*-1,3,4-*oxadiazolo*[3,2-a]*pyridylium*-2-*olate* (14) (2.36 g, 82%), white leaflets, m.p. 199—210 °C (Found: C, 75.0; H, 4.1; N, 9.7. $C_{18}H_{12}N_2O_2$ requires C, 75.0; H, 4.15; N, 9.7%); $\nu_{max.}$ (Nujol) 1 795, 1 770, and 1 645 cm^{-1}; $\lambda_{max.}$ (EtOH) 225 (ε 21 000), 266 (31 700), and 315 nm (21 000); *m/z* 288 (M^+, base peak), 230, 218, 203, 103, and 77.

By the same procedure, *N*-(α-naphthyl)-*N'*-(1,2-dihydro-2-oxo-4,6-diphenyl-1-pyridyl)urea (8) (4.31 g, 0.01 mol) yielded the product (14) (1.58 g, 55%).

(b) *From* 1-*Amino*-4,6-*diphenyl*-2(1H)-*pyridone* (3) *and* N,N'-*carbonyldi-imidazole*. *N,N'*-Carbonyldi-imidazole (1.62 g, 0.01 mol) was added to a solution of (3) (2.62 g, 0.01 mol) in *p*-xylene (50 ml). After 5 h under reflux the reaction mixture was cooled and the solvent removed under reduced pressure to give a residual oil, which, treated with absolute EtOH (20 ml), gave N,N'-*bis*-(1,2-*dihydro*-2-*oxo*-4,6-*diphenyl*-1-*pyridyl*)*urea* (1.24 g, 45%) as white crystals, m.p. 236—237 °C (Found: C, 76.3; H, 4.7; N, 10.15. $C_{35}H_{26}N_4O_3$ requires C, 76.35; H, 4.7; N, 10.2%); $\nu_{max.}$ (Nujol) 3 200, 1 730, 1 650, 760, and 700 cm^{-1}; *m/z* 550 (M^+), 288 (base peak), 261, 247, 218, 203, 103, and 77. The mother-liquor was concentrated to afford compound (14) (1 g, 37%), m.p. 199—200 °C (from benzene).

(c) *From the iminophosphorane* (12). A stream of dry carbon dioxide was passed through a stirred solution of 1-triphenylphosphoranylideneamino-4,6-diphenyl-2(1*H*)-pyridone (12) (5.22 g, 0.001 mol) in dry benzene (50 ml) at room temperature for 1 h. After cooling, the separated solid was collected by filtration and recrystallized from benzene to give compound (14) (2.68 g, 93%).

5,7-*Diphenyl*-1,3,4-*thiadiazolo*[3,2-a]*pyridylium*-2-*olate* (15).—(a) *From the urea* (11). The procedure (a) described for (14) but using *N*-phenyl-*N'*-(1,2-dihydro-2-thioxo-4,6-diphenyl-1-pyridyl)urea (11) (3.97 g, 0.01 mol) gave the *product* (15) (2.64 g, 87%) as yellow crystals (from Cl_3CH), m.p. 270 °C (Found: C, 71.15; H, 4.05; N, 9.1; S, 10.35. $C_{18}H_{12}N_2OS$ requires C, 71.05; H, 3.95; N, 9.2; S, 10.5%); $\nu_{max.}$ (Nujol) 1 655 cm^{-1} (C=O); $\lambda_{max.}$ 209 (ε 41 200), 255 (40 300) and 329 nm (31 000); *m/z* 304 (M^+, base peak), 275, 247, 203, 115, 103, and 77.

(b) *From the iminophosphorane* (13). The procedure (c) described for (14), but using the 1-triphenylphosphoranylideneamino-4,6-diphenylpyridine-2(1*H*)-thione (13) (5.22 g, 0.01 mol) gave the product (15) (88%).

5,7-*Diphenyl*-1,3,4-*oxadiazolo*[3,2-a]*pyridylium*-2-*aminides* (16)—(18).—(a) *From ureas and thioureas*. In a typical experiment, triphenylphosphine (3.14 g, 0.012 mol) in carbon tetrachloride (20 ml) was added dropwise to a solution of *N*-phenyl-*N'*-(1,2-dihydro-2-oxo-4,6-diphenyl-1-pyridyl)urea (7) (3.81 g, 0.01 mol) and triethylamine (1.21 g, 0.012 mol) in dichloromethane (50 ml). A deep red colouration immediately developed, after 6 h under gentle reflux the solution was set aside at room temperature. Evaporation and recrystallization from MeOH gave 5,7-*diphenyl*-1,3,4-*oxadiazolo*[3,2-a]*pyridylium*-2-(*phenylaminide*) (16) (2.83 g, 78%), orange leaflets, m.p. 207—208 °C (Found: C, 79.25; H, 4.65; N, 11.5. $C_{24}H_{17}N_3O$ requires C, 79.35; H, 4.7; N, 11.55%); $\nu_{max.}$ (Nujol) 1 630 cm^{-1} (C=N); $\lambda_{max.}$ (EtOH) 245 (ε 36 300), 274 (26 300), and 335 nm (23 600); *m/z* 363 (M^+, base peak), 247, 218, 203, 91, and 77.

In a similar manner the following derivatives were prepared: 5,7-*diphenyl*-1,3,4-*oxadiazolo*[3,2-a]*pyridylium*-2-(α-*naphthylaminide*) (17) (76%), orange crystals, m.p. 235—236 °C (Found: C, 81.3; H, 4.55; N, 10.15. $C_{28}H_{19}N_3O$ requires C, 81.35; H, 4.6; N, 10.15%); $\nu_{max.}$ (Nujol) 1 640 cm^{-1} (C=N); *m/z* 413 (M^+), 294 (base peak), 293, 247, 218, 203, 167, and 117; 5,7-*Diphenyl*-1,3,4-*oxadiazolo*[3,2-a]-*pyridylium*-2-*ethoxycarbonylaminide* (18) (61%), yellow leaflets, m.p. 225—230 °C (Found: C, 69.95; H, 4.6; N, 11.75. $C_{21}H_{17}N_3O_3$ requires C, 70.2; H, 4.75; N, 11.7%); $\nu_{max.}$ (Nujol) 1 680 (C=O) and 1 630 cm^{-1} (C=N); δ[$(CD_3)_2$-SO] 1.39 (t, 3 H, CH_3), 4.18 (q, 2 H, $-O-CH_2-$), and 7.59—8.05 (m, 12 H, aromatic); *m/z* 359 (M^+), 314, 286, 247 (base peak), 218, 202, 191, and 103.

(b) *From the iminophosphorane* (12). In a typical experiment, phenyl isocyanate (1.19 g, 0.01 mol) was added dropwise to a stirred solution of 1-triphenylphosphoranylideneamino-4,6-diphenyl-2(1*H*)-pyridone (12) (5.22 g, 0.01 mol) in dry benzene (50 ml). The resultant red solution was stirred at room temperature for 15 h. Evaporation and recrystallization from MeOH afforded the mesoionic compound (16) (2.94 g, 81%). Similarly, the reaction of (12) with phenyl isothiocyanate under same condition leads to (16) (86%).

By this procedure the mesoionic compounds (17) (80%) and (18) (72%) were prepared.

5,7-*Diphenyl*-1,3,4-*thiadiazolo*[3,2-a]*pyridylium*-2-*aminides* (19) *and* (20).—(a) *From ureas*. The procedure (a) described for 5,7-diphenyl-1,3,4-oxadiazolo[3,2-*a*]pyridylium-2-aminides, but using (11), gave 5,7-*diphenyl*-1,3,4-*thiadiazolo*[3,2-a]*pyridylium*-2-(*phenylaminide*) (19) (80%), yellow crystals, m.p. 320 °C (Found: C, 76.1; H, 4.65; N, 10.95; S, 8.55. $C_{24}H_{17}N_3S$ requires C, 76.0; H, 4.5; N, 11.05; S, 8.45%); $\nu_{max.}$ (Nujol) 1 555 cm^{-1} (C=N); $\lambda_{max.}$ (EtOH) 260 (ε 22 200), 284 (21 300), and 334 nm (14 000); *m/z* 379 (M^+, base peak), 275, 262, 230, 203, and 77.

(b) *From* 1-*amino*-4,6-*diphenylpyridine*-2(1H)-*thione* (4). Phenyl isothiocyanate (1.35 g, 0.01 mol) was added dropwise to 1-amino-4,6-diphenylpyridine-2(1*H*)-thione (4) (2.78 g, 0.01 mol) in dry acetonitrile (60 ml). The mixture was stirred at room temperature for 24 h. Concentration and recrystallization from MeOH gave (19) (65%).

By a similar procedure was prepared 5,7-*diphenyl*-1,3,4-*thiadiazolo*[3,2-a]*pyridylium*-2-(*ethoxycarbonylaminide*) (20) (78%), pale yellow leaflets, m.p. 285 °C (Found: C, 67.25; H, 4.45; N, 10.85; S, 8.3. $C_{21}H_{17}N_3O_2S$ requires C, 67.2; H, 4.55; N, 11.2; S, 8.55%); $\nu_{max.}$ (Nujol) 1 610 and 1 550 cm^{-1} (C=N); δ($CDCl_3$) 1.31 (t, 3 H, CH_3), 4.22 (q, 2 H, $-O-CH_2-$), and 7.56—8.07 (m, 12 H, aromatic); *m/z* 375 (M^+), 330, 302 (base peak), 301, 262, and 203.

(c) *From the iminophosphorane* (13). The procedure (c) described for (16) by using (13) gave (19) (80%) and (20) (70%).

5,7-*Diphenyl*-1,3,4-*oxadiazolo*[3,2-a]*pyridylium*-2-*thiolate* (21).—Carbon disulphide (3 g, 0.04 mol) was added slowly with stirring at room temperature to a solution of 1-triphenylphosphoranylideneamino-4,6-diphenyl-2(1*H*)-pyridone (12) (5.2 g, 0.01 mol) in dry benzene (50 ml). The mixture was kept for 20 h. After cooling, the precipitate was collected by filtration, and recrystallization from benzene gave the *product* (21) (2.31 g, 76%), yellow crystals, m.p. 215—216 °C (Found: C, 71.0; H, 3.95; N, 9.2; S, 10.3. $C_{18}H_{12}N_2OS$ requires C, 71.05; H, 3.95; N, 9.2; S, 10.55%); $\nu_{max.}$ (Nujol) 1 640 and 1 430 cm^{-1} (C=S); $\lambda_{max.}$ (EtOH) 247 (ε 41 800), 280 (42 200), and 370 nm (21 300); *m/z* 304 (M^+), 272, 247, 244 (M^+ — COS, base peak), 218, 203, 191, and 77.

5,7-*Diphenyl*-1,3,4-*thiadiazolo*[3,2-a]*pyridylium*-2-*thiolate* (22).—The procedure described for (21) but using (13) (0.01 mol) gave the *product* (22) (80%), yellow prisms, m.p. 235 °C (Found: C, 67.45; H, 3.55; N, 8.85; S, 20.05. $C_{18}H_{12}N_2S_2$ requires C, 67.5; H, 3.8; N, 8.75; S, 20.0%); $\nu_{max.}$ (Nujol) 1 610 and 1 035 cm^{-1} (C=S); $\lambda_{max.}$ (EtOH) 260 (ε 7 100), 293 (7 300), and 330 nm (5 600); *m/z* 320 (M^+), 287 (base peak), 230, 202, and 77.

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