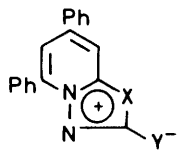
Fused Mesoionic Heterocycles: Synthesis of 1,3,4-Triazolo[3,2-*a*]pyridine Derivatives[1]

Pedro Molina,* Mateo Alajarin, Antonio Arques, Raimundo Benzal, and Higinio Hernandez
Departamento de Quimica Organica, Facultad de Ciencias, Universidad de Murcia, Murcia, Spain

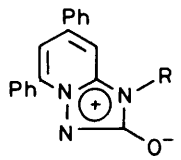
A number of mesoionic derivatives of 1,3,4-triazolo[3,2-*a*]pyridine have been prepared. The 1,3,4-oxadiazolo[3,2-*a*]pyridylium-2-aminides [(**14**)—(**19**)], available from 1,3,4-oxadiazolo[3,2-*a*]pyridylium-2-olate (**12**) and *N*-aryliminotriphenylphosphoranes, undergo base-catalysed isomerization to the corresponding 1,3,4-triazolo[3,2-*a*]pyridylium-2-olates [(**20**)—(**25**)]. 1-Amino-2-methylthio-4,6-diphenylpyridinium iodide (**27**), reacts under basic conditions with aryl isothiocyanates to yield the corresponding 1,3,4-triazolo[3,2-*a*]pyridylium-2-thiolates [(**36**)—(**40**)]. Compounds [(**14**)—(**17**)] react with arylmethylamines to yield the guanidine derivatives [**43**)—(**46**)]; these cyclize on treatment with base giving the mesoionic 1,3,4-triazolo[3,2-*a*]pyridylium-2-aminides [(**47**)—(**50**)]. The reactions of (**14**) and (**16**) with aniline and *p*-chloroaniline respectively, lead directly to the corresponding mesoionic compounds (**51**) and (**52**).

Our interest in the preparation of fused mesoionic compounds has encouraged us to look for specific routes to derivatives of 1,3,4-triazolo[3,2-*a*]pyridine [(**1**)—(**3**)]. Previously, we have reported the preparation and characterization of mesoionic compounds derived from 1,3,4-oxadiazolo[3,2-*a*]pyridine[2,3] [(**4**)—(**6**)] and 1,3,4-thiadiazolo[3,2-*a*]pyridine[3] [(**7**)—(**9**)]. Compound (**10**), formed from (**11**) and sodium azide,[4] was the first bicyclic derivative to be prepared, but it has remained the sole example of the triazolo.

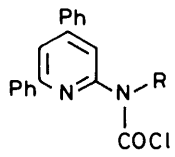
We report here attempts to synthesize 1,3,4-triazolo[3,2-*a*]-pyridylium-2-olate, -2-thiolate, and -2-aminide by two approaches: (*a*) ring interconversion of mesoionic precursors [for the series (**1**) and (**2**)]; (*b*) from compounds which contain the pyridine moiety [for the series (**3**)].



(**1**) X = NR Y = O (**4**) X = O Y = O (**7**) X = S Y = O
(**2**) X = NR Y = S (**5**) X = O Y = S (**8**) X = S Y = S
(**3**) X = NR Y = NAr (**6**) X = O Y = NAr (**9**) X = S Y = NAr



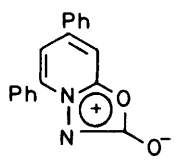
(**10**)



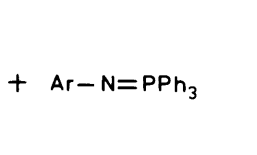
(**11**)

Results and Discussion

1,3,4-*Triazolo*[3,2-a]*pyridylium*-2-*olates*.—5,7-Diphenyl-1,3,4-oxadiazolo[3,2-*a*]pyridylium-2-olate (**12**) reacted with *N*-aryliminotriphenylphosphoranes (**13**), readily available from arylamines and triphenylphosphine dibromide,[5] in toluene at reflux temperature for 10 h to give the corresponding 5,7-diphenyl-1,3,4-oxadiazolo[3,2-*a*]pyridylium-2-aminides (**14**)—(**19**), isolated as orange crystalline solids in good yields (75—91%) (Table 1). Two possible routes to the 2-aminides may be envisaged, involving either (i) condensation of the iminophosphorane (**13**) with the valence tautomer isocyanate to give the carbodi-imide, which cyclize spontaneously to the 2-aminide, or (ii) direct condensation of (**13**) with the carbonyl group of the mesoionic 2-olate (**12**).



(**12**)

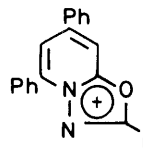


(**13**)

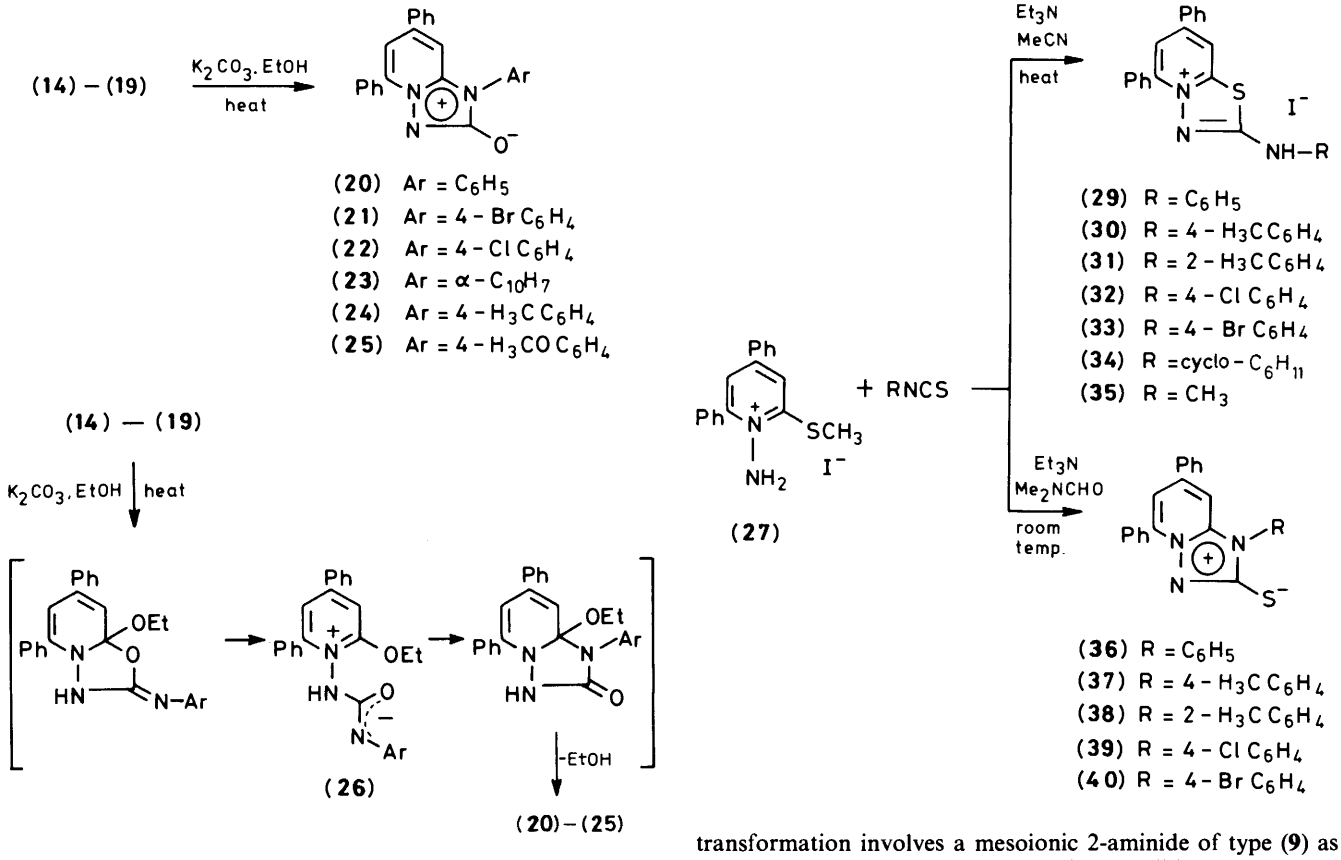
This conversion demonstrates a useful alternative preparation of the 2-aminides (**14**)—(**19**), previously prepared by reaction of 1-triphenylphosphoranylideneamino-4,6-diphenyl-2-pyridone with aryl isothiocyanates or isocyanates.[2,3]

When a solution of one of the mesoionic 2-aminides (**14**)—(**19**) was treated with potassium carbonate in ethanol at reflux temperature for 2 h, the corresponding 1-aryl-5,7-diphenyl-1,3,4-triazolo[3,2-*a*]pyridylium-2-olate (**20**)—(**25**) was isolated as a crystalline solid in excellent yield (85—96%) (Table 2). Presumably, this isomerization involves nucleophilic attack at the 5-position of the five-membered ring to give the betaine (**26**), which undergoes cycloelimination. No method of interconverting the mesoionic systems (**6**) and (**1**) has been reported previously.[6]

The pairs of mesoionic isomers (**14**)—(**19**) and (**20**)—(**25**) show distinct spectral properties. The i.r. spectra of the 1,3,4-



(**14**) Ar = C_6H_5
(**15**) Ar = 4-BrC_6H_4
(**16**) Ar = 4-ClC_6H_4
(**17**) Ar = α-$C_{10}H_7$
(**18**) Ar = 4-$H_3CC_6H_4$
(**19**) Ar = 4-$H_3COC_6H_4$



triazolo[3,2-*a*]pyridylium-2-olates (**20**)—(**25**) show a strong absorption band in the 1 670 cm^{-1} region which can be attributed to carbonyl stretching; it is similar in position to the carbonyl band shown by the monocyclic series.[6,7] The i.r. spectra of the isomeric 2-aminides (**14**)—(**19**) show strong absorption in the region 1 650—1 620 cm^{-1} which can be attributed to exocyclic C=N stretching. The absence of isocyanate bands in the i.r. spectra of (**20**)—(**25**) supports their formulation as cyclic mesoionic structures rather than the alternative valence tautomers. The mass spectra of (**14**)—(**19**) and (**20**)—(**25**) also differ. Both systems give a molecular ion as base peak, but the 2-olates (**20**)—(**25**) show the characteristic fragment ion (M^+ – NCO), whereas in the spectra of the isomeric 2-aminides (**14**)—(**19**) this fragment is absent. This clearly distinguishes between the two skeletal types (**1**) and (**6**). U.v. spectra of (**20**)—(**25**) are similar to those of the analogous monocyclic systems[7] and are consistent with a mesoionic structure.

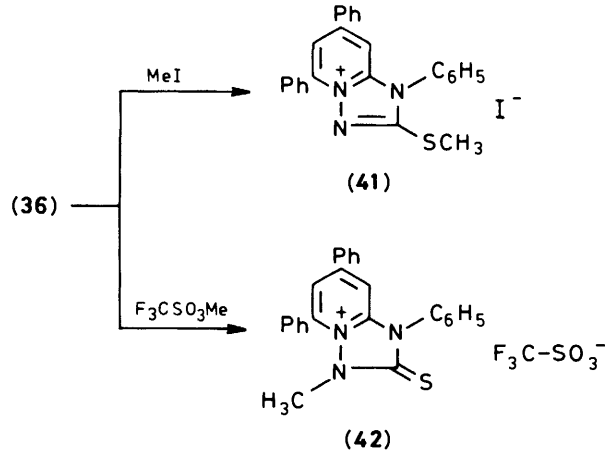
1,3,4-*Triazolo*[3,2-a]*pyridylium*-2-*thiolates*.—1-Amino-2-methylthio-4,6-diphenylpyridinium iodide (**27**), readily available from 1-amino-4,6-diphenylpyridine-2-thione and methyl iodide,[8] reacts with aliphatic and aromatic isothiocyanates (**28**) in acetonitrile in the presence of triethylamine giving the previously unreported 2-aryl(alkyl)amino-5,7-diphenyl-1,3,4-thiadiazolo[3,2-*a*]pyridylium iodides (**29**)—(**35**), as yellow crystalline solids in high yields (70—92%) (Table 3). However, when the reaction is carried out in dimethylformamide at room temperature with a slight excess of triethylamine 1-aryl-5,7-diphenyl-1,3,4-triazolo[3,2-*a*]pyridylium-2-thiolates (**36**)—(**40**) were isolated as orange crystalline solids in high yields (79—85%) (Table 4).

The conversion (**29**)—(**33**) ⟶ (**36**)—(**40**) is achieved in almost quantitative yield by treatment with triethylamine in dimethylformamide at room temperature. We believe that this transformation involves a mesoionic 2-aminide of type (**9**) as intermediate which, under the reaction conditions, rearranges to the mesoionic 2-thiolate. This assumption was supported by the direct conversion of 1,3,4-thiadiazolo[3,2-*a*]pyridylium-2-aminides under the same conditions into the corresponding 1,3,4-triazolo[3,2-*a*]pyridylium-2-thiolates. This isomerization is conceptually similar to that reported in the monocyclic series for the interconversion of 1,3,4-thiadiazolium-2-aminides into 1,3,4-triazolium-2-thiolates.[9] The conversions of 1,3,4-oxadiazolo[3,2-*a*]pyridylium-2-aminide into 1,3,4-triazolo[3,2-*a*]-pyridylium-2-olate and of 1,3,4-thiadiazolo[3,2-*a*]pyridylium-2-aminide into 1,3,4-triazolo[3,2-*a*]pyridylium-2-thiolate provide two examples of useful interconversion of pairs of fused mesoionic isomers by exchange of exocyclic and endocyclic heteroatoms or grouping.

Compounds (**29**)—(**35**) show in their i.r. spectra absorption due to N–H stretching at 3 170—3 160 cm^{-1}, together with the characteristic absorptions of the pyridinium ring at 1 620 and 1 600 cm^{-1}. The n.m.r. spectra show two doublets at δ 9 and 8.2 (*J* 2 Hz) due to *meta*-coupling of the pyridinium ring protons, together with a multiplet at δ 7—8 due to the aromatic protons; in addition compounds (**30**), (**31**), and (**35**) show a singlet attributable to the methyl group at δ 2.3, 2.15, and 3, respectively.

Support for structures (**36**)—(**40**) is clearly provided by spectral data. The i.r. spectra show absorption at 1 380 cm^{-1} attributable to thione stretching, similar in position to the thione stretching shown by the monocyclic 1,2,4-triazolium-2-thiolates.[6] This wavenumber is lower than that shown by the isomeric 1,3,4-thiadiazolo[3,2-*a*]pyridylium-2-aminides.[3] Mass spectra show the expected molecular ions as base peaks, and the fragmentation patterns are similar to those reported for the monocyclic series.[9b] The u.v. spectra show absorption around 360 nm, similar to the analogous monocyclic system,[9b] and also consistent with a mesoionic structure.

The mesoionic compounds (**36**)—(**40**) show informative differences in their reactions towards methyl iodide and methyl trifluoromethanesulphonate. This is exemplified by the

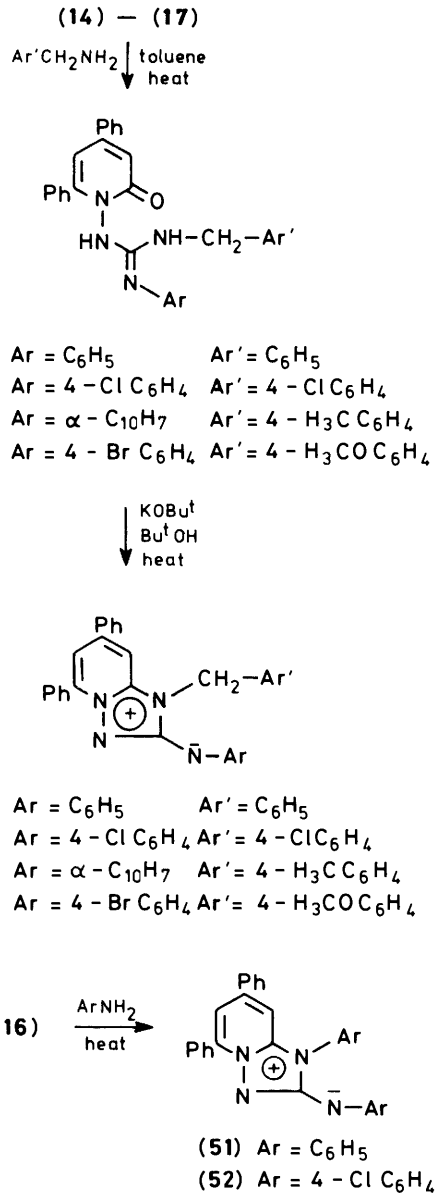


reaction of compound (**36**) with methyl iodide to give the corresponding *S*-methyl derivative (**41**), whereas with methyl trifluoromethanesulphonate the *N*-methyl derivative (**42**) is formed. The n.m.r. spectrum of (**41**) shows a singlet at δ 3.65 (*S*-CH_3), in that of (**42**) the signal corresponding to the *N*-CH_3 group appears as a singlet at δ 4.6.

1,3,4-*Triazolo*[3,2-a]*pyridylium*-2-*aminides*.—1,3,4-Oxadiazolo[3,2-*a*]pyridylium-2-aminides react with aryl-methylamines in toluene solution at reflux temperature for 24 h giving the guanidine derivatives (**43**)—(**46**) as crystalline solids in high yields (81—96%) (Table 5). The i.r. spectra of (**43**)—(**46**) show absorption due to N–H stretching at 3 500—3 100 cm^{-1} and to the carbonyl group at 1 650—1 645 cm^{-1}. The ($M^+ - H_2O$) ion provides the base peak in the mass spectra of (**44**)—(**46**), which also show fragments corresponding to ($M^+ - CH_2Ar'$); the molecular ion shows very low intensity. For compound (**43**) the fragment at *m/z* 91 is the base peak. In the n.m.r. spectra the methylene group appears as a singlet at δ 4.16—4.47.

The guanidine derivatives (**43**)—(**46**) undergo base-catalysed cyclization by the action of potassium t-butoxide in t-butyl alcohol at reflux temperature (24 h) to give the corresponding 1-substituted 5,7-diphenyl-1,3,4-triazolo[3,2-*a*]pyridylium-2-aminides (**47**)—(**50**) as orange crystals in high yields (78—93%) (Table 6). The i.r. spectra of (**43**)—(**46**) show strong absorption in the region 1 570—1 550 cm^{-1}, which can be attributed to C=N stretching; this wavenumber is similar to that reported for the monocyclic 1,2,4-triazolium-2-aminides.[9c] In addition, the i.r. spectra show no N–H absorption bands nor a carbodi-imide stretching vibration (2 155—2 130 cm^{-1}). The mass spectra show the expected molecular ions and the fragment ($M^+ - CH_2Ar'$) provides the base peak. The n.m.r. spectra are consistent with a mesoionic system. Thus, the signals corresponding to N–CH_2Ar' appear at δ 5.85—5.50, showing a downfield shift (*ca.* 1.3—1.1 p.p.m.) with respect to the N–CH_2Ar' group of the precursor guanidine derivatives. This deshielding may be attributed to a combination of the partial positive charge associated with the heterocycle and a ring current characterizing the aromaticity of the mesoionic system.[9d] The u.v. spectra are similar to those of the analogous monocyclic systems.

When the mesoionic 2-aminide (**14**) reacted with aniline in toluene for a long period (48 h), the 1,3,4-triazolo[3,2-*a*]-pyridylium-2-aminide (**51**) was isolated as orange crystals in high yield (90%). A similar result was achieved from the reaction of the 2-aminide (**16**) with *p*-chloroaniline to give (**52**). Spectral data of (**51**) and (**52**) are similar to those of the 2-aminides (**47**)—(**50**). This procedure for the preparation of



1,3,4-triazolo[3,2-*a*]pyridylium-2-aminides is unsatisfactory if the aryl groups at the 1- and 2-positions are different: this leads to a mixture of isomers.

The dipole moments of compounds (**20**) (8.7 D), (**36**) (9.6 D), and (**47**) (8.4 D) in benzene solution are in excellent agreement with the mesoionic structures indicated.[10]

Experimental

M.p.s were determined with a Kofler hot-stage microscope. Spectral characterizations were performed with the following instruments: i.r., Nicolet-FT 5DX; ^1H n.m.r., Varian FT-80 ($SiMe_4$ internal reference; all chemical shifts expressed as δ values); mass spectra (70 eV), Hewlett-Packard 5993 C; u.v. Varian 634 spectrophotometer. Combustion analyses were performed with a Perkin-Elmer 240 C instrument.

Reagents.—5,7-Diphenyl-1,3,4-oxadiazolo[3,2-*a*]-pyridylium-2-olate[3] (**12**), *N*-aryliminotriphenylphosphoranes[5] (**13**), and 1-amino-2-methylthio-4,6-diphenylpyridinium iodide[8] (**27**) were prepared following the methods described in the literature.

General Procedure for the Preparation of 1,3,4-*Oxadiazolo*[3,2-a]*pyridylium-2-aminides* (**14**)—(**19**).—5,7-Diphenyl-1,3,4-oxadiazolo[3,2-*a*]pyridylium-2-olate (**12**) (0.576 g, 2 mmol) in dry toluene (30 ml) and the appropriate *N*-aryliminotriphenylphosphorane (**13**) (2 mmol) were refluxed for 10 h. The solvent was removed (30 °C; 20 mmHg) and the product crystallized from ethanol. The following 1,3,4-oxadiazolo[3,2-*a*]pyridylium-2-olates were obtained (yields, m.p.s, and analyses are given in Table 1): 2-(4-*bromophenyl*)*aminide* (**15**), $\nu_{max.}$(Nujol) 3 060, 1 640, 1 630, 1 570, 1 560, 1 470, 1 410, 1 390, 1 380, 1 230, 1 190, 930, 880, 760, 740, and 700 cm^{-1}; *m/z* (%) 443 (M^+ + 2, 95), 442 (100), 441 (M^+, 93), 286 (60), 218 (25), 203 (27), and 77 (30); 2-(4-*chlorophenyl*)*aminide* (**16**), $\nu_{max.}$(Nujol) 3 060, 1 640, 1 620, 1 480, 1 470, 1 400, 1 200, 1 190, 930, 870, 830, 770, and 700 cm^{-1}; *m/z* (%) 399 (M^+ + 2, 30), 397 (M^+, 100), 287 (10), 247 (30), 218 (25), 202 (20), 127 (10), 125 (25), and 77 (20); 2-(4-*methylphenyl*)*aminide* (**18**), $\nu_{max.}$(Nujol) 3 060, 1 630, 1 600, 1 560, 1 460, 1 440, 1 260, 1 180, 1 140, 850, 840, and 700 cm^{-1}; *m/z* (%) 377 (M^+, 100), 362 (40), 247 (35), 218 (20), 203 (20), 105 (25), 91 (15), and 77 (24); 2-(4-*methoxyphenyl*)*aminide* (**19**), $\nu_{max.}$(Nujol) 3 060, 1 640, 1 630, 1 500, 1 460, 1 400, 1 240, 1 190, 1 180, 940, 930, 840, 780, 770, and 700 cm^{-1}; *m/z* (%) 393 (M^+, 100), 285 (45), 218 (30), 202 (15), and 77 (35).

General Procedure for the Preparation of 1-*Aryl*-5,7-*diphenyl*-1,3,4-*triazolo*[3,2-a]*pyridylium-2-olates* (**20**)—(**25**).—Potassium carbonate (0.276 g, 2 mmol) was added to a solution of 1,3,4-oxadiazolo[3,2-*a*]pyridylium-2-aminide (1 mmol) in anhydrous ethanol (20 ml). The mixture was stirred and heated at reflux for 2 h. After cooling, the salt was separated by filtration and the filtrate concentrated to dryness to afford a crude product which, recrystallized from ethanol, gave 1,3,4-triazolo[3,2-*a*]pyridylium-2-olate. The following compounds were obtained (yields, m.p.s, and analyses are given in Table 2): 1,5,7-*triphenyl* (**20**), $\nu_{max.}$(Nujol) 3 060, 1 675, 1 630, 1 550, 1 500, 1 200, 1 190, 780, 770, 760, 720, and 700 cm^{-1}; *m/z* (%) 363 (M^+, 100), 362 (96), 321 (M^+ − NCO, 28), 203 (10), 202 (12), 115 (8), 102 (12), and 77 (20); 1-(4-*bromophenyl*)-5,7-*diphenyl* (**21**), $\nu_{max.}$(Nujol) 3 060, 1 675, 1 550, 1 490, 1 200, 1 120, 1 070, 1 010, 870, 770, 750, 730, 710, and 700 cm^{-1}; $\lambda_{max.}$(EtOH) 267 nm (ε 62 500); *m/z* (%) 443 (M^+ + 2, 98), 442 (100), 441 (M^+, 96), 440 (81), 309 (M^+ − NCO, 20), 220 (87), 219 (60), 203 (45), 202 (66), 167 (48), 155 (30), 115 (45), 102 (93), and 77 (60); 1-(4-*chlorophenyl*)-5,7-*diphenyl* (**22**), $\nu_{max.}$(Nujol) 3 060, 1 670, 1 630, 1 550, 1 490, 1 420, 1 200, 1 120, 1 090, 1 010, 870, 840, 780, 760, 750, 730, and 700 cm^{-1}; $\lambda_{max.}$(EtOH) 265 nm (ε 68 700); *m/z* (%) 399 (M^+ + 2, 35), 397 (M^+, 99), 396 (100), 355 (M^+ − NCO, 33), 320 (30), 319 (32), 218 (25), 217 (25), 203 (40), 202 (55), 167 (30), 115 (37), 102 (75), and 77 (45); 1-(1-*naphthyl*)-5,7-*diphenyl* (**23**), $\nu_{max.}$(Nujol) 3 060, 1 675, 1 630, 1 550, 1 480, 1 200, 1 170, 1 130, 1 090, 870, 800, 780, 760, 750, 740, 710, and 700 cm^{-1}; $\lambda_{max.}$(EtOH) 267 nm (ε 81 400); *m/z* (%) 413 (M^+, 72), 412 (100), 372 (31), 371 (M^+ − NCO, 44), 203 (13), 202 (22), 178 (15), 153 (17), 127 (70), 126 (42), 115 (73), 101 (25), and 77 (75); 1-(4-*methylphenyl*)-5,7-*diphenyl* (**24**), $\nu_{max.}$(Nujol) 3 060, 1 670, 1 630, 1 550, 1 510, 1 420, 1 200, 1 180, 1 120, 820, 770, 760, 750, 720, and 700 cm^{-1}; $\lambda_{max.}$(EtOH) 266 nm (ε 68 700); *m/z* (%) 377 (M^+, 100), 376 (97), 335 (M^+ − NCO, 32), 203 (18), 202 (25), 115 (28), 102 (65), 91 (51), 89 (30), and 77 (55); 1-(4-*methoxyphenyl*)-5,7-*diphenyl* (**25**), $\nu_{max.}$(Nujol) 3 060, 1 670, 1 630, 1 550, 1 510, 1 300, 1 250, 1 200, 1 170, 1 120, 1 030, 850, 840, 770, 750, and 700 cm^{-1}; $\lambda_{max.}$(EtOH) 266 nm (ε 72 100); *m/z* (%) 393 (M^+, 100), 392 (71), 351 (M^+ − NCO, 40), 203 (16), 202 (21), 115 (30), 102 (33), 92 (22), 91 (16), and 77 (65).

General Procedure for the Preparation of 2-*Aryl*(*alkyl*)*amino*-5,7-*diphenyl*-1,3,4-*thiadiazolo*[3,2-a]*pyridinium Iodides* (**29**)—(**35**).—1-Amino-2-methylthio-4,6-diphenylpyridinium iodide (**27**) (0.42 g, 1 mmol) in dry acetonitrile (30 ml) and equimolecular amounts of triethylamine and the appropriate isothiocyanate were stirred at reflux for 6—10 h. The solvent was removed (30 °C; 20 mmHg) and the resulting solid crystallized from methanol. The following 1,3,4-thiadiazolo-[3,2-*a*]pyridinium iodides were obtained (yields, m.p.s, and analyses are given in Table 3): 5,7-*diphenyl*-2-*phenylamino* (**29**), $\nu_{max.}$(Nujol) 3 160, 3 040, 1 610, 1 560, 1 540, 1 500, 1 450, 1 410, 1 280, 1 260, 1 220, 880, 770, 760, 700, and 690 cm^{-1}; *m/z* (%) 379 (M^+ − IH, 55), 302 (5), 263 (7), 203 (16), 128 (100), 118 (5), 115 (27), and 77 (12); 5,7-*diphenyl*-2-(4-*methylphenyl*)*amino* (**30**), $\nu_{max.}$(Nujol) 3 160, 3 040, 1 600, 1 560, 1 535, 1 510, 1 460, 1 400, 1 385, 1 320, 1 275, 1 245, 1 215, 885, 810, 775, 765, and 700 cm^{-1}; *m/z* (%) 393 (M^+ − IH − 1, 98), 263 (100), 230 (40),

Table 1. 5,7-Diphenyl-1,3,4-oxadiazolo[3,2-*a*]pyridylium-2-aminides

Compound	Crystal form	Yield (%)	M.p. (°C)	Lit.[a] m.p. (°C)	Found (%) C	H	N	Formula	Required (%) C	H	N
(**14**)	Orange needles	89	206—207	206—207							
(**15**)	Orange needles	75	255—256		65.1	3.6	9.4	$C_{24}H_{16}BrN_3O$	65.2	3.65	9.5
(**16**)	Yellow needles	87	236—238		72.25	4.0	10.5	$C_{24}H_{16}ClN_3O$	72.45	4.05	10.6
(**17**)	Orange needles	91	235—236	235—236							
(**18**)	Yellow needles	75	204—205		79.4	5.0	11.1	$C_{25}H_{19}N_3O$	79.6	5.1	11.1
(**19**)	Orange needles	81	214—215		76.2	4.8	10.6	$C_{25}H_{19}N_3O_2$	76.3	4.8	10.7

[a] Ref. 2.

Table 2. 1-Aryl-5,7-diphenyl-1,3,4-triazolo[3,2-*a*]pyridylium-2-olates

Compound	Crystal form	Yield (%)	M.p. (°C)	Solvent	Found (%) C	H	N	Formula	Required (%) C	H	N
(**20**)	White needles	85	203—204	EtOH	79.15	4.7	11.4	$C_{24}H_{17}N_3O$	79.3	4.7	11.6
(**21**)	White needles	94	262—263	EtOH	64.9	3.6	9.4	$C_{24}H_{16}BrN_3O$	65.2	3.65	9.5
(**22**)	White needles	91	254—255	EtOH	72.2	3.9	10.5	$C_{24}H_{16}ClN_3O$	72.45	4.05	10.6
(**23**)	White needles	96	223—224	EtOH	81.1	4.55	10.0	$C_{28}H_{19}N_3O$	81.3	4.6	10.2
(**24**)	White needles	87	244—245	EtOH	79.4	5.0	11.0	$C_{25}H_{19}N_3O$	79.6	5.1	11.1
(**25**)	White needles	93	186—188	EtOH	76.1	4.75	10.6	$C_{25}H_{19}N_3O_2$	76.3	4.8	10.7

Table 3. 2-Aryl(alkyl)amino-5,7-diphenyl-1,3,4-thiadiazolo[3,2-*a*]pyridylium iodides

Compound	Crystal form	Yield (%)	M.p. (°C)	Solvent	Found (%) C	H	N	Formula	Required (%) C	H	N
(**29**)	Yellow needles	83	298—300	MeOH	56.7	3.6	8.35	$C_{24}H_{18}N_3IS$	56.8	3.6	8.3
(**30**)	Yellow needles	93	328—330	MeOH	57.4	4.0	7.85	$C_{25}H_{20}N_3IS$	57.6	3.9	8.1
(**31**)	Yellow needles	90	305—307	MeOH	57.5	3.8	7.95	$C_{25}H_{20}N_3IS$	57.6	3.9	8.1
(**32**)	Yellow needles	88	332—334	MeOH	53.1	3.0	7.9	$C_{24}H_{17}N_3ClIS$	53.2	3.2	7.75
(**33**)	Yellow needles	85	320—322	MeOH	49.3	2.8	7.3	$C_{24}H_{17}N_3BrIS$	49.2	2.9	7.2
(**34**)	Yellow needles	70	301—303	MeOH	56.3	4.9	8.3	$C_{24}H_{24}N_3IS$	56.15	4.7	8.2
(**35**)	Yellow needles	72	296—297	MeOH	51.5	3.5	9.3	$C_{19}H_{16}N_3IS$	51.25	3.6	9.4

Table 4. 1-Aryl-5,7-diphenyl-1,3,4-triazolo[3,2-*a*]pyridylium-2-thiolates

Compound	Crystal form	Yield (%)	M.p. (°C)	Solvent	Found (%) C	H	N	Formula	Required (%) C	H	N
(**36**)	Orange needles	79	125—126	MeOH	75.6	4.6	11.0	$C_{24}H_{17}N_3S$	76.0	4.5	11.1
(**37**)	Orange needles	85	193—194	MeOH	76.35	4.8	10.6	$C_{25}H_{19}N_3S$	76.3	4.8	10.7
(**38**)	Orange needles	83	135—136	MeOH	76.25	4.7	10.5	$C_{25}H_{19}N_3S$	76.3	4.9	10.7
(**39**)	Orange needles	80	130—131	MeOH	69.5	3.8	10.4	$C_{24}H_{16}ClN_3S$	69.7	3.9	10.15
(**40**)	Orange needles	81	198—199	MeOH	63.0	3.5	9.3	$C_{24}H_{16}BrN_3S$	62.9	3.5	9.2

218 (20), 203 (25), 202 (15), 115 (20), and 77 (10); δ[$(CD_3)_2SO$] 9.00 (1 H, d), 8.30 (1 H, d), 7.0—8.2 (14 H, m), and 2.30 (3 H, s); 5,7-*diphenyl*-2-(2-*methylphenyl*)*amino* (**31**), $\nu_{max.}$(Nujol) 3 160, 3 040, 1 620, 1 600, 1 560, 1 540, 1 500, 1 460, 1 410, 1 380, 1 310, 1 280, 1 260, 1 200, 890, 770, 750, and 700 cm^{-1}; *m/z* (%) 393 (M^+ − IH, 4), 263 (10), 230 (18), 219 (13), 202 (10), 163 (6), 132 (8), 131 (39), 128 (100), 115 (15), and 77 (15); δ[$(CD_3)_2SO$] 9.00 (1 H, d), 8.20 (1 H, d), 7.1—8.1 (14 H, m), and 2.15 (3 H, s); 5,7-*diphenyl*-2-(4-*chlorophenyl*)*amino* (**32**), $\nu_{max.}$(Nujol) 3 165, 3 040, 1 610, 1 560, 1 535, 1 495, 1 460, 1 440, 1 405, 1 380, 1 320, 1 090, 1 015, 830, 770, and 700 cm^{-1}; *m/z* (%) 415 (18), 413 (45), 263 (21), 262 (15), 230 (10), 228 (10), 203 (24), 202 (26), 152 (15), 128 (100), 115 (44), and 77 (16); 5,7-*diphenyl*-2-(4-*bromophenyl*)-*amino* (**33**), $\nu_{max.}$(Nujol) 3 160, 3 040, 1 610, 1 560, 1 540, 1 495, 1 460, 1 430, 1 410, 1 390, 1 325, 1 300, 1 220, 1 080, 1 025, 935, 835, 770, and 700 cm^{-1}; *m/z* (%) 459 (16), 457 (16), 263 (9), 228 (8), 203 (27), 189 (16), 128 (100), 115 (32), and 77 (10); 5,7-*diphenyl*-2-*cyclohexylamino* (**34**), $\nu_{max.}$(Nujol) 3 160, 3 025, 1 610, 1 570, 1 530, 1 500, 1 450, 1 420, 1 400, 1 370, 1 340, 1 280, 1 190, 1 080, 900, 880, 770, 765, and 700 cm^{-1}; *m/z* (%) 386 (80), 385 (14), 288 (7), 263 (28), 254 (5), 230 (21), 228 (6), 203 (15), 128 (100), 115 (25), and 77 (30); 5,7-*diphenyl*-2-*methylamino* (**35**), $\nu_{max.}$(Nujol) 3 140, 3 060, 1 610, 1 590, 1 540, 1 520, 1 500, 1 460, 1 420, 1 400, 1 290, 1 265, 1 210, 1 160, 1 035, 880, 770, and 700 cm^{-1}; δ[$(CD_3)_2SO$] 9.20 (1 H, d), 8.30 (1 H, d), 7.5—8.2 (11 H, m), and 3.00 (3 H, s); *m/z* (%) 318 (59), 317 (73), 288 (13), 277 (72), 263 (55), 254 (20), 230 (34), 228 (11), 219 (20), 203 (26), 128 (100), 115 (36), and 77 (25).

General Procedure for the Preparation of 1-*Aryl*-5,7-*diphenyl*-1,3,4-*triazolo*[3,2-a]*pyridylium*-2-*thiolates* (**36**)—(**40**).—1-Amino-2-methylthio-4,6-diphenylpyridinium iodide (**27**) (0.42 g, 1 mmol) in dry dimethylformamide (15 ml), triethylamine (2 mmol), and the appropriate aryl isothiocyanate (1 mmol) were stirred at room temperature for 12 h. The mixture was poured into ice–water((30 ml) and the precipitated solid filtered off and recrystallized from methanol to give the corresponding 1,3,4-triazolo[3,2-*a*]pyridylium-2-thiolate. By the above procedure the following compounds were obtained (yields, m.p.s, and analyses are given in Table 4): 1,5,7-*triphenyl* (**36**), $\nu_{max.}$(Nujol) 3 060, 1 610, 1 570, 1 550, 1 520, 1 470, 1 450, 1 400, 1 380, 1 210, 1 180, 1 150, 1 000, 770, and 700 cm^{-1}; *m/z* (%) 379 (M^+, 100), 321 (80), 302 (40), 275 (20), 263 (45), 202 (20), 115 (15), and 77 (10); 5,7-*diphenyl*-1-(4-*methylphenyl*) (**37**), $\nu_{max.}$(Nujol) 1 610, 1 570, 1 540, 1 510, 1 450, 1 400, 1 380, 1 220, 1 190, 1 160, 920, 830, 760, 720, and 700 cm^{-1}; *m/z* (%) 393 (M^+, 100), 376 (80), 353 (20), 335 (25), 294 (10), 293 (8), 263 (40), 230 (50), 219 (20), 203 (35), 115 (20), and 77 (7); $\lambda_{max.}$(EtOH) 246 nm (ε 18 800); 5,7-*diphenyl*-1-(2-*methylphenyl*) (**38**), $\nu_{max.}$(Nujol) 3 060, 1 605, 1 580, 1 560, 1 480, 1 460, 1 405, 1 375, 1 300, 1 250, 1 210, 1 180, 1 160, 1 110, 920, 880, 770, 740, and 700 cm^{-1}; *m/z* (%) 393 (M^+, 24), 360 (15), 263 (46), 230 (10), 203 (15), 202 (17), 131 (100), 115 (41), 104 (30), 91 (8), and 77 (43); $\lambda_{max.}$(EtOH) 260 nm (ε 17 300); 5,7-*diphenyl*-1-(4-*chlorophenyl*) (**39**), $\nu_{max.}$(Nujol) 3 040, 1 605, 1 580, 1 565, 1 560, 1 480, 1 460, 1 430, 1 400, 1 380, 1 280, 1 210, 1 180, 1 160, 1 085, 920, 835, 760, and 700 cm^{-1}; *m/z* (%) 415 (M^+ + 2, 25), 413 (M^+, 65), 263 (9), 262 (11), 230 (7), 203 (31), 202 (32), 159 (12), 152 (12), 128 (7), 115 (100), 102 (25), and 77 (33); $\lambda_{max.}$(EtOH) 300 (ε 17 900) and 265 nm (18 300); 5,7-*diphenyl*-1-(4-*bromophenyl*) (**40**), $\nu_{max.}$(Nujol) 3 040, 1 600, 1 540, 1 520, 1 460, 1 420, 1 400, 1 380, 1 310, 1 280, 1 250, 1 210, 1 180, 1 150, 1 070, 1 000, 910, 870, 830, 770, and 700 cm^{-1}; *m/z* (%) 459 (M^+ + 2, 30), 254 (37), 238 (17), 230 (12), 228 (10), 215 (13), 213 (13), 205 (35), 203 (30), 202 (32), 196 (14), 128 (24), 115 (100), 90 (35), and 77 (61); $\lambda_{max.}$(EtOH) 296 (ε 18 800) and 264 nm (20 400).

Reaction of Methyl Iodide with 1-*Aryl*-5,7-*diphenyl*-1,3,4-*triazolo*[3,2-a]*pyridylium*-2-*thiolates*.—1-Aryl-5,7-diphenyl-1,3,4-triazolo[3,2-*a*]pyridylium-2-thiolate (1 mmol) in dry dichloromethane (30 ml) and methyl iodide (2 mmol) were stirred at room temperature for 3 h. The solvent was removed under reduced pressure (30 °C; 20 mmHg) and the product recrystallized from ethanol to give the corresponding 2-methylthio-1,3,4-triazolo[3,2-*a*]pyridinium iodide. By this procedure the following compounds were obtained: 1,5,7-*triphenyl* (**41**) (80%), yellow needles, m.p. 280—282 °C (Found: C, 58.0; H, 3.9; N, 8.1. $C_{25}H_{20}IN_3S$ requires C, 57.6; H, 3.9; N, 8.1%); $\nu_{max.}$(Nujol) 1 615, 1 560, 1 510, 1 450, 1 430, 1 375, 1 350, 1 340, 1 290, 1 270, 1 210, 890, 760, 730, and 700 cm^{-1}; δ[$(CD_3)_2SO$] 9.30 (1 H, d), 8.50 (1 H, d), 7.6—8.4 (15 H, m), and 3.65 (3 H, s); 5,7-*diphenyl*-1-(4-*methylphenyl*) (86%), yellow needles, m.p. 329—331 °C (Found: C, 58.25; H, 4.2; N, 7.8. $C_{26}H_{22}IN_3S$ requires C, 58.3; H, 4.1; N, 7.85%); $\nu_{max.}$(Nujol)

Table 5. Guanidine derivatives

Compound	Crystal form	Yield (%)	M.p (°C)	Solvent	Found (%) C	H	N	Formula	Required (%) C	H	N
(43)	White needles	84	192—193	EtOH	78.9	5.6	11.8	$C_{31}H_{26}N_4O$	79.15	5.5	11.9
(44)	White needles	81	233—235	EtOH	68.75	4.4	10.4	$C_{31}H_{24}ClN_4O_2$	69.0	4.5	10.4
(45)	White needles	87	228—230	EtOH	80.6	5.6	10.4	$C_{36}H_{30}N_4O$	80.9	5.7	10.5
(46)	White needles	96	180—181	EtOH	66.2	4.7	9.6	$C_{32}H_{27}BrN_4O_2$	66.3	4.8	9.65

Table 6. 1-Substituted 5,7-diphenyl-1,3,4-triazolo[3,2-*a*]pyridylium-2-aminides

Compound	Crystal form	Yield (%)	M.p. (°C)	Solvent	Found (%) C	H	N	Formula	Required (%) C	H	N
(47)	Red needles	87	274—275	Benzene	82.1	5.25	12.3	$C_{31}H_{24}N_4$	82.3	5.35	12.4
(48)	Orange needles	93	253—255	Benzene	71.2	4.1	10.6	$C_{31}H_{22}Cl_2N_4$	71.4	4.25	10.7
(49)	Orange needles	89	257—259	Benzene	83.5	5.4	10.8	$C_{36}H_{28}N_4$	83.7	5.5	10.8
(50)	Orange needles	91	210—211	Benzene	68.2	4.5	9.9	$C_{32}H_{25}BrN_4O$	68.5	4.5	10.0
(51)	Red needles	90	273—275	Benzene	81.9	5.0	12.6	$C_{30}H_{22}N_4$	82.2	5.1	12.8
(52)	Orange needles	92	290—292	Benzene	70.85	3.85	10.9	$C_{30}H_{20}Cl_2N_4$	71.0	4.0	11.0

1 615, 1 525, 1 510, 1 460, 1 425, 1 405, 1 376, 1 275, 1 210, 765, 735, and 700 cm^{-1}; δ[$(CD_3)_2SO$] 9.10 (1 H, d), 8.50 (1 H, d), 7.6—8.4 (14 H, m), 3.60 (3 H, s), and 2.50 (3 H, s); 5,7-*diphenyl*-1-(2-*methylphenyl*) (85%), yellow needles, m.p. 314—316 °C (Found: C, 58.3; H, 4.2; N, 7.9. $C_{26}H_{22}IN_3S$ requires C, 58.3; H, 4.1; N, 7.85%); $\nu_{max.}$(Nujol) 3 040, 1 610, 1 570, 1 540, 1 500, 1 460, 1 420, 1 400, 1 380, 1 360, 1 260, 1 200, 1 110, 880, 850, 770, 730, 710, and 700 cm^{-1}; δ[$(CD_3)_2SO$] 9.10 (1 H, d), 8.40 (1 H, d), 7.5—8.3 (14 H, m), 3.50 (3 H, s), and 2.35 (3 H, s); 5,7-*diphenyl*-1-(4-*chlorophenyl*) (80%), yellow needles, m.p. 303—305 °C (Found: C, 54.1; H, 3.4; N, 7.5. $C_{25}H_{19}ClIN_3S$ requires C, 54.0; H, 3.4; N, 7.6%), $\nu_{max.}$(Nujol) 3 030, 1 610, 1 600, 1 555, 1 540, 1 490, 1 460, 1 420, 1 400, 1 380, 1 260, 1 110, 890, 840, 770, 740, and 700 cm^{-1}; δ[$(CD_3)_2SO$] 9.20 (1 H, d), 8.55 (1 H, d), 7.6—8.4 (14 H, m), and 3.65 (3 H, s); 5,7-*diphenyl*-1-(4-*bromophenyl*) (79%), yellow needles, m.p. 290—292 °C (Found: C, 50.3; H, 3.15; N, 7.2. $C_{25}H_{19}BrIN_3S$ requires C, 50.0; H, 3.2; N, 7.0%); $\nu_{max.}$(Nujol) 3 040, 1 610, 1 560, 1 540, 1 490, 1 460, 1 430, 1 380, 1 270, 1 210, 1 110, 1 060, 1 010, 900, 840, 770, 730, and 700 cm^{-1}; δ[$(CD_3)_2SO$] 9.25 (1 H, d), 8.30 (1 H, d), 7.4—8.2 (14 H, m), and 3.70 (3 H, s).

Compound (**36**), treated with methyl trifluoromethanesulphonate, gave 3-*methyl*-1,5,7-*triphenyl*-2-*thioxo*-1,3,4-*triazolo*[3,2-a]*pyridinium trifluoromethanesulphonate* (**42**) (82%), yellow prisms, m.p. 320—322 °C (Found: C, 57.4; H, 3.7; N, 7.8. $C_{26}H_{20}F_3N_3O_3S_2$ requires C, 57.45; H, 3.7; N, 7.7%); $\nu_{max.}$(Nujol) 3 060, 1 610, 1 570, 1 560, 1 500, 1 450, 1 400, 1 380, 1 310, 1 200, 1 150, 1 060, 760, 750, 720, and 700 cm^{-1}; δ[$(CD_3)_2SO$] 9.30 (1 H, d), 9.15 (1 H, d), 7.6—8.8 (15 H, m), and 4.60 (3 H, s).

General Procedure for the Preparation of Guanidine Derivatives (**43**)—(**46**).—5,7-Diphenyl-1,3,4-oxadiazolo[3,2-*a*]pyridylium-2-aminide (2 mmol) in dry toluene (40 ml) and the appropriate arylmethylamine (2.4 mmol) were heated at reflux for 24 h. After cooling, the solvent was removed (50 °C; 20 mmHg) and the resulting oil treated with cold ether gave a solid which crystallized from ethanol to yield the corresponding *N*-(1,2-dihydro-2-oxo-4,6-diphenyl-1-pyridyl)guanidine derivative. According to this procedure the following compounds were obtained (yields, m.p.s, and analyses are given in Table 5): N′-*benzyl*-N″-*phenyl* (**43**), $\nu_{max.}$(Nujol) 3 320, 3 060, 3 040, 1 645, 1 605, 1 590, 1 570, 1 550, 1 500, 1 250, 875, 775, 765, 750, and 700 cm^{-1}; *m/z* (%) 470 (M^+, 5), 452 (5), 379 (6), 322 (4), 261 (12), 248 (10), 218 (15), 203 (11), 115 (18), 91 (100), and 77 (40); N′-(4-*chlorobenzyl*)-N″-(4-*chlorophenyl*) (**44**), $\nu_{max.}$(Nujol) 3 300, 3 260, 1 645, 1 570, 1 560, 1 490, 1 250, 1 090, 1 010, 860, 820, 770, 760, 700, and 690 cm^{-1}; δ($CDCl_3$–CF_3CO_2H) 6.7—8.1 (20 H, m) and 4.30 (2 H, s); 542 (M^+ + 4, 2), 540 (M^+ + 2, 12), 538 (M^+, 20), 520 (100), 397 (35), 230 (20), 218 (32), 203 (18), and 77 (35); N′-(4-*methylbenzyl*)-N″-(1-*naphthyl*) (**45**), $\nu_{max.}$(Nujol) 3 450, 3 190, 3 040, 1 650, 1 610, 1 580, 1 560, 1 520, 1 490, 1 370, 1 100, 860, 840, 780, 770, 750, 700, and 690 cm^{-1}; δ($CDCl_3$–CF_3CO_2H) 6.7—8.3 (23 H, m), 4.16 (2 H, s), and 2.33 (3 H, s); *m/z* (%) 534 (M^+, 15), 516 (100), 519 (28), 413 (43), 247 (32), 230 (18), 218 (27), 203 (25), and 77 (41); N′-(4-*methoxybenzyl*)-N″-(4-*bromophenyl*) (**46**), $\nu_{max.}$(Nujol) 3 420, 3 295, 3 200, 1 640, 1 600, 1 580, 1 530, 1 510, 1 490, 1 400, 1 245, 1 180, 1 040, 830, 810, 770, 760, and 700 cm^{-1}; δ($CDCl_3$–CF_3CO_2H) 6.6—8.5 (20 H, m), 4.47 (2 H, s), and 3.80 (3 H, s); *m/z* (%) 580 (M^+ + 2, 9), 578 (M^+, 10), 562 (98), 560 (100), 443 (26), 441 (28), 247 (42), 230 (15), 218 (26), 203 (20), and 77 (40).

General Procedure for the Preparation of 1-*Substituted* 5,7-*Diphenyl*-1,3,4-*triazolo*[3,2-a]*pyridylium-2-aminides* (**47**)—(**52**).—*Method A: From guanidine derivatives and arylmethyl amines.* Potassium t-butoxide (0.49 g, 4 mmol) was added to a solution of the guanidine derivative (2 mmol) in t-butyl alcohol (30 ml). A deep red colouration immediately developed; after 24 h under gentle reflux the solution was set aside at room temperature. The precipitated solid, separated by filtration and recrystallized from benzene, gave the corresponding 1,3,4-triazolo[3,2-*a*]pyridylium-2-aminide. The following compounds were obtained (yields, m.p.s, and analyses are given in Table 6): 1-*benzyl*-5,7-*diphenyl*-2-*phenylaminide* (**47**), $\nu_{max.}$(Nujol) 3 060, 1 640, 1 610, 1 570, 1 550, 1 490, 1 440, 1 200, 1 160, 770, 760, 740, and 700 cm^{-1}; δ[$(CD_3)_2SO$] 7.0—8.3 (22 H, m) and 5.50 (2 H, s); $\lambda_{max.}$(EtOH) 257 nm (ε 55 600); *m/z* (%) 452 (M^+, 50), 451 (30), 375 (40), 362 (25), 361 (20), 319 (15), 230 (40), 202 (15), 167 (61), 115 (15), 91 (100), and 77 (42); 1-(4-*chlorobenzyl*)-5,7-*diphenyl*-2-(4-*chlorophenyl*)*aminide* (**48**), $\nu_{max.}$(Nujol) 3 060, 1 640, 1 590, 1 560, 1 540, 1 480, 1 180, 1 170, 1 160, 830, 770, and 700 cm^{-1}; δ[$(CD_3)_2SO$] 7.1—8.3 (20 H, m) and 5.53 (2 H, s); $\lambda_{max.}$(EtOH) 261 nm (ε 84 500); *m/z* (%) 522 (M^+ + 2, 14), 521 (13), 520 (M^+, 30), 519 (12), 396 (18), 395 (10), 360 (20), 235 (40), 230 (25), 202 (30), 127 (54), 126 (28), 125 (100), 115 (22), 91 (30), and 77 (52); 1-(4-*methylbenzyl*)-5,7-*diphenyl*-2-(1-*naphthyl*)*aminide* (**49**), $\nu_{max.}$(Nujol) 3 060, 1 640,

1 590, 1 570, 1 540, 1 490, 1 200, 1 160, 1 140, 800, 790, 780, 770, 760, and 695 cm $^{-1}$; δ[$(CD_3)_2SO$] 6.9—8.4 (23 H, m), 5.57 (2 H, s), and 2.30 (3 H, s); $\lambda_{max.}$(EtOH) 262 nm (ε 89 800); *m/z* (%) 516 (M^+, 40), 411 (20), 231 (60), 230 (15), 202 (15), 167 (15), 127 (20), 115 (35), 105 (100), 91 (27), and 77 (50); 1-(*4-methoxybenzyl*)-*5,7-diphenyl*-2-(*4-bromophenyl*)*aminide* (**50**), $\nu_{max.}$(Nujol) 3 060, 1 630, 1 590, 1 560, 1 540, 1 470, 1 240, 1 200, 830, 770, 760, and 695 cm $^{-1}$; δ[$(CD_3)_2SO$] 7.1—8.4 (20 H, m), 5.58 (2 H, s), and 3.83 (3 H, s); $\lambda_{max.}$(EtOH) 261 nm (ε 83 500); *m/z* (%) 562 (M^+ + 2, 10), 560 (M^+, 10), 442 (20), 441 (10), 440 (13), 439 (10), 230 (9), 202 (12), 180 (15), 122 (20), 121 (100), 115 (10), 91 (15), and 77 (30).

Method B. From 1,3,4-*oxadiazolo*[3,2-a]*pyridylium*-2-*aminides and arylamines.* 5,7-Diphenyl-1,3,4-oxadiazolo[3,2-*a*]-pyridylium-2-aminide (1 mmol) in dry toluene (30 ml) and the appropriate arylamine (1 mmol) were stirred at reflux for 48 h. After cooling, the solvent was removed under reduced pressure (50 °C; 20 mmHg) and the resulting red material treated with cold benzene gave a solid which was recrystallized from benzene to give the corresponding 1,3,4-triazolo[3,2-*a*]pyridylium-2-aminide. The following compounds were obtained (yields, m.p.s, and analyses are given in Table 6): 1,*5,7-triphenyl*-2-*phenylaminide* (**51**), $\nu_{max.}$(Nujol) 3 060, 1 630, 1 610, 1 570, 1 560, 1 490, 1 200, 770, 760, 750, and 700 cm $^{-1}$; $\lambda_{max.}$(EtOH) 258 nm (ε 69 500); *m/z* (%) 438 (M^+, 100), 422 (40), 361 (35), 320 (10), 319 (10), 318 (10), 242 (30), 230 (40), 202 (25), 189 (20), 177 (15), and 77 (50); 1-(*4-chlorophenyl*)-*5,7-diphenyl*-2-(*4-chlorophenyl*)-*aminide* (**52**), $\nu_{max.}$(Nujol) 3 060, 1 640, 1 610, 1 570, 1 540, 1 480, 1 200, 830, 760, and 700 cm $^{-1}$; $\lambda_{max.}$(EtOH) 262 nm (ε 72 800); *m/z* (%) 508 (M^+ + 2, 65), 507 (52), 506 (M^+, 99), 505 (35), 492 (40), 490 (55), 452 (20), 320 (25), 319 (50), 318 (16), 236 (50), 230 (25), 203 (22), 202 (35), 167 (25), 115 (75), 102 (46), 99 (53), 91 (52), and 77 (100).

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