Bridgehead Nitrogen Heterocycles. Synthesis of [1,2,4]Triazolo[1,5-*a*]pyridin-1-ium and Pyrido[2,1-*f*][1,2,4]triazin-9-ium Derivatives [1]

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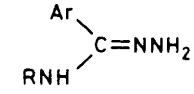
A number of derivatives of bridgehead nitrogen heterocycles from pyrylium salts and amidrazones have been prepared. 2-Methylthio-4,6-diphenylpyrylium tetrafluoroborate (13) reacts with N^3-aryl substituted amidrazones to yield derivatives of [1,2,4]triazolo[1,5-*a*]pyridin-1-ium tetrafluoroborates [(17)—(21)]. 2-Ethoxycarbonyl-4,6-diphenylpyrylium (14) reacts with N^3-aryl substituted amidrazones to give 4-oxopyrido[2,1-*f*][1,2,4]triazin-9-ium derivatives [(23)—(27)]. Compound (14) also reacts under neutral conditions with unsubstituted amidrazones to yield the corresponding pyridinium salts [(29)—(33)]; these cyclised on treatment with base giving the zwitterionic 4-oxidopyrido[2,1-*f*][1,2,4]triazin-9-ium compounds [(34)—(39)].

The reaction of primary amino groups with several pyrylium salts to give the corresponding pyridinium cations, has been comprehensively reviewed; [2] however, reactions of pyrylium salts with amidrazones have not received very much attention and only two reactions have been reported by Katritzky and his co-workers. In both cases the starting pyrylium salt used was the 2,4,6-triphenylpyrylium and different products were obtained according to the type of amidrazone employed, *e.g.* N^3-aryl substituted amidrazones react to give the corresponding pyridinium salts which can be converted into carbodiimides;[3] however, unsubstituted amidrazones lead to the bicyclic pyrazolo[1,5-*a*]pyrimidine ring system.[4]

We report here attempts to synthesize bridgehead nitrogen heterocycles such as [1,2,4]triazolo[1,5-*a*]pyridinium (15) and pyrido[2,1-*f*][1,2,4]triazinium (16) by reaction of 2-functionalized pyrylium salts with N^3-aryl substituted (1)—(6) and unsubstituted (7)—(12) amidrazones.

Two different pyrylium salts have been used: 2-methylthio-4,6-diphenylpyrylium tetrafluoroborate (13), available from 4,6-diphenylpyran-2-thione and trimethyloxonium tetrafluoroborate,[5] and 2-ethoxycarbonyl-4,6-diphenylpyrylium tetrafluoroborate, readily available from ethyl pyruvate, benzylideneacetophenone, and boron trifluoride–diethyl ether.[6]



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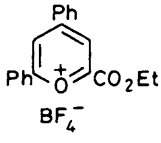
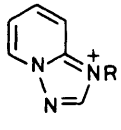
(2) Ar = Ph R = 4-MeC_6H_4
(3) Ar = 4-$O_2NC_6H_4$ R = Ph
(4) Ar = 4-$O_2NC_6H_4$ R = 4-MeC_6H_4
(5) Ar = Ph R = 4-BrC_6H_4
(6) Ar = Ph R = 4-ClC_6H_4
(7) Ar = Ph R = H
(8) Ar = 4-MeC_6H_4 R = H
(9) Ar = 4-$O_2NC_6H_4$ R = H
(10) Ar = 4-$H_3OCC_6H_4$ R = H
(11) Ar = 4-ClC_6H_4 R = H
(12) Ar = 2-Pyridyl R = H

(13)



(14)



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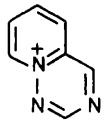

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Results and Discussion

Reaction of the Pyrylium Salt (13) *with* N^3*-Aryl Amidrazones.*—The pyrylium salt (13) reacts with N^3-aryl substituted amidrazones (1)—(5) at reflux temperature in dry acetonitrile giving the corresponding 1,2-diaryl-5,7-diphenyl[1,2,4]-triazolo[1,5-*a*]pyridinium tetrafluoroborates (17)—(21) as crystalline solids in moderate yields (50—66%) (Table 1). The i.r. spectra of these bicyclic salts show an absorption at 1 650 cm^{-1} which can be attributed to the C=N stretching vibration. The n.m.r. spectra do not show signals of pyridinium ring protons, and the mass spectra show the expected ion peak at (M^+ − HBF_4); the base peak occurs at (M^+ − HBF_4 − ArCN).

Compound (13) reacts with the amidrazone (5) at room temperature in dry ethanol in a short period of time to give the monocyclic salt (22) as a crystalline solid in moderate yield (46%). Support for the formula (22) is clearly provided by the i.r. spectrum which shows strong bands at 1 700 cm^{-1} due to the carbonyl group and at 3 280 cm^{-1} corresponding to the NH group, in addition to the absorption at 1 630 cm^{-1} attributable to the C=N stretching vibration. Attempted purification of compound (22) by crystallization in boiling ethanol failed, because under these conditions it easily undergoes cyclization to the bicyclic compound (21).

Reaction of the Pyrylium Salt (14) *with* N^3*-Aryl Substituted Amidrazones.*—Compound (14) reacts with amidrazones (1) (2), (4), (5), and (6) at room temperature in dry acetonitrile for 18 h to give 2,3-diaryl-6,8-diphenyl-4-oxopyrido[2,1-*f*][1,2,4]-triazinium tetrafluoroborates (23)—(27) as yellow crystalline solids in 60—93% yields (Table 2). Similar results were achieved when the reaction was carried out at reflux temperature in methanol for 8 h; however, under these conditions but

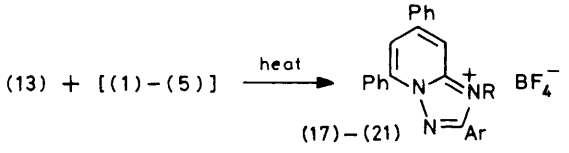
Table 1. [1,2,4]Triazolo[1,5-*a*]pyridinium tetrafluoroborates

Compd.	Crystal form	Yield (%)	M.p. (°C)	Solvent	Found (%) C	H	N	Formula	Required (%) C	H	N
(17)	Prism	66	294—295	EtOH	70.25	4.3	8.0	$C_{30}H_{22}BF_4N_3$	70.49	4.30	8.21
(18)	Needles	62	319—320	EtOH	70.95	4.6	8.0	$C_{31}H_{24}BF_4N_3$	70.93	4.57	8.00
(19)	Needles	50	262—263	EtOH	64.35	3.75	10.35	$C_{30}H_{21}BF_4N_4O_2$	64.74	3.77	10.07
(20)	Prism	60	261—262	EtOH	65.25	4.05	9.85	$C_{31}H_{23}BF_4N_4O_2$	65.35	4.04	9.83
(21)	Prism	64	275—276	EtOH	61.25	3.5	7.0	$C_{30}H_{21}BBrF_4N_3$	61.01	3.55	7.11

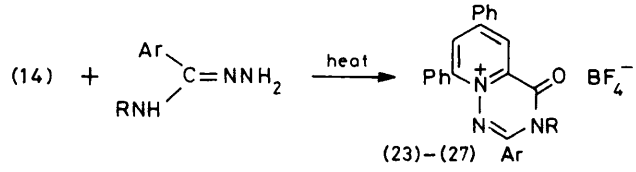
Table 2. 4-Oxopyrido[2,1-*f*][1,2,4]triazinium tetrafluoroborates

Compd.	Crystal form	Yield [a] (%)	M.p. (°C)	Solvent	Found (%) C	H	N	Formula	Required (%) C	H	N
(23)	Prism	93	192—193	EtOH	69.1	4.1	7.75	$C_{31}H_{22}BF_4N_3O$	69.01	4.08	7.79
(24)	Needles	91	194—195	EtOH	69.4	4.5	7.55	$C_{32}H_{24}BF_4N_3O$	69.49	4.34	7.59
(25)	Prism	70	241—242	EtOH	65.45	3.95	9.5	$C_{32}H_{23}BF_4N_4O_3$	65.52	3.92	9.55
(26)	Needles	60	243—245	EtOH	60.05	3.35	6.7	$C_{31}H_{21}BBrF_4N_3O$	60.19	3.39	6.79
(27)	Needles	64	188—190	EtOH	64.95	3.65	7.3	$C_{31}H_{21}BClF_4N_3O$	64.91	3.66	7.32

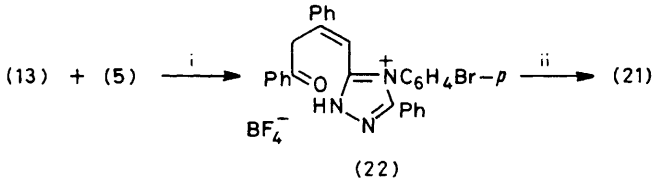
[a] Procedure A.

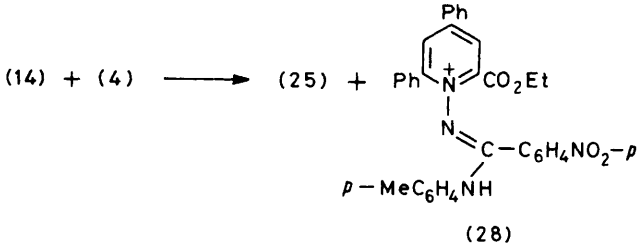


(17) Ar = Ph R = Ph
(18) Ar = Ph R = 4-MeC_6H_4
(19) Ar = 4-$O_2NC_6H_4$ R = Ph
(20) Ar = 4-$O_2NC_6H_4$ R = 4-MeC_6H_4
(21) Ar = Ph R = 4-BrC_6H_4



(23) Ar = Ph R = Ph
(24) Ar = Ph R = 4-MeC_6H_4
(25) Ar = 4-$O_2NC_6H_4$ R = 4-MeC_6H_4
(26) Ar = Ph R = 4-BrC_6H_4
(27) Ar = Ph R = 4-ClC_6H_4





Reagents: i, EtOH, room temp.; ii, EtOH, heat

in the presence of triethylamine, the products were found to be the expected 4-oxopyrido[2,1-*f*][1,2,4]triazinium tetrafluoroborate (24) (83%) and the [1,2,4]tetrazolo[1,5-*a*]pyridinium tetrafluoroborate (18) (6%). This result indicates that intramolecular nucleophilic attack could occur on the 2-position of the intermediate pyridinium derivative (28) followed by de-ethoxycarbonylation.

The i.r. spectra of compounds (23)—(27) show strong absorption in the carbonyl region (1 720—1 730 cm^{-1}) and two bands at 1 600 and 1 620 cm^{-1} respectively attributable to the pyridinium ring. The n.m.r. spectra show two doublets at δ 8.5 and 8.0 (*J* 2 Hz) corresponding to the pyridinium ring protons.

Compound (14) reacts with the amidrazone (4) at room temperature in dry methanol for 5 min to give the oxopyrido-[2,1-*f*][1,2,4]triazinium derivative (25) (21%) and the pyridinium salt (28) (54%). The i.r. spectrum of (28) shows strong bands at 1 750 cm^{-1} due to the ester group and at 3 280 cm^{-1} corresponding to the NH stretching vibration in addition to the characteristic bands of the pyridinium ring (1 600 and 1 620 cm^{-1}). The n.m.r. spectrum shows the typical signals of the CO_2Et group and the two doublets corresponding to the pyridinium ring protons. Pyridinium (28), on heating in methanol, cyclised to give the bicyclic salt (25). Similar compounds have been previously reported.[7,8]

Reaction of the Pyrylium Salt (14) *with Unsubstituted Amidrazones* (7)—(12).—When this reaction was performed at room temperature in methanol in the presence of triethylamine, the cyclised zwitterionic species 2-substituted 4-oxido-6,8-diphenylpyrido[2,1-*f*][1,2,4]triazinium (34)—(39) were obtained as crystalline solids in 61—94% yields (Table 3).

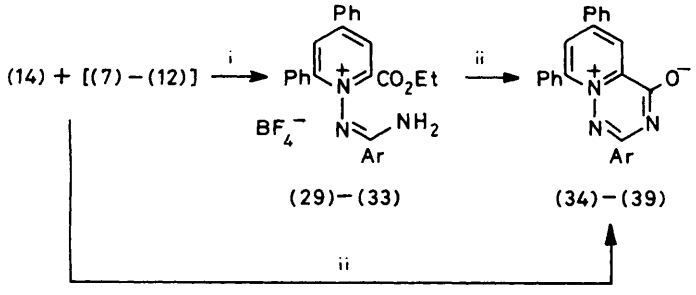
However, when the reaction was carried out without addition of triethylamine, the only products obtained were the 1-[amino(aryl)methylene]amino-2-ethoxycarbonyl-4,6-diphenylpyridinium tetrafluoroborates (29)—(33) in 65—80% yields (Table 4), which, after isolation, underwent cyclization to give the corresponding bicyclic zwitterionic compounds on treatment with triethylamine in methanol at room temperature.

Table 3. 4-Oxidopyrido[2,1-*f*][1,2,4]triazinium zwitterions

Compd.	Crystal form	Yield (%)	M.p. (°C)	Solvent	Found (%) C	H	N	Formula	Required (%) C	H	N
(34)	Needles	65	296—298	EtOH	79.95	4.55	11.15	$C_{25}H_{17}N_3O$	80.0	4.53	11.20
(35)	Needles	69	275—276	EtOH	79.9	4.95	10.7	$C_{26}H_{19}N_3O$	80.20	4.88	10.79
(36)	Needles	94	288—289	EtOH	71.3	3.7	13.05	$C_{25}H_{16}N_4O_3$	71.42	3.80	13.33
(37)	Prism	69	310—312	EtOH	76.9	4.45	10.2	$C_{26}H_{19}N_3O_2$	77.03	4.69	10.37
(38)	Needles	69	258—260	EtOH	73.3	3.8	10.45	$C_{25}H_{16}ClN_3O$	73.26	3.90	10.25
(39)	Needles	61	270—271	EtOH	76.35	4.1	14.7	$C_{24}H_{16}N_4O$	76.59	4.25	14.89

Table 4. 1-[Amino(aryl)methylene]amino-2-ethoxycarbonyl-4,6-diphenylpyridinium tetrafluoroborates

Compd.	Crystal form	Yield (%)	M.p. (°C)	Solvent	Found (%) C	H	N	Formula	Required (%) C	H	N
(29)	Prism	76	274—275	EtOH	63.5	4.9	8.05	$C_{27}H_{24}BF_4N_3O_2$	63.65	4.71	8.25
(30)	Prism	78	278—279	EtOH	64.05	4.85	7.85	$C_{28}H_{26}BF_4N_3O_2$	64.24	4.27	8.03
(31)	Needles	79	183—185	EtOH	62.3	4.85	7.8	$C_{28}H_{26}BF_4N_3O_3$	62.33	4.82	7.79
(32)	Prism	65	243—245	EtOH	59.3	4.5	7.5	$C_{27}H_{23}BClF_4N_3O_2$	59.61	4.23	7.72
(33)	Prism	80	277—278	EtOH	60.95	4.35	11.15	$C_{26}H_{23}BF_4N_4O_2$	61.17	4.50	10.98



(29) Ar = Ph
(30) Ar = 4-MeC_6H_4
(31) Ar = 4-$MeOC_6H_4$
(32) Ar = 4-ClC_6H_4
(33) Ar = 2-Pyridyl

(34) Ar = Ph
(35) Ar = 4-MeC_6H_4
(36) Ar = 4-$O_2NC_6H_4$
(37) Ar = 4-$MeOC_6H_4$
(38) Ar = 4-ClC_6H_4
(39) Ar = 2-Pyridyl

Reagents: i, MeOH, room temp.; ii, MeOH–Et_3N, room temp.

Compound (14) reacts with the amidrazone (9) to give the bicyclic compound (36) even under neutral conditions.

Compounds (29)—(33) show in their i.r. spectra absorptions due to the stretching vibration of the NH group (3 280—3 460 cm^{-1}), to the ester group (1 745—1 750 cm^{-1}) and to the C=N group (1 640—1 670 cm^{-1}) together with the characteristic absorptions for the pyridinium ring (1 620 and 1 600 cm^{-1}) and for the anion BF_4^- (1 060 cm^{-1}). The n.m.r. spectra show two doublets at δ 8.8 and 8.6 (*J* 2 Hz), due to the *meta* coupling of the pyridinium ring protons, together with the quadruplet at δ 4.4 and the triplet at δ 1.28 due to the methylene and methyl group, respectively.

Support for structures (34)—(39) is clearly provided by their i.r. and n.m.r. spectra. The i.r. spectra show an absorption at 1 640—1 660 cm^{-1} due to the vibration of the C=N group and at 1 600 and 1 620 cm^{-1} due to the pyridinium ring, but there are no absorptions due either to the amino and ester groups or to the anion. The n.m.r. spectra show, as the only characteristic signals, two doublets at low field, δ 9.2 and 8.6 (*J* 2 Hz), corresponding to the pyridinium ring protons.

Experimental

All m.p.s were determined with a Kofler hot-stage microscope and are uncorrected. Spectral characterizations were performed with the following instruments: i.r., Perkin-Elmer Infracord 457; ^1H n.m.r. Varian FT-80 ($SiMe_4$ internal reference), all chemical shifts expressed as δ values. Mass Spectra (70 eV) were obtained with a Hewlett-Packard 5 980 A instrument. Combustion analyses were performed with a Perkin-Elmer 240-C instrument.

Reagents.—2-Methylthio-4,6-diphenylpyrylium tetrafluoroborate [5] (13), 2-ethoxycarbonyl-4,6-diphenylpyrylium tetrafluoroborate [6] (14), N^3-aryl substituted amidrazones [3] (1)—(6) and unsubstituted amidrazones [9,10] (7)—(12) were prepared following the methods described in the literature.

General Procedure for the Preparation of [1,2,4]*Triazolo*-[1,5-a]*pyridin*-1-*ium Tetrafluoroborates.*—2-Methylthio-4,6-diphenylpyrylium (13) (0.366 g, 1 mmol) in dry acetonitrile (20 ml) and an equimolar amount of N^3-aryl substituted amidrazone were refluxed for 9 h. The solvent was removed (30 °C/20 mmHg) and the residue crystallised by addition of EtOH (15 ml). The following [1,2,4]triazolo[1,5-*a*]pyridin-1-ium derivatives were obtained (yields, m.p.s, and analyses are given in Table 1): 1,2,5,7-*tetraphenyl*- (17), $\nu_{max.}$ (Nujol) 1 650, 1 570, 1 500, 1 060, 770, 710, and 700 cm^{-1}; δ($CDCl_3$) 8.16—7.01 (22 H, m); *m*/*z* (%) 423 (M^+ − HBF_4, 8), 347 (3), 320 (100), 224 (10), 218 (13), 115 (23), 103 (20), and 77 (33); 2,5,7-*triphenyl*-1-p-*tolyl*- (18), $\nu_{max.}$ (Nujol) 1 650, 1 600, 1 560, 1 510, 1 060, 840, 830, 760, 750, 700, and 690 cm^{-1}; δ($CDCl_3$) 7.3—7.9 (21 H, m) and 2.5 (3 H, s); *m*/*z* (%) 437 (M^+ − HBF_4, 3), 361 (14), 334 (29), 105 (20), 103 (100), 91 (35), and 77 (55); 2-p-*nitrophenyl*-1,5,7-*triphenyl*- (19), $\nu_{max.}$ (Nujol) 1 650, 1 560, 1 530, 1 360, 870, 865, 860, 775, 710, 700, and 690 cm^{-1}; δ[$(CD_3)_2SO$] 7.4—8.5 (21 H, m); *m*/*z* (%) 468 (M^+ − HBF_4, 2) 346 (3), 321 (40), 148 (16), 122 (53), and 77 (100); 2-p-*nitrophenyl*-5,7-*diphenyl*-1-p-*tolyl*- (20), $\nu_{max.}$ (Nujol) 1 650, 1 600, 1 560, 1 520, 1 350, 1 060, 860, 770, and 720 cm^{-1}; δ[$(CD_3)_2SO$] 7.0—8.1 (20 H, m) and 2.2 (3 H, s); *m*/*z* (%) 482 (M^+ − HBF_4, 4), 335 (100), 148 (15), and 103 (24); 1-p-*bromophenyl*-2,5,7-*triphenyl*- (21), $\nu_{max.}$ (Nujol) 1 650, 1 560, 1 510, 1 060, 770, 710, and 700 cm^{-1}; δ[$(CD_3)_2SO$] 7.3—8.2 (21

H, m); *m/z* (%) 503 ($M^+ + 2 - HBF_4$, 3), 501 ($M^+ - HBF_4$, 2), 400 (30), 398 (28), 103 (100), and 77 (46).

4-p-*Bromophenyl*-5-*phenyl*-3-(2,4-*diphenyl*-4-*oxobut*-1-*enyl*)-1,2,4-*triazol*-4-*ium Tetrafluoroborate* (22).—2-Methylthio-4,6-diphenylpyrylium tetrafluoroborate (13) (0.5 g, 0.00136 mol) was dissolved in dry ethanol (15 ml) and N^3-*p*-bromophenylbenzamidrazone (5) (0.37 g, 0.00136 mol) was added. The solution was stirred at 20 °C for 5 min and the precipitated yellow solid was separated as a crude product (46%), m.p. 189 °C; $\nu_{max.}$ (Nujol) 3 280, 1 700, 1 630, 1 600, 1 580, 1 520, 1 500, 1 270, 1 230, 1 160, 1 060, 1 000, 870, 850, 790, 760, 755, and 700 cm^{-1}. This compound (0.3 g, 5.24 mmol) was refluxed in absolute ethanol (5 ml) for 2 h and gave, on cooling, the corresponding [1,2,4]triazolo[1,5-*a*]pyridinium tetrafluoroborate (21) (67%) previously described.

General Procedures for the Preparation of 4-*Oxopyrido*[2,1-f]-[1,2,4]*triazin*-9-*ium Tetrafluoroborates.*—*Procedure A.* 2-Ethoxycarbonyl-4,6-diphenylpyrylium (14) (0.392 g, 0.001 mol) in dry acetonitrile (15 ml) and equimolar amounts of N^3-aryl substituted amidrazones were stirred at room temperature for 18 h. The solvent was removed (30 °C, 20 mmHg) and the resulting product crystallised from ethanol. The following pyrido[2,1-*f*][1,2,4]triazin-9-ium tetrafluoroborates were obtained (yields, m.p.s, and analyses are given in Table 2): 4-*oxo*-2,3,6,8-*tetraphenyl*- (23), $\nu_{max.}$ (Nujol) 1 720, 1 640, 1 550, 1 500, 1 290, 1 060, 900, 770, 740, 720, and 700 cm^{-1}; δ ($CDCl_3$) 6.8—7.8 (20 H, m), 8.0 (1 H, d, *J* 2 Hz), and 8.5 (1 H, d, *J* 2 Hz); 4-*oxo*-2,6,8-*triphenyl*-3-p-*tolyl*- (24), $\nu_{max.}$ (Nujol) 1 720, 1 630, 1 550, 1 280, 1 060, 770, 730, and 700 cm^{-1}; δ ($CDCl_3$) 2.1 (3 H, s), 6.5—8.0 (19 H, m), 8.1 (1 H, d, *J* 2 Hz), and 8.5 (1 H, d, *J* 2 Hz); 2-p-*nitrophenyl*-4-*oxo*-6,8-*diphenyl*-3-p-*tolyl*- (25), $\nu_{max.}$ (Nujol) 1 720, 1 630, 1 600, 1 335, 1 060, 900, 870, 860, 770, 760, 730, and 700 cm^{-1}; δ [$(CD_3)_2SO$] 2.26 (3 H, s), 7.29—8.33 (18 H, m), 9.09 (1 H, d, *J* 2 Hz), and 9.17 (1 H, d, *J* 2 Hz); 3-p-*bromophenyl*-4-*oxo*-2,6,8-*triphenyl*- (26), $\nu_{max.}$ (Nujol) 1 720, 1 635, 1 550, 1 280, 1 060, 770, 730, and 700 cm^{-1}; δ($CDCl_3$) 6.7—7.9 (19 H, m), 8.0 (1 H, d, *J* 2 Hz), and 8.45 (1 H, d, *J* 2 Hz); 3-p-*chlorophenyl*-4-*oxo*-2,6,8-*triphenyl*- (27), $\nu_{max.}$ (Nujol) 1 730, 1 620, 1 610, 1 550, 1 490, 1 280, 1 060, 900, 830, 760, and 700 cm^{-1}; δ($CDCl_3$) 6.6—7.8 (19 H, m), 8.0 (1 H, d, *J* 2 Hz), 8.45 (1 H, d, *J* 2 Hz).

Procedure B. Pyrylium salt (14) (0.392 g), methanol (15 ml), and N^3-aryl substituted amidrazones were refluxed for 3 h. On cooling, the product separated as crystalline solid.

Procedure C. Pyrylium salt (14) (1.18 g, 3 mmol), methanol (30 ml), Et_3N (0.3 ml), and N^3-*p*-tolylbenzamidrazone (2) were refluxed for 8 h. The solvent was removed (30 °C/20 mmHg) and the product extracted with CH_2Cl_2 (20 ml), washed with water (10 ml), dried (Na_2SO_4), and evaporated at 20 °C/20 mmHg. The resulting mixture was crystallised from EtOH giving (24) (82%); (18) (6%) was separated from the mother-liquor.

2-*Ethoxycarbonyl*-4,6-*diphenyl*-1-[p-*nitrophenyl*-(p-*tolylamino*)*methylene*]*aminopyridinium Tetrafluoroborate* (28).—2-Ethoxycarbonyl-4,6-diphenylpyrylium tetrafluoroborate (14) (0.326 g, 0.8 mmol) in methanol (20 ml) and N^3-*p*-tolyl-*p*-nitrobenzamidrazone (4) (0.225 g, 0.8 mmol) were stirred at room temperature for 5 min. The precipitated yellow solid (28) (57%) was separated m.p. 218—222 °C (decomposes); $\nu_{max.}$ (Nujol) 3 280, 1 750, 1 620, 1 600, 1 580, 1 520, 1 350, 1 259, 1 200, 1 080, 1 000, 870, 860, 810, 770, 730, and 710 cm^{-1}; δ[$(CD_3)_2SO$] 9.9 (1 H, s), 8.7 (1 H, d), 8.29 (1 H, d), 6.9—8.1 (18 H, m), 4.23 (2 H, q), 2.25 (3 H, s), and 1.21 (3 H, t). Compound (25) (21%) was crystallised from the mother-liquor; it was also obtained by heating compound (28) in ethanol for 4 min.

General Procedure for the Formation of 4-*Oxidopyrido*[2,1-f][1,2,4]*triazin*-9-*ium Zwitterions.*—2-Ethoxycarbonyl-4,6-diphenylpyrylium tetrafluoroborate (14) (0.5 g, 1.27 mmol) was suspended in methanol (5 ml) and equimolar amounts of the benzamidrazone and triethylamine were added. The solution was stirred at 20 °C for 12 h. The precipitated yellow solid was filtered off and recrystallised. The following pyrido[2,1-*f*]-[1,2,4]triazin-9-ium zwitterions were obtained (m.p.s, yields, and analyses are given in Table 3): 4-*oxido*-2,6,8-*triphenyl*- (34), $\nu_{max.}$ (Nujol) 1 640, 1 615, 1 475, 1 440, 1 430, 1 300, 960, 890, 780, and 760 cm^{-1}; δ[$(CD_3)_2SO$] 9.5 (1 H, d, *J* 2 Hz), 8.58 (1 H, d, *J* 2 Hz), and 7.3—8.1 (15 H, m); 4-*oxido*-6,8-*diphenyl*-2-p-*tolyl*- (35), $\nu_{max.}$ (Nujol) 1 650, 1 620, 1 480, 1 440, 1 410, 970, 900, 840, 800, 770, 760, 745, 730, and 710 cm^{-1}; δ[$(CD_3)_2SO$] 9.5 (1 H, d, *J* 2 Hz), 8.6 (1 H, d, *J* 2 Hz), 7.3—8.2 (14 H, m), and 2.33 (3 H, s); 2-p-*nitrophenyl*-4-*oxido*-6,8-*diphenyl*- (36), $\nu_{max.}$ (Nujol) 1 640, 1 620, 1 530, 1 440, 1 410, 1 380, 1 350, 875, 860, 800, 780, 770, and 720 cm^{-1}; δ [$(CD_3)_2SO$] 9.3 (1 H, d, *J* 2 Hz), 8.56 (1 H, d, *J* 2 Hz), 7.4—8.2 (14 H, m); 2-p-*methoxyphenyl*-4-*oxido*-6,8-*diphenyl*- (37), $\nu_{max.}$ (Nujol) 1 640, 1 620, 1 600, 1 450, 1 410, 1 400, 1 160, 900, 850, 800, 765, 750, 725, and 700 cm^{-1}; δ[$(CD_3)_2SO$] 9.3 (1 H, d, *J* 2 Hz), 8.6 (1 H, d, *J* 2 Hz), 7.38—8.1 (14 H, m), and 3.71 (3 H, s); 2-p-*chlorophenyl*-4-*oxido*-6,8-*diphenyl*- (38), $\nu_{max.}$ (Nujol) 1 640, 1 610, 1 590, 1 570, 1 470, 1 440, 1 400, 1 385, 1 080, 1 010, 960, 895, 840, 790, 760, and 740 cm^{-1}; δ[$(CD_3)_2SO$] 9.2 (1 H, d, *J* 2 Hz), 8.6 (1 H, d, *J* 2 Hz), and 7.4—8.1 (14 H, m); 4-*oxido*-6,8-*diphenyl*-2-*pyridyl*- (39), $\nu_{max.}$ (Nujol) 1 645, 1 620, 1 490, 1 440, 1 410, 1 400, 970, 910, 800, 780, 750, 730, 720, and 700 cm^{-1}; [$(CD_3)_2SO$] 9.35 (1 H, d, *J* 2 Hz), 8.6 (1 H, d, *J* 2 Hz), and 7.6—8.4 (14 H, m).

General Procedure for the Preparation of 1-[*Amino*(*aryl*)-*methylene*]*amino*-2-*ethoxycarbonyl*-4,6-*diphenylpyridinium Tetrafluoroborates.*—2-Ethoxycarbonyl-4,6-diphenylpyrylium tetrafluoroborate (14) (0.5 g) was suspended in methanol (5 ml) and an equimolar amount of the benzamidrazone was added gradually. The solution was stirred at 20 °C for 12 h and the precipitated yellow solid was filtered off and recrystallised. The following 2-ethoxycarbonyl-4,6-diphenylpyridinium tetrafluoroborates were obtained (m.p.s, yields, and analyses are given in Table 4): 1-[*amino*(*phenyl*)*methylene*]*amino*- (29), $\nu_{max.}$ (Nujol) 3 460, 3 370, 3 280, 1 745, 1 660, 1 620, 1 600, 1 560, 1 430, 1 280, 1 250, 1 210, 1 060, 770, 740, and 700 cm^{-1}; δ[$(CD_3)_2SO$] 8.82 (1 H, d), 8.58 (1 H, d), 7.45—8.20 (15 H, m), 4.41 (2 H, q), 3.81 (2 H, s), and 1.29 (3 H, t); 1-[*amino*(p-*tolyl*)*methylene*]*amino*- (30), $\nu_{max.}$ (Nujol) 3 460, 3 370, 3 280, 1 750, 1 660, 1 620, 1 600, 1 550, 1 430, 1 060, 910, 870, 830, 760, and 700 cm^{-1}; δ[$(CD_3)_2SO$] 8.81 (1 H, d, *J* 2 Hz), 8.60 (1 H, d, *J* 2 Hz), 8.20—7.27 (14 H, m), 4.35 (2 H, q), 3.90 (2 H, s), 2.33 (3 H, s), and 1.20 (3 H, t); 1-[*amino*-(p-*methoxyphenyl*)*methylene*]*amino*- (31), $\nu_{max.}$ (Nujol) 3 460, 3 370, 3 280, 1 750, 1 660, 1 630, 1 620, 1 430, 1 270, 1 250, 1 215, 1 190, 1 060, 910, 850, 780, 770, 740, and 710 cm^{-1}; δ[$(CD_3)_2SO$] 8.7 (1 H, d, *J* 2 Hz), 8.6 (1 H, d, *J* 2 Hz), 7.05—8.2 (14 H, m), 4.41 (2 H, q), 3.91 (2 H, s), 3.71 (3 H, s), and 1.29 (3 H, t); 1-[*amino*(p-*chlorophenyl*)*methylene*]*amino*- (32), $\nu_{max.}$ (Nujol), 3 280, 3 370, 3 460, 1 750, 1 660, 1 620, 1 600, 1 555, 1 430, 1 060, 910, 870, 755, and 700 cm^{-1}; δ [$(CD_3)_2SO$] 8.80 (1 H, d, *J* 2 Hz), 8.60 (1 H, d, *J* 2 Hz), 7.6—8.2 (14 H, m), 4.41 (2 H, q), 3.8 (2 H, s), and 1.28 (3 H, s); 1-[*amino*(2-*pyridyl*)*methylene*]-*amino*- (33) $\nu_{max.}$ (Nujol) 3 320, 1 740, 1 640, 1 630, 1 600, 1 500, 1 060, 770, 740, and 710 cm^{-1}; δ[$(CD_3)_2SO$] 8.81 (1 H, d, *J* 2 Hz), 8.6 (1 H, d, *J* 2 Hz), 7.6—8.3 (14 H, m), 4.40 (2 H, q), 3.90 (2 H, s), and 1.28 (3 H, s).

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