Reactions of Pyryliums with Mono- and asym-Di-substituted Hydrazines

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Literature data on the title reactions are reviewed and further examples given particularly with dialkylhydrazines and hydrazones. Compounds derived from 2-ethoxycarbonyl-4,6-diphenylpyrylium tend to cyclise and new examples of the dihydropyrazoloquinoline (27) and oxidopyrido[1,2-*b*]pyridazinium [(62)—(64)] ring systems are described.

RECENT work from this laboratory has emphasised the synthetic utility of the general sequence (1) ⟶ (5) to transform the primary aliphatic and aromatic amino-functions (2) into others by reaction with cyclic oxoniums (pyryliums) (1), *via* the cyclic azonium (3).[1] We are now investigating the potential utilisation of cyclic azoniums (3) in which the R-group is linked by a nitrogen atom; the present paper records investigation of the preparation of such compounds by the reaction of pyryliums with mono- and di-substituted hydrazines.

There is considerable, scattered literature work on this topic, but it has only been reviewed in part.[2] We review previous work, and our new results, on reactions of pyryliums with five classes of hydrazines in turn: (i) monoalkyl (aryl) hydrazines (6), (ii) dialkyl (aryl) hydrazines (7), (iii) acyl and thioacyl hydrazides (8), (iv) other hydrazines monosubstituted with an electron-withdrawing group (9), and (v) hydrazones (10).

Monoalkyl (or Aryl) Hydrazines.—Much work has been done,[3] and the reactions are often complex. The triphenylpyrylium perchlorate (11) with PhN_2H_3 gives (13); this is converted by refluxing in acetic acid into the pyridinium (15). In refluxing ethanol (13) gives (20), the latter loses $PhCOCH_3$ with acid to form the pyrazole (22).[4] Snieckus[5] found that the reaction of MeN_2H_3 with pyryliums gave products of types (21), (23), and (16) together with diazepines, depending on the pyrylium substituents, anion, solvent, and reaction time.

We found that the ethoxycarbonylpyrylium (24) and phenylhydrazine in cold ethanol gave solely the hydrazone (25) which showed the CH_2 singlet at δ 4.06 in addition to the Et peaks: on heating in ethanol it cyclised to the pyrazoline (26a). In refluxing acetic acid containing BF_3–diethyl ether, (25) cyclised to the dihydropyrazoloquinoline (27), a ring system previously reported by Elguero *et al.*[6] The structure (27) was supported by analysis and by ν(C=O) at 1 695 cm^{-1}. The ^1H n.m.r. showed the aromatic and ethyl protons signals and additionally a CH_2 singlet at δ 3.55 and a :CH. singlet at 6.29. ^{13}C N.m.r. data are in agreement with this structure. The conversion (25)→(27) probably involves (26a) as an intermediate. Reaction of (24) with *p*-nitrophenylhydrazine gave only the pyrazoline (26b).

Dialkyl (or Aryl) Hydrazines.—Reactions with pyryliums proceed smoothly. Schneider reported the conversion of 2-methyl-4,6-diphenylpyrylium iodide into the salts (28) and (29),[7] and Schmidt and Berger the preparation of (17).[8]

Reaction of 1,1-dimethylhydrazine with triphenylpyrylium (12) in dichloromethane gives the pyrazolinium cation (30) identified by ^1H and ^{13}C n.m.r. spectroscopy. Particularly significant in the ^1H n.m.r. spectra, there were two AB quartets for the methylene groups and two singlets for the *N*-methyls [Balaban and Silhan similarly found two AB-quartets for the methylene group of (20)]. However, in cold methanol, this reaction gave the hydrazone (14): this on treatment with pyridine and perchloric acid gave initially the pyrazolium (31) which at 100 °C was converted into the dimethylaminopyridinium perchlorate (17), m.p. 209 °C, previously reported[8] with m.p. 177 °C. Later, we found that in refluxing methanol the desired tetrafluoroborate (18) could be formed directly in 82% yield. Compound (19) was similarly prepared from 1-aminopiperidine. The more reactive pyrylium (24) gave (32) directly in cold ethanol, whereas from the less reactive oxadiazolium (33)[10] it was necessary to isolate intermediate (35) and cyclise to (34) in refluxing $HClO_4$–HOAc (*cf.* ref. 11).

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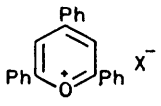
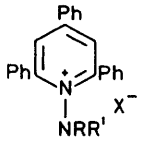
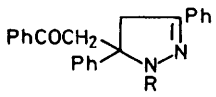


(11) X = ClO_4
(12) X BF_4

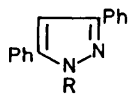
PhCO·CH:CPhCH$_2$CPh:NR
(13) R = NHPh
(14) R = NMe_2



(15) R = Ph, R′ = H, X = ClO_4
(16) R = Me, R′ = H
(17) R = R′ = Me, X = ClO_4
(18) R = R′ = Me X = BF_4
(19) R,R′ = $(CH_2)_5$, X = BF_4

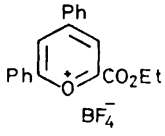


(20) R = Ph
(21) R = Me



(22) R = Ph
(23) R = Me

Various attempts were made to transfer the dimethylamino-group of (18) to nucleophilic centres (pyridine, triphenylphosphine, and malonate anions). Starting material was recovered, or under forcing conditions tri-



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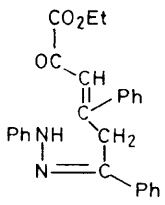

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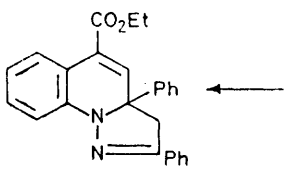
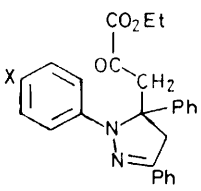


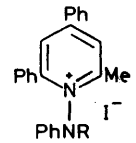
(27)



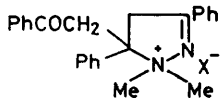
(26) a; X = H
b; X = NO_2

phenylpyridine was isolated with indications that elimination to give the imine MeN=CH_2 had occurred (*cf.* ref. 12).

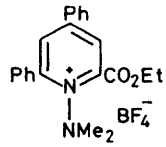
Acylhydrazides.—We recently reported the smooth reaction of various acylhydrazines RCONHNH_2 with 2,4,6-triphenylpyrylium to give compounds of type (36):[13] the corresponding sulphur derivatives were stable only as salts. Neidlein and Witerzens converted 2,4,6-trimethylpyrylium into salts analogous to (38), (39), (41), and (42);[14] the salt corresponding to (40) had



(28) R = Me
(29) R = Ph



(30) X = BF_4
(31) X = $C10_4$



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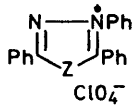
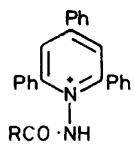


(33) Z = O
(34) Z = $NNMe_2$

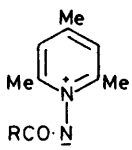
PhCO·NH·NPh·CPh:N·NMe_2
(35)

been reported earlier,[15] as had the analogue from 2,6-dimethyl-4-ethylpyrylium.[15] However, semicarbazide with triphenylpyrylium was reported to give only the bis-semicarbazone (44).[16]

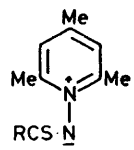
Under the previous conditions with benzohydrazide,[13] the triphenylpyrylium tetrafluoroborate (12) gave the



(36) R = alkyl or aryl
(37) R = NH_2

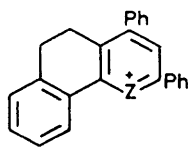


(38) R = alkyl or aryl
(39) R = PhNH
(40) R = NH_2

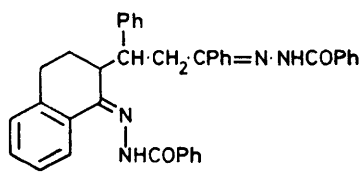


(41) R = NH_2
(42) R = PhNH
(43) R = aryl

$NH_2CO·NH·N=CPh·CH=CPh·CH_2·CPh=N·NH·CONH_2$
(44)



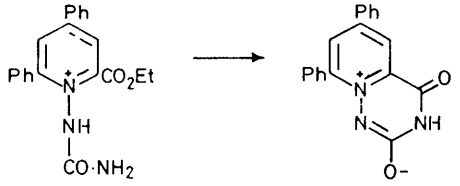
(45) Z = O
(46) Z = NNCOPh



(47)

expected salt (36; R = Ph), but the tricyclic pyrylium (45) formed a mixture of the imide (46) and the bis-hydrazone (47).

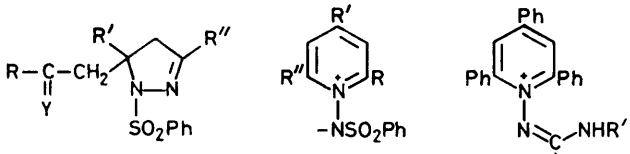
In our hands semicarbazide reacted smoothly with (12) and (24) to form the ureido-derivatives (37) and (48), respectively. The ethoxycarbonylurea (48) cyclised on



(48) (49)

treatment with potassium carbonate in dimethoxyethane to give the zwitterionic (49): a similar compound has been previously reported.[17]

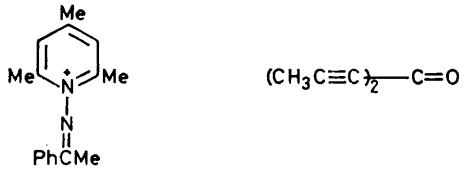
Other Monosubstituted Hydrazines with Electron-withdrawing Groups.—Lempert treated benzenesulphonohydrazide both with triphenyl- and other substituted pyryliums and obtained pyrazoliums of type (50) or (51); in some cases these could be converted into the corresponding imines (52).[18] Amidrazones react smoothly with triphenylpyrylium to give (53).[19]



(50) Y = O
(51) Y = NNHSO$_2$Ph (52) (53)

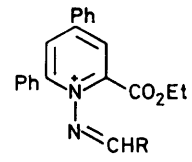
Hydrazones.—Acetophenone hydrazone with trimethylpyrylium yields the cation (54).[14] Analogous 4-pyridones have been prepared by ring closure of the bis-acetylene (55),[20] and from 1-aminopyridiniums.[21]

The triphenylpyrylium (12) did not give the expected product with benzaldehyde hydrazone. The more reactive 2-ethoxycarbonylpyrylium (24) gave *N*-alkylideneaminopyridiniums (56) and (57) with aldehyde hydr-

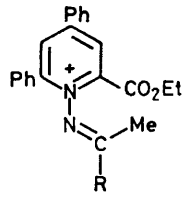


(54) (55)

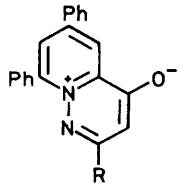
azones, and (58)—(61) with ketone hydrazones. Treatment of the ketone derivatives with K_2CO_3 in THF at 20 °C gave the cyclised oxidopyrido[1,2-*b*]pyridaziniums (62)—(64): reduced [22] and fully aromatic [23] derivatives of this ring system have previously been reported.



(56) R = Ph
(57) R = *p*-MeC$_6$H$_4$



(58) R = Ph
(59) R = *p*-BrC$_6$H$_4$
(60) R = *p*-MeC$_6$H$_4$
(61) R = 4-pyridyl



(62) R = Ph
(63) R = *p*-BrC$_6$H$_4$
(64) R = *p*-MeC$_6$H$_4$

EXPERIMENTAL

I.r. spectra were measured for samples in $CHBr_3$ solution, and n.m.r. spectra (60 and 100 MHz) for solutions in $CDCl_3$ or $(CD_3)_2SO$ ($SiMe_4$ as internal reference). When substances are stated to be identical, this refers to comparison by m.p., mixed m.p., and i.r. spectra.

The following were prepared by the literature methods indicated: 2,4,6-Triphenylpyrylium tetrafluoroborate (12), m.p. 252 °C (lit.,[24] m.p. 253—255 °C); 2-ethoxycarbonyl-4,6-diphenylpyrylium tetrafluoroborate (24), m.p. 168—170 °C (lit.,[25] m.p. 153 °C); 2,3,5-triphenyloxadiazolium perchlorate (33), m.p. 272 °C (lit.,[10] m.p. 272 °C decomp.); 2,4-diphenylbenzo[*h*]chromenylium tetrafluoroborate (45), m.p. 265 °C (lit.,[26] m.p. 270 °C); 1-benzamido-2,4,6-triphenylpyridinium (36), m.p. 218—220 °C (lit.,[13b] m.p. 204 °C).

5-Ethoxycarbonyl-1,3-diphenylpent-3-ene-1,5-dione 1-Phenylhydrazone (25).—2-Ethoxycarbonyl-4,6-diphenylpyrylium tetrafluoroborate (2 g, 5 mmol), MeOH (20 ml), and phenylhydrazine (2.16 g, 10 mmol) were stirred at 20 °C for 30 min. The *hydrazone* separated (1.5 g, 73% yield), m.p. 131 °C (prisms from MeOH) (Found: C, 75.5; H, 5.9; N, 6.7. $C_{26}H_{24}N_2O_3$ requires C, 75.7; H, 5.8; N, 6.8%); $\nu_{max.}$ ($CHBr_3$) 3 280, 1 705, 1 670, 1 600, 1 560, 1 510, 1 500, 1 490, 1 450, 1 370, 1 290, 1 230, 760, and 750 cm^{-1}; δ ($CDCl_3$) 8.85 (1 H, s), 7.4 (15 H, m), 6.5 (1 H, s), 4.22 (2 H, q), 4.06 (2 H, s), and 1.3 (3 H, t).

5-(2-Ethoxycarbonyl-2-oxoethyl)-1,3,5-triphenyl-2-pyrazoline (26a).—5-Ethoxycarbonyl-1,3-diphenylpent-3-ene-1,5-dione 1-phenylhydrazone (0.28 g, 0.68 mmol) was refluxed in EtOH (8 ml) for 1 h. On cooling the *pyrazoline* (0.25 g, 89%) separated as prisms, m.p. 118—119 °C from EtOH (Found: C, 75.6; H, 5.9; N, 6.7. $C_{26}H_{24}N_2O_3$ requires C, 75.7; H, 5.8; N, 6.8%); $\nu_{max.}$ ($CHBr_3$) 1 690, 1 600, 1 560, 1 500, 1 450, 1 355, 1 300, 1 250, and 750 cm^{-1}; δ ($CDCl_3$) 7.3 (15 H, m), 4.28 (2 H, q), 3.90 (2 H, dd, *J* 18 Hz), 3.68 (2 H, dd, *J* 18 Hz), and 1.35 (3 H, t).

5-Ethoxycarbonyl-3,3a-dihydro-2,3a-diphenylpyrazolo-

[1,5-a]*quinoline* (27).—5-Ethoxycarbonyl-1,3-diphenylpent-3-ene-1,5-dione 1-phenylhydrazone (0.42 g, 0.001 mol), glacial HOAc (5 ml), and BF_3·Et_2O (45%, 0.5 ml) were refluxed for 15 min, and the solvent removed at 20 °C/20 mmHg. The red crude *product* was recrystallised from 95% EtOH (0.20 g, 51% yield), m.p. 155 °C (yellow prisms from 95% EtOH) (Found: C, 79.1; H, 5.6; N, 6.9. $C_{26}H_{22}N_2O_2$ requires C, 79.2; H, 5.6; N, 7.1%); $\nu_{max.}$ ($CHBr_3$) 1 695, 1 600, 1 590, 1 480, 1 315, 1 250, 1 090, 770, and 750 cm^{-1}; δ ($CDCl_3$) 7.4 (14 H, m), 6.29 (1 H, s), 4.3 (2 H, q), 3.55 (2 H, s), and 1.35 (3 H, t); ^{13}C n.m.r., δ ($CDCl_3$) 14 (q, Me), 48 (t, C-3), 61 (t, OCH_2), 68 (s, C-3a), 116 (s, C-5), 121 (d, C-4), 131 (m, aromatics), 145 (s, C-2), and 162 (s, C=O).

5-(2-*Ethoxycarbonyl*-2-*oxoethyl*)-1-p-*nitrophenyl*-3,5-*diphenyl*-2-*pyrazoline* (26b).—2-Ethoxycarbonyl-4,6-diphenylpyrylium tetrafluoroborate (1 g, 2.55 mmol) and *p*-nitrophenylhydrazine (0.382 g, 2.55 mmol) in EtOH (50 ml), were stirred at 20 °C for 2 h. The *pyrazoline* (0.7 g, 59%) separated and formed prisms, m.p. 150—152 °C from MeOH (Found: C, 68.4; H, 4.9; N, 9.1. $C_{26}H_{23}N_3O_5$ requires C, 68.3; H, 5.0; N, 9.2%); $\nu_{max.}$ ($CHBr_3$) 1 700, 1 600, 1 580, 1 500, 1 450, 1 335, 1 305, 1 250, 840, 760, and 750 cm^{-1}; δ ($CDCl_3$) 7.4 (14 H, m), 4.3 (2 H, q), 4.06 (2 H, dd, *J* 18 Hz), 3.68 (2 H, dd, *J* 18 Hz), and 1.36 (3 H, t).

1,1-*Dimethyl*-5-*phenacyl*-3,5-*diphenyl*-2-*pyrazolinium Tetrafluoroborate* (30).—2,4,6-Triphenylpyrylium tetrafluoroborate (1 g, 2.5 mmol), dimethylhydrazine (0.18 ml, 0.0025 mol), and CH_2Cl_2 (10 ml) were stirred for 15 min, then HOAc (0.1 ml) was added. After 1 h the *pyrazolinium salt* started to separate (0.7 g, 61%), m.p. 154—155 °C (prisms from EtOH–Me_2CO) (Found: C, 65.7; H, 5.4; N, 6.1. $C_{25}H_{25}BF_4N_2O$ requires C, 65.8; H, 5.5; N, 6.1%); $\nu_{max.}$ ($CHBr_3$) 3 060, 2 940, 1 680, 1 610, 1 600, 1 570, 1 500, 1 450, 1 360, 1 310, 1 230, 1 080, 760, and 740 cm^{-1}; δ [$(CD_3)_2$SO; 60 MHz] 8.2—7.7 (15 H, m), 5.1 (2 H, q, *J* 18 Hz), 4.2 (2 H, q, *J* 18 Hz), 3.75 (3 H, s), and 2.9 (3 H, s); ^{13}C n.m.r., δ [$(CD_3)_2$SO] 175 (s, C-3), 52—43 (m, C-4, N*Me*,N*Me'*, and 5-CH_2), 194 (s, C=O), and 136—117 (aromatics).

1,3,5-*Triphenylpent*-3-*ene*-1,5-*dione* 1-NN-*Dimethylhydrazone* (14).—To 2,4,6-triphenylpyrylium tetrafluoroborate (10 g, 25 mmol) and MeOH (100 ml), was added at 20 °C dimethylhydrazine (3.6 ml, 50 mmol). After 1 min the *hydrazone* crystallised (6.7 g, 73%), m.p. 107—109 °C (prisms from absolute EtOH) (Found: C, 81.3; H, 6.6; N, 7.4. $C_{25}H_{24}N_2O$ requires C, 81.5; H, 6.5; N, 7.6%); $\nu_{max.}$ ($CHBr_3$) 3 060, 2 960, 2 890, 2 860, 2 820, 2 780, 1 690, 1 620, 1 600, 1 580, 1 500, 1 490, 1 430, 1 330, 1 310, 1 070, 1 020, 1 000, 980, and 700 cm^{-1}; δ ($CDCl_3$, 60 MHz) 7.45 (15 H, m), 6.8 (1 H, s), 4.05 (2 H, s), and 2.7 (6 H, s).

1,1-*Dimethyl*-5-*phenacyl*-3,5-*diphenylpyrazolinium Perchlorate* (31).—1,3,5-Triphenylpent-3-ene-1,5-dione 1-*NN*-dimethylhydrazone (1 g, 2.7 mmol), pyridine (5 ml), and $HClO_4$ (0.2 ml) were kept at 20 °C for 1 min. Pyridine was removed at 20 mmHg/100 °C and EtOH–Et_2O (10 ml) were added to give the *pyrazolinium salt* (0.5 g, 40%) m.p. 135 °C (prisms from absolute EtOH) (Found: C, 64.3; H, 5.5; N, 5.9. $C_{25}H_{25}ClN_2O_5$ requires C, 64.0; H, 5.4; N, 6.0%); $\nu_{max.}$ ($CHBr_3$) 3 060, 3 040, 2 980, 2 960, 2 940, 1 685, 1 605, 1 595, 1 580, 1 570, 1 500, 1 450, 1 360, 1 310, 1 230, 1 110, 1 000, 760, and 745 cm^{-1}; δ [$(CD_3)_2$SO, 60 MHz] 8.2—7.7 (15 H, m), 5.0 (2 H, q, *J* 18 Hz), 4.15 (2 H, q, *J* 18 Hz), 3.7 (3 H, s), and 2.9 (3 H, s).

1-*Dimethylamino*-2,4,6-*triphenylpyridinium Perchlorate* (17).—Hydrazone (14) (3 g, 8.1 mmol), pyridine (15 ml), and 78% aqueous $HClO_4$ (0.7 ml) were heated at 100 °C for 3 h. Pyridine was removed at 20 mmHg/100 °C and the residue was crystallised from EtOH to give the pyridinium (1 g, 27%), m.p. 209 °C (prisms from EtOH) (lit.,[8] m.p. 177 °C) (Found: C, 66.4; H, 5.1; N, 5.9. Calc. for $C_{25}H_{23}ClN_2O_4$: C, 66.6; H, 5.1; N, 6.2%); $\nu_{max.}$ ($CHBr_3$) 3 060, 2 960, 1 620, 1 600, 1 500, 1 495, 1 445, 1 415, 1 250, 1 090, 890, and 760 cm^{-1}; δ ($CDCl_3$, 60 MHz) 7.55 (17 H, m) and 2.5 (6 H, s).

1-*Dimethylamino*-2,4,6-*triphenylpyridinium Tetrafluoroborate* (18).—2,4,6-Triphenylpyrylium tetrafluoroborate (10 g, 0.025 mol), dimethylhydrazine (3.6 ml, 0.05 mol), and MeOH (100 ml) were kept at 20 °C for 30 min and then refluxed for 5 h. Solvent was removed at 20 mmHg/100 °C when Et_2O (20 ml) was added; the *pyridininum salt* separated (9 g, 82%), m.p. 199 °C (prisms from absolute EtOH) (Found: C, 68.3; H, 5.2; N, 6.3. $C_{25}H_{23}BF_4N_2$ requires C, 68.5; H, 5.3; N, 6.4%); $\nu_{max.}$ ($CHBr_3$) 3 050, 2 920, 1 610, 1 590, 1 500, 1 490, 1 440, 1 410, 1 355, 1 280, 1 235, 1 050, 925, 895, and 755 cm^{-1}; δ ($CDCl_3$, 60 MHz) 7.4 (17 H, m) and 2.45 (6 H, s).

1-*Piperidino*-2,4,6-*triphenylpyridinium Tetrafluoroborate* (19).—2,4,6-Triphenylpyrylium tetrafluoroborate (5 g, 0.013 mol), 1-aminopiperidine, and MeOH (50 ml) were stirred at 20 °C for 30 min, and then refluxed for 15 h. Solvent was removed at 20 mmHg/100 °C and Et_2O (10 ml) added to give the *pyridinium* (3 g, 48%), m.p. 225—227 °C (prisms from absolute EtOH) (Found: C, 70.3; H, 5.9; N, 5.8. $C_{28}H_{27}BF_4N_2$ requires C, 70.3; H, 5.7; N, 5.8%); $\nu_{max.}$ ($CHBr_3$) 3 060, 2 940, 2 850, 1 615, 1 595, 1 555, 1 490, 1 440, 1 410, 1 275, 1 235, 1 050, 910, 880, and 755 cm^{-1}; δ ($CDCl_3$, 60 MHz) 8.2—7.6 (17 H, m), 2.95 (4 H, m), and 1.0 (6 H, m).

1-*Dimethylamino*-2-*ethoxycarbonyl*-4,6-*diphenylpyridinium Tetrafluoroborate* (32).—2-Ethoxycarbonyl-4,6-diphenylpyrylium tetrafluoroborate (0.78 g, 2 mmol) was suspended in absolute EtOH (8 ml) and *NN*-dimethylhydrazine (0.12 g, 2 mmol) was added dropwise. The solution was stirred at 20 °C for 12 h, when the *pyridinium* separated (0.50 g, 58% yield), m.p. 202—203 °C (prisms from EtOH) (Found: C, 60.7; H, 5.3; N, 6.4. $C_{22}H_{23}BF_4N_2O_2$ requires C, 60.8; H, 5.3; N, 6.4%); $\nu_{max.}$ ($CHBr_3$) 1 740, 1 620, 1 600, 1 380, 1 300, 1 255, 1 210, 1 060, 780, and 755 cm^{-1}; δ ($CDCl_3$) 7.65 (12 H, m), 4.5 (2 H, q), 2.88 (6 H, s), and 1.4 (3 H, t).

2-*Benzoyl*-4,4-*dimethyl*-1-*phenylbenzohydrazide Hydrazone* (35).—2,3,5-Triphenyl-1,3,4-oxadiazolium perchlorate (7.1 g, 18 mmol), dimethylhydrazine (2.73 ml, 36 mmol), and MeOH (76 ml) were stirred at 20 °C for 24 h. The *hydrazone* crystallised (4 g, 62%), m.p. 165 °C (prisms from EtOH) (Found: C, 73.5; H, 6.1; N, 15.6. $C_{22}H_{22}N_4O$ requires C, 73.7; H, 6.2; N, 15.6%); $\nu_{max.}$ ($CHBr_3$) 3 060, 2 980, 2 900, 2 860, 2 820, 2 780, 1 690, 1 600, 1 580, 1 550, 1 490, 1 465, 1 340, 1 290, 1 270, 1 225, 1 070, 1 025, 960, 940, 800, 775, and 750 cm^{-1}; δ ($CDCl_3$, 60 MHz) 8 (3 H, m), 7.2 (13 H, m), and 2.65 (6 H, s).

4-*Dimethylamino*-1,3,5-*triphenyl*-s-*triazolium Perchlorate* (34).—2-Benzoyl-4,4-dimethyl-1-phenylbenzohydrazide hydrazone (35) (3.2 g, 9 mmol), HOAc (11 ml), and $HClO_4$ (1 ml) were refluxed for 30 min. On cooling, the *triazolium salt* crystallised (1.9 g, 48%), m.p. 302—303 °C (needles from Me_2CO) (Found: C, 59.8; H, 4.5; N, 12.6. $C_{22}H_{21}ClN_4O_4$ requires C, 59.9; H, 4.8; N, 12.7%); $\nu_{max.}$ ($CHBr_3$) 3 060, 2 960, 2 800, 1 600, 1 550, 1 500, 1 480, 1 450, 1 375, 1 300, 1 090, 1 025, 790, 765, and 740 cm^{-1}; δ [$CDCl_3$–$(CD_3)_2$SO, 60 MHz] 8.1—7.4 (15 H, m) and 2.9 (6 H, s).

5,6-*Dihydro*-2,4-*diphenylbenzo*[h]*quinoline* 1-*Benzoylimide* (46).—2,4-Diphenylbenzo[*h*]chromenylium tetrafluoroborate (10 g, 23 mmol), benzohydrazide (6.39 g, 0.047 mol),

and EtOH (160 ml) were refluxed for 26 h. The cold reaction mixture was filtered and the solvent removed at 20 mmHg/100 °C. Addition of Et_2O (50 ml) gave a crude product (6.3 g). This (2.3 g) was treated with KOH (0.26 g) in MeOH (10 ml) at 20 °C for 20 min. The solution was filtered and solvent removed at 20 mmHg/100 °C. The residue was partially soluble in hot toluene from which the *benzoylimine* (200 mg, 5%) crystallised as prisms (m.p. 198—200 °C) (Found: C, 84.8; H, 6.1; N, 5.3. $C_{32}H_{24}N_2O$ requires C, 84.9; H, 6.2; N, 5.3%); $\nu_{max.}$ ($CHBr_3$) 3 050, 2 940, 1 610, 1 590, 1 550, 1 490, 1 440, 1 410, 1 335, 1 295, 1 200, 1 025, 900, 785, 765, and 700 cm^{-1}; δ ($CDCl_3$, 60 MHz) 7.9—7.1 (20 H, m) and 2.9 (4 H, s).

The residue insoluble in toluene crystallised from absolute EtOH to yield the *bishydrazone* (47) (2 g, 40%), m.p. 244—246 °C as prisms (Found: C, 79.3; H, 5.4; N, 9.5. $C_{39}H_{31}N_4O_2$ requires C, 79.7; H, 5.3; N, 9.6%); $\nu_{max.}$ ($CHBr_3$) 3 220, 3 060, 2 980, 2 820, 1 675, 1 670, 1 575, 1 520, 1 480, 1 445, 1 410, 1 350, 1 340, 1 270, 1 180, 1 025, 870, 800, 780, and 760 cm^{-1}.

2,4,6-*Triphenyl*-1-*ureidopyridinium Tetrafluoroborate* (37).—2,4,6-Triphenylpyrylium tetrafluoroborate (1 g, 2.5 mmol) in EtOH (7.5 ml) and CH_2Cl_2 (7.5 ml), and semicarbazide hydrochloride (0.281 g, 2.5 mmol) and sodium hydroxide (0.1 g, 2.5 mmol) in water (3 ml) were mixed and refluxed for 12 h. The solvent was removed (30 °C, 20 mmHg) and the product extracted with CH_2Cl_2 (20 ml). Et_2O (10 ml) precipitated the *pyridinium* (0.7 g, 62%), prisms m.p. 216—219 °C from EtOH (Found: C, 63.5; H, 4.6; N, 9.1. $C_{24}H_{20}BF_4N_3O$ requires C, 63.6; H, 4.4; N, 9.3%); $\nu_{max.}$ ($CHBr_3$) 3 450, 3 350, 3 200, 1 680, 1 620, 1 600, 1 510, 1 460, 1 420, 1 340, 1 250, 1 075, 885, 760, and 740 cm^{-1}; δ [$(CD_3)_2SO$] 8.5 (1 H, s), 7.9 (17 H, m), and 6.12 (2 H, s).

2-*Ethoxycarbonyl*-4,6-*diphenyl*-1-*ureidopyridinium Tetrafluoroborate* (48).—2-Ethoxycarbonyl-4,6-diphenylpyrylium tetrafluoroborate (1 g, 2.55 mmol) in EtOH (7.5 ml) and CH_2Cl_2 (7.5 ml), and semicarbazide hydrochloride (0.284 g, 2.55 mmol) and sodium hydroxide (0.1 g, 2.55 mmol) in water (3 ml) were mixed and refluxed for 3 h. The solvent was removed (30 °C/20 mmHg) and the product extracted with CH_2Cl_2 (10 ml). Et_2O (10 ml) precipitated the *pyridinium* (0.63 g, 56%), prisms m.p. 185—186 °C from EtOH (Found: C, 56.1; H, 4.4; N, 9.1. $C_{21}H_{20}BF_4N_3O_3$ requires C, 56.1; H, 4.4; N, 9.3%); $\nu_{max.}$ ($CHBr_3$) 3 440, 3 340, 3 210, 1 745, 1 690, 1 620, 1 600, 1 070, and 765 cm^{-1}; δ [$(CD_3)_2SO$] 8.83 (1 H, d), 8.68 (1 H, d), 6.57 (2 H, s), 7.9 (11 H, m), 4.44 (2 H, q), and 1.38 (3 H, t).

6,8-*Diphenyl*-4-*oxo*-3H-*pyrido*[2,1-f]-1,2,4-*triazinium* 2-*Oxide* (49).—2-Ethoxycarbonyl-4,6-diphenyl-1-ureidopyridinium tetrafluoroborate (0.100 g, 0.22 mmol) in dimethoxyethane (4 ml) and potassium carbonate (0.06 g, 0.44 mmol) were stirred at 20 °C for 2 h. Water (20 ml) was added and the whole extracted with CH_2Cl_2 (30 ml). The dry (Na_2SO_4) extracts were evaporated (20 °C/20 mmHg) to give the *oxide* (0.58 g, 83%), prisms m.p. >325 °C from EtOH (Found: C, 72.2; H, 4.0; N, 13.1. $C_{19}H_{13}N_3O_2$ requires C, 72.4; H, 4.1; N, 13.3%); $\nu_{max.}$ ($CHBr_3$) 1 710, 1 630, 1 610, 1 560, 1 480, 1 440, 1 400, 830, 760, and 745 cm^{-1}; δ [$(CD_3)_2SO$] 8.52 (1 H, d), 8.2 (1 H, d), and 7.35 (11 H, m).

General Procedure for the Preparation of 1-*Alkylideneamino*-2-*ethoxycarbonyl*-4,6-*diphenylpyridinium Salts*.—2-Ethoxycarbonyl-4,6-diphenylpyrylium tetrafluoroborate (24) (1 g) was suspended in EtOH (10 ml) and an equimolecular amount of the alkylidenehydrazone was added gradually. The solution was refluxed for 4 h and the pyridinium was precipitated with Et_2O (5 ml).

1-*Benzylidenamino*- (56) (68%), m.p. 195 °C (prisms from EtOH) (Found: C, 65.4; H, 4.7; N, 5.4. $C_{27}H_{23}BF_4N_2O_2$ requires C, 65.6; H, 4.6; N, 5.6%); $\nu_{max.}$ ($CHBr_3$) 1 745, 1 620, 1 600, 1 570, 1 250, 1 060, and 770 cm^{-1}; δ [$(CD_3)_2SO$] 9.05 (1 H, s), 8.95 (1 H, d), 8.75 (1 H, d), 7.85 (15 H, m), 4.37 (2 H, q), and 1.2 (3 H, t); 2-*ethoxycarbonyl*-1-(p-*tolylideneamino*)-4,6-*diphenylpyridinium tetrafluoroborate* (57) (43%), prisms m.p. 156—158 °C from EtOH (Found: C, 66.4; H, 4.9; N, 5.2. $C_{28}H_{25}BF_4N_2O_2$ requires C, 66.2; H, 4.9; N, 5.5%); $\nu_{max.}$ ($CHBr_3$) 1 745, 1 620, 1 600, 1 560, 1 245, 1 190, 900, 820, 770, and 730 cm^{-1}; δ ($CDCl_3$) 8.7 (1 H, s), 8.29 (1 H, d), 7.95 (1 H, d), 7.4 (14 H, m), 4.23 (2 H, q), 2.24 (3 H, s), and 1.1 (3 H, t); 1-(1-*phenyl*)*ethylideneamino*- (58) (54%), m.p. 195—196 °C (prisms from EtOH) (Found: C, 65.9; H, 5.0; N, 5.4. $C_{28}H_{25}BF_4N_2O_2$ requires C, 66.1; H, 4.9; N, 5.5%); $\nu_{max.}$ ($CHBr_3$) 1 745, 1 620, 1 600, 1 570, 1 370, 1 250, 1 205, 1 060, 770, and 760 cm^{-1}; δ ($CDCl_3$) 8.55 (1 H, d), 8.21 (1 H, d), 7.6 (15 H, m), 4.42 (2 H, q), 2.2 (3 H, s), and 1.3 (3 H, t); 1-(1-p-*tolyl*)-*ethylideneamino*- (60) (41%), m.p. 200—201 °C (prisms from EtOH) (Found: C, 66.4; H, 4.9; N, 5.4. $C_{29}H_{27}BF_4N_2O_2$ requires C, 66.7; H, 5.1; N, 5.4%); $\nu_{max.}$ ($CHBr_3$) 1 745, 1 620, 1 600, 1 370, 1 345, 1 315. 1 250, 1 205, 1 060, 770, and 760 cm^{-1}; δ [$(CD_3)_2SO$] 8.99 (1 H, d), 8.1 (1 H, d), 7.8 (14 H, m), 4.35 (2 H, q), 2.39 (3 H, s), 2.18 (3 H, s), and 1.21 (3 H, t); 1-(1-p-*bromophenyl*)*ethylideneamino*- (59) (35%), m.p. 209—211 °C (prisms from EtOH) (Found: C, 57.2; H, 3.9; Br, 13.7; N, 4.7. $C_{28}H_{24}BBrF_4N_2O_2$ requires C, 57.3; H, 4.1; Br, 13.6; N, 4.8%); $\nu_{max.}$ ($CHBr_3$) 1 745, 1 620, 1 600, 1 370, 1 350, 1 310, 1 250, 1 205, 1 060, 780, and 770 cm^{-1}; δ [$(CD_3)_2SO$] 8.99 (1 H, d), 8.1 (1 H, d), 7.9 (14 H, m), 4.35 (2 H, q), 2.18 (3 H, s), and 1.21 (3 H, t).

3-*Ethoxycarbonyl*-4,6-*diphenyl*-1-[1-(4-*pyridyl*)*ethylideneamino*]*pyridinium Tetrafluoroborate* (61).—2-Ethoxycarbonyl-4,6-diphenylpyrylium tetrafluoroborate (0.78 g, 2 mmol) and 4-acetylpyridine hydrazone (0.270 g, 2 mmol) in MeOH (8 ml) were stirred at 20 °C for 0.5 h. The 4-*acetyl*-N-(1-*ethoxycarbonyl*-1-*oxo*-3,5-*diphenylpent*-2,4-*dienyl*)-*pyridininm hydrazone tetrafluoroborate* was separated (0.93 g, 88%), m.p. 146—149 °C (decomp.), prisms from EtOH (Found: C, 61.3; H, 4.9; N, 7.9. $C_{27}H_{26}BF_4N_3O_3$ requires C, 61.5; H, 4.9; N, 7.9%); $\nu_{max.}$ ($CHBr_3$) 3 370, 3 270, 3 170, 1 710, 1 685, 1 500, 1 450, 1 370, 1 260, 1 210, 1 060, 770, 760, 750, and 730 cm^{-1}; δ [$(CD_3)_2SO$] 7.7 (15 H, m), 6.72 (1 H, s), 6.24 (1 H, s), 4.14 (2 H, q), 1.54 (3 H, s), and 1.26 (3 H, t). This compound (0.200 g, 0.38 mmol) was refluxed in absolute EtOH (5 ml) during 3 h to give, from the cooled solution, 2-*ethoxycarbonyl*-4,6-*diphenyl*-1-[1-(4-*pyridyl*)*ethylideneamino*]*pyridinium tetrafluoroborate* (0.140 g, 73%), m.p. 171—176 °C (decomp.), prisms from EtOH (Found: C, 63.4; H, 4.6; N, 8.2. $C_{27}H_{24}BF_4N_3O_2$ requires C, 63.6; H, 4.7; N, 8.2%); $\nu_{max.}$ ($CHBr_3$) 1 735, 1 620, 1 600, 1 410, 1 370, 1 345, 1 310, 1 250, 1 210, 1 060, 1 010, 900 860, 825, 765, and 755 cm^{-1}; δ [$(CD_3)_2SO$] 8.9 (1 H, d), 8.73 (1 H, d), 8.0 (14 H, m), 4.28 (2 H, q), 2.12 (3 H, s), and 2.14 (3 H, t).

General Procedures for the Formation of 4-*Oxidopyrido*-[1,2-b]*pyridazinium Zwitterions*.—*Procedure A*. The 1-alkylidenamino-2-ethoxycarbonylpyridinium (0.200 g), 1,2-dimethoxyethane (5 ml), and NaH (equimolecular) were stirred for 3 h at −5 °C under N_2. The precipitated yellow solid in CH_2Cl_2 (15 ml) was washed with water (10 ml), dried (Na_2SO_4), and evaporated at 20 °C/20 mmHg.

Procedure B. Pyridinium salt (0.200 g), dry THF (5 ml), and potassium carbonate (equimolecular) were stirred for 5 h at 20 °C and then treated as in A above.

4-*Oxido*-2,6,8-*triphenylpyrido*[1,2-b]*pyridazinium zwitterion* (62). This compound (50% procedure A, 68% procedure B) had m.p. 288—289 °C (prisms from EtOH) (Found: C, 83.0; H, 4.8; N, 7.4. $C_{28}H_{18}N_2O$ requires C, 83.4; H, 4.8; N, 7.5%); $\nu_{max.}$ ($CHBr_3$) 1 590, 1 580, 1 480, 1 465, 1 455, 1 430, 1 400, 945, and 770 cm^{-1}; δ ($CDCl_3$) 8.98 (1 H, d), 7.51 (16 H, m), and 6.92 (1 H, s).

2-p-*Bromophenyl*-4-*oxido*-6,8-*diphenylpyrido*[1,2-b]*pyridazinium zwitterion* (63). This compound (38% procedure A, 73% procedure B) had m.p. 238—240 °C (prisms from EtOH) (Found: C, 66.1; H, 3.6; Br, 17.0; N, 6.0. $C_{26}H_{17}BrN_2O{\cdot}H_2O$ requires C, 66.2; H, 4.0; Br, 17.0; N, 5.9%); $\nu_{max.}$ ($CHBr_3$) 3 400 (H_2O), 1 590, 1 570, 1 480, 1 450, 945, 825, and 760 cm^{-1}; δ ($CDCl_3$) 8.95 (1 H, d), 7.6 (15 H, m), and 6.86 (1 H, s).

4-*Oxido*-6,8-*diphenyl*-2-p-*tolylpyrido*[1,2-b]*pyridazinium zwitterion* (64). This compound (32% procedure A, 68% procedure B) had m.p. 249—250 °C (prisms from EtOH) (Found: C, 83.3; H, 5.1; N, 7.2. $C_{27}H_{20}N_2O$ requires C, 83.5; H, 5.1; N, 7.2%); $\nu_{max.}$ ($CHBr_3$) 1 590, 1 575, 1 485, 1 465, 1 450, 945, 820, and 760 cm^{-1}; δ ($CDCl_3$) 8.97 (1 H, d), 7.45 (15 H, m), 6.92 (1 H, s), and 2.28 (3 H, s).

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