Heterocycles in Organic Synthesis. Part 19.[1] Thermolysis of Pyridinium *N*-Acylimines: a New Preparation of Isocyanates [2]

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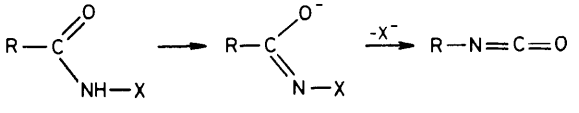
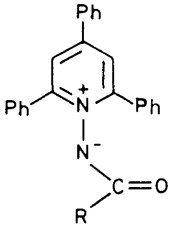
2,4,6-Triphenylpyrylium perchlorate converts hydrazides into the 1-amidopyridinium perchlorates (25) which are easily deprotonated to the free pyridinium 1-acylimines (8). These are alternatively prepared by acylation of the 1-amino-2,4,6-triphenylpyridinium cation. The 1-acylimines undergo smooth thermolysis to 2,4,6-triphenylpyridine and the corresponding isocyanates, constituting a practical synthetic method for the latter. 1-Thioamidosalts (28) were prepared: the corresponding 1-thioacylimines are unstable and decompose to the corresponding cyanides and sulphur.

CLASSICAL preparations of isocyanates (7) involve the rearrangement of anions (3) and (4) of *N*-halogenoamides (1) [3] or hydroxamic acids (2),[4] or of acyl azides (5).[5] In each of these species (3)—(5), X is a leaving group: other parts of this series [6] have emphasised 2,4,6-triphenylpyridine as a good leaving group and the present paper describes a new synthesis of isocyanates based on the thermolysis of 2,4,6-triphenylpyridine *N*-acylimines (8).

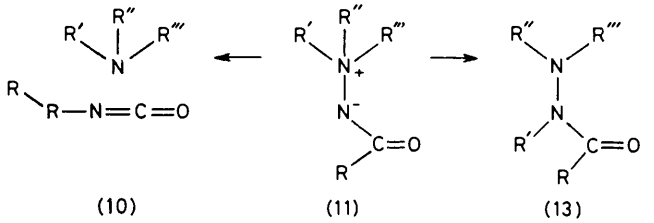


(1) X = Cl or Br
(2) X = OH
(3) X = Cl or Br
(4) X = OH
(5) X = N_2^+
(6) X = pyridinium ring
(7)



(8)
(9) R = Ph

Gibson and Murray [7] and independently Smith and Briggs [8] first observed the thermolysis of an amine-imide of type (11) ⟶ (10); the trimethyl derivative



(10) (11) (13)
(12) R′ = R″ = R‴ = Me; R = Ph

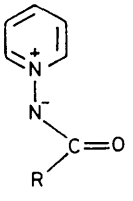
(11) gave trimethylamine and phenyl isocyanate (isolated as trimer). Other amine-imides of type (11) rearrange to the acyltrialkylhydroazines (13);[9] both reactions (11) ⟶ (10) + (13) can occur simultaneously,[10] in proportions which depend on steric factors.[11]

McKillip *et al.*[12] first proposed reactions of trimethylamine-imides of type (11) as a preparative method for isocyanates: two isocyanates were isolated as monomers and the reaction was employed to produce polyfunctional isocyanates to initiate polymerisation. For related work see ref. 13; the field has been reviewed.[14]

The thermolysis of pyridine *N*-benzoylimide (14) and heteroaromatic analogues was studied by Tamura *et al.*:[15] for example heating (14) at 190 °C gave pyridine (27%) and diphenylurea (30%).

Preparation of N-*Acylimines by Acylation.*—We have previously described [16] the benzoylation of 1-aminopyridinium iodide to give (14) (following Okamoto *et al.*) [17] and we have now prepared the *p*-tolyl analogue (15) similarly.

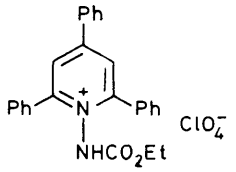
2,4,6-Triphenylpyrylium perchlorate reacts with ethyl carbazate to give the *N*-(ethoxycarbamoyl) derivative (16) together with a by-product to which we have assigned a pyrazoline structure (17) on spectral evidence (see Experimental section). Similar results have been previously reported for benzenesulphonhydrazide.[18] 1-Amino-2,4,6-trimethylpyridinium perchlorate (18) was made from t-butyl carbazate ($NH_2NHCO_2Bu^t$) and 2,4,6-trimethylpyrylium perchlorate; loss of the t-butyl group and decarboxylation occurred during the reaction.



(14) R = Ph
(15) R = *p*-$CH_3C_6H_4$

We also made the triphenyl analogue (19) analogously; however a better preparation of this 1-amino-perchlorate (19) was found to be from the treatment of 1-(2-pyridyl)-2,4,6-triphenylpyridinium perchlorate [19] (20) with hydrazine. Direct reaction of hydrazine with 2,4,6-triarylpyrylium salts gives 1,2-diazepines [20] which are difficult to rearrange into the isomeric pyridine 1-imine derivatives.[21] Similar elimination of 2-aminopyridine from (20) and reclosure to a new pyridine ring was achieved with aniline (in the presence of t-butyl-lithium) to give (21).

The amino-perchlorate (19) reacted with acetone, benzaldehyde, and 2,4-dichlorobenzaldehyde to give the



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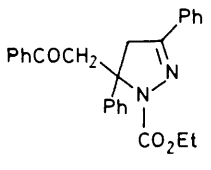

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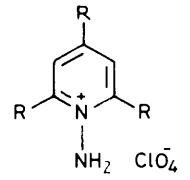
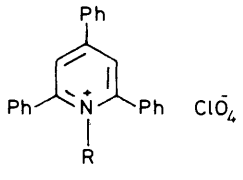


(18) R = Me (19) R = Ph

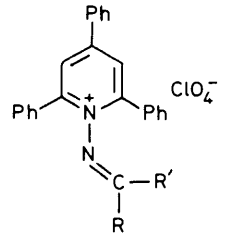


(20) R = 2-pyridyl
(21) R = Ph

imine perchlorates (22)—(24): similar compounds have been prepared from the 1-aminopyridinium cation by Okamoto *et al.*[22] In the presence of K_2CO_3, the amino-perchlorate (19) underwent acylation by acid chlorides to yield a series of acylimines of type (8) (Table 1).

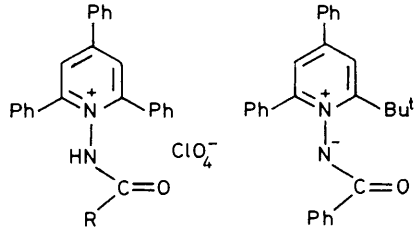
Preparation of N-*Acylimines from Hydrazines.*—2,4,6-Triphenylpyrylium perchlorate reacts with acylhydrazines to yield the 1-amidopyridinium perchlorates (25) (Table 2). Neidlein and Witerzens [23] recently reacted 2,4,6-trimethylpyrylium perchlorate with various acylhydrazines to give analogues of (25) (*cf.* also ref. 18). The perchlorates (25) are readily converted to the free 1-acylimines (8) by base (Table 1). The t-butylimine (27) was made similarly from benzhydrazide and 2-t-butyl-4,6-diphenylpyrylium perchlorate without isolation of the intermediate salt.

2,4,6-Triphenylpyrylium perchlorate and thiobenzhydrazide gave the 1-thioamido-perchlorate, but this salt



(22) R = R' = Me
(23) R = H, R' = Ph
(24) R = H, R' = 2,4-$Cl_2C_6H_4$

was unstable; in particular it decomposed on attempted deprotonation. It was therefore decided to pyrolyse the



(25) (26) R = Ph (27)

salts directly, and our attention moved from the perchlorates to the analogous tetrafluoroborates. 2,4,6-Triphenylpyrylium tetrafluoroborate with a series of thioacylhydrazines gave the corresponding 1-thioamido-tetrafluoroborates (28): these compounds decomposed rapidly in solution and often could not be satisfactorily recrystallised or analysed (see Table 3).

TABLE 1

Pyridine *N*-acylimides (8)

R	Method [a]	M.p. (°C)	Crystallisation solvent [b]	Yield (%)	Formula	Found (%) C	Found (%) H	Found (%) N	Calc. (%) C	Calc. (%) H	Calc. (%) N
Me	A	209	Benzene	76	$C_{25}H_{20}N_2O$	82.5	5.6	7.4	82.4	5.4	7.6
n-C_3H_7	B	174	Benzene	64	$C_{27}H_{24}N_2O$			7.2			7.1
Ph	A	204	Benzene	82	$C_{30}H_{22}N_2O$	84.5	5.1	6.4	84.5	5.2	6.6
p-MeC_6H_4	A	201	Benzene	79	$C_{31}H_{24}N_2O$	84.2	5.5	6.4	84.5	5.5	6.4
p-$MeOC_6H_4$	A	201	Benzene	78	$C_{31}H_{24}N_2O_2$	81.1	5.3	6.4	81.5	5.3	6.1
p-ClC_6H_4	B	186	Benzene	73	$C_{30}H_{21}N_2O$			5.7			6.0
$PhCH_2$	B	167	Benzene	85	$C_{31}H_{24}N_2O$			6.3			6.3
PhCH:CH	B	197	Benzene	66	$C_{32}H_{24}N_2O$			6.0			6.1
p-$NO_2C_6H_4$	B	226	CH_3Cl	79	$C_{30}H_{21}N_3O_3$	75.9	4.6	9.0	76.4	4.4	8.7

[a] Method A by deprotonation of amido-perchlorates. Method B by acylation of *N*-amino-perchlorates. [b] All compounds crystallised as prisms.

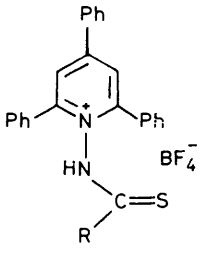
TABLE 2

N-Amidopyridinium perchlorates (25) [a]

R	M.p. (°C)	Yield (%)	Formula	Found (%) C	Found (%) H	Found (%) N	Reqd. (%) C	Reqd. (%) H	Reqd. (%) N
Me	267	85	$C_{25}H_{21}ClN_2O_5$	64.3	4.6	6.1	64.6	4.5	6.0
Ph	128	83	$C_{20}H_{23}ClN_2O_5$	68.5	4.5	5.1	68.4	4.3	5.3
p-MeC_6H_4	245	66	$C_{31}H_{25}ClN_2O_5$	68.3	4.7	5.0	68.8	4.6	5.1
p-$MeOC_6H_4$	250	70	$C_{31}H_{25}ClN_2O_6$	66.3	4.6	5.2	66.8	4.4	5.0

[a] All these compounds crystallised as prisms from EtOH.

Reaction of N-*Acylimines with Amines*.—We initially attempted to trap the isocyanates formed from thermo-



(28)

lytic reactions of type (6) ⟶ (7) as ureas (30) by reaction with amines (29). Ureas were indeed obtained

In refluxing xylene, (14) gave the symmetrical urea with *p*-toluidine; no reaction occurred in refluxing toluene. By contrast, (9) reacted in toluene at 100 °C, but still gave a mixture of the symmetrical and unsymmetrical ureas.

$$R'NH_2 \xrightarrow{RNCO} RNHCONHR' \xrightarrow{R'NH_2} R'NHCONHR'$$
(29) (30) (31)

Preparation of Isocyanates.—However, the *N*-acylimines (8) thermolysed smoothly to give excellent yields of the isocyanates which were characterised by i.r. spectroscopy and by reaction with aniline to give the corresponding unsymmetrical ureas (Table 5).

The present route complements the Curtius reaction

TABLE 3

Preparation and thermolysis of thioamidopyridinium tetrafluoroborates

	Thiohydrazides (32)			Thioamidopyridinium tetrafluoroborates (28)						Nitriles (34)			
R	M.p. (°C)	Lit. M.p. (°C)	Ref.	M.p. (°C)	Crystal form	Yield (%)	Formula	N (%) Found	N (%) Reqd.	Yield (%)	M.p. (°C)	Lit. m.p. (°C)	Ref.
Ph	67—70	72—73	*a*	122 (decomp.)	Prisms	93	$C_{30}H_{23}N_2SBF_4$			98	*b*		
p-MeC_6H_4	135—137	137—138	*a*	152 (decomp.)	Prisms	90	$C_{31}H_{25}N_2SBF_4$	5.3	5.1	99	33 [c]	29.5	*d*
p-$MeOC_6H_4$	124—126	125—126	*a*	127 (decomp.)	Prisms	95	$C_{31}H_{25}N_2OBF_4$			100	57 [e]	59	*f*
p-ClC_6H_4	122—124	123—124	*a*	158 (decomp.)	Prisms	95	$C_{30}H_{22}ClN_2SBF_4$	5.2	5.0	100	93 [g]	90	*h*

[a] K. A. Jensen and C. Pedersen, *Acta Chem. Scand.*, 1961, **15**, 1097. [b] The nitrile was characterised by comparing the i.r. spectrum with the published spectrum, C. J. Pouchert, ' The Aldrich Library of Infrared Spectra,' Aldrich Chemical Co. Inc., 1970, p. 825. [c] Footnote *b*, p. 827. [d] ' Beilstein's Handbuch der Organischen Chemie ', eds. B. Prager, P. Jacobson, P. Schmidt and D. Stern, Verlag von Julius Springer, Berlin, 1926, vol. 9. p. 489. [e] Footnote *b*, p. 828. [f] Footnote *d*, 1927, vol. 10, p. 168. [g] Footnote *b*, p. 827. [h] Footnote *d*, p. 341.

(Table 4), but in most cases these were the *symmetrical* ureas (31) derived from two molecules of the added amine. Only with the hindered *N*-methylaniline, and the weakly basic 2-aminopyridine were poorish yields of the corresponding unsymmetrical urea (30) obtained

for the formation of isocyanates.[5] Although recently mild methods utilising Me_3SiN_3 [25] and diphenylphosphoryl azide [26] have been developed, for cases in which the use of azides or nitrous acid in the preparation of the acid azide is a source of difficulty it could be the method

TABLE 4

Thermal reactions of *N*-acylimines with amines

Compound	*N*-Acylimines R	Amines	Moles of amine per mole of *N*-acylimine	Temp. (°C)	Time (h)	Product	Yield (%)	M.p. (°C)	Lit. m.p. (°C)	Ref.
(14)	Ph	*p*-$MeC_6H_4NH_2$	3	190	2	$(p\text{-}MeC_6H_4NH)_2CO$	75	264	263	*a*
	Ph	*p*-$MeOC_6H_4NH_2$	1	190	2	$(p\text{-}MeOC_6H_4NH)_2CO$	79	234	234	*b*
	Ph	*p*-$ClC_6H_4NH_2$	3	190	1.5	$(p\text{-}ClC_6H_4NH)_2CO$	75	270 (sublimed)	275 sublimed)	*c*
	Ph	PhNHMe	5	190	3	PhNHCON(Me)Ph	20	101—102	104—105	*d*
(15)	*p*-MeC_6H_4	$PhNH_2$	1	185	2	$(PhNH)_2CO$	85	233—235	235	*e*
(9)	Ph	*p*-$MeC_6H_4NH_2$	1	190	2	$(p\text{-}MeC_6H_4NH)_2CO$	95	263	263	*a*
	Ph	2-$C_5H_4NNH_2$	5	190	2	(2-NC_5H_4)NHCONHPh	50	187—189	185—186	*f*
	Ph	$PhCH_2NH_2$	6	185	2	$(PhCH_2NH)_2CO$	80	169	167	*g*

[a] ' Beilstein's Handbuch der Organischen Chemie' , eds. B. Prager, P. Jacobson, P. Schmidt, and D. Stern, Verlag von Julius Springer, Berlin, 1929, vol. XII, p. 941. [b] ' Beilstein's Handbuch der Organischen Chemie ', ed. F. Richter, Second Supplement, Springer-Verlag, Berlin, 1950, vol. XIII, p. 252. [c] Footnote *a*, p. 615. [d] D. G. Crosby and C. Niemann, *J. Amer. Chem. Soc.*, 1954, **76**, 4458. [e] Footnote *a*, p. 352. [f] ' Beilstein's Handbuch der Organischen Chemie ', ed. F. Richter, Second Supplement, Springer-Verlag, Berlin, 1953, vol. XXII, p. 330. [g] Footnote *a*, p. 1051.

(Table 3). Similar results were reported [7] for the thermolysis of (12) in *p*-bromoaniline. Amine–urea exchange reactions are well documented: [24] they proceed less readily with hindered and weakly basic amines.[24d]

of choice. The intermediate *N*-acylimines are stable crystalline compounds convenient to store.

Pyrolysis of 1-*Thioamidopyridinium Salts* (28).—Treatment of the salts (28) with base led to complete decomposition. Thermolysis of the salts (28) with

triphenylpyridine gave the nitriles RCN by loss of sulphur (Table 3). Analogously thiatriazoles (33) [prepared from thiohydrazides (32)] thermolyse to

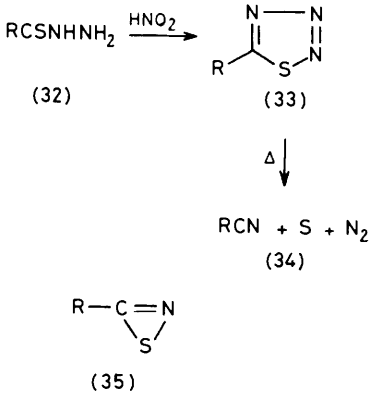
TABLE 5

Preparation of isocyanates by pyrolysis of 2,4,6-triphenylpyridinium *N*-acylimines (8) (at 220 °C at 1 mmHg)

		Urea (RNHCONHPh)		
R in (8)	Yield (%)	M.p. (°C)	Lit. m.p. (°C)	Ref.
Me	95	148 [a]	149—150	*c*
n-C_3H_7	94	115 [a]	114—116	*d*
Ph	86	212 [a]	212—213 [b]	*b*
p-MeC_6H_4	95	212 [a]	212—213	*e*
p-$MeOC_6H_4$	93	183 [a]	184	*f*
p-ClC_6H_4	89	234 [a]	237—238	*g*
$PhCH_2$	76	166 [a]	168	*h*
PhCH:CH	90	219 [a]	217	*i*

[a] The isocyanate was reacted with aniline. [b] The isocyanate was reacted with *p*-toluidine (in this case R = *p*-MeC_6H_4), 'Beilstein's Handbuch der Organischen Chemie', eds. B. Prager, P. Jacobson, P. Schmidt, and D. Stern, Verlag von Julius Springer, Berlin, 1929, vol. XII, p. 941. [c] Footnote *b*, p. 348. [d] 'Beilstein's Handbuch der Organischen Chemie', ed. F. Richter, First Supplement, Verlag von Julius Springer, Berlin, 1933, vol. XII, p. 231. [e] Footnote *b*, p. 941. [f] A. F. M. Fahmy and S. A. Esawy, *Indian J. Chem.*, 1973, **11**, 871. [g] Footnote *b*, p. 615. [h] Footnote *b*, p. 1050. [i] Footnote *b*, p. 355.

cyanide and sulphur (34).[27] Attempts to react (28) with various amines did not yield significant amounts of thioureas: possibly the production of cyanide from both (28) and (33) involves three-membered ring intermediates of type (35).



EXPERIMENTAL

The following were prepared by the literature method quoted: pyridine *N*-benzoylimide, m.p. 177—179 °C (lit.,[16] 179—180 °C).

Pyridine N-p-Tolylimide (15).—1-Aminopyridinium iodide and *p*-tolyl chloride gave, by the method reported for the benzoyl analogue,[16] the *imine* (30%) which separated from benzene as prisms, m.p. 168—170 °C (Found: C, 73.1; H, 5.7; N, 12.8. $C_{13}H_{12}N_2O$ requires C, 73.5; H, 5.6; N, 13.2%); $\nu_{max.}$ (Nujol) 3 020, 1 620, 1 590, 1 550, 1 510, 1 400, 1 340, 1 300, 1 250, 1 210, 1 180, 1 100, 1 050, 1 020, 980, 950, 900, 860, 840, 760, 750, 680, and 640 cm^{-1}; δ(D_2O; 60 MHz) 8.9—7.6 (9 H, m) and 2.8 (3 H, s).

1-Ethoxycarbamoyl-2,4,6-triphenylpyridinium Perchlorate (16) *and 1-Ethoxycarbonyl-3,5-diphenyl-5-phenacyl-2-pyrazoline* (17).—Ethyl carbazate (3.06 g) and 2,4,6-triphenylpyrylium perchlorate (12.24 g) were refluxed 12 h in ethanol (150 ml). Some perchlorate (16) separated on cooling, more was obtained by evaporation and treatment with ether. Evaporation of the ether gave the pyrazoline (17). The *perchlorate* (16) (9.1 g, 61%) formed prisms (from ethanol), m.p. 210—212 °C (Found: C, 62.9; H, 4.7; N, 5.5. $C_{26}H_{23}ClN_2O_6$ requires C, 63.1; H, 4.7; N, 5.7%); $\nu_{max.}$ (Nujol) 3 180—3 140, 1 745, 1 620, 1 595, 1 575, 1 560, 1 490, 1 410, 1 260—1 230, 1 120—1 040, 920, 890, 770, and 750 cm^{-1}; δ($CDCl_3$) 8.00 (2 H, s, arom.), 7.95—7.25 (15 H, m, arom.), 4.0—3.6 (2 H, q, *J* 7.5 Hz, CH_2), and 0.85 (3 H, t, *J* 7.5 Hz, CH_3). The *pyrazoline* (17) (4.7 g, 39%) (from dioxan–water) had m.p. 140—141 °C (Found: C, 75.3; H, 5.8; N, 6.7. $C_{25}H_{24}N_2O_3$ requires C, 75.7; H, 5.8; N, 6.8%); $\nu_{max.}$ (Nujol) 1 700 (ketone C=O), 1 680 (amide C=O), 1 595, 1 500, 1 480, 1 450, 1 425, 1 365, 1 330, 1 315, 1 305, 1 255, 1 230, 1 210, 1 175, 1 110, 1 030, 1 015, 1 000, 765, 755, 720, 700, and 690 cm^{-1}; δ($CDCl_3$) 8.15—7.10 (15 H, m, ArH), 4.40—3.50 (6 H, m, 3 × CH_3), and 1.15 (3 H, t, *J* 7 Hz, CH_3).

1-Amino-2,4,6-trimethylpyridinium Perchlorate (18) (with Dr. J. SUWINSKI).—t-Butyl carbazate (0.216 g) and 2,4,6-trimethylpyrylium perchlorate (0.362 g) were refluxed in 95% ethanol (4 ml) for 4 h. On cooling the *perchlorate* separated; it crystallised as prisms (from ethanol), m.p. 178—180 °C (Found: N, 12.0. $C_8H_{13}ClN_2O_4$ requires N, 11.8%).

1-Amino-2,4,6-triphenylpyridinium Perchlorate (19).—(i) t-Butyl carbazate (1.6 g), 2,4,6-triphenylpyrylium perchlorate (4.08 g), and amyl alcohol (25 ml) were refluxed for 12 h. On cooling an oil precipitated: it was taken up in hot ethanol and on cooling gave the *amino-perchlorate* (19) (0.5 g, 35%) which separated from ethanol as prisms, m.p. 161—163 °C (Found: C, 65.2; H, 4.7; N, 6.6. $C_{23}H_{19}ClN_2O_4$ requires C, 65.4; H, 4.5; N, 6.3%); $\nu_{max.}$ (Nujol) 3 340, 3 280—3 160, 1 620, 1 575, 1 530, 1 490, 1 410, 1 245—1 230, 1 110—1 060, 770, 725, and 695 cm^{-1}; δ($CDCl_3$) 8.00—7.25 (17 H, m, ArH) and 5.50 (2 H, s, NH_2).

(ii) 1-(2-Pyridyl)-2,4,6-triphenylpyridinium perchlorate [19] (4.9 g, 0.01 mol), hydrazine hydrate (5 g, 0.15 mol), and ethanol (50 ml) were refluxed for 4 h. A precipitate separated on cooling and was crystallised from ethanol to give the perchlorate (19) (3.6 g, 85%), m.p. and mixed m.p. 161—163 °C.

Reaction of 1-(2-Pyridyl)-2,4,6-triphenylpyridinium Perchlorate with Aniline.—t-Butyl lithium (1.4 ml of 15% solution in pentane) was added to 1-(2-pyridyl)-2,4,6-triphenylpyridinium perchlorate (1.79 g, 0.003 5 mol) in aniline (15 ml) and ether (15 ml). After stirring at −10 °C for 1.5 h, 1,2,4,6-tetraphenylpyridinium perchlorate (21) (1.5 g, 87%) separated, m.p. 261—163 °C (lit.,[28] 260 °C).

N-(2,4,6-Triphenylpyridinio)benzylideneamine Perchlorate (23).—Trimethylamine (0.10 g) was added to 1-amino-2,4,6-triphenylpyridinium perchlorate (0.42 g) and benzaldehyde (0.106 g) in dichloromethane (10 ml) and the mixture stirred 6 h at 20 °C. Ether then precipitated the *imine perchlorate* (23) (0.35 g, 70%) which after recrystallisation from methanol had m.p. 226—228 °C (Found: C, 70.0; H, 4.5; N, 5.5. $C_{30}H_{23}ClN_2O_4$ requires C, 70.5; H, 4.5; N, 5.5%); $\nu_{max.}$ (Nujol) 1 620, 1 600, 1 595, 1 560, 1 490, 1 450, 1 415, 1 240, 1 225, 1 110—1 070, 840, 770, 760, 745, 700, and 685 cm^{-1}; δ($CDCl_3$; 60 MHz) 8.65 (1 H, s), 7.95 (2 H, s), and 7.90—7.60 (20 H, m); δ(CF_3CO_2H; 60 MHz) 8.35 (2 H, s) and 8.20—7.20 (21 H, m).

The following were similarly prepared: N-(2,4,6-*triphenylpyridinio*)-2,4-*dichlorobenzylideneamine* (24) (67%),

m.p. 194—195 °C (from ethanol) (Found: C, 61.8; H, 3.6; N, 4.8. $C_{30}H_{21}Cl_3N_2O_4$ requires C, 62.1; H, 3.6; N, 4.8%); $\nu_{max.}$ (Nujol) 1 620, 1 600, 1 580, 1 570, 1 490, 1 415, 1 110—1 070, 885, 760, 730, and 690 cm^{-1}; δ(CF_3CO_2H; 60 MHz) 8.72 (1 H, s), 8.25 (2 H, s), and 8.1—7.0 (18 H, m); δ($CDCl_3$; 60 MHz) 8.85 (1 H, s) and 8.10—7.10 (20 H, m), and *-isopropylideneamine* (22) (75%) (prepared in aqueous acetone solvent), m.p. 182—186 °C (from methanol) (Found: N, 5.8. $C_{26}H_{23}N_2ClO_4$ requires N, 6.0%); $\nu_{max.}$ (Nujol) 1 630, 1 615, 1 595, 1 575, 1 560, 1 540, 1 490, 1 415, 1 235, 1 185, 1 110—1 070, 880, 795, 760, 750, and 695 cm^{-1}; δ(CF_3CO_2H; 60 MHz) 8.25 (2 H, s), 8.15—7.5 (15 H, m), 1.90 (3 H, s), and 1.68 (3 H, s).

2,4,6-*Triphenylpyridine* 1-*Acylimines* (8) *by Acylation* (*Procedure B of Table* 1).—Potassium carbonate (0.28 g, 0.002 mol) was added to 1-amino-2,4,6-triphenylpyridinium perchlorate (0.4 g, 0.001 mol) in acetone (5 ml) and water (1 ml), with stirring. After 10 min, the acid chloride (0.001 mol) in acetone (3 ml) was added at 20 °C and the whole stirred for 1 h. Volatiles were evaporated at 40 °C at 15 mmHg, water (20 ml) and chloroform (50 ml) were added. The dried ($MgSO_4$) chloroform layer was evaporated and the residue crystallised from benzene.

1-*Amido*-2,4,6-*triphenylpyridinium Perchlorates* (25).—2,4,6-Triphenylpyrylium perchlorate (0.01 mol), the acid hydrazide (0.012 mol), and ethanol (40 ml) were refluxed for 24 h. On cooling and addition of ether the *perchlorate* separated and was crystallised from ethanol (for details see Table 2).

2,4,6-*Triphenylpyridine* 1-*Acylimines* (8) (*Method A of Table* 1).—The perchlorate (25) (0.005 mol) in methanol (10 ml) was treated with potassium hydroxide (0.005 5 mol) in methanol (5 ml) at 20 °C. After stirring 20 min, the solution was filtered and the filtrate evaporated to give the *imine* which crystallised from benzene (for details see Table 1).

2-*t-Butyl*-4,6-*diphenylpyridine* N-*Benzoylimide* (27).—Benzhydrazide (3.12 g, 0.023 mol) and 2-t-butyl-4,6-diphenylpyrylium perchlorate (9.2 g, 0.023 mol) were converted by application of the general method for the preparation of (25) and method A for preparation of (8) into the *t-butyl imine* (2.8 g, 30%), which formed as prisms, m.p. 207—209 °C (from benzene) (Found: C, 82.8; H, 6.6; N, 6.7. $C_{28}H_{26}N_2O$ requires C, 82.7; H, 6.4; N, 6.8%); $\nu_{max.}$ (Nujol) 1 620, 1 600, 1 560, 1 460, 1 405, 1 330, 1 340, 1 300, 1 220, 1 150, 1 190, 1 080, 1 060, 1 020, 905, 880, 800, 750—780, 710, and 700 cm^{-1}; δ($CDCl_3$; 60 MHz) 8.4—7.4 (17 H, m) and 2.1 (9 H, s).

1-*Thioamido*-2,4,6-*triphenylpyridinium Tetrafluoroborates* (28).—2,4,6-Triphenylpyrylium tetrafluoroborate (0.01 mol) and the thiohydrazide (0.015 mol) were stirred in ethanol (150 ml) for 4 h at 20 °C. The tetrafluoroborate separated (see Table 3).

Pyrolysis of 2,4,6-*Triphenylpyridine* N-*Acylimines* (8) (*Table* 4).—The *N*-acylimine (0.01 mol) was dried for 5 h at 90 °C at 0.5 mmHg. It was then heated in an oil bath rapidly to 150 °C then gradually to 220 °C either at 0.5—2 or 12—15 mmHg in a distillation apparatus cooled in liquid nitrogen. The isocyanate distilled over at temperatures from 150 °C.

The ureas were prepared by adding the isocyanate to aniline (2 ml) in dry benzene (15 ml).

Pyrolysis of 1-*Thioamido*-2,4,6-*triphenylpyridinium Tetrafluoroborates* (*Table* 5).—The tetrafluoroborate (0.002 mol) and 2,4,6-triphenylpyridine (3 g) were mixed, dried at 40 °C and 5 mmHg, and heated at 110—150 °C and 0.2 mmHg. The nitrile distilled or sublimed and was characterised as in Table 3.

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