## Heterocycles in Organic Synthesis. Part 22.<sup>1</sup> The Conversion of Amines to Thiocarbonate Esters and Thiocyanates <sup>2</sup>

By Alan R. Katritzky,\* Urban Gruntz, Nicola Mongelli, and Marcos C. Rezende, School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ

Primary amines with 2,4,6-triphenylpyrylium perchlorate give 1-substituted pyridinium perchlorates which with potassium ethyl xanthate readily produce S-alkyl-O-ethyl dithiocarbonates. Primary amines with 2,4,6-triphenyl-pyrylium thiocyanate form 1-substituted-2,4,6-triphenylpyridinium thiocyanates which thermolyse smoothly to the corresponding alkyl and aralkyl thiocyanates

MANY sulphur-containing compounds, and particularly thiocyanates and isothiocyanates, are important as fungicides, herbicides, and insecticides. S-Linked functional groups are usually introduced into organic compounds by the substitution of C-H (e.g. sulphonation, thiocyanation), C-halogen (nucleophilic displacements *inter alia* by phase transfer catalysis<sup>3</sup>), or C-oxygen bonds (recent work describes the displacement of OH by CH<sub>3</sub>COS <sup>4</sup> and Me<sub>2</sub>NCSS <sup>5</sup> via 2-fluoropyridinium cations, see also ref. 6). Little work has involved the replacement of C-N bonds, except in the diazotisation of aromatic amines.

Previous parts of this series have demonstrated that the conversion of primary amines into pyridinium cations by pyrylium salts, and subsequent nucleophilic displacement allows replacement of the  $\rm NH_2$  group by other functionality, including bonds to halogen,<sup>7</sup> oxygen,<sup>8</sup> and nitrogen.<sup>9</sup> We now report on the substitution of the NH<sub>2</sub> group by S-linked functions.

Preparation of Xanthate Esters.-The 1-substituted-



2,4,6-triphenylpyridinium salts (3) and (8) (Tables 1 and 2) were prepared by standard methods from the amines (1) and triphenylpyrylium salts (2) and (7). Potassium

	Pvridi	nium perchlo	rate	(3)		E	tOCS	SR:Y	ield, n.	cher characterisations				
	<u>M.n.</u>	Lit. m.p.	Lit.	Wt.	EtOCS.	x	Vol	ť	Yield	C	D-Et	S	-R	Other
R	(°Ć)	(°C)	ref.	(g)	Wt. (g)	Туре	(ml)	(h)	(%)	СН3	b CH2	ά-H	Other H	charactn.
Me	215	214 - 215.5	d	<b>2.5</b>	1.2	$C_{6}H_{6}$	50	5	<b>4</b> 0	1.8	<b>5.0</b>	3.9		е
Et <sup>f</sup>	175—176			2.6	1.2	C <sub>6</sub> H <sub>6</sub>	50	4	64	1.8	<b>5.0</b>	(3 H, s) 3.4 (2 H,	1.6 (3 H,	е
Bu <sup>n ø</sup>	187—188			2.7	1.2	C <sub>6</sub> H <sub>6</sub>	50	4	80	h	<b>5.0</b>	q, f 7 Hz 3.33.6	1.2 - 2.3	е
PhCH <sub>2</sub>	196	196—198	i	2.1	1.0	EtOH	30	2	73	1.6	4.8	(2 H, III) 4.5 (2 H a)	(10 H, III) 7.5 (5 H c)	j
$MeC_{6}H_{4}CH_{2}(p)$ <sup>k</sup>	132—133	174176	i	2.0	1.0	EtOH	30	2	84	1.6	4.8	(2 H, s) 4.5 (2 H, s)	(3 H, s) 2.5 (3 H, s) 7.3	е
$\mathrm{ClC}_{6}\mathrm{H}_{4}\mathrm{CH}_{2}(p)$	142—143	143	i	3.0	1.2	EtOH	30	2	81	1.6	4.8	4.5 (2 H. s)	(4 H, s) 7.5 (4 H, s)	е
$MeOC_6H_4CH_2(p)$ <sup>1</sup>	146—148			2.8	1.1	EtOH	30	2	88	1.6	4.8	4.5 (2 H, s)	7.0 (2 H, d, J 9 Hz) 7.4 (2 H, d, J 9 Hz) 3.9 (3 H, s)	m

TABLE 1 Reactions of 1-substituted-2,4,6-triphenylpyridinium perchlorates (3) with potassium ethyl xanthate (4, R' = Et)

<sup>e</sup> P.p.m. on 8 scale from internal Me<sub>4</sub>Si at 60 MHz in CCl<sub>4</sub>. <sup>b</sup> Triplets with J 7 Hz. <sup>c</sup> Quartets with J 7 Hz. <sup>d</sup> K. Dimroth, K. Wolf, and H. Kroke, Annalen, 1964, **678**, 183. <sup>e</sup> Identical by spectral comparison with authentic samples prepared by reaction of EtOCS<sub>2</sub>K with the corresponding halide RX (see A. I. Vogel, 'A Textbook of Practical Organic Chemistry,' 3rd edn., Longmans, Green and Co. Ltd., London, 1961, p. 499). <sup>f</sup> Found: C, 68.9; H, 5.1; N, 3.4. C<sub>25</sub>H<sub>22</sub>ClNO<sub>4</sub> requires C, 68.9; H, 5.1; N, 3.2%. <sup>e</sup> Found: C, 69.6; H, 5.7; N, 2.8. C<sub>27</sub>H<sub>26</sub>ClNO<sub>4</sub> requires C, 69.9; H, 5.6; N, 3.0%. <sup>k</sup>Overlapped by multiplet at 81.2–2.3. <sup>i</sup> Ref. 9. <sup>j</sup> np<sup>21</sup> 1.6007, lit., np<sup>30</sup> 1.5952 (C. Djerassi, M. Gorman, F. X. Markley, and E. B. Oldenburg, J. Amer. Chem. Soc., 1955, **77**, 568. <sup>k</sup> Found: C, 71.2; H, 5.4; N, 2.8. C<sub>21</sub>H<sub>26</sub>ClNO<sub>4</sub>·H<sub>2</sub>O requires C, 71.5; H, 5.2; N, 2.7%. <sup>i</sup> Found: C, 70.3; H, 4.9; N, 2.9. C<sub>31</sub>H<sub>26</sub>ClNO<sub>5</sub> requires C, 70.5; H, 4.9; N, 2.7%. <sup>m</sup> np<sup>21</sup> 1.5960, N. N. Mel'nikov, A. F. Prokof'eva, T. P. Krylova, N. A. Popovkina, N. N. Khvorostukhina, and I. L. Vladimirova, Khim. Org. Soedinenii Fosfora, Akad. Nauk S.S.S.R., Otdel Obshch. Tekh. Khim., 1967, 256 (Chem. Abs. 1968, **69**, 2627h).

alkyl xanthates (4) were obtained from the corresponding potassium alkoxide and  $CS_2$ .

The N-alkylpyridinium salts (3; R = Me, Et, Bu<sup>n</sup>) underwent nucleophilic substitution to yield the corresponding O-ethyl S-alkyl dithiocarbonates (6; R' = Et) with potassium ethyl xanthate (4; R' = Et) in moderate to good yield (Table 1) in refluxing benzene. No reactions with the N-alkyl salts occurred in acetonitrile or ethanol, but the more reactive benzyl salts (3;  $R = PhCH_2$ , p-MeC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>, p-OMeC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>, and p-ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>) on refluxing in ethanol readily gave the dithiocarbonates (6; R' = Et) in good yield (Table 1).

These experiments in solution were more satisfactory than others in which we thermolysed dry mixtures of tetrafluoroborates (8) and potassium alkyl xanthates (4). Using the xanthates derived from methanol, ethanol, and isopropyl alcohol (4;  $\mathbf{R}' = \mathbf{M}\mathbf{e}, \mathbf{E}\mathbf{t}, \mathbf{P}\mathbf{r}^i$ ) gave some of the desired O,S-dialkyl dithiocarbonates (6), but the yields were often low and the products grossly contaminated, except in the simplest reaction of (4;  $\mathbf{R}' = \mathbf{M}\mathbf{e}$ ) with (8;  $\mathbf{R} = \mathbf{M}\mathbf{e}$ ) when 70% of O-methyl S-methyl dithiocarbonate was obtained. N.m.r. spectra suggested that in some of the other cases  $O \longrightarrow S$ -alkyl migration had partially occurred.

We also used potassium t-butyl xanthate (4;  $R = Bu^t$ ) in the expectation that the dithiocarbonate (11) thus formed would thermolyse spontaneously into isobutene (12) and the acid (13) which would, in turn, give the thiol (14) and COS. Using the benzyl and ethyl tetrafluoroborates (8;  $R = CH_2Ph$ , Et), toluene- $\alpha$ -thiol and ethanethiol were indeed obtained, but they were grossly contaminated with side-reaction products (for details see Table 2).

Preparation of Alkyl Thiocyanates (15).—The preparation of 2,4,6-triphenylpyrylium thiocyanate (9) from the corresponding hydrogen sulphate and ammonium thiocyanate proceeds in good yield, as reported by Balaban and Paraschiv.<sup>10</sup> We now find that this thiocyanate (9) reacts with a variety of primary amines

## TABLE 2

Reaction of N-substituted 2,4,6-triphenylpyridinium tetrafluoroborates (8) with alkyl potassium xanthates (4)

Pyridi	nium	(8) D	0000 1	2 (4)		
cettamaore	Wt.	( <sup>0</sup> ) K	Wt.	<b>A</b> (4)	Yield (	%)
N-Subst.	(g)	R′	(g)	$T(^{\circ}C)$	R'OCS2R	RSH
Me	2.0	Me	1.0	130	70 ª	
Et	2.0	Me	1.0	130	37 5	
	<b>2.0</b>	$\mathbf{Bu^t}$	1.3	130		60 <sup>b</sup>
Bun	<b>2.2</b>	$\mathbf{Et}$	1.1	130	50 <sup>b</sup>	
	2.2	Pri	1.2	130	70 <sup>b</sup>	
PhCH <sub>2</sub>	2.4	$\mathbf{Bu^t}$	1.3	130		90 s, c

<sup>a</sup> Identical by spectral comparison with authentic sample prepared by reaction of MeOCS<sub>2</sub>K with MeI. <sup>b</sup> Crude products. <sup>c</sup> Mercury dibenzyl sulphide, m.p. 117—118 °C, lit., m.p. 121— 121.5 °C (A. Gutmann, *Ber.*, 1916, **49**, 954).

(including primary and secondary carbylamines, hydroxyamines, benzylamines, and arylamines) (1) in ethanol or chloroform solvents at 20 °C to give the corresponding 1-substituted-2,4,6-triphenylpyridinium thiocyanates



(10) in yields of 52-97% (average of 14 different amines 75%) (Table 3).

When heated at 150—185 °C at 0.1—1 mmHg, these 1-substituted pyridinium thiocyanates (10) smoothly decomposed to give the corresponding alkyl and benzyl

TABLE 3

Preparation of 1-substituted-2,4,6-triphenylpyridinium thiocyanates (10)

			Prepa	ration					_							
				Vield			Mn	F	oun	d (%	)		Re	equir	ed (%	6)
1-Subst.	Solv.",b	<i>t</i> /h	Solv. <sup>b, c</sup>	%	Solv. <sup>b,d</sup>	Cryst."	(°C)	Ċ	Н	N	s	Formula	C	н	N	s
Me	$\mathbf{E}$	16	EE	75	EA-M	N	183 - 184	78.4	5.3	7.2	8.4	C.,H.N.S	78.9	5.3	7.3	8.4
Et	E	16	EE	<b>72</b>	T–EA	N	165 - 167	79.1	5.6	6.9	8.2	C <sub>26</sub> H <sub>22</sub> N <sub>2</sub> S	79.2	5.6	7.1	8.1
[CH,],OH	С	20	EA	96	T–EA	Р	177 - 179	76.0	5.5	6.9	7.7	C <sub>26</sub> H <sub>22</sub> N <sub>2</sub> OS	76.1	5.4	6.8	7.8
Pr <sup>n</sup>	E	24	EA	64	T–EA	N	140-141			7.2	8.1	C <sub>27</sub> H <sub>24</sub> N <sub>2</sub> S			6.9	7.8
[CH,],OH	С	<b>26</b>	EA	70	D	N	183 - 185	<b>76.0</b>	5.6	6.5	7.7	C <sub>27</sub> H <sub>24</sub> N <sub>2</sub> OS	76.4	5.7	6.6	7.5
Bun	E	<b>24</b>	EE	73	D	N	168 - 170	79.3	6.2	7.0	7.6	$C_{28}H_{26}N_2S$	79.6	6.2	6.6	7.6
Bui	Е	24	E	63	E	$\mathbf{P}$	222 - 224			7.0	7.4	C <sub>28</sub> H <sub>26</sub> N <sub>2</sub> S			6.6	7.6
n-C <sub>s</sub> H <sub>11</sub>	E	20	EA–EE	70	E-EE	$\mathbf{P}$	142 - 143			6.6	7.5	C <sub>22</sub> H <sub>28</sub> N <sub>2</sub> S			6.4	7.3
NN'-tetra- methylenebis	E	16	f	52	AC	Ν	218220			6.9	8.3	$C_{52}H_{42}N_4S_2$			7.1	8.1
Ph	С	20	EE	97	E-EE	N	244 - 245			6.6	7.4	C, H. N.S			6.3	7.2
PhCH,	Е	18	f	82	PR-D	N	159 - 161			6.1	7.0	C <sub>a1</sub> H <sub>a4</sub> N <sub>5</sub> S			6.1	7.0
PhCH,CH,	С	<b>24</b>	EA–D	64	$\mathbf{PR}$	Р	177 - 179			5.6	7.1	$C_{32}H_{26}N_{2}S$			6.0	6.8
$MeC_{6}H_{4}CH_{2}(p)$	С	20	A-EE	80	A-EE	Р	115—116	78.5	5.7	<b>5.5</b>	6.5	C <sub>32</sub> H <sub>26</sub> N <sub>2</sub> S, H <sub>2</sub> O	78.7	5.7	5.7	6.6
4-Picolyl	Е	16	Е	92	C–B	Р	140 - 142	<b>78.6</b>	5.1	9.0	6.7	C <sub>30</sub> H <sub>23</sub> N <sub>3</sub> S	78.8	5.1	9.2	7.0

• Solvent for reaction. • A = acetone, AC = acetic acid, B = benzene, C = chloroform, D = 1,4-dioxan, E = ethanol, EA = ethyl acetate, EE = diethyl ether, M = methanol, PR = n-propanol, T = tetrahydrofuran. • Solvent added to triturate gum. • Solvent for recrystallisation. • N = needles, P = prisms. <sup>J</sup> Product precipitated after evaporation of solvent.

TABLE 4

Pyrolysis of 1-substituted-2,4,6-triphenylpyridinium thiocyanates (10)

Pyridinium thiocy	ranate (10)			Pyrolysis		Yie		
R	Wt. (g)	Flux (g) <sup>a</sup>	$T(^{\circ}C)$	P[mmHg]	<i>t/</i> h	RSCN	R-N=C=S	Charactn.
Me	1.5	1.5	170	1	1.5	95	0	b, c, d
Et	1.6		166	1	1	90	5	c, d
Pr <sup>n</sup>	1.5	1.5	170	1	1.5	81	5	d, e
ICH.J.OH	1.7		185	0.1	1	67	0	d, f
Bun	2.2		168	0.5	1	87	5	c, d
Bui	1.5	1.5	170	1.5	1.5	87	4	d
n-C.H.,	1.0		170	1	1	82	6	d
PhCH	1.0	1.0	150	0.5	1	83	9	c, d, g
PhCH.CH.	1.0	1.0	180	0.5	1	65	30	<i>d</i> -
$MeC_{\bullet}H_{\bullet}CH_{\bullet}(\phi)$	1.0		150	0.5	1	84	7	d, h

<sup>a</sup> Weight of 2,4,6-triphenylpyridine used as flux. <sup>b</sup>  $n_{\rm D}^{17}$  1.4760, lit.,  $n_{\rm D}^{12.5}$  1.4764 (J. Hawthorne, J. Chem. Soc., 1906, 89, 562). <sup>c</sup> I.r. of product compared with i.r. of authentic sample (E. Lieber, C. N. R. Rao, and J. Ramachandran, Spectrochim. Acta, 1959, 13, 296). <sup>d</sup> I.r. and n.m.r. spectra compatible with assigned structure (see Table 5). <sup>e</sup> I.r. spectrum compared with i.r. of authentic isothiocyanate (G. L. Caldow and H. W. Thompson, Spectrochim. Acta, 1959, 13, 212). <sup>f</sup>  $n_{\rm D}^{22}$  1.4910, lit.,  $n_{\rm D}^{20}$  1.4981 (Z. J. Vejdělek, V. Trčka, and V. Vyšatová, Chem. Listy, 1954, 48, 685). <sup>g</sup> M.p. of thiocyanate 36 °C; lit., m.p. 36—38 °C; (L. Henry, Ber., 1869, 2, 638). <sup>k</sup> I.r. and n.m.r. spectrum of product compared with i.r. and n.m.r. of authentic sample (T. E. Parks and L. A. Spurlock, J. Org. Chem., 1973, 38, 3922).

## TABLE 5

Spectral data of alkyl thiocyanates (15) and isothiocyanates (16)

	I.r.	(film)	<sup>1</sup> H N.m.r. in CCl <sub>4</sub> ( <b>§</b> , p.p.m.)								
R	$(\mathrm{cm}^{-1})$	$(\mathrm{cm}^{-1})$	-CH-SCN	CH-NCS	Other						
Me	2 0755	• •	2.6 (s)								
Et	2 160s	2.080w	2.9 (2 H. a. 17 Hz)	3.4 (g, 17 Hz)	1.5 (3 H, t, / 7 Hz)						
Pr <sup>n</sup>	2 140s	2 100w, 2 060w	2.9 (2 H, t, J 7 Hz)	3.4 (t, $J$ 7 Hz)	1.1 (3 H, t, $J$ 7 Hz); 1.5–2.2 (2 H, sextet)						
[CH <sub>2</sub> ] <sub>3</sub> OH	2 140s		2.9—3.4 (2 H, m)		1.8 - 2.3'(2 H, m); 3.6 - 3.9 (2 H, m) [2.9 - 3.4 (1 H, m)]						
Bun	2 160s	2 100w	2.9 (2 H. t. / 6 Hz)	3.5 (2 H. t. / 6 Hz)	1.1-2.1 (4 H, m); $0.8-1.1$ (3 H, m)						
Bui	2 150s	2 100	2.9 (2 H, d, J 6 Hz)	3.35 (d, J 6 Hz)	1.5—2.3 (1 H, septet) 1.1 (6 H, d, <i>I</i> 6 Hz)						
n-C.H.,	2 150s	2 100	2.9 (2 H. t. / 7 Hz)	3.4 (t. $I 7$ Hz)	2.1 - 1.1 (6 H, m), $1.1 - 0.7$ (3 H, m)						
PhCH	2 140s	2 080	4.05 (2 H. s)	<b>4.6</b> (s)	7.3 (5 H, s)						
PhCH <sub>2</sub> CH <sub>2</sub>	2 070s	2 090, 2 050	3.0 (4 H, s) <sup>a</sup>	3.4 (2 H, t, J 6 Hz) ª	7.2 (5 H, s)						
$MeC_6H_4CH_2(p)$	2 150s	2 040	4.05 (2 H, s)	<b>4.5</b> (s)	7.2 (4 H, s) 2.3 (3 H, s)						

<sup>a</sup> The four methylene protons of  $PhCH_2CH_2SCN$  absorb as a singlet at 3.0 p.p.m. The small triplet at 3.0 p.p.m., due to the methylene protons in  $PhCH_2CH_2NCS$ , overlaps with the singlet at 3.0 p.p.m.

thiocyanates in 81–95% yield (Table 4): only for 2phenylethyl thiocyanate was the yield appreciably lower (65%) due to the formation of a sizeable amount of isothiocyanate (16) (30%). Pyrolysis of the 1-phenyl derivative failed to yield phenyl thiocyanate. In some pyrolyses, 2,4,6-triphenylpyridine was used as a flux to reduce the m.p. of the mixture to 150–180 °C.

Most of the thiocyanates prepared contained small quantities (up to 5%) of the corresponding isothiocyanate, as determined by n.m.r. spectroscopy (Table 5) and v.p.c. analysis. The products were characterised by spectral data (Table 5) and by comparison with literature data.

Conclusions.—The only previously reported general methods for direct replacements of amino-groups by S-linked functionality have been restricted to diazotisable aromatic amines:  $ArN_2^+$  is converted into  $ArSCSOEt,^{11}$  or  $ArSSAr.^{12}$  Kröhnke <sup>13</sup> reported the reaction of the pyridinium derivative (17) with potassium xanthate to give the bisxanthate (18). Treatment of the *o*-hydroxybenzylammonium cations (19) gave the cyclic thiocarbamate (20).<sup>14</sup>

The presently described methods constitute efficient and useful general conversions of primary aliphatic amines into S-linked functional groups which fill a previous gap in synthetic methods.





EXPERIMENTAL

Preparation of Pyridinium Perchlorates (3).—2,4,6-Triphenylpyrylium perchlorate <sup>15</sup> (ca. 10 mmol) and an equimolar amount of the corresponding amine were stirred in EtOH (50 ml) at room temperature for 8—12 h. The solvent was then evaporated under reduced pressure, and the pyridinium perchlorate (3) was washed with Et<sub>2</sub>O, filtered, and crystallised from EtOH.

Preparation of S-Alkyl O-Ethyl Dithiocarbonates (6; R' = Et) from Potassium Ethyl Xanthate (4; R' = Et) and

Pyridinium Perchlorates (3).—Method A. The appropriate pyridinium perchlorate (3) (ca. 5 mmol) and potassium ethyl xanthate (ca. 7 mmol) were refluxed in EtOH (30 ml) for 2 h. After cooling, the precipitated 2,4,6-triphenylpyridine and the potassium perchlorate formed were removed by filtration and the yellow filtrate evaporated under reduced pressure. The remaining oil was extracted with Et<sub>2</sub>O (50 ml), and the ethereal extracts washed with water and dried (MgSO<sub>4</sub>). Evaporation of the Et<sub>2</sub>O yielded the crude S-alkyl O-ethyl dithiocarbonate (6;  $\mathbf{R}' = \mathbf{Et}$ ) which was slightly contaminated with 2,4,6-triphenylpyridine. The product was purified by column chromatography (silica 60, elution with n-hexane).

Method B. The appropriate pyridinium perchlorate (3) (ca. 5 mmol) and potassium ethyl xanthate (ca. 7 mmol) were refluxed in benzene (50 ml) for 4-6 h. After cooling the solution was filtered and the filtrate evaporated under reduced pressure. Addition of cold EtOH (30 ml) to the residue, followed by filtration, eliminated 2,4,6-triphenylpyridine from the mixture. The ethanolic filtrate was evaporated under reduced pressure, the remaining oil extracted with 50 ml of Et<sub>2</sub>O, and the extracts washed with water and dried (MgSO<sub>4</sub>). Evaporation of the solvent yielded the crude product (6) which was purified as above, in A.

Preparation of OS-Dimethyl Dithiocarbonate.—Well mixed dry N-methyl-2,4,6-triphenylpyridinium tetra-fluoroborate <sup>16</sup> (8; R = Me) (2.0 g, 4.9 mmol) and dry potassium methyl xanthate (4; R' = Me) (1.0 g, 6.8 mmol) were heated in a distillation apparatus at 130—140 °C under reduced pressure (1—3 mmHg) for ca. 1 h. The OS-dimethyl dithiocarbonate (0.42 g, 70% yield) distilled out of the reaction mixture and was collected in a trap cooled with liquid nitrogen. The product was characterised by comparison with the n.m.r. and i.r. spectra of an authentic sample, prepared from potassium methyl xanthate and methyl iodide.

Preparation of 2,4,6-Triphenylpyrylium Thiocyanate (9) (cf. ref. 10).—The pseudo-base (6.5 g, 20 mmol), obtained from 2,4,6-triphenylpyrylium perchlorate by treatment with NaOAc, was dissolved in boiling 95% EtOH (80 ml). To this solution was added aqueous ammonium thiocyanate (15 g in 15 ml of water) and hot 1N-sulphuric acid (200 ml). A red solid started to precipitate. The solution was cooled, filtered, and the red crystals washed with water (2  $\times$  50 ml) and Et<sub>2</sub>O (3  $\times$  40 ml). The product (6.8 g, 93%) was crystallised from HOAc to give red needles, m.p. 189—191 °C (lit.,<sup>10</sup> m.p. 192 °C).

General Procedure for the Preparation of Pyridinium Thiocyanates (10) (Table 3).—The amine (10 mmol) was stirred at 20 °C with 2,4,6-triphenylpyrylium thiocyanate (9) (10 mmol) in either EtOH or CHCl<sub>3</sub> (see Table 3) (30 ml) for the appropriate time. The solvent was then evaporated at 60 °C at 20 mmHg and the residue triturated with an appropriate solvent (see Table 3) until crystallisation. The crude pyridinium thiocyanate was recrystallised (see Table 3).

Preparation of Alkyl Thiocyanates (15) from the Pyridinium Thiocyanates (10).—The dry pyridinium thiocyanate (10) (ca. 3 mmol) and an equal weight of 2,4,6-triphenylpyridine were heated for 1—1.5 h in a distillation apparatus under reduced pressure (0.5—1.5 mmHg). The alkyl thiocyanate (15) was collected in a trap, cooled with liquid nitrogen, and characterised by i.r. and n.m.r. spectroscopy. The proportion (5—10%) of the admixed corresponding isothiocyanate (16) was determined by n.m.r. integration of the peaks of the methylene protons CH<sub>2</sub>SCN and CH<sub>2</sub>NCS, and also by gas chromatography.

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