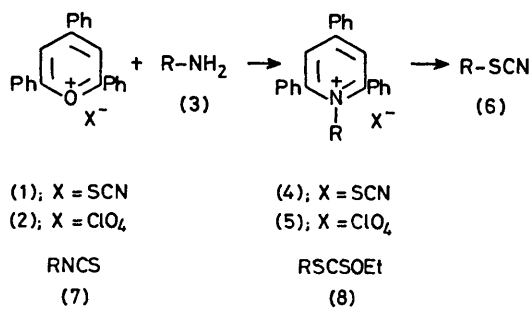


## Conversion of Primary Aliphatic Amines into Thiocyanates and Thiocarbonate Esters<sup>1</sup>

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**Summary** 2,4,6-Triphenylpyrylium thiocyanate converts primary aliphatic amines into 1-substituted-2,4,6-triphenylpyridinium thiocyanates which smoothly pyrolyse to 2,4,6-triphenylpyridine and the corresponding alkyl thiocyanate; 1-substituted-2,4,6-triphenylpyridinium perchlorates give *S*-alkyl *O*-ethyl dithiocarbonates with potassium ethyl xanthate.

salts (4) forms 2,4,6-triphenylpyridine and the corresponding alkyl thiocyanate (6), in excellent yield, and with only low proportions of the isothiocyanate isomers (7)



No general synthetically useful procedure has been previously reported for the conversion of aliphatic amines into *S*-linked functional groups. We now find that readily available<sup>2</sup> crystalline 2,4,6-triphenylpyrylium thiocyanate (1) reacts with alkyl and aralkyl primary amines (3) to give 1-substituted-2,4,6-triphenylpyridinium thiocyanates (4) in high yield (Table 1).<sup>†</sup> Gently heating the pyridinium

<sup>†</sup> Satisfactory analytical data were obtained for all new compounds.

TABLE I

Preparation and pyrolysis of 1-substituted-2,4,6-triphenylpyridinium thiocyanates (4)<sup>a</sup>

R in (4) and (6)	Preparation of (4)		Pyrolysis of (4)			Yields (%)	
	Yield (%)	M.p. (°C)	Temp. (°C)	Pressure (mmHg)	Time (h)	RSCN	RNCS
Methyl .. .. .	75	183—184	170	1	1.5	95	0
Ethyl .. .. .	72	165—167	166	1	1	90	5
n-Propyl .. .. .	64	140—141	170	1	1.5	81	5
n-Butyl .. .. .	86	168—170	168	0.5	1	87	5
i-Butyl .. .. .	63	222—224	170	1.5	1.5	87	4
3-Hydroxypropyl .. .. .	81	183—185	184	0.1	1	67	—
n-Pentyl .. .. .	70	142—143	170	1	1	82	6
Phenylethyl .. .. .	64	177—179	180	0.5	1	65	30
Benzyl .. .. .	82	159—161	150	0.5	1	83	9
4-Picolyl .. .. .	92	140—142	—	—	—	—	—

<sup>a</sup> Compounds (4) were prepared by reaction of equimolar amounts of (1) with the corresponding amine (3) in chloroform or ethanol solvent.

TABLE 2

Reaction of *N*-substituted-2,4,6-triphenylpyridinium perchlorates (5) with potassium ethyl xanthate

R in (5)	Solvent	Time (h)	Yield of RSCSOEt %
Me	C <sub>6</sub> H <sub>6</sub>	5	40 <sup>a</sup>
Et	C <sub>6</sub> H <sub>6</sub>	4	64 <sup>a</sup>
Bu <sup>n</sup>	C <sub>6</sub> H <sub>6</sub>	4	80 <sup>a</sup>
PhCH <sub>2</sub>	EtOH	2	73 <sup>b</sup>
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	EtOH	2	84 <sup>a</sup>
<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	EtOH	2	88 <sup>c</sup>
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	EtOH	2	81 <sup>a</sup>

<sup>a</sup> Identical by i.r. 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 including Qualitative Organic Analysis,' 3rd edn., Longmans, London, 1956, p. 499). <sup>b</sup>  $n_D^{25} = 1.6007$ , lit.,  $n_D^{20} = 1.5952$  (C. Djerassi, M. Gorman, F. X. Markley, and E. B. Oldenberg, *J. Amer. Chem. Soc.*, 1955, **77**, 568). <sup>c</sup>  $n_D^{25} = 1.5963$ , lit.,  $n_D^{20} = 1.5960$  [N. N. Mel'nikov, A. F. Prokof'eva, T. P. Krylova, N. A. Popovkima, N. N. Khrorostukhina, and I. L. Vladimirova, *Khim. Org. Soedin. Fosfora, Akad. Nauk. S.S.S.R., Otd. Obshch. Tekh. Khim.*, 1967, 256 (*Chem. Abs.*, 1968, **69**, 2627h)].

<sup>1</sup> Cf. the series 'Heterocycles in Organic Synthesis,' for Part XIII see B. J. Graphakos, A. R. Katritzky, and G. Lhommet, *J.C.S. Perkin I*, in the press.

<sup>2</sup> A. T. Balaban and M. Paraschiv, *Rev. Roumaine Chim.*, 1974, **19**, 1731.

<sup>3</sup> A. T. Balaban and C. Toma, *Tetrahedron*, Suppl. 7, 1966, 1.

<sup>4</sup> Cf. D. S. Tarbell and D. K. Fukushima, *Org. Synth.*, 1955, Col. Vol. III, 809.

<sup>5</sup> C. F. H. Allen and D. D. MacKay, *Org. Synth.*, 1943, Col. Vol. II, 580.

(Table 1). This method compares favourably with procedures commencing from halide and thiocyanate salts which can give significant quantities of the isothiocyanate isomer.

*N*-Alkyl-2,4,6-triphenylpyridinium perchlorates (5) (readily available from the primary amines and 2,4,6-triphenylpyrylium perchlorate<sup>3</sup>), when heated to reflux in benzene with potassium ethyl xanthate, give moderate to good yields of the corresponding *S*-alkyl *O*-ethyl dithiocarbonate (8) (Table 2). The corresponding *N*-benzyl perchlorates (5) react more readily and ethanol is satisfactory as solvent: good yields of the *S*-benzyl *O*-ethyl dithiocarbonates (8) are obtained (Table 2).

The foregoing synthetic procedures complement those available in the aromatic amine series *via* diazotization<sup>4,5</sup> and allow the conversion of primary alkyl and aralkyl amines into a variety of *S*-linked substituents.

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