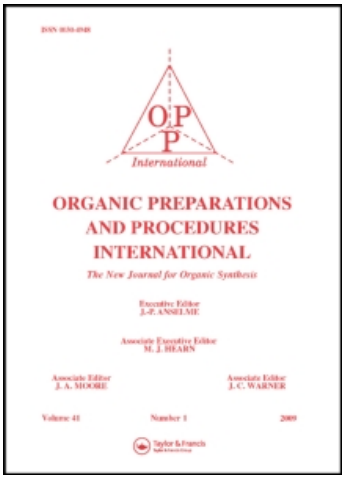

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AN ALTERNATIVE TO THE LEUCKART METHOD FOR THE CONVERSION OF PRIMARY AMINES INTO THIOLS

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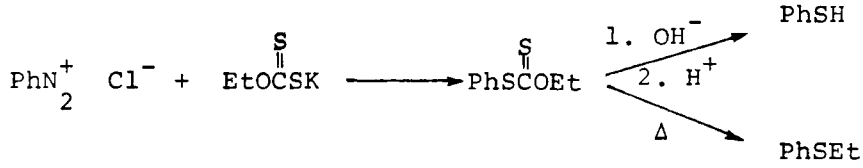
The Leuckart[1] method involves the decomposition of diazoxanthates by gentle warming (70°) in weakly acidic cuprous media to the corresponding aryl xanthates, which afford arylthiols on alkaline hydrolysis and aryl thioethers on warming.[2] The action of alkyl halides on potassium xanthate yields xanthate esters which can be purified by distillation. Alkali al-

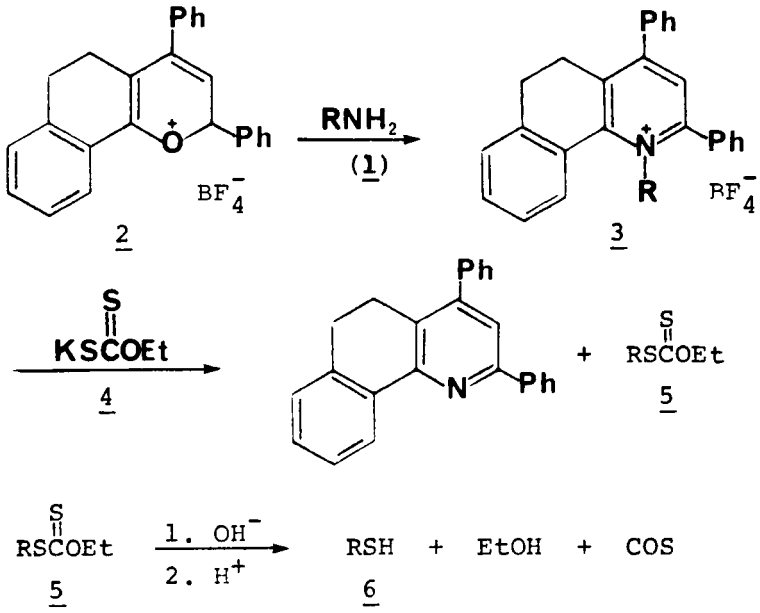


koxides decompose these xanthates to mercaptans, an alcohol and salts of the alkylthiocarbonic acid;[3] xanthates can also be reduced in excellent yields to mercaptans by lithium aluminium hydride.[4] In a previous article,

various procedures for the conversion of primary amines into fatty-acid esters,[5] and N-piperidine derivatives were investigated.[6] It was found that N-alkyl- or N-arylpyridinium salts could be converted to potassium ethyl xanthate with the formation of xanthogenates. We now report the conversion of primary amines to sulfur-linked functions.

The 1-substituted 5,6-dihydro-2,4-diphenylnaphtho[1,2-b]pyridinium

tetrafluoroborates (3) were prepared by standard methods (Table 1) from the amines (1) and the tricyclic pyrylium cation (2).[6,7] The N-alkyl and N-benzyl substituted pyridinium tetrafluoroborates were best prepared at 30°



a) R = CH_3 b) R = C_2H_5 c) R = CH_2=$CHCH_2$

d) R = $CH_3(CH_2)_2CH_2$ e) R = C_6H_5 f) R = p-$CH_3C_6H_4$

g) R = $C_6H_5CH_2$ h) R = $C_6H_5CH_2CH_2$ i) R = p-$CH_3OC_6H_4CH_2$

j) R = p-$ClC_6H_4CH_2$ k) R = 2-pyridyl l) R = 4-pyridyl

and the N-aryl analogues at reflux in methanol. These compounds (3) were characterized by their elemental analysis and spectral data;their IR-spectra show the typical tetrafluoroborate peak at 720-700 cm^{-1} and characteristic ring-stretching bands at 1630-1620 and 1600-1570 cm^{-1} for the pyridinium cation. Proton H_B is highly shielded in the aryl derivatives but not for the N-butyl compounds (3d), as expected. The pyridinium ring-proton H_A is deshielded due to the ring currents of the 2- and 4-phenyl groups but is relatively unaffected by the nature of the N-substituent. The $-CH_2-CH_2$ signal remains relatively constant for aryl N-substituents. In the N-

TABLE 1. 1-Substituted 5,6-Dihydro-2,4-Diphenylnaphtho[1,2-b] Pyridinium Tetrafluoroborates (3)

Cpd	mp[a] (°C)	Yield (%)	Elemental Analysis			NMR(δ) ArH	-CH_2-CH_2-	Alkyl
			C	H	N			
3a	156	70	71.76 (71.92)	5.06 (5.00)	3.22 (3.07)	7.5(14H,s), 5.8(1H,m)	2.7-3.1 (4H,s)	2.3-2.9 (3H,s)
3b	122	74	72.19 (72.29)	5.35 (5.30)	3.12 (3.19)	7.8(14H,s), 5.7(1H,m)	2.9-3.2 (4H,s)	4.3-4.7 (2H,t),2.2 -2.8(3H,m)
3c	164	67	72.92 (72.74)	5.21 (4.98)	3.04 (3.09)	7.3(14H,s), 5.7(1H,m)	2.8-3.2 (4H,s)	4.9(5H,m)
3d	98	66	72.99 (73.16)	5.87 (5.63)	2.94 (2.78)	7.4-8.0 (15H,m)	2.8-3.2 (4H,s)	4.5-4.9(2H, t),0.5-1.7 (7H,m)
3e	274	90	74.88 (74.92)	4.83 (4.60)	2.82 (2.57)	7.1-7.9(19H, m),6.1-6.4 (1H,m)	2.3-3.1 (4H,s)	
3f	296	93	75.18 (74.96)	5.09 (4.98)	2.74 (2.76)	7.1-8.4 (19H,m)	2.6 (4H,s)	2.7(3H,s)
3g	193	91	75.18 (75.04)	5.09 (5.07)	2.74 (2.79)	6.8-7.9(19H, m),6.3-6.6 (1H,d)	2.7-3.4 (4H,s)	3.8(2H,s)
3h	242	80	75.46 (75.26)	5.34 (5.08)	2.67 (2.82)	7.5(20H,m)	2.6(4H,b)	6.8(2H,s) 5.5(2H,s)
3i	196	85	73.22 (73.46)	5.18 (5.34)	2.59 (2.36)	7.1-8.5 (19H,m)	2.6-3.5 (4H,s)	4.9(2H,s), 2.8(3H,s)
3j	190	82	70.42 (70.03)	4.58 (4.45)	2.57[b] (2.59)	6.5-7.9(18H, m),5.8-6.1 (1H,m)	2.3-2.8 (4H,s)	3.8(2H,s)
3k	258	70	72.32 (72.75)	4.62 (4.34)	5.62 (5.41)	7.9-8.5(2H, m),6.1-6.5 (2H,m)	2.4-3.0 (4H,s)	
3l	256	76	72.32 (72.45)	4.62 (4.51)	5.62 (5.77)	6.9-7.8(19H, m)	2.6-3.1 (4H,s)	

a) Crystallized from 2-propanol. b) Calcd.: Cl,6.51; Found, Cl, 6.58.

(2-pyridyl)pyridinium compound 3k, two protons appear at δ 7.9 and the other two-protons appear at δ 6.5.

TABLE 2. Representative nmr Spectral Data of Xanthates (5).[a,b]

R	Yield	O-Et		S-R	
	(%)	CH_3	CH_2	α-H	other-H
5a	43	1.6	4.8	3.7(3H,s)	
5b	60	1.8	4.9	3.5(2H,q)	1.4(3H,t)
5d	70	1.7	4.8	3.4(2H,m)	1.7(10H,m)
5e	73	1.5	4.9	4.6(2H,s)	7.6(5H,s)
5i	85	1.6	4.9	4.7(2H,s)	7.2(2H,d),7.5 (2H,d),3.8(3H,s)
5j	80	1.6	4.8	4.7(2H,s)	7.5(4H,s)

a) Identical by spectral comparison and physical constants with authentic samples.[8,9,14]

b) Ppm on δ scale from internal TMS at 60 MHz in $CDCl_3$.

Potassium alkyl xanthates (4), obtained from the corresponding potassium alkoxide and carbon disulphide with the N-alkylpyridinium salts (3), underwent nucleophilic substitution to yield the corresponding O-ethyl-S-alkyl dithiocarbonates (5) in moderate to good yield in refluxing acetone (Table 2). The only previously reported general methods for direct replacements of amino-groups S-linked functionality have been restricted to diazotizable aromatic amines. ArN_2^+ is converted into ArSC(S)OEt[8] or ArSSAr.[9] The present method constitutes efficient, safe and general conversion of primary aliphatic and aromatic amines into S-linked functional groups.

EXPERIMENTAL SECTION

IR and nmr spectra were measured with Perkin Elmer 237 and R 12 (60 MHz) instruments (TMS as internal standard). Mps. are uncorrected and were determined using Gallenkamp melting point apparatus.

Preparation of Pyridinium tetrafluoroborates (3).- The pyrylium tetrafluoroborate[7] (20 mmol) and the primary amine (25 mmol) were stirred in methanol

(30 ml) to give the pyridinium tetrafluoroborates as colourless crystalline solid which were crystallized from isopropyl alcohol (Table 1).

Preparation of Xanthates (5).- A mixture of 20 mmol of N-substituted pyridinium tetrafluoroborates (3) and potassium ethylxanthate (4, 30 mmol) was refluxed in acetone (50 ml) over a period of 3 hrs. After filtration of potassium tetrafluoroborate and evaporation of the solvent, the residue was treated with cold dil. hydrochloric acid (20% v/v) to pH 1 to dissolve 5,6-dihydro-2,4-diphenylnaphtho[1,2-b]pyridine. The resulting reaction mixture was extracted with ether (100 ml, three times). The ethereal extracts were washed with water and dried ($MgSO_4$). Evaporation of the ether yielded the crude S-alkyl-O-ethyl dithiocarbonate (5) which was purified by distillation under reduced pressure; alternatively it was hydrolyzed directly to the corresponding mercaptans. In the case of 2- or 4-mercaptopyridines (6k and 6l), the residue was treated with formamide (20 ml) to dissolve 5,6-dihydro-2,4-diphenylnaphtho[1,2-b]pyridine after removal of potassium tetrafluoroborate and evaporation of the solvent. The residual product could be hydrolyzed directly to 2- or 4-mercaptopyridines which would then be separated and purified.

Preparation of Mercaptans.- The xanthate ester (60 mmol) was refluxed in a solution of sodium ethoxide in absolute ethyl alcohol (60 ml., 10% w/v) with efficient stirring for 2 hrs. The reaction mixture was acidified with conc. hydrochloric acid and the mercaptan was extracted with ether and the organic layer was washed with water, dried over sodium sulphate and evaporated. The crude mercaptans were isolated by distillation (Table 3) and identified by comparison of their physical constants with those of authentic samples.

TABLE 3. Yields and Physical Constants of Xanthates (5)[a] and of Mercaptans (6).

R	RSC(S)OEt(5) Yield (%)	bp. (°C)	D_4^t	n_D^t	RSH(6) Yield (%)	bp. (°C)	n_D^t	Ref.
a	43	184	1.1189(25°)					10
b	60	200	1.0865(19°)	1.5370 (18°)	70	36	1.4270 (25°)	10,11
c	62	230			65	68	0.925(23°)	12
d	70	270			60	97	1.4401(25°)	13
e					72	169	1.5880(20°)	14
f					71	195		13
g	73	147/4mm		1.6007(21°)	76	194	1.5751(20°)	4
h	80	163/3mm			85	95/3mm	1.5816(20°)	4
i	80	108/ 0.1mm	1.180(20°)	1.5960(20°)	78	90/ 0.5mm	1.573(20°)	15
j					82	202	1.5893(20°)	16
k					63	128/C_6H_6 (mp.)		17
l					58	177/C_6H_6 (mp.)		18

a) Refractive indices were determined by use of an Abbé type refractometer with water-jacketed prisms.

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