Heterocycles in Organic Synthesis. Part 13.[1] The Reaction of 2,4-Diphenylthiopyrylium Perchlorate with Amines

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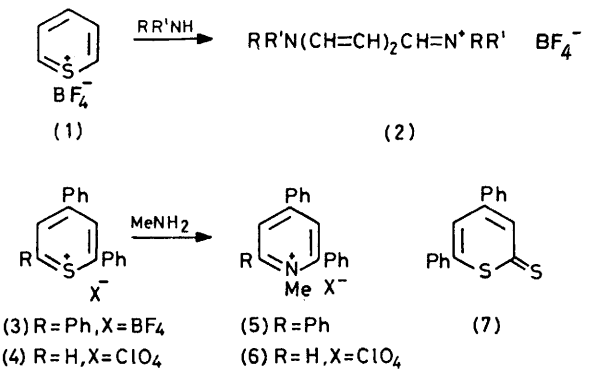
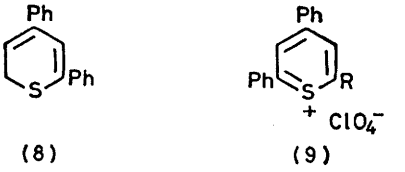
The title cation abstracts hydride from aliphatic amines yielding the corresponding thiopyran: with methylamine some pyridinium cation is also found. With aniline, and its *N*- and ring-substituted and hetero-analogues, fair yields of novel thiopyrylium dyes are obtained.

THE reaction of primary amines with pyrylium salts has been extensively investigated as a means of converting the amino-function into a good leaving group, and thus replacing it by other functionality.[2] Pyrylium cations with free α-positions are easily hydrolysed,[3] and we therefore considered the use of the analogous thiopyrylium salts. Previous reports of reaction of amines with non-functionalized thiopyrylium cations are sparse: the parent (1) reacts with various primary or secondary amines to give open-chain cations (2),[4] and 2,4,6-triphenylthiopyrylium tetrafluoroborate (3) gives the pyridinium salt (5) with methylamine, but does not react with aromatic amines.[4]



2,4-Diphenylthiopyrylium perchlorate (4) is readily available in quantity by the oxidation of the thiopyran-2-thione (7):[5] it reacts with methylamine to give 12—18% of the pyridinium perchlorate (6) (which showed the expected spectroscopic properties), together with 45% of a highly insoluble compound, the analysis for which was consistent with its formulation as 4,6-diphenyl-2*H*-thiopyran (8), but which may be an oligomer of this structure. Because of insolubility and non-volatility,



n.m.r. and mass spectra were unavailable; the i.r. was uninformative. However, perchloric acid in acetic acid reconverted (8) into the perchlorate (4) in 78% yield. The same thiopyran (8) was obtained from the perchlorate (4) by reaction with triethylamine, ethylamine, and benzylamine in yields of 72, 18, and 12%. In these reactions the thiopyrylium cation is acting as a hydride abstractor, but attempts to use this property in synthetically useful applications were unrewarding.[6]

2,4-Diphenylthiopyrylium perchlorate (4) reacts with aromatic amines to form the novel thiopyrylium dyes (9): fair to moderate yields are obtained with aniline, *N*-methylaniline, ring substituted anilines, and pyridylamines (Table 1). The dyes show strong absorption in their u.v.–visible spectra at 560—600 and 350—370 nm, except for the pyridyl derivatives for which these bands occur at *ca.* 425 and 300 nm (Table 2). In the n.m.r. spectrum, the 3-H and 5-H protons in the thiopyrylium ring give two peaks between δ 8.3 and 8.8 (Table 2) and show a very slight *meta*-coupling.

TABLE 1

Reactions of 2,4-diphenylthiopyrylium perchlorate with aromatic amines

R	Solvent for recrystallisation	Yield (%)	Crystal form	M p (°C)	Found (%) C	H	N	Formula	Required (%) C	H	N
4-$H_2NC_6H_4$	EtOH–$CHCl_3$	52	Blue needles	160—162	62.2	4.1	3.4	$C_{23}H_{18}ClNO_4S\cdot0.75H_2O$	62.3	4.4	3.2
4-MeNHC_6H_4	EtOH–$CHCl_3$	58	Blue needles	206—208	63.0	4.6	3.3	$C_{24}H_{20}ClNO_4S\cdot0.25H_2O$	62.9	4.5	3.1
3-Me-4-$H_2NC_6H_3$	EtOH–$CHCl_3$	41	Blue needles	249—250	62.9	4.6	3.0	$C_{24}H_{20}ClNO_4S\cdot0.25H_2O$	62.9	4.5	3.1
2-Me-4-$H_2NC_6H_3$	EtOH–$CHCl_3$	65	Blue needles	165—168	63.6	4.7	3.2	$C_{24}H_{20}ClNO_4S$	63.5	4.4	3.1
3-MeO-4-$H_2NC_6H_3$	EtOH–$CHCl_3$	60	Blue needles	247—248	60.9	4.7	3.0	$C_{24}H_{20}ClNO_5S$	61.3	4.3	3.0
2-MeO-4-$H_2NC_6H_3$	EtOH–$CHCl_3$	63	Blue needles	164—165	61.2	4.4	2.6	$C_{24}H_{20}ClNO_5S$	61.3	4.3	3.0
2-Cl-4-$H_2NC_6H_3$	EtOH–$CHCl_3$	67	Purple needles	170—172			2.4	$C_{23}H_{17}Cl_2NO_4S\cdot H_2O$			2.8
6-H_2N-3-pyridyl	EtOH	42	Green needles	279—280	59.4	4.0	5.9	$C_{22}H_{17}ClN_2O_4S\cdot H_2O$	59.7	4.3	6.3
4-Me-6-H_2N-3-pyridyl	EtOH	48	Green-yellow needles	255—256	60.2	4.2	6.0	$C_{23}H_{20}ClN_2O_4S$	60.6	4.4	6.1
4-$Me_2NC_6H_4$	EtOH	49	Blue needles	283—285*	64.2	4.7	3.0	$C_{25}H_{22}ClNO_4S$	64.2	4.7	3.0

* Lit., 265—266 °C (R. Wizinger and P. Ulrich, *Helv. Chim. Acta*, 1956, **39**, 215).

TABLE 2

Spectroscopic data for 2-aminoaryl-4,6-diphenylthiopyrylium perchlorates

R	$\lambda_{max.}$/cm^{-1}	log ε (l mol^{-1} cm^{-1})	^{1}H n.m.r.: δ (p.p.m. at 60 MHz) 3-H	5-H
4-$H_2NC_6H_4$	584 (4.21)	367 (4.27)	8.67	8.49
4-MeNHC_6H_4	596 (4.32)	368 (4.38)	8.49	8.31
3-Me-4-$H_2NC_6H_3$	588 (4.19)	366 (4.28)	8.78	8.62
2-Me-4-$H_2NC_6H_3$	566 (4.16)	356 (4.17)	8.78	8.62
3-MeO-4-$H_2NC_6H_3$	588 (4.19)	366 (4.23)	8.67	8.49
2-MeO-4-$H_2NC_6H_3$	566 (4.16)	356 (4.17)	8.68	8.52
2-Cl-4-$H_2NC_6H_3$	588 (4.06)	367 (4.52)	8.49	8.31
6-H_2N-3-pyridyl	425 (3.38)	302 (3.54)	8.50	8.34
4-Me-6-H_2N-3-pyridyl	424 (3.36)	298 (3.48)	8.69	8.51
4-$Me_2NC_6H_4$	610 (4.49)	378 (4.41)	8.52	8.41

EXPERIMENTAL

The i.r. spectra were taken with a Perkin-Elmer model 125 spectrophotometer as Nujol mulls and as bromoform solutions. N.m.r. spectra at 100 and 60 MHz were taken with Varian HA 100 and Perkin-Elmer R12 instruments ($SiMe_4$ as internal standard). Mass spectroscopy measurements were carried out on a Perkin-Elmer–Hitachi RMU21 spectrometer with 70V ionizing potential. M.p.s were determined using a Kofler hot-stage microscope.

2,4-Diphenylthiopyrylium Perchlorate.—Hydrogen peroxide (30%, 34 ml) was added to 4,6-diphenylthiopyran-2-thione (4,6-diphenyl-α-dithiopyrone [7]) (16.8 g, 0.06 mol) suspended in HOAc (680 ml) and the mixture maintained at 40 °C. After 2 h, 70% $HClO_4$ (21 ml) was added and the volume reduced to 50% at 40 °C/15 mmHg. Ether (300 ml) was added: yellow needles of 2,4-diphenylthiopyrylium perchlorate separated and were recrystallized from HOAc containing 1% $HClO_4$ (15.7 g, 75%), m.p. 156—157 °C (lit.,[5] m.p. 155—156 °C, 66%).

1-Methyl-2,4-diphenylpyridinium Perchlorate and 4,6-Diphenyl-2H-thiopyran.—Methylamine (0.62 g) in ethanol (5 ml) was added to 2,4-diphenylthiopyrylium perchlorate (1 g) in ethanol (10 ml). The mixture was refluxed for 2 h, and the solid which separated (A) was filtered off. Ether (30 ml) was added to the filtrate to give *1-methyl-2,4-diphenylpyridinium perchlorate* which crystallized from methanol as needles (0.12 g, 12%), m.p. 154—155 °C (Found: C, 62.7; N, 3.8; H, 4.7. $C_{18}H_{16}ClNO_4$ requires C, 62.5; N, 4.0; H, 4.6%); $\nu_{max.}$ 1 630 cm^{-1} (C=N); δ($CDCl_3$) 9.05 (1 H, d, H-6), 8.4—7.5 (12 H, m, Ar), 6.1 (3 H, s, NMe). In $HCONMe_2$ as solvent the yield was 18%.

The insoluble solid (A) filtered from the hot reaction mixture was *4,6-diphenyl-2H-thiopyran* (0.32 g, 45%) and it crystallized from chloroform as yellow needles, m.p. 219—220 °C (Found: C, 81.5; H, 5.2; S, 12.9. $C_{17}H_{14}S$ requires C, 81.6; H, 5.6; S, 12.8%); $\nu_{max.}$ 760 cm^{-1}.

Preparation of 5-Mercapto-3,5-diphenylpenta-2,4-dienylideneammonium Perchlorates.—2,4-Diphenylthiopyrylium perchlorate (1 g, 2.87 mmol) and the amine (5.74 mmol) were heated in ethanol (10 ml) at 40—45 °C. The deep blue reaction mixture was stirred for 2 h and then kept at 20 °C: the dye then separated, for details see Table 1.

In the reactions with 2-aminopyridine and 2-amino-4-methylpyridine, the yields were increased by adding Et_2O to the filtrate, removing the separated 2-aminopyridinium perchlorate, and evaporating the solvent. The residue was treated with perchloric acid (0.3 ml) in chloroform to give more product.

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