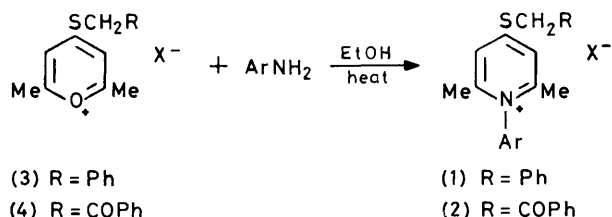


The Reaction between 4-Methoxy-2,6-dimethylpyrylium Perchlorate and Amines. Isolation of Both 4-Iminopyran† Salts and Pyridinium Salts in the Reaction with Primary Amines

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Both 4-aryliminio-2,6-dimethylpyran salts (5)† and 1-aryl-4-methoxy-2,6-dimethylpyridinium salts (13) can be isolated from the reaction between 4-methoxy-2,6-dimethylpyrylium perchlorate (12) and aromatic primary amines, the ratio of products depending upon the basicity of the amine. Separation of the mixture by conversion of the iminiopyran salts into the hitherto unknown 4-arylimino-2,6-dimethylpyrans (6) is described. Secondary aromatic amines studied gave only 2-(2,6-dimethylpyran-4-ylidenemethyl)-4-methoxy-6-methylpyrylium perchlorate (18), and the well-known reaction with methylamine was found to give an additional product not previously recorded, 2,6-dimethyl-4-methyliminiopyran perchlorate (21m) in 21% yield. I.r., ¹H n.m.r., and mass spectra of iminiopyran salts, iminopyrans, and pyridinium salts are discussed.

WHILE attempting to prepare pyridinium salts [(1), (2)] from pyrylium salts [(3), (4)] by the method of King and his co-workers¹ (Scheme 1), we observed that the course of the reaction depended on the nature of the aromatic amine. Aniline in refluxing 95% ethanol gave, respectively, compounds (1f) and (2f), but *p*-nitroaniline under the same conditions gave a product containing no sulphur, which proved in both cases to be the iminiopyran salt (5a), readily convertible into the iminopyran (6a) on treatment with sodium hydrogen carbonate. Dibenzyl disulphide and 2,5-diphenyl-1,4-dithiin (7),² respectively, were isolated from the reaction mixtures, confirming that the thioether side chains had been displaced. The reaction between the pyrylium salt (3) and *p*-nitroaniline in dry acetonitrile, however, gave the expected pyridinium salt (1a).



SCHEME 1

Iminopyran salts of types (8) and (9) have been described several times,³⁻¹³ though only one example of type (9) derived from a primary aliphatic amine ($R^1 = Pr^1$, $R^2 = H$)¹³ and none derived from a primary aromatic amine (9; $R^1 = Ar$, $R^2 = H$) has been re-

† X-Ray crystallographic data (see ref. 18) indicate that these compounds should be named as iminiopyran salts and not, as is the usual practice, aminopyrylium salts.

¹ L. C. King, F. J. Ozog, and J. Moffat, *J. Amer. Chem. Soc.*, 1951, **73**, 300.

² T. B. Johnson, R. C. Moran, and E. F. Kohman, *J. Amer. Chem. Soc.*, 1913, **35**, 450.

³ R. M. Anker and A. H. Cook, *J. Chem. Soc.*, 1946, 117.

⁴ F. Gaudemar-Bardonne, *Ann. Chim. (France)*, 1958, **3**, 52.

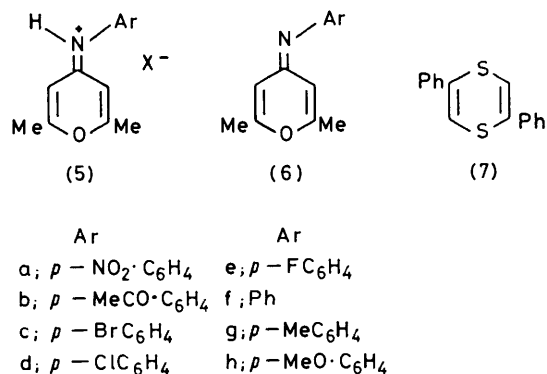
⁵ H. Strzelecka, *Ann. Chim. (France)*, 1966, **1**, 201.

⁶ J. A. Van Allen, G. A. Reynolds, and C. C. Petropoulos, *J. Heterocyclic Chem.*, 1972, **9**, 783.

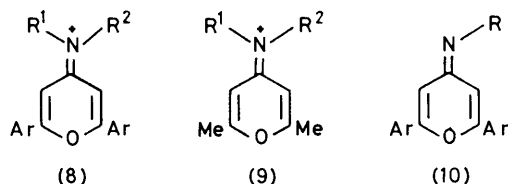
⁷ C. C. Petropoulos, *J. Polymer Sci., Part A-I, Polymer Chem.*, 1972, **10**, 957.

ported. Iminopyrans (10) have had fewer reports^{5,11,12,14} and the 2,6-dimethyl derivatives (11) none to date.

Suspecting that displacement of the 4-substituent of a



suitably substituted pyrylium salt by an aromatic amine might provide a general route to iminiopyran salts (5), we selected 4-methoxy-2,6-dimethylpyrylium perchlorate



(12) for a more detailed study, since it has been shown¹⁵ that a methoxy-group in pyrylium salts is more easily displaced than an alkylthio-group. Equimolar quantities of the salt (12) and the aromatic amine were heated

⁸ S. V. Krivun, A. I. Buryak, and S. N. Baranov, *Dopovidi Akad. Nauk Ukrain, R.S.R. Ser. B.*, 1972, **34**, 931.

⁹ G. I. Zhungietu and B. P. Sukhanyuk, *Khim. geterotsikl. Soedinenii*, 1972, **8**, 1531.

¹⁰ G. I. Zhungietu, E. A. Revenko, and F. N. Chukhrii, *Khim. geterotsikl. Soedinenii*, 1973, **9**, 347.

¹¹ J. A. Van Allen and S. Chie Chang, *J. Heterocyclic Chem.*, 1974, **11**, 1065.

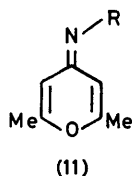
¹² S. Sib, *Tetrahedron*, 1975, **31**, 2229.

¹³ J. A. Van Allen, G. A. Reynolds, J. T. Alessi, S. Chie Chang, and R. C. Jones, *J. Heterocyclic Chem.*, 1971, **8**, 919.

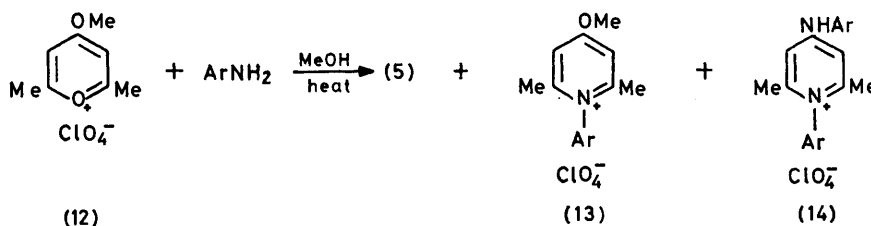
¹⁴ H. Strzelecka, M. Simalty-Siemiatycki, and C. Prévost, *Compt. rend.*, 1964, **258**, 6167.

¹⁵ L. C. King and F. J. Ozog, *J. Org. Chem.*, 1955, **20**, 448.

under reflux in methanol (Scheme 2), and the crude products after removal of methanol were investigated by ^1H n.m.r. From a series of eight *para*-substituted



anilines the iminiopyran salt (5) was formed in each case, together with the corresponding methoxy-pyridinium salt (13) (with the exception of the *p*-nitro- and *p*-acetyl compounds). Compound (13a) was prepared by independent synthesis (Scheme 3), and was shown by ^1H n.m.r. not to be present in the crude product from



SCHEME 2

compound (12) and *p*-nitroaniline. The relative percentages of compounds (5) and (13) as a function of the *para*-substituent on the aniline are given in Table 1.

TABLE 1

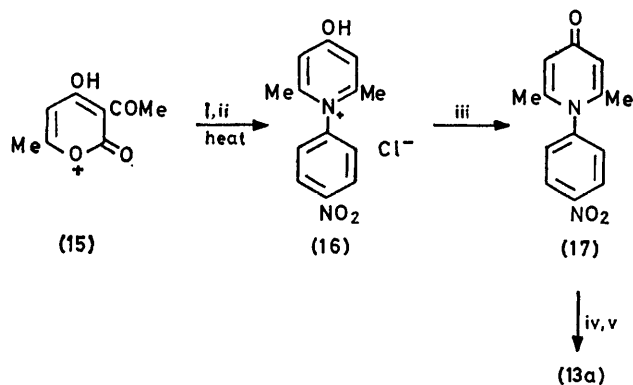
Relative yields of compounds (5) and (13) from pyrylium salt (12) as a function of the *para*-substituent of the reacting aniline

<i>para</i> -Subst.	Yield (%)	
	(5)	(13)
NO ₂	100	0
COMe	100	0
Br	61	39
Cl	67	33
F	53	47
H	43	57
Me	41	59
MeO	32	68

There is seen to be a qualitative correlation between the predominant position of attack on the pyrylium salt, and the electronic effects of the *para*-substituent on the amine. Anilines with an electron-withdrawing group (the 'softer' amines) gave products resulting from predominant attack at the 4-position of the pyrylium salt, whereas those with an electron-releasing group (the 'harder' amines) from attack predominantly at the 2-position. We observed only very small traces of compounds (14) resulting from substitution by two moles of the aromatic amine, and contrary to the report by Anker and Cook,³ none in the case of aniline itself. When however two moles of aniline were used, compound (14f) (18%) was detected (^1H n.m.r.) together with products (5f) (32%) and (13f) (50%).

Mixtures of iminiopyran (5) and pyridinium (13) salts were separated by shaking first with chloroform and sodium hydrogen carbonate solution, then by evaporation of the chloroform to give a mixture of the iminiopyran (6) and the pyridinium salt (13). This was readily separated by extraction with ether, in which the iminiopyran was soluble. Pure compounds (6), obtained by evaporation and sublimation, were readily converted to iminiopyran salts (5) or (19) by treatment respectively with hydrochloric acid and sodium perchlorate, or with dimethyl sulphate and sodium perchlorate. The nitro-derivative (6a) also gave the methiodide (19a; X = I) on treatment with methyl iodide. Iminopyrans (6c-h) were found to be unstable at room temperature, darkening considerably within a few days. Decomposition was quite rapid above 100 °C.

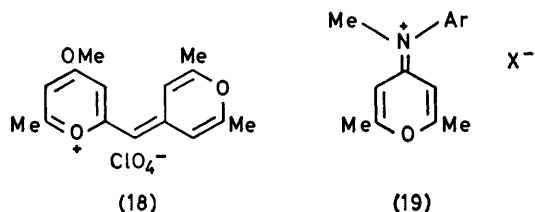
Sterically hindered amines failed to give products by substitution. *o*-Nitroaniline did not react even after prolonged reflux (1 week). Van Allen and Chie Chang¹¹



SCHEME 3 Reagents: i, *p*-nitroaniline; ii, conc. HCl; iii, NaHCO₃; iv, CF₃CO₂Me; v, NaClO₄

found that *o*-nitroaniline reacted with 4-chloro-2,6-diphenylpyrylium perchlorate, but not with the 4-methoxy-derivative. *N*-Methylaniline, *N*-ethylaniline, and *p*-chloro-*N*-ethylaniline also failed to displace the methoxy-group of the pyrylium salt (12), giving instead as the only isolable product the pyrylocyanine (18), identical with that reported by Anker and Cook³ from the reaction between the salt (12), and sodium acetate, or triethylamine. This result is surprising since secondary aliphatic amines are known to displace the 4-methoxy-group of compound (12) readily,^{3,6,15} as are the secondary aromatic amines 2,3-dihydroindole⁹ and hexahydro-carbazole.¹⁰

It appears that the relative rate of reaction of amines at the 2- and 4-positions of the pyrylium salt (12) depends both on electronic and on steric factors. Secondary



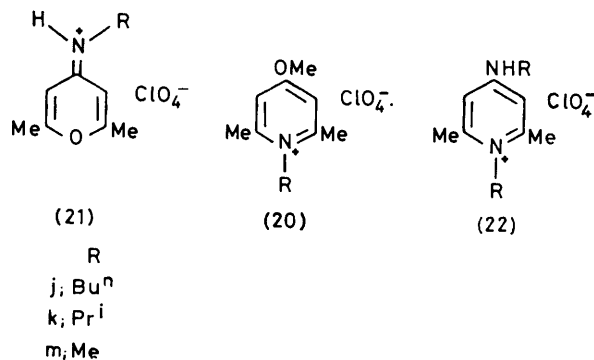
amines cannot give rise to pyridinium salts, so compound (18) or products of type (9) result, though a second molecule of amine can add to the 2-position of iminiopyrans (9) under more vigorous conditions.⁶ With primary amines, the rate of reaction at the 2-position to give pyridinium salts increases relative to the rate at the 4-position as the basicity of the amine increases, unless there is a steric constraint which discourages recyclisation of the open-chain intermediate. Thus the salt (12) is reported to give the pyridinium derivative (20j) with butylamine, while the more crowded isopropylamine gives the iminiopyran salt (21k).¹³ However, the authors do not give yields, nor do they state whether or not other products are formed.

Anker and Cook³ observed that compound (12) with 1 mol of methylamine gave both the pyridinium salt (20m) and the product from attack by 2 molecules of amine (22m). This reaction is the accepted method for making the salt (20m) (in only 42% yield).¹⁶ King and Ozog¹⁵ have rationalised the formation of the aminopyridinium salt (22m) in terms of further attack by methylamine on the methoxypyridinium salt (20m) rather than on an iminiopyran intermediate (21m). On repeating this reaction, we find that *three* compounds are formed: (20m) (42%), (21m) (21%), and (22m) (37%) as determined by ¹H n.m.r. spectroscopy. This accounts for the low yield observed in the preparation of pyridinium salt (20m).¹⁶ Compounds (20m) and (22m) were isolated by fractional crystallisation and shown to be identical with those described by Anker and Cook.³ The iminiopyran salt (21m) could not be obtained free from traces of contaminants (20m) and (22m), though it was purified sufficiently for positive characterisation by i.r. and ¹H n.m.r. spectroscopy. Its high solubility in methanol explains why it has not been reported before, and its presence in the reaction mixture suggests that it might also be an intermediate in the formation of the aminopyridinium salt (22m). Thus the scope of the reaction between the pyrylium salt (12) and primary aliphatic amines needs to be investigated, since even these relatively highly basic amines appear to give significant yields of iminiopyran salts (21).

* Available as Supplementary Publication No. SUP 22323 (7 pp.); for details see Notice to Authors No. 7, *J.C.S. Perkin I*, 1977, Index issue.

¹⁰ K. Dimroth, *Angew. Chem.*, 1960, **72**, 331.

¹H N.m.r. and i.r. data are recorded in Tables 2–5.* The ¹H n.m.r. spectra of compounds (5), (6), and (19) are temperature dependent, owing to isomerisation about the C=N bond. Thus in certain solvents, and for certain aryl substituents the 2- and 6-methyl signals coalesce at room temperature, as do the 3- and 5-hydrogen atom signals of the pyran ring. In other cases they appear as separate signals. This phenomenon will be discussed elsewhere.¹⁷



The i.r. spectra of compounds (5) as perchlorate salts all show three bands in the N–H stretching region, comprising two medium intensity, broad absorptions near 3 250 and 3 100 cm⁻¹ and a sharper, weak absorption near 3 200 cm⁻¹. Repeated recrystallisation from D₂O causes all three to disappear, and be replaced by a broad band near 2 320 cm⁻¹. In contrast compound (5a) as the bromide salt shows only one broad band at 2 710 cm⁻¹, which is replaced by sharp bands at 2 175 and 2 080 cm⁻¹ after recrystallisation from D₂O. The molecular structure of (5a) as the bromide salt, determined by X-ray crystallography,¹⁸ shows a hydrogen bond between the N–H group and the bromide ion. Merényi¹⁹ comments that N–H absorption bands must be observed in iminium salts with complex anions to prevent the appearance of strong hydrogen bonded shifts. The N–H bending mode in the perchlorate salts (5) is assigned to a broad, weak absorption near 740 cm⁻¹. The C=N stretching mode of the iminium salts (5) and (19) is assigned to an intense band near 1 660 cm⁻¹, which predictably shifts to higher frequency (near 1 680 cm⁻¹) in the free bases (6). The methoxypyridinium salts (13) all show an intense band near 1 345 cm⁻¹ which probably arises from the ether function.

The mass spectra of compounds (6) show the molecular ion as the base peak, with prominent peaks at *M* – 43, *M* – 55, and *m/e* 134, 108, 93, and 43. Spectra for compounds (5) and (19) are essentially the same as those of the corresponding free bases (6). The molecular ion is also observed for the methoxypyridinium salts (13), but the base peak is at *M* – 15 due to de-*O*-methylation. Losses of CO and then of H⁺ occur as major processes

¹⁷ M. P. Sammes and K. L. Yip, in preparation.

¹⁸ R. L. Harlow, S. H. Simonsen, and M. P. Sammes, in preparation.

¹⁹ R. Merényi, *Adv. Org. Chem.*, 1976, **9**, part 1, p. 75.

(substantiated by prominent metastable peaks). Cleavage of the C-N bond to give a substituted phenyl fragment is also a significant process.

EXPERIMENTAL

I.r. spectra were recorded for Nujol mulls on a Perkin-Elmer 577 spectrophotometer; ^1H n.m.r. spectra on a Perkin-Elmer R-20 spectrometer; and mass spectra on a Hitachi RMS-4 spectrometer. Spectroscopic data for com-

ether. Treatment of the residue with HBF_4 (5 ml; 40%) followed by recrystallisation from EtOH gave 4-(benzylthio)-2,6-dimethylpyrylium tetrafluoroborate (3; $\text{X} = \text{BF}_4^-$); M^+ 306; ν_{max} 1 632, 1 533 (pyrylium ion), and 1 062 cm^{-1} (BF_4^-); $\delta[(\text{CD}_3)_2\text{SO}]$ 7.95 (2 H, s), 7.5—7.2 (5 H, m), 4.71 (2 H, s), and 2.69 (6 H, s). Similarly 2,6-dimethyl-4-(phenacylthio)pyrylium bromide was converted into the tetrafluoroborate (4; $\text{X} = \text{BF}_4^-$); ν_{max} 1 683 (C=O), 1 636, 1 532 (pyrylium ion), and 1 062 cm^{-1} (BF_4^-); $\delta[(\text{CD}_3)_2\text{SO}]$

TABLE 6
Physical and analytical data for new compounds

Compd.	X	Yield (%) ^a	M.p. (°C)	Cryst. form	Solvent ^b	Found (%)			Formula	Required (%)		
						C	H	N		C	H	N
(1a)	BF_4	24	163—166	Plates	A	52.8	4.3	6.0	$\text{C}_{20}\text{H}_{22}\text{BF}_4\text{NOS}^d$	52.7	4.6	6.1
(1f)	BF_4	61	164—166	Plates	A	61.0	5.1	3.6	$\text{C}_{20}\text{H}_{19}\text{BF}_4\text{N}_2\text{O}_5\text{S}$	61.1	5.1	3.6
(2f)	BF_4	22		Plates	A	59.6	4.5	3.2	$\text{C}_{21}\text{H}_{20}\text{BF}_4\text{NO}_2\text{S}$	59.9	4.8	3.3
(3)	BF_4	82	143—145	Prisms	A	52.6	4.5	9.9 ^e	$\text{C}_{14}\text{H}_{15}\text{BF}_4\text{OS}$	52.9	4.7	10.1 ^e
(4)	BF_4	83	175—177	Prisms	A	52.0	4.4	9.5 ^e	$\text{C}_{15}\text{H}_{15}\text{BF}_4\text{O}_2\text{S}$	52.0	4.4	9.3 ^e
(5a)	Br	66	193—195	Needles	A	48.1	4.2	8.6	$\text{C}_{13}\text{H}_{13}\text{BrN}_2\text{O}_3$	48.0	4.0	8.6
(5a)	BF_4	21	168—170	Needles	A	47.0	3.9	8.2	$\text{C}_{13}\text{H}_{13}\text{BF}_4\text{N}_2\text{O}_3$	47.0	3.9	8.4
(5a)	ClO_4	80	184—186	Needles	A	45.3	3.7	7.9	$\text{C}_{13}\text{H}_{13}\text{ClN}_2\text{O}_7$	45.3	3.8	8.1
(5b)	ClO_4	64	135—138 (decomp.)	Needles	A	52.4	4.9	3.8	$\text{C}_{15}\text{H}_{16}\text{ClNO}_6$	52.7	4.7	4.1
(5c)	ClO_4	82	249—259 (decomp.)	Needles	A + B	41.3	3.4	3.7	$\text{C}_{13}\text{H}_{13}\text{BrClNO}_5$	41.2	3.5	3.7
(5d)	ClO_4	98	220—233 (decomp.)	Plates	A + B	46.4	4.0	4.2	$\text{C}_{13}\text{H}_{13}\text{Cl}_2\text{NO}_5$	46.7	3.9	4.2
(5e)	ClO_4	96	155—157	Needles	A + B	49.3	4.2	4.4	$\text{C}_{13}\text{H}_{13}\text{ClFNO}_5$	49.2	4.1	4.4
(5f)	ClO_4	62	174—175	Needles	A + B	52.1	5.3	4.3	$\text{C}_{28}\text{H}_{34}\text{Cl}_2\text{N}_2\text{O}_{11}^f$	52.2	5.3	4.3
(5g)	ClO_4	75	190—195 (decomp.)	Needles	A + B	53.5	5.0	4.3	$\text{C}_{14}\text{H}_{16}\text{ClNO}_5$	53.6	5.1	4.5
(5h)	ClO_4	80	215—222 (decomp.)	Needles	A + B	51.2	5.1	4.2	$\text{C}_{14}\text{H}_{16}\text{ClNO}_6$	51.0	4.9	4.3
(6a)		69	150—153	Prisms	g	63.6	4.6	11.6	$\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_3$	63.9	4.9	11.5
(6b)		70	114—115	Prisms	g	72.0	6.5	5.5	$\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_5^e$	72.0	6.4	5.6
(6c)		44	117	Prisms	g	56.2	4.5	4.9	$\text{C}_{13}\text{H}_{12}\text{BrNO}$	56.1	4.4	5.0
(6d)		51	124—126	Prisms	g	66.9	5.1	5.9	$\text{C}_{13}\text{H}_{12}\text{ClNO}$	66.8	5.1	6.0
(6e)		27	102—103	Prisms	g	71.6	5.6	6.5	$\text{C}_{13}\text{H}_{12}\text{FNO}$	71.9	5.6	6.5
(6f)		22	72—73	Needles	g	78.0	6.5	7.1	$\text{C}_{13}\text{H}_{12}\text{NO}$	78.4	6.6	7.0
(6g)		17	111	Needles	g	78.9	7.2	6.8	$\text{C}_{14}\text{H}_{15}\text{NO}$	78.8	7.1	6.6
(6h)		17	98	Needles	g	73.4	6.7	6.2	$\text{C}_{14}\text{H}_{15}\text{NO}_2$	73.3	6.6	6.1
(13a)	ClO_4	95	244—252 (decomp.)	Needles	A	46.6	4.2	7.6	$\text{C}_{14}\text{H}_{16}\text{ClN}_2\text{O}_7$	46.9	4.2	7.8
(13c)	ClO_4	27	205—210	Prisms	A + B	42.5	3.8	3.5	$\text{C}_{14}\text{H}_{15}\text{BrClNO}_5$	42.8	3.9	3.6
(13d)	ClO_4	18	177—180	Plates	A + B	48.3	4.3	3.9	$\text{C}_{14}\text{H}_{15}\text{Cl}_2\text{NO}_5$	48.3	4.3	4.0
(13e)	ClO_4	34	134—135	Prisms	A + B	50.4	4.7	4.1	$\text{C}_{14}\text{H}_{15}\text{ClFNO}_5$	50.7	4.6	4.2
(13f)	ClO_4	49	153—154	Plates	A + B	53.4	5.1	4.4	$\text{C}_{14}\text{H}_{16}\text{ClNO}_5$	53.6	5.1	4.5
(13g)	ClO_4	53	115—116	Prisms	A + B	54.9	5.5	4.4	$\text{C}_{15}\text{H}_{16}\text{ClNO}_5$	55.0	5.3	4.3
(13h)	ClO_4	54	127	Needles	A + B	52.3	5.3	4.2	$\text{C}_{15}\text{H}_{16}\text{ClNO}_6$	52.4	5.3	4.1
(16)	Cl	70	225—227	Prisms	A	55.4	4.7	9.7	$\text{C}_{13}\text{H}_{13}\text{ClN}_2\text{O}_3$	55.6	4.6	10.0
(17)		71	219—221	Needles	A	59.5	5.4	10.7	$\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_4^d$	59.1	5.4	10.6
(19a)	ClO_4	93	208—210	Plates	A	46.8	4.2	7.6	$\text{C}_{14}\text{H}_{15}\text{ClN}_2\text{O}_7$	46.9	4.2	7.8
(19a)	I	86	(decomp.)	Prisms	B + C	43.5	3.9	7.0	$\text{C}_{14}\text{H}_{15}\text{IN}_2\text{O}_3$	43.5	3.9	7.3
(19c)	ClO_4	75	132—137	Plates	A + B	42.6	3.8	3.6	$\text{C}_{14}\text{H}_{15}\text{BrClNO}_5$	42.8	3.9	3.6
(19d)	ClO_4	71	120—125	Plates	A + B	48.1	4.6	3.7	$\text{C}_{14}\text{H}_{15}\text{Cl}_2\text{NO}_5$	48.3	4.3	4.0

^a Of isolated material. ^b Solvents: A, EtOH; B, Et₂O; C, Me₂CO. ^c % Sulphur. ^d Monohydrate. ^e Hemihydrate. ^f Hemietanolate. ^g Purified by sublimation.

ounds (5), (6), (13), and (19) are presented in Tables 2—5,* and physical and microanalytical data in Table 6.

2,6-Dimethylpyran-4-thione,¹ 2,6-dimethyl-4-phenacylthiopyrylium bromide,¹ 4-methoxy-2,6-dimethylpyrylium perchlorate,³ and 4-chloro-N-ethylaniline,²⁰ were prepared by known methods.

Preparation of Substituted 4-Mercaptopyrylium Tetrafluoroborates (3) and (4).—2,6-Dimethylpyran-4-thione (0.005 mol) and benzyl bromide (0.005 mol) were heated under reflux in acetone (1 h). The mixture was cooled and evaporated and the residue washed with benzene and then

* See footnote on p. 1375.

²⁰ R. M. Roberts and P. J. Vogt, *Org. Synth.*, Coll. Vol. V, 1963, 420.

7.97 (2 H, s), 8.2—7.5 (5 H, m), 5.32 (2 H, s), and 2.70 (6 H, s).

Reaction of Pyrylium Salts (3) and (4) with Aromatic Amines.—With aniline. The 4-(benzylthio)pyrylium salt (3; $\text{X} = \text{BF}_4^-$) (0.001 mol) and aniline (0.001 mol) were heated under reflux in 95% EtOH (1.5 ml) for 30 min. The solvent was evaporated off and the residue triturated with Et₂O and recrystallised from 95% EtOH to give the pyridinium salt (1f); ν_{max} 1 627, 1 548 (pyridinium ion), and 1 062 cm^{-1} (BF_4^-); $\delta(\text{CDCl}_3)$ 7.7—7.2 (10 H, m), 4.41 (2 H, s), and 2.26 (6 H, s). Similarly, from the 4-(phenacylthio)pyrylium salt (4) was prepared the pyridinium salt (2f); ν_{max} 1 683 (C=O), 1 622, 1 542 (pyridinium ion), and 1 063 cm^{-1} (BF_4^-).

With *p*-nitroaniline in ethanol. The salt (4; X = Br) (0.005 mol) and *p*-nitroaniline (0.005 mol) were heated under reflux in 95% EtOH (7.5 ml) for 2 h. The solution was cooled, Et₂O (25 ml) added, and the precipitate separated and recrystallised from 95% EtOH to give 2,6-dimethyl-4-(*p*-nitrophenyliminio)pyran bromide (5a; X = Br); ν_{\max} 2 710 (NH), 1 664 (pyrylium ion), 1 515, and 1 348 cm⁻¹ (NO₂). Evaporation of the ethereal filtrate, and recrystallisation of the residue from 95% EtOH gave 2,5-diphenyl-1,4-dithiin (7) as yellow plates, m.p. 119° (lit.,² 118—119°); identical (i.r.)^{21a} with an authentic sample.

Compound (5a) was also obtained (48%) when the pyrylium salt (3) was used in place of the pyrylium salt (4). Dibenzyl disulphide, m.p. 70—71° (lit.,²² 71.5—72°) was obtained from the ethereal filtrate; M^+ 246; identical (i.r.)^{21b} with an authentic sample.

With *p*-nitroaniline in acetonitrile. The pyrylium salt (3; X = Br) (0.002 mol) and *p*-nitroaniline (0.002 mol) were heated under reflux in MeCN (3 ml) for 2 h. The solvent was removed, the red tarry residue triturated with 40% HBF₄, and the resulting solid recrystallised from 95% EtOH to give the pyridinium salt (1a); M^+ 351; ν_{\max} 1 628, 1 546 (pyridinium ion), 1 531, 1 351 (NO₂), and 1 065 cm⁻¹ (BF₄⁻); δ [(CD₃)₂NCDO] 8.62 (2 H, m), 8.13 (5 H, m), 8.05 (2 H, s), 4.71 (2 H, s), and 2.42 (6 H, s).

Reactions of 4-Methoxy-2,6-dimethylpyrylium Perchlorate with Aromatic Amines.—Primary amines. The pyrylium salt (12) (0.005 mol) and the appropriate aniline (0.005 mol) were heated under reflux in dry MeOH (6.5 ml) for 4 h. Dry Et₂O (50 ml) was added with vigorous stirring to the cooled product, and the precipitate was filtered off and washed with Et₂O. The relative amounts of iminiopyran salt (5) and of pyridinium salt (13) in the crude product were determined by ¹H n.m.r. [(CD₃)₂SO] (Table 1). Actual yields of compounds (13) are given in Table 6.

With *o*-nitroaniline. Only starting materials were recovered after reflux periods of 1 h or 1 week in dry MeOH. When dry EtOH was used as the solvent, the product consisted of 4-ethoxy-2,6-dimethylpyrylium perchlorate together with unchanged amine.

Secondary amines. 4-Chloro-*N*-ethylaniline, under the conditions used for primary amines yielded only starting materials and the pyrylocyanine (18) (3%); m.p. 260° (decomp.) [lit.,³ 260° (decomp.)] (Found: C, 52.4; H, 4.95; Cl, 10.2. Calc. for C₁₅H₁₇ClO₇: C, 52.25; H, 5.0; Cl, 10.3%); M^+ 245; ν_{\max} 3 068, 1 648, 1 542, 1 515, and 1 095 cm⁻¹; λ_{\max} 204 (log ϵ 4.16), 260 (4.08), 320 (3.66), 450 (4.56), and 471 nm (4.78); δ [(CD₃)₂NCDO] 7.37 (1 H, s), 7.07—6.94 (2 H, dd), 6.64 (1 H, s), 5.81 (1 H, s), 4.13 (3 H, s), 2.71 (3 H, s), 2.45 (3 H, s), and 2.37 (3 H, s). Use of *N*-methylaniline or *N*-ethylaniline in place of 4-chloro-*N*-ethylaniline, and increase in heating time to 20 h, gave the product (18) in 15% yield together with starting materials.

Separation of Compounds (5) and (13).—The crude mixture prepared as above was suspended in CHCl₃ (25 ml), and shaken vigorously with saturated aqueous NaHCO₃ (20 ml). The aqueous layer was extracted (3 × 5 ml CHCl₃) and the combined CHCl₃ layers were dried (MgSO₄) and evaporated to dryness. The residue was triturated with Et₂O (4 × 15 ml), and the remaining solid recrystallised (EtOH—Et₂O) to give the appropriate pyridinium salt (13). The Et₂O solution from the trituration was evaporated,

and the residue sublimed three times (100 °C and 10⁻² Torr) to give the corresponding 4-aryliminopyran (6). Yields are recorded in Table 6.

Preparation of 4-(*N*-Aryliminio)-2,6-dimethylpyran Perchlorates (5).—The appropriate 4-aryliminopyran (6) (0.000 5 mol) was suspended in water (1 ml) and acidified with conc. HCl (5 drops). The mixture was warmed to give a clear solution, 70% NaClO₄ (3 ml) was added, and the product was triturated to give a homogeneous suspension. This was filtered, and the residue of compound (5) washed with water (2 ml). Yields are recorded in Table 6.

Preparation of 4-(*N*-Aryl-*N*-methyliminio)-2,6-dimethylpyran Perchlorates (19).—The appropriate 4-aryliminopyran (6) (0.000 4 mol) was suspended in MeOH (0.5 ml) and Me₂SO₄ (0.000 8 mol) was added. The mixture was heated on a steam-bath for 10 min, treated with 70% NaClO₄ (3 ml), triturated to give a homogeneous suspension, and filtered. The residue of compound (19) was washed with water (2 ml).

Preparation of Compound (13a).—4-Hydroxy-2,6-dimethyl-1-(*p*-nitrophenyl)pyridinium chloride (16). 3-Acetyl-4-hydroxy-6-methyl-2-pyrone (15) (0.01 mol) and *p*-nitroaniline (0.01 mol) were heated under reflux in conc. HCl (10 ml) for 3 h. The solution was cooled in ice and filtered, and the residue recrystallised from EtOH to give the chloride (16); ν_{\max} 2 340 (OH), 1 640 (pyridinium salt), 1 521, and 1 353 cm⁻¹ (NO₂); δ [(CD₃)₂SO] 8.49 (2 H, m), 7.91 (2 H, m), 7.36 (2 H, s), and 2.19 (6 H, s).

2,6-Dimethyl-1-(*p*-nitrophenyl)-4-pyridone (17). The chloride (16) (0.005 mol) was triturated with saturated aqueous NaHCO₃ (15 ml) on a steam-bath for 15 min. The mixture was cooled and filtered, and the residue recrystallised from absolute EtOH to give the pyridone (17); M^{++} 244; ν_{\max} 3 380 (H₂O), 1 640 (pyridone), 1 520, and 1 349 cm⁻¹ (NO₂); δ (CDCl₃) 8.50 (2 H, m), 7.63 (2 H, m), 6.27 (2 H, s), 3.19 (2 H, s), and 1.95 (6 H, s).

4-Methoxy-2,6-dimethyl-1-(*p*-nitrophenyl)pyridinium perchlorate (13a). The pyridone (17) (0.001 mol), and CF₃SO₃Me (0.002 mol) in dry CH₂Cl₂ (10 ml) were stirred at room temperature for 10 h. The solvent was evaporated off, the residue triturated with 70% NaClO₄ (3 ml), and the precipitated solid recrystallised from ethanol to give the pyridinium perchlorate (13a).

Reaction between Compound (12) and Methylamine.—The preparation was carried out as described by King and Ozog¹⁵ for the corresponding iodide (0.01 mol scale). The mixture was cooled and dry Et₂O (300 ml) added slowly with vigorous stirring to give a mixture of salts (2.14 g), shown by ¹H n.m.r. [(CD₃)₂SO] to comprise compounds (20 m) (42%), (21 m) (21%), and (22 m) (37%). Recrystallisation from MeOH (4 times) gave the pure methoxy-pyridinium salt (20 m), m.p. 186—188° (lit.,³ 187°); ν_{\max} 1 639, 1 583 (pyridinium ion), 1 341 (MeO), and 1 098 cm⁻¹ (ClO₄⁻); δ [(CD₃)₂SO] 7.46 (2 H, s), 4.04 (3 H, s), 3.89 (3 H, s), and 2.70 (6 H, s). Dilution of the mother liquors from the first recrystallisation of the salt (20 m) with two volumes of Et₂O, and recrystallisation of the precipitate from MeOH (5 times), gave the pure methylaminopyridinium salt (22 m), m.p. 222—224° (lit.,³ 224°); ν_{\max} 3 350 (NH), 1 650, 1 565 (pyridinium ion), and 1 085 cm⁻¹ (ClO₄⁻); δ [(CD₃)₂SO] 8.15 (1 H, br, q, *J* 5.1 Hz), 6.74 (1 H, s), 6.66 (1 H, s), 3.68 (3 H, s), 2.85 (3 H, d, *J* 5.1 Hz), and 2.54 (6 H, br, s). Dilution of the mother liquor (above) with a

²¹ Standard Grating Spectra, Sadtler Research Laboratories, Inc.; (a) 1974, spectrum 31194; (b) 1969, spectrum 15336.

²² H. J. Backer and P. L. Stedehouder, *Rec. Trav. chim.*, 1933, 52, 437.

further large volume of Et_2O gave a solid which was triturated with sufficient MeOH to dissolve about one third. The MeOH solution was evaporated to give the iminiopyran salt (21 m) contaminated with a small amount of pyridinium salt (20m); ν_{max} 3 308 (NH), 1 672 (C=N), 1 612, 1 583 (ring), and 1 098 cm^{-1} (ClO_4^-);

$\delta[(\text{CD}_3)_2\text{SO}]$ 7.01 (1 H, d, J 2.5 Hz), 6.66 (1 H, d, J 2.5 Hz), 3.04 (3 H, d, J 4.5 Hz), 2.48 (3 H, s), and 2.44 (3 H, s).

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