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The synthesis is described of fluorescent and coloured pyrylium and pyridinium salts, including water-soluble derivatives, designed to serve as marker reagents for primary amines.

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The transformation of pyrylium salts with primary amines to pyridinium salts in organic solvents is the basis for a two-step functionalisation of amines [1]. Recently, this transformation became feasible in aqueous media by the use of water-soluble pyrylium salts [2]. Thus the aminoacid lysine and the peptide glycine-glycine were converted in water solution into pyridinium salts. The high selectivity and almost quantitative yields of the pyrylium into pyridinium conversion suggested the application of pyrylium salts as covalent labels for the detection of primary amino compounds in organic and aqueous systems.

We now report the synthesis of fluorescent and of coloured pyrylium and pyridinium salts, including water-soluble examples, which are of potential interest as marker reagents.

Fluorescent Pyrylium Salts.

The highly fluorescent and commercially available 2,5-diphenyloxazole [3] was acetylated under the usual Friedel-Crafts conditions leading to 5-(4-acetylphenyl)-2-phenyloxazole (**1**) in good yields. As with sulphonation [4] and nitration [5], acetylation occurred in the *para*-position of the 5-phenyl ring as demonstrated by ^{13}C nmr spectroscopy. Aldol condensation of ketone **1** with benzaldehyde (**2**) furnished the benzylidene derivative **3**.

Scheme I

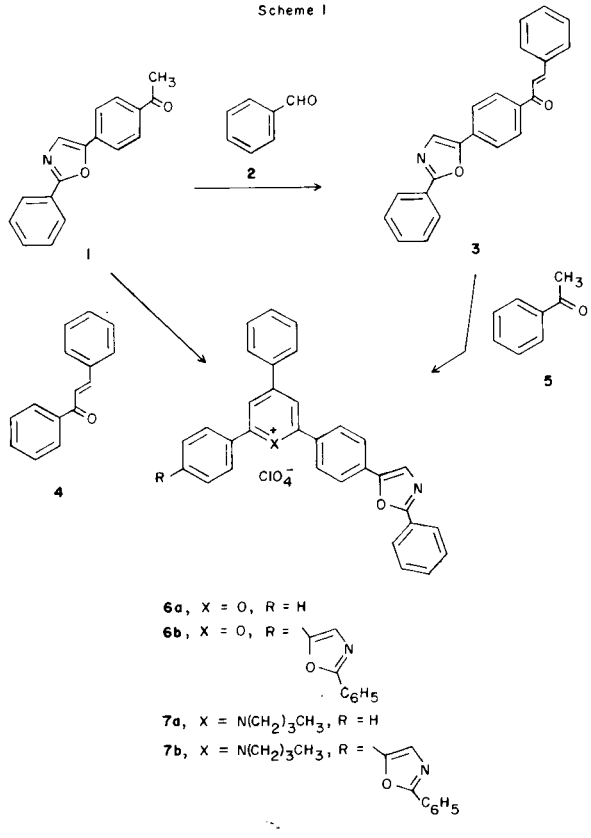


Table 1

Preparative and Analytical Data of Pyrylium Salts **6**, **9**, **11**, **14** and **15**

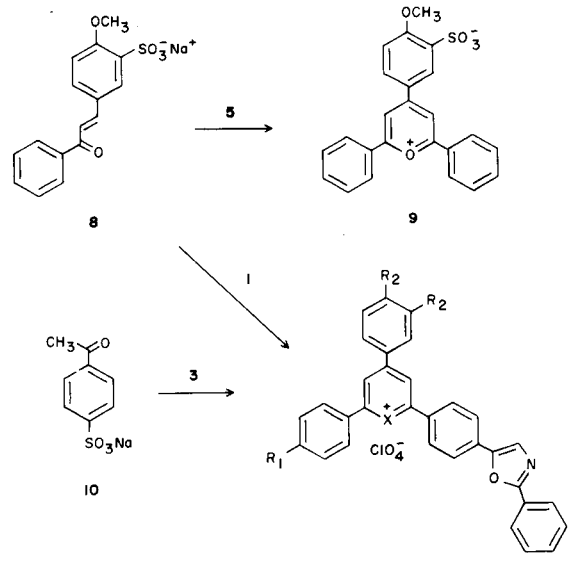
Compound No.	Prepared from Aldehyde/Chalcone	Prepared from Ketone	Yield (%)	Mp (°C)	Formula	Analysis (%) Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
6a	—	4	1	40	239 [a]	$C_{32}H_{22}ClNO_6 \cdot H_2O$	67.48	4.21	2.46	67.36	3.88	2.36
	—	3	5	70								
6b [b]	—	3	1	75	194	$C_{41}H_{27}ClN_2O_7 \cdot \frac{1}{2}HClO_4$	66.08	3.65	3.76	65.69	4.01	3.47
9 [c]	—	8	5	65	>300	$C_{24}H_{18}O_5S \cdot 2H_2O$	63.43	4.84	—	63.49	4.45	—
11b	—	3	10	70	>300	$C_{32}H_{22}ClNO_9S \cdot H_2O$	59.13	3.71	2.15	59.11	3.72	2.15
14a	**13b**	—	5	85	>300	$C_{23}H_{17}ClO_6$	65.03	4.03	—	64.83	4.19	—
14b [c]	**13b**	—	10	85	>300	$C_{23}H_{16}O_8S_2 \cdot H_2O$	54.80	3.60	—	55.13	3.74	—
15a [d]	—	—	—	98	>300	$C_{25}H_{19}ClO_7$	64.31	4.12	—	64.36	4.12	—
15b [c,d]	—	—	—	95	>300	$C_{25}H_{18}O_9S_2 \cdot H_2O$	55.16	3.70	—	54.84	3.88	—

[a] Purified by refluxing in acetic acid. [b] Sesquiperchlorate. [c] Zwitterion. [d] Prepared by acetylation of **14a** and **14b**, respectively.

Treatment of ketone **1** and chalcone **4** [6] with perchloric acid gave moderate yields of the pyrylium perchlorate **6a**; high yields of **6a** were obtained by similar reaction of **3** with acetophenone (**5**) (Table 1). The pyrylium salt **6b**, containing two diphenyloxazole moieties, was not obtained through 2:1 condensation of **1** with **2**. However, the synthesis of **6b** was accomplished by reaction of chalcone **3** and **1**. Treatment with *n*-butylamine converted **6a** and **6b** smoothly into the pyridinium salts **7a** and **7b**, respectively.

Attaching sulphonic groups to the aryl substituent renders pyrylium cations water-soluble [2]. Anticipated problems in the direct sulphonation of arylpyrylium salts suggested the construction of the pyrylium ring from appropriately functionalised components. Acidic condensation of **1** with the water-soluble chalcone **8** gave, as shown spectroscopically, only minor quantities of pyrylium salt **11a** [^{13}C nmr (deuteriochloroform/trifluoroacetic acid): *e.g.* 177.0 (s), 174.5 (s), 170.0 (s), 116.0 (d) ppm, (pyrylium ring carbons)]. The main product obtained was the symmetrical pyrylium salt **9**, isolated as betaine. The structure of **9** was confirmed ^{13}C nmr spectroscopically and by unequivocal synthesis from **8** and acetophenone (**5**). The formation of **9** is explained by *retro*-aldol reaction of **8** and subsequent condensation of the more reactive ketone **5** with 4-methoxy-3-sulphonylbenzaldehyde [7].

Scheme 2



IIa, X = O, R_1 = H, R_2 = OCH_3, R_3 = SO_3H

IIb, X = O, R_1 = SO_3H, R_2 = R_3 = H

12, X = $N(CH_2)_3CH_3$, R_1 = SO_3H, R_2 = R_3 = H

The low reactivity of **1** was overcome by treatment of the deriving benzylidene derivative **3** with sodium 4-acetylbenzenesulphonate (**10**). This gave the water-soluble,

Table 2

^{13}C NMR Spectra [a] of Pyrylium Salts **6**, **9**, **11** and Pyridinium Salts **7** and **12**

Compound No.	Pyrylium or Pyridinium Ring Carbons					Oxazole Ring Carbons			Other signals
	2 (s)	3 (d)	4 (s)	5 (d)	6 (s)	2 (s)	4 (d)	5 (s)	
6a	172.4	115.3	167.7	115.3	169.3	163.0	116.1	152.5	137.0 (d), 136.6 (d), 136.4 (d), 132.4 (s), 130.9 (s), 130.5 (d), 129.8 (s), 129.3 (d), 128.5 (d), 128.2 (d), 126.8 (s), 118.7 (s)
6b	170.2	116.3	168.3	116.3	170.2	163.2	116.3	152.5	137.2 (d), 132.2 (s), 130.8 (d), 130.6 (d), 130.3 (d), 129.6 (d), 128.6 (d), 126.9 (s), 118.7 (s)
11b	170.3	116.2	168.4	116.2	170.3	163.2	116.2	152.5	147.6 (s, *C*SO_3H), 136.7 (d), 132.3 (d), 131.6 (s), 131.5 (s), 130.8 (d), 130.6 (d), 130.4 (d), 129.7 (d), 129.1 (s), 128.6 (d), 128.3 (d), 127.0 (s), 118.7 (s)
7a	155.7	[b]	157.5	[b]	155.7	163.4	115.9	153.4	136.2 (s), 134.8 (s), 132.9 (d), 132.8 (s), 131.6 (d), 131.2 (s), 129.7 (d), 129.3 (s), 128.8 (d), 127.9 (d), 127.6 (d), 127.4 (d), 126.2 (d), 125.6 (d), 118.7 (s), 54.0 (t, NCH_2), 30.1 (t, CH_2), 17.2 (t, CH_2), 11.8 (q, CH_3)
7b	155.8	[b]	157.9	[b]	155.8	163.1	115.1	152.9	137.1 (d), 135.0 (d), 133.6 (s), 132.8 (s), 131.8 (s), 130.5 (d), 130.3 (d), 128.4 (d), 128.1 (d), 127.2 (d), 126.5 (d), 118.8 (s), 55.2 (t, NCH_2), 32.4 (t, CH_2), 19.2 (t, CH_2), 11.8 (q, CH_3)
12	155.7	[b]	157.6	[b]	155.7	162.8	115.4	152.9	143.9 (s, *C*SO_3H), 137.0 (d), 136.0 (s), 135.0 (s), 133.5 (s), 133.0 (s), 131.6 (d), 130.6 (d), 130.2 (d), 129.8 (d), 128.5 (d), 128.2 (d), 127.9 (d), 127.3 (d), 127.0 (d), 126.6 (d), 118.7 (s), 67.1 (t, NCH_2), 19.2 (t, CH_2), 13.6 (t, CH_2), 12.1 (q, CH_3)
9	171.2	113.7	164.8	113.7	171.2	—	—	—	163.2 (s, 4-phenyl C-4), 136.1 (d, 2, 6-phenyl C-4), 135.9 (d), 131.0 (s), 130.5 (d), 128.4 (d), 125.7 (s), 124.5 (s), 114.2 (d), 56.7 (q, OCH_3)

[a] Recorded in deuteriochloroform/trifluoroacetic acid. [b] Superimposed by aromatic signals.

fluorescent pyrylium perchlorate **11b**, which could be converted into the pyridinium **12** with *n*-butylamine in dichloromethane or water. The ^{13}C nmr spectra of the oxazole containing pyrylium cations **6** and **11** display the signals for the pyrylium carbons in the characteristic range: 172.4-169.3 ppm (α-carbons), 116.3-115.3 ppm (β-carbons), 168.4-167.7 ppm (γ-carbons) (Table 2). Protonation of the oxazole nitrogen in trifluoroacetic acid solution has little effect on the chemical shift of the oxazole C-2 and C-3 carbons. However, the oxazole C-4 carbon is considerably more shielded and resonances near 116 ppm [1 (deuteriochloroform): 125.3 ppm], due to the lowered aromaticity of the heterocyclic ring (Table 2). Whereas the *N*-butyl carbons of the pyridiniums **7a,b** show the expected chemical shift, the $^{+}N\text{-}CH_2$ carbon of the water-soluble analogue **12** is shifted downfield while the other methylene carbons experience a significant *para*-magnetic shift (Table 2). Some of the ultraviolet and fluorescence spectra are given in Table 3. Although the pyrylium cations fluoresce relatively readily, the corresponding pyridinium cations show less intense emission.

Table 3

UV-Visible Spectra and Fluorescence Spectra of Oxazole Containing Pyrylium and Pyridinium Salts [a]

Compound No.	UV-Visible λ max (nm)	Fluorescence λ em (nm)	Fluorescence λ ex (nm)
1	315	365 [b]	315
6b	324	387	319
7a	305	445	315
7b	314	[c]	315
11b	330	395	319
12	314	388	339

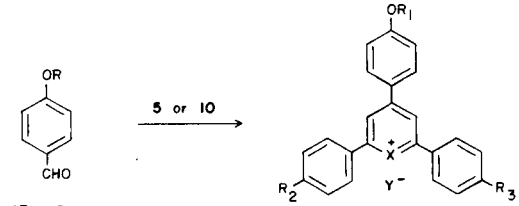
[a] Recorded in methanol with perchloric acid (*ca.* 10^{-2} *M*) in concentration *ca.* 2×10^{-5} *M*. [b] Concentration *ca.* 10^{-7} *M*. [c] Weak yellow fluorescence.

Coloured Pyrylium Salts.

Highly conjugated pyridinium betaines are dyestuffs [8]. It was expected, that *p*-hydroxyphenylpyridinium salts **14** should form intensively coloured vinylogous pyrones **17** with base.

The water-insoluble pyrylium salt **14a** and its water-soluble analogue **14b** were obtained by acidic condensation of the appropriate acetophenone **5** or **10** with 4-acetoxybenzaldehyde (**13b**) (Table 1). The acetoxy group was hydrolytically cleaved to hydroxyl under the reaction conditions employed. Similar reaction of ketones **5** and **10** with phenol **13a** gave some of the pyrylium **14** but only in unsatisfactory yields and contaminated with intractable impurities. Refluxing **14a** and **14b** in acetic anhydride afforded the acetylated salts **15a** and **15b**, respectively. As shown by elemental anlaysis, the pyryliums **14b** and **15b** were isolated as betaines.

SCHEME 3

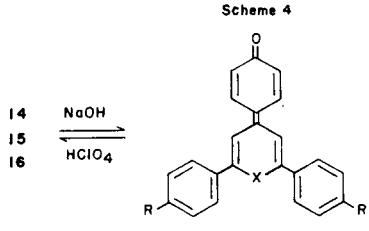


13a, R = H
13b, R = $COCH_3$

	X	Y	R_1	R_2	R_3
14a	O	ClO_4	H	H	H
14b	O	—	H	SO_3H	SO_3^-
15a	O	ClO_4	$COCH_3$	H	H
15b	O	—	$COCH_3$	SO_3H	SO_3^-
16a	N-$CH_2C_6H_5$	ClO_4	$COCH_3$	H	H
16b	N-$(CH_2)_3CH_3$	ClO_4	H	SO_3H	SO_3H
16c	N-$(CH_2)_4CH(NH_2)COOH$	ClO_4	H	SO_3H	SO_3H

Whereas reaction of **14a** with amines gave the violet vinylogous pyrone **17a**, the acetylated analogue **15a** was converted into the pyridinium salt **16a** on treatment with benzylamine. The ^{13}C nmr spectra of salts **14** and **15** were fully assigned by off-resonance decoupling, chemical shift considerations and by comparison with known data for aryl-pyrylium and -pyridinium salts [9] (Table 4).

Scheme 4



17a, X = O, R = H
17b, X = O, R = SO_3^-
18a, X = N-$CH_2C_6H_5$, R = H
18b, X = N-$(CH_2)_3CH_3$, R = SO_3^-
18c, X = N-$(CH_2)_4CH(NH_2)COO^-$, R = SO_3^-

The pyryliums **15a, 15b** and pyridinium **16a** were deacetylated in aqueous sodium hydroxide (0.4 *M*) leading to the highly coloured vinylogous pyrons **17a, 17b** and the pyridone **18a**. These transformations can be unambiguously monitored by uv-visible spectroscopy (Table 5). The use of pyryliums **15** as marker reagent for primary amines is exemplified in the reaction of **15b** with butylamine or lysine hydrochloride in buffer solution (*p*H = 10.5). The

Table 4

^{13}C NMR Spectra [a] of Pyrylium Salts **14, 15** and Pyridinium Salt **16a**

Compound No.	Heterocyclic Ring Carbons 2,6 (s)	3,5 (d)	4 (s)	α-Aryl Substituent 1 (s)	2,6 (d)	3,5 (d)	4	γ-Aryl Substituent 1 (s)	2,6 (d)	3,5 (d)	4 (s)	Other Signals
14a	168.0	117.0	165.7	129.0	128.2	129.7	134.5 (d)	122.6	133.5	112.2	163.1	—
14b	167.9	117.3	165.8	128.6	126.8	129.5	153.0 (s)	123.0	133.8	113.0	163.4	—
15a	169.8	114.8	163.9	128.9	128.7	129.8	135.0 (d)	129.7	131.8	123.3	155.9	[c]
15b	169.6	115.0	164.1	129.5	127.0	130.0	153.2 (s)	130.0	132.3	123.5	156.0	[e]
16a	156.5	124.3	154.5	[b]	[b]	[b]	133.0 (d)	[b]	131.1	123.2	155.9	[f]

[a] Recorded in d_6-dimethyl sulphoxide. [b] Not assigned. [c] Also 168.7 (s, C=O), 20.9 (q, CH_3). [e] Also 169.0 (s, C=O), 21.1 (q, CH_3). [f] Also 168.8 (s, C=O), 129.0, 128.7, 128.4, 128.1, 126.2, 126.0, 57.2 (t, CH_2), 20.8 (q, CH_3).

Table 5

UV-Visible Spectra [a] of Pyrylium Salts **14, 15** and Pyridinium Salt **16**

Compound No.	Spectra in Methanol/-Perchloric Acid λ max (nm)	ε (× 10^4)	Compound No.	Spectra in Sodium Hydroxide (0.4 *M*) λ max (nm)	ε (× 10^4)
14a	420	5.8	**17a**	474	3.8
15a	405	5.8			
14b	428	3.7	**17b**	478	2.2
	406	3.5			
15b	398	3.9			
16a	358	3.9	**18a**	417	7.3
	320	3.6			
16b [b]	343	—	**18b** [c]	417	—
16c [b]	343	—	**18c** [c]	417	—

[a] Concentration of compounds 2 × 10^{-5} *M*/l. [b] In aqueous solution acidified with perchloric acid (70%) to *p*H = 1. [c] In aqueous buffer solution at *p*H = 10.5.

formation of the pyridones **18b, 18c** and the deacetylated pyridinium salts **16b, 16c**, respectively, was detected by uv spectroscopy of the reaction mixture at *p*H = 10.5 and *p*H = 1 (Table 7). However, relatively high amine concentrations (*ca.* 10^{-2}*M*/l) are necessary to provide appropriate reaction times in aqueous medium.

We have thus shown, that suitable pyrylium salts convert primary amino groups into fluorescent or into highly coloured derivatives in organic or aqueous solution. However, the applicability of this technique in aqueous systems is limited due to the relatively high amine concentrations required for a reasonable reaction time.

EXPERIMENTAL

Melting points were determined with a Thomas Model 40 (Kofler Type) hot stage apparatus and are uncorrected. The ^{1}H nmr spectra were recorded on a Varian EM-360 and the chemical shifts are given in ppm relative to TMS as internal standard. The ^{13}C nmr spectra were recorded on a JEOL FX-100 (25.5 MHz) and chemical shifts are referenced to the deuterium signal of the solvent (deuteriochloroform: 77.0 ppm, d_6-dimethyl sulphoxide: 39.5 ppm). The uv spectra were taken on a Pye Unicam PU 8800 and the fluorescence spectra on a Perkin Elmer MPF 44A (spectra are uncorrected). Elemental analysis were carried out by Dr. W. King in this department.

5-(4-Acetylphenyl)-2-phenyloxazole (**1**).

To a solution of 2,5-diphenyloxazole (20 g, 90 mmoles) in dry carbon disulfide was added anhydrous alumninum chloride (72 g, 540 mmoles). The mixture was refluxed with stirring and then acetyl chloride (20 g, 180 mmoles) was added to maintain gentle reflux. After further reflux for 7 hours the solvent was distilled off and the remaining residue quenched with ice. The precipitation was filtered off, washed with hydrochloric acid (2*M*), dried *in vacuo* and subsequent column chromatography (silica, ethyl acetate/hexane 1:8) furnished 16.6 g (70%) **1** after recrystallisation from the eluent as plates, mp 107-108°; ^{1}H nmr (deuteriochloroform): 2.65 (s, CH_3, 3H), 7.40-7.70 (m, 5H), 7.85 and 8.10 (A_2B_2 system, J = 8 Hz, 4H), 8.05-8.35 (m, 1H); ^{13}C nmr (deuteriochloroform): 196.6 (s, C=O), 161.5 (s, oxazole C-2), 125.3 (d, oxazole C-4), 149.7 (s, oxazole C-5), 131.6 [s, 5-phenyl C-1, Δ = 0.4 (10)], 123.5 (d, 5-phenyl C-2,6, Δ = 1.3), 128.7 (d, 5-phenyl C-3,5, Δ = 0.2), 136.0 (s, 5-phenyl C-4, Δ = 1.3), 126.7 (s, 2-phenyl C-1, Δ = 1.3), 126.1 (d, 2-phenyl C-2,6, Δ = 0.2), 128.6 (d, 2-phenyl C-3,5, Δ = 0.2), 130.4 (d, 2-phenyl C-4, Δ = 0.2), 26.2 (q, CH_3); (deuteriochloroform/trifluoroacetic acid): 202.1 (s, C=O), 162.4 (s, oxazole C-2), 152.5 (s, oxazole C-5), 116.3 (d, oxazole C-3), 129.1 (s, 5-phenyl C-1), 125.3 (d, 5-phenyl C-2,6), 130.2 (d, 5-phenyl C-3,5), 137.9 (s, 5-phenyl C-1), 119.7 (s, 2-phenyl C-1), 128.1 (d, 2-phenyl C-2,6), 130.0 (d, 2-phenyl C-3,5), 136.0 (d, 2-phenyl C-4).

Anal. Calcd. for $C_{17}H_{13}NO_2$: C, 77.57; H, 4.94. Found: C, 77.39; H, 4.99.

1-[4-(2-Phenyloxazol-5-yl)phenyl]-3-phenyl-2-ethen-1-one (**3**).

A mixture of **1** (1.3 g, 5 mmoles) and benzaldehyde (**2**) (0.53 g, 5 mmoles) in ethanol (40 ml) was heated to 60°. After addition of sodium hydroxide (1.5 *M*, 6.6 ml) heating was continued for 2 hours. The mixture was cooled and left at 0° overnight. The precipitation was filtered off. Recrystallisation from ethanol gave 1.62 g (93%) **3**, mp 181-182°; ^{1}H nmr (deuteriochloroform/trifluoroacetic acid): 7.50-8.20 (m, 10H), 8.25-8.60 (m, 7H); ^{13}C nmr (deuteriochloroform/trifluoroacetic acid): 115.0 (d, oxazole C-3), 119.0 (s), 121.2 (d), 125.7 (d), 128.4 (d), 129.4 (d), 130.6 (d), 132.5 (d), 133.8 (s), 136.9 (d), 139.7 (s), 151.2 (s), 153.4 (s), 162.8 (s, oxazole C-2), 195.2 (s, C=O); ms: m/e 351 (M^+, 100).

Anal. Calcd. for $C_{24}H_{17}NO_2$: C, 82.04; H, 4.87; N, 3.98. Found: C, 81.65; H, 4.77; N, 3.83.

General Procedure for the Preparation of Pyrylium Salts **6, 9, 11** and **14**.

To a mixture of the aldehyde (5 mmoles) or chalcone (10 mmoles) and the ketone (10 mmoles) in acetic anhydride (10 ml) was slowly added perchloric acid (70%, 3 ml, 35 mmoles) so that the temperature was kept at 100-105°. After complete addition, stirring was continued for 4 hours at ambient temperature. The pyrylium salts were precipitated by dropwise addition to ethyl acetate (400 ml), filtered off, suspended in anhydrous ethanol (20 ml) and reprecipitated with ethyl acetate/diethyl ether (300 ml, 1:1). After filtration, the pyrylium salts were dried at 100° over phosphorus pentoxide. In the preparation of **6b** and **11b** the reaction mixture was heated for 10 minutes at 100°. The analytical and spectroscopic properties of the pyrylium salts are given in Tables 1, 2, 4, 6.

Table 6

^{1}H NMR Spectra [a] of Pyrylium Salts **14, 15** and Pyridinium Salt **16a**

Compound No.	Heterocyclic Ring H-3,5 (s, 2H)	α-Aryl Substituent	γ-Aryl Substituent A_2B_2 System	J_{AB} (Hz)	Other Signals
14a	9.10	7.85-8.20 (m, 4H) 8.65-8.95 (m, 6H)	7.20 and 7.95	9	—
14b	9.15	8.15 and 8.75 (A_2B_2 system, J_{AB} = 8 Hz, 8H)	7.30 and 8.85	9	—
15a	9.35	7.90-8.15 (m, 4H), 8.65-9.00 (m, 6H)	7.75 and 8.10	9	2.30 (s, CH_3, 3H)
15b	9.40	8.15 and 8.80 (A_2B_2 system, J_{AB} = 8 Hz, 8H)	7.75 and 8.90	9	2.35 (s, CH_3, 3H)
16a	8.60	7.10-7.70 (m, 10H)	6.80 and 7.35	8	2.35 (s, CH_3, 3H), 5.75 (s, CH_2, 2H), 7.80 (s, arom, 5H)

[a] Recorded in d_6-dimethyl sulphoxide.

Table 7

Preparative and Analytical Data of Pyridinium Salts **7, 12** and **16a**

Compound No.	*N*-Substituent	Procedure	Yield (%)	Mp (°C)	Formula	Analysis (%) Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
7a	*n*-butyl	A	83	141-142 [a]	$C_{36}H_{31}ClN_2O_5$	71.28	5.11	4.62	70.98	5.35	4.89
7b	*n*-butyl	A	95	149	$C_{45}H_{36}ClN_3O_6 \cdot 3/2H_2O$	69.54	5.05	5.40	69.45	4.95	5.30
12 [b]	*n*-butyl	A	80	199-201	$C_{36}H_{31}ClN_2O_8S \cdot 2H_2O \cdot ½HClO_4$	55.95	4.65	3.62	56.15	4.76	3.66
		B	75								
16a	benzyl	A	90	97-99	$C_{32}H_{26}ClNO_6$	69.19	4.68	2.52	69.42	4.75	2.86

[a] Recrystallisation from methanol. [b] Sesquiperchlorate.

Acetylation of Pyrylium Salts **14**.

A suspension of pyrylium salts **14** (10 mmoles) in acetic anhydride (40 ml) was heated at 100° (**14a**) or 150° (**14b**) for 10 hours (**14a**) or 48 hours (**14b**). The pyrylium salts **15** were precipitated by dropwise addition of the reaction mixture to ethyl acetate (400 ml), filtered off and dried at 100° over phosphorus pentoxide (Tables 1, 4, 6).

Procedures for the Conversion of Pyrylium Salts into Pyridinium Salts. Procedure A.

To the pyrylium salt (1 mmole) in the dichloromethane (5 ml) a solution of the amine (for **6a, 6b, 15a**: 2 mmoles; **11b**: 3 mmoles) in dichloromethane (2 ml) was added. After stirring for 1 hour at room temperature glacial acetic acid (0.1 ml) was added and stirring was continued for 3 hours. The pyridinium salts were precipitated with diethyl ether (200 ml), filtered off and dried over phosporus pentoxide. The pyridinium salts were purified by recrystallisation or by stirring in acetone (10 ml, containing 0.1 ml perchloric acid) and reprecipitated with diethyl ether (20 ml). Analytical and spectroscopic properties of the pyridinium salts are given in Tables 2, 4, 6, 7.

Procedure B.

To a stirred solution of amine (2 mmoles) in sodium hydrocarbonate/-sodium carbonate buffer solution (10 ml, *p*H = 10.5) the pyrylium salt (0.5 mmole) was added in small portions. After 15 hours, the mixture was acidified with perchloric acid (70%) to *p*H = 1, concentrated *in vacuo* and added dropwise to acetone (150 ml). The precipitated pyrdinium salt was filtered off, washed with acetone and dried over phosphorus pentoxide. Purification as described in procedure A.

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[10] $\Delta = \delta_{calcd} - \delta_{obs}$, where δ_{calcd} is calculated from known substitution shift parameters [D. F. Ewing, *Org. Magn. Reson.*, 505 (9179)] and values for 2,5-diphenyloxazole.