Pyrylium-mediated Transformations of Natural Products. Part 8.[1] Kinetics of Nucleophilic Displacements with Pyridines as Leaving Groups in Aqueous Solution.

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Good second-order kinetics were found with k_2 values which were *ca.* 50 times less for piperidine displacements in H_2O than in chlorobenzene solutions, as expected from the polarity increase. Rates for thioglycolate dianion displacements were about five times faster than for piperidine. The rate dependence on pyridine leaving group structure paralleled that previously found for non-aqueous solutions except that an additional SO_3^- substituent group showed a small rate-decreasing effect.

Earlier Parts have described the preparation of water-soluble pyrylium salts containing one or more sulphonic or carboxylic acid groups attached to aryl groups in the pyrylium ring. We have reported the kinetics of the reactions of such pyrylium salts with water and the equilibria existing between the pyrylium salt, the corresponding unsaturated 1,5-diketone, and the enolate anion of this diketone.[2] We also previously considered the reactions of such pyrylium salts with primary amines from both the kinetic[3] and preparative points of view.[4] Finally we have shown that the corresponding pyridinium salts can undergo nucleophilic displacement reactions in which the pyridine behaves as the leaving group.[1] In all these respects, the water-soluble pyrylium–pyridinium chemistry parallels that previously carried out in non-aqueous solvents.[5]

This paper is concerned with the kinetics of the nucleophilic displacement reactions occurring in aqueous solution and was undertaken to give information that should be of assistance in applying this method for the conversion of primary amino functionality into other groups under mild conditions in aqueous solution.

Preparation of Compounds.—The pentacyclic pyrylium perchlorate (**5a**) was prepared by the previously reported method.[1] Four further pyrylium perchlorates (**1a**)—(**4a**) were prepared by two different approaches depending on the type of product: (a) for the symmetrical pentacyclic compound (**4a**), α-tetralone (2.5 mol) and the appropriately functionalised benzaldehyde (1 mol) were condensed with perchloric acid; (b) for the unsymmetrical tricyclic compounds (**1a**)—(**3a**), the intermediate chalcone was reacted with the corresponding methyl ketone.

A series of pyridinium salts was prepared (Tables 1 and 2) from pyryliums (**1a**)—(**5a**). Two methods were used: (a) each pyrylium was reacted with benzylamine and n-butylamine in methylene dichloride; subsequent addition of acetic acid yielded the corresponding pyridinium salts;[6] (b) reactions with lysine and glycylglycine were carried out in aqueous buffer solution at pH 10; acidification with perchloric acid gave the products.[1]

N.m.r. Spectra.—The pyridinium salts, all of which had m.p. > 300 °C, and which in some cases gave poor analytical results, were all characterised by their ^{1}H and ^{13}C n.m.r. spectra.

The ^{1}H n.m.r. spectra [Supplementary Publication No. SUP 56313 (8 pp.)†], obtained in CF_3CO_2H, showed the characteristic methoxy singlet near δ 4.15 [except for (**4b** and **c**)] and the multiplet for CH_2CH_2 near δ 3. The α-methylene group

† For details of Supplementary Publications see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1985, Issue 1.

Table 1. *N*-Substituted pyridinium perchlorates; preparation

Compound	Recrystallisation solvent	Colour[a]	Procedure	Yield (%)
(**1b**)	Acetone	Orange	A	64
(**2b**)	Acetone–Et_2O	Yellow	A	65
(**3b**)	Acetone–Et_2O	Yellow	A	68
(**4b**)	Acetone	Orange	A	63
(**5b**)	EtOH–Et_2O	Pale yellow	A	46
(**1c**)	Acetone	Orange	A	55
(**2c**)	Acetone–Et_2O	Yellow	A	53
(**3c**)	Acetone–Et_2O	Yellow	A	58
(**4c**)	Acetone	Orange	A	54
(**5c**)[b]	EtOH–Et_2O	Pale yellow	A	57
(**2d**)[c]	EtOH–Et_2O	Yellow	B	42
(**5d**)[b,c]	EtOH–Et_2O	Orange	B	69
(**5e**)[b]	EtOH	Yellow	B	39

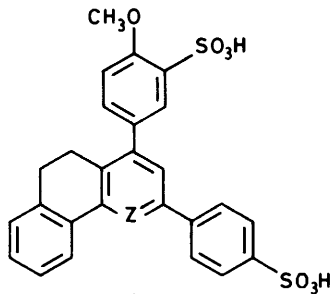
[a] All crystallised as prisms and had m.p. > 300 °C. [b] Identical by spectral comparison with compounds described in ref. 5. [c] Bisperchlorate.

in the N-substituent appears at δ 5.1—5.75 for the *N*-benzyl- and *N*-glycyl-glycine derivatives. These shifts are downfield from the corresponding shifts obtained in D_2O[4a] for water-soluble 2,4,6-triarylpyridinium salts. Integration of the aromatic region using the OMe and CH_2CH_2 peaks as standard shows acceptable agreement between the values expected and those actually found.

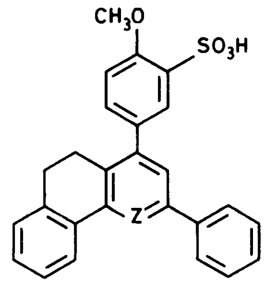
The ^{13}C n.m.r. spectra provided excellent criteria for both structure and purity. Chemical shifts for the pyrylium ring carbon atoms of pyrylium salts (**1a**)—(**5a**) are given in SUP 56313. The symmetrical compounds (**4a**) and (**5a**) gave just three peaks and the unsymmetrical compounds (**1a**)—(**3a**) five peaks in this region: the positions for the individual α (δ 165.0—170.3 p.p.m.), β (δ 118.2—126.3 p.p.m.), and γ (δ 166.0—168.4 p.p.m.) carbon atoms are very close to those reported for analogous compounds without water-solubilising groups.[7] The same applies for (**1a**) (C-2, δ 170.3; C-3, 120.5; C-4, 166.1; C-5, 126.3; C-6, 166.1 p.p.m.) compared with the reported[4] 2-(4-carboxyphenyl)-substituted compound (C-2, δ 170.5; C-3, 119.5; C-4, 166.2; C-5, 126.0; C-6, 165.5 p.p.m.). The other peaks for (**1a**)—(**5a**) are recorded in SUP 56313; some of the assignments are tentative.

The ^{13}C n.m.r. spectra of the pyridinium salts are recorded in SUP 56313. The five [or three for symmetrical (**1**) and (**2**) derivatives] peaks for the pyridinium ring carbon atoms are clearly observed in the expected regions: the α (δ 153.1—158.3 p.p.m.), β (δ 126.2—128.5 p.p.m.), and γ (δ 151.8—158.4 p.p.m.) positions are in agreement with previous work.[4,7]

The *N*-substituent peaks (SUP 56313) are also clearly



(1)



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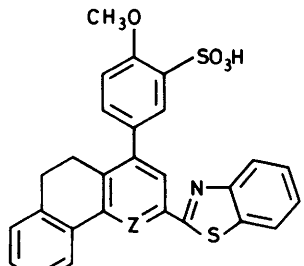

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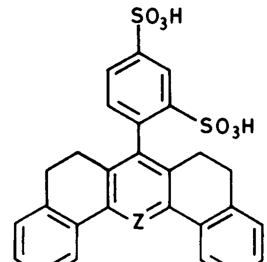

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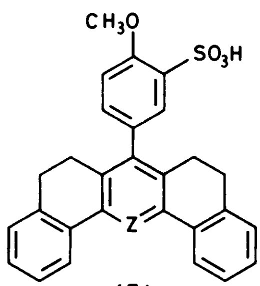
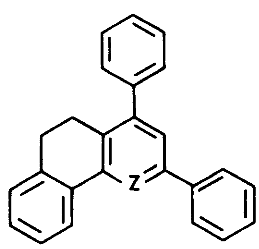


(5)

a ; Z = O^+, ClO_4^-
b ; Z = N^+CH_2Ph, ClO_4^-
c ; Z = N^+Bu^n, ClO_4^-
d ; Z = $N^+(CH_2)_4CH(NH_2)CO_2H$, ClO_4^-
e ; Z = $N^+CH_2CONHCH_2CO_2H$, ClO_4^-



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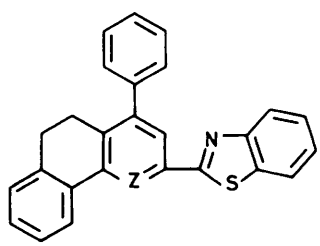

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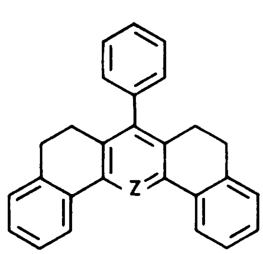

(8)

distinguished: (a) the *N*-butyl substituent shows the α-CH_2 group at δ 65.0—66.9 p.p.m. and the β-, γ-, and δ-carbon atoms at δ 32.4—32.8, 18.8—19.8, and 12.0—13.5 p.p.m., respectively; (b) for the lysine substituent, the α-CH_2 group appears at δ 63.2—64.3 p.p.m. and the β-, γ-, δ-, and ε-carbon atoms at δ 29.5—29.7, 21.3—21.9, 24.6—25.1, and 54.0—54.1 p.p.m., respectively; (c) the glycylglycine derivative depicts the α-CH_2 group at δ 65.0 p.p.m. and the β-, γ-, and δ-carbon atoms at δ 170.9, 41.5, and 174.2 p.p.m., respectively; (d) for the *N*-benzyl compounds, the CH_2 peak is clearly observed at δ 64.1—66.8 p.p.m.; the assignments for the phenyl carbon atoms, however, are tentative.

Table 2. *N*-Substituted pyridinium perchlorates; elemental analyses

Compound	Found (%) C	H	N	Molecular Formula	Required (%) C	H	N
(1b)	54.5	4.6	3.2	$C_{33}H_{26}ClNO_{11}S_2 \cdot 2H_2O$	53.0	4.0	1.9
(2b)	55.7	4.5	2.1	$C_{33}H_{26}ClNO_8S \cdot 4H_2O$	56.3	4.9	2.0
(3b)	57.7	4.1	2.6	$C_{34}H_{27}ClN_2O_8S_2 \cdot H_2O$	57.6	4.1	4.0
(4b)	51.1	3.9	1.8	$C_{34}H_{26}ClNNa_2O_{10}S_2 \cdot 2H_2O$	51.7	3.8	1.8
(5b)	63.0	4.7	2.8	$C_{35}H_{30}ClNO_8S$	63.7	4.6	2.1
(1c)	48.2	4.9	2.8	$C_{30}H_{27}ClNNaO_{11}S \cdot 3H_2O$	47.8	4.4	1.9
(2c)	53.6	4.6	1.4	$C_{30}H_{27}ClNNaO_8S \cdot 3H_2O$	53.5	4.9	2.1
(3c)	56.3	4.6	2.4	$C_{31}H_{29}ClN_2O_8S_2$	56.7	4.5	2.1
(4c)	47.5	4.3	2.1	$C_{31}H_{28}ClNNa_2O_{10}S_2 \cdot 3H_2O$	48.1	4.4	1.8
(2d)	49.5	4.6	3.7	$C_{32}H_{33}Cl_2N_2O_{14}S$	49.8	4.3	3.6

Table 3. First- (k_1) and second- (k_2) order rate constants for the reactions of *N*-substituted pyridinium perchlorates with piperidine in water at 80 °C

Compound	N^a	r^b	Slope 10^5k_2/l mol^{-1} s$^{-1\,c}$	% error in k_2	Intercept 10^6k_1/s$^{-1\,c,d}$	% error	$10^3k_1/(k_2 + 10k_1)^e$
(1b)	4	0.9999	34.8 ± 1.1	3	171 ± 52	30	33
(2b)	3	0.9999	58.9 ± 3.9	7	(0 ± 20)		2
(3b)	3	0.9999	243 ± 15	6	⩽ 6 (−4 ± 10)		2
(4b)	3	0.9988	640 ± 200	31	(100 ± 100)		24
(5b)	5	0.9992	2 210 ± 120	5	287 ± 26	9	11
(1c)	3	0.9999	0.0805 ± 0.0011	2	⩽ 0.04 (−0.02 ± 0.06)		33
(2c)	3	0.9995	0.091 ± 0.017	19	⩽ 0.7 (−0.2 ± 0.9)		88
(3c)	3	0.9998	0.162 ± 0.017	10	⩽ 0.6 (−0.2 ± 0.8)		79
(4c)	3	0.9999	0.375 ± 0.011	2	(0.0 ± 0.4)		56
(5c)	4	0.9975	2.06 ± 0.29	14	(0 ± 17)		90
(2d)	3	0.9995	1.31 ± 0.25	19	(0 ± 10)		88
(5d)	5	0.9912	15.8 ± 2.8	18	(66 ± 70)		90
(5e)	4	0.9946	18.7 ± 4.0	21	⩽ 46 (−30 ± 76)		72

[a] Number of runs. [b] Correlation coefficient. [c] 90% Confidence limit. [d] Values in parentheses are not significantly different from zero. [e] k_1 in s^{-1}, k_2 in mol^{-1} s^{-1}, *i.e.* percentage reaction by S_N1 route at [Nucleophile] = 10^{-1}M.

The shifts for the substituent carbons are in the same range as previously reported for the same *N*-substituents of water-soluble pyridiniums in D_2O[4] and for other pyridiniums in $CDCl_3$,[7] except that the α-carbon atom shifts are at lower field than for the corresponding monocyclic pyridiniums.

The remaining peaks are given in SUP 56313. Some of the assignments are clear, particularly for OCH_3 (δ 55.7—56.1 p.p.m.) and CH_2CH_2 (δ 26.1—28.3 p.p.m.) in the aliphatic region corresponding peaks were previously described.[4,7] However, in the aromatic region, although the assignments for 1′- and 4′-carbon atoms are clear,[4] those for the other peaks are tentative.

Reactions with Piperidine.—These reactions were carried out at 80 °C in water and followed spectrophotometrically under pseudo-first-order conditions, as already described.[8] Observed rate constants were calculated from the slope of the plots of ln $[a/(a - x)]$ *versus* time (see Experimental section). Such plots showed linearity up to 80% conversion, except for the tricyclic *N*-butyl substituted compounds (**1c**)—(**3c**), which exhibited curvature after 50% conversion possibly because of competitive ring opening to the divinylogous amide. Plots of the pseudo-first-order rate constants *versus* nucleophile concentration gave straight lines which passed through the origin within experimental error except for (**4b**) and (**5b**). The reasons for these non-zero intercepts are discussed in the following paper.[9] The k_2 and k_1 constants, derived from the slopes and intercepts, respectively, of the plots are collected in Table 3.

In Table 6, the k_2 values of Table 3 are compared with those for the analogous compounds (without water-solubilising groups) (**6**)—(**8**) for the reaction with piperidine in chlorobenzene solution. The following conclusions are apparent.

(a) In the pentacyclic series the rate constants in H_2O are less than those in PhCl by factors of 90 and 300 for the *N*-benzyl-substituted compounds (**5b**) and (**4b**), respectively. In the tricyclic series the rate constants in H_2O are less than in PhCl by factors of 160 and 280 for the *N*-benzyl-substituted compounds (**2b**) and (**1b**), respectively.[10]

We have shown earlier that the rate constants of these reactions decrease with increasing solvent polarity:[11,12] there is a correlation between log k_2 and the E_T solvent parameter[13] of the form $\log k_2 = -0.064\,E_T + 0.141$. Using E_T values of 63.1 and 37.4 for water and chlorobenzene,[13] respectively, the rate constants in water should be 0.0022 times those in chlorobenzene; this figure is in general agreement with the results of Table 6.

(b) The introduction of SO_3^- substituents is rate reducing: thus (**4**) is slower than (**5**) by factors of 3.5 and 6.5 in the *N*-benzyl and *N*-n-butyl series; (**1**) is slower than (**2**) by factors of 1.7 and 1.1 in the same two series. This abnormal effect of the sulphonate anion is discussed in the following paper.[9]

(c) The overall order of the rates for leaving groups of (**5**), (**4**) > (**3**) > (**2**), (**1**) is as expected from the work in chlorobenzene solution.[10,14,15]

Reactions with Thioglycolate Dianion.—Runs were carried out at 80 °C in water at pH *ca.* 12 (pk_1 3.68, pk_2 10.68 for thioglycolic acid:[16] thus the majority species was the dianion).

The pseudo-first-order plots showed linearity up to 80% conversion, except for the tricyclic *N*-butyl-substituted

Table 4. First- (k_1) and second- (k_2) order rate constants for the reactions of *N*-substituted pyridinium perchlorates with $^-SCH_2CO_2^-$ in water at 80 °C

			Slope		Intercept			
Compound	N^a	r^b	10^5k_2/l mol^{-1} s$^{-1\,c}$	% error in k_2	10^6k_1/s$^{-1\,c,d}$	% error in intercept	$10^3k_1/(k_2 + 10k_1)^e$	k_2 (thioglycolate)/k_2 (piperidine)
(1b)	3	0.9989	155 ± 45	29	82 ± 20	30	35	4.5
(2b)	4	0.9991	183 ± 16	8	92 ± 10	12	33	3
(3b)	3	0.9988	1 830 ± 550	30	< 47 (6 ± 40)		<2.5	7.5
(4b)	3	0.9999	5 650 ± 55	1	21 ± 2	7	36	9
(5b)	4	0.9991	22 200 ± 1 900	8	< 100 (40 ± 60)		<0.4	10
(1c)	3	0.9999	0.631 ± 0.026	4	0.4 (0.03 ± 0.40)		<37	8.5
(2c)	3	0.9995	0.718 ± 0.027	4	< 0.45 (0.04 ± 0.40)		<38	8
(3c)	3	0.9999	0.807 ± 0.011	2	< 0.3 (0.09 ± 0.20)		<27	5
(4c)	3	0.9999	1.81 ± 0.04	2	< 0.6 (−0.02 ± 0.60)		<25	5.7
(5c)	3	0.9996	8.94 ± 0.15	16	< 20.5 (−2 ± 23)		<70	4.3
(2d)	3	0.9999	1.52 ± 0.11	7	< 6 (−1 ± 7)		<80	1.2
(5d)	4	0.9959	5.8 ± 1.1	18	< 30 (12 ± 15)		<84	0.4
(5e)	4	0.9886	188 ± 59	31	< 51 (−9 ± 60)		<21	10

[a] Number of runs. [b] Correlation coefficient. [c] 90% Confidence limit. [d] Values in parentheses are not significantly different from zero. [e] *i.e.* percentage reaction by S_N1 route at [Nucleophile] = 10^{-1}M (k_1 in s^{-1}, k_2 in l mol^{-1} s^{-1} units).

Table 5. First- (k_1) and second- (k_2) order rate constants for the reactions of 14-benzyl-5,6,8,9-tetrahydro-7-(4-methoxy-3-sulphophenyl)-dibenzo[*c,h*]acridinium perchlorate (**5b**) with nucleophiles in water at 80 °C

			Slope		Intercept				
Nucleophile	N^a	r^b	10^5k_2	% error	$10^6k_1^{c,d}$	% error	$10^3k_1/(k_2 + 10k_1)^e$	k_2/k_2(piperidine) parent compound	k_2/k_2(piperidine)[17] MeI
$^-SCH_2CO_2^-$	4	0.9991	22 200 ± 1 900	8	100(40 ± 60)		0.4	10	5.0
Piperidine	5	0.9992	2 210 ± 120	5	287 ± 26	9	11	1	1
NaN_3	3	0.9999	1 360 ± 30	2	274 ± 8	3	17	0.62	0.030
NH_2CSNH_2	4	0.9938	880 ± 20	23	303 ± 66	22	26	0.39	0.93
KI	4	0.9948	610 ± 130	21	334 ± 52	16	35	0.28	1.3
KSCN	3	0.9996	610 ± 100	16	317 ± 46	15	34	0.28	0.25
Pyridine	4	0.9944	104 ± 23	22	280 ± 30	11	73	0.047	0.0085
KBr	3	0.9999	96.4 ± 8.1	8	299 ± 8	3	76	0.044	0.031

[a] Number of runs. [b] Correlation coefficient. [c] 90% Confidence limit. [d] Values in parentheses are not significantly different from zero. [e] *i.e.* percentage reaction by S_N1 route at [Nucleophile] = 10^{-1}M.

Table 6. Comparison of second-order rate constants k_2 in water and in chlorobenzene solution for reactions with piperidine

	10^3k_2/l mol^{-1} s^{-1} (PhCl) at 80 °C		$k_2(H_2O)/k_2$(PhCl) at 80 °C	
Series	*N*-benzyl	*N*-n-butyl	*N*-benzyl	*N*-n-butyl
(1)	96.6[a]	0.127[b]	0.0036	0.0063
(2)			0.0061	0.0072
(3)	*c*	0.35[d]		0.0046
(4)	1 960[a]	0.575[e]	0.0033	0.0055
(5)			0.0113	0.0358

[a] Measured at 80 °C in PhCl from ref. 10. [b] Extrapolated from value measured at 100 °C in PhCl from ref. 14, using $\Delta H^{\ddagger}_{373}$ 20 kcal mol^{-1} and $\Delta S^{\ddagger}_{373}$ −20 cal mol^{-1} K^{-1}. [c] Not described. [d] Extrapolated from value measured at 100 °C in PhCl from ref. 15, using $\Delta H^{\ddagger}_{373}$ 20 kcal mol^{-1} and $\Delta S^{\ddagger}_{373}$ −18 cal mol^{-1} K^{-1}. [e] Extrapolated from value measured at 100 °C in PhCl from ref. 14, using $\Delta H^{\ddagger}_{373}$ 20 kcal mol^{-1} and $\Delta S_{373}^{\ddagger}$ −17 cal mol^{-1} K^{-1}.

compounds (**1c**)—(**3c**), which exhibited curvature after 50% conversion. Plots of the pseudo-first-order rate constants *versus* nucleophile concentration gave straight lines which passed through the origin within the experimental error except for (**1b**), (**2b**), and (**4b**). The reasons for these non-zero intercepts are discussed in the following paper.[9] Table 4 lists the k_2 and k_1 rate constants and also gives the ratios k_2 (thioglycolate)/k_2 (piperidine). Except for the lysine derivatives, an exception which is explained later, the rates are all substantially faster (by a factor of 3—10) for the thioglycolate dianion. This rate increase is expected: HS^- reacts with MeI more rapidly than piperidine by a factor of 5 in MeOH at 25 °C.[17]

Reaction of Lysine and Glycylglycine Derivatives.—The lysine derivatives (**2d**) and (**5d**) react with piperidine 14 and 8 times as rapidly as do their *N*-n-butyl analogues. The increased reactivity found with piperidine may be rationalised in terms of hydrogen-bonding of the piperidine NH with the CO_2^- group of the lysine residue in the transition state: no such effect applies to the reaction with thioglycolate as nucleophile. This hydrogen-bonding would also explain the low ratios found for the lysine derivatives in the last column of Table 4.

The corresponding factors for the glycylglycine derivative (**5e**) are 9 and 21. These significant factors are in marked contrast to the low reactivity found for the *N*-ethoxycarbonylmethyl derivatives in the 2,4,6-triphenylpyridinium series:[18] this was ascribed to steric prevention of overlap of the C–N σ-bond with the π-orbital of C=O during the nucleophilic approach. Examination of models shows that, in the pentacyclic series, the substituted carbonyl group is less constrained, and offers more possibility for overlap of the incoming nucleophile with the C=O π* orbital, thus enhancing the rate in the normal manner found for rates of α-substituted carbonyl compounds.

Reaction of Pentacyclic N-*Benzylpyridinium* (**5b**) *with Various Nucleophiles.*—The k_2 and k_1 values are collected in Table 5. Comparison of the k_2/k_2 (piperidine) values for the parent compounds and for the reaction of the same nucleophiles with

MeI in methanol at 25 °C[17] (last column of Table 5) shows correspondence within a factor of 2 except for N_3^- and for pyridine (which react much more rapidly than expected), and for I^- (which reacts less rapidly).

Experimental

^1H N.m.r. spectra were recorded with a Varian EM-360L spectrometer; a JEOL FX-100 spectrometer was used for ^{13}C n.m.r. spectra; $SiMe_4$ was used as internal reference. U.v. spectra were obtained on a Pye-Unicam SP 8-200 spectrophotometer and i.r. spectra were run on a Perkin-Elmer 297 spectrophotometer.

The following compounds were made by the literature methods quoted: sodium 3-formyl-6-methoxybenzenesulphonate,[4a] 2-acetylbenzothiazole,[19] sodium 5-(1-oxo-2-tetralinylidenemethyl)-2-methoxybenzenesulphonate,[4a] 5,6,8,9-tetrahydro-7-(4-methoxy-3-sulphophenyl)dibenzo[*c,h*]xanthylium perchlorate (**5a**),[1] 14-butyl-5,6,8,9-tetrahydro-7-(4-methoxy-3-sulphophenyl)dibenzo[*c,h*]acridinium perchlorate (**5c**),[1] 14-(5-carboxy-5-aminopentyl)-5,6,8,9-tetrahydro-7-(4-methoxy-3-sulphophenyl)dibenzo[*c,h*]acridinium perchlorate (**5d**),[1] and 14-(carboxymethylcarbamoylmethyl)-5,6,8,9-tetrahydro-8-(4-methoxy-3-sulphophenyl)dibenzo[*c,h*]acridinium perchlorate (**5e**).[1]

5,6,8,9-*Tetrahydro*-7-(2,4-*disulphophenyl*)*dibenzo*[c,h]*xanthylium Perchlorate* (**4a**).—Perchloric acid (70%, 2.5 ml) was added dropwise to sodium 4-formylbenzene-1,3-disulphonate (2.5 g, 8.7 mmol), α-tetralone (3.2 g, 0.022 mol), and acetic anhydride (2.5 ml) with stirring. The temperature was kept at 100 °C for 1.5 h. On cooling to room temperature, 1:1 acetone–ether (50 ml) was added to give a yellow solid. The precipitated perchlorate was filtered off, washed with anhydrous ether (3 × 20 ml), and dried over P_2O_5 to give the product as yellow prisms (1.7 g, 31%), m.p. > 300 °C (Found: C, 42.4; H, 3.0. $C_{27}H_{19}ClNa_2O_{11}S{\cdot}5H_2O$ requires C, 42.9; H, 3.8%).

5,6-*Dihydro*-2-*phenyl*-4-(4-*methoxy*-3-*sulphophenyl*)*benzo*-[h]*chromenylium Perchlorate* (**2a**).—Perchloric acid (70%, 2 ml) was added dropwise to sodium 5-(1-oxo-2-tetralinylidenemethyl)-2-methoxybenzonesulphonate (2 g, 5.5 mmol), acetophenone (0.65 g, 5.5 mmol), and acetic anhydride (5 ml) with stirring. The temperature was kept at 100 °C for 1 h. On cooling to room temperature 1:1 acetone–ether (50 ml) was added to give a yellow solid. The precipitated perchlorate was filtered off, washed with anhydrous ether (3 × 20 ml), and dried over P_2O_5 to give the product as yellow prisms (1.5 g, 49%), m.p. > 300 °C (Found: C, 47.3; H, 4.9. $C_{26}H_{20}ClNaO_9S{\cdot}5H_2O$ requires C, 47.5; H, 4.6%).

5,6-*Dihydro*-2-(4-*sulphophenyl*)-4-(4-*methoxy*-3-*sulphophenyl*)*benzo*[h]*chromenylium Perchlorate* (**1a**).—Perchloric acid (70%, 3 ml) was added dropwise to sodium 5-(1-oxo-2-tetralinylidenemethyl)-2-methoxybenzenesulphonate (25 g, 6.83 mmol), sodium 4-acetylbenzenesulphonate (1.5 g, 6.83 mmol), and acetic anhydride (7 ml) with stirring. The temperature was kept at 100 °C for 1 h. On cooling to room temperature, acetone (25 ml) was added to give a yellow solid. The precipitated perchlorate was filtered off, washed with anhydrous ether (3 × 25 ml), and dried over P_2O_5 to give the product as yellow prisms (2 g, 47%), m.p. > 300 °C (Found: C, 42.9; H, 3.7. $C_{26}H_{20}ClO_{12}S_2{\cdot}4H_2O$ requires C, 43.4; H, 3.9%).

5,6-*Dihydro*-2-(*benzothiazolyl*)-4-(4-*methoxy*-3-*sulphophenyl*)*benzo*[h]*chromenylium Perchlorate* (**3a**).—Perchloric acid (70%, 5 ml) was added dropwise to sodium 5-(1-oxo-2-tetralinylidenemethyl)-2-methoxybenzenesulphonate (5 g, 13.6 mmol), 2-acetylbenzothiazole (2.4 g, 13.6 mmol), and acetic anhydride (12 ml) with stirring. The temperature was kept at 100 °C for 1 h. On cooling to room temperature, 1:1 acetone–ether (50 ml) was added to give a yellow solid. The precipitated perchlorate was filtered off, washed with anhydrous ether (3 × 30 ml), and dried over P_2O_5 to give the product as yellow prisms (3.3 g, 44%), m.p. > 300 °C (Found: C, 51.8; H, 3.6. $C_{27}H_{20}ClO_9NS_2{\cdot}1H_2O$ requires C, 52.3; H, 3.6%).

Preparation of Pyridinium Perchlorates (*Table* 1).—*Method A*. To a suspension of the pyrylium (2 mmol) in CH_2Cl_2 (10 ml) was added dropwise a solution of the amine (6 mmol) in CH_2Cl_2 (4 ml). The mixture was stirred for 1 h at room temperature. AcOH (1 ml) was added, and the red solution stirred for 1 h. Dilution with ether (150 ml) gave a solid which was filtered off, stirred with 1:1 acetone–ether (40 ml) containing $HClO_4$ (4 drops). The pyridinium salt was filtered off, washed with anhydrous ether (3 × 15 ml), and dried over P_2O_5.

Method B. The pyrylium salt (2 mmol) was added portionwise with stirring over a period of 6 h to the amine hydrochloride (5.5 mmol) in buffer solution (10 ml; pH 10). After stirring at 25 °C for 48 h, the reaction mixture was acidified with 70% $HClO_4$ (pH 2—3). The gum formed was washed with water and dissolved in hot ethanol. Dropwise addition to a large excess of ether (250—300 ml) gave a solid. The pyridinium was filtered off, washed with anhydrous ether (3 × 15 ml), and dried over P_2O_5.

Kinetic Measurements.—Kinetics were followed by u.v. spectrophotometry, monitoring the decrease of absorbance of pyridinium cation at a fixed wavelength, using the procedure already described.[11] In typical runs under pseudo-first-order conditions the concentration of pyridinium was *ca.* 10^{-5} mol l^{-1}.

Pseudo-first-order rate constants ($k_{obs.}$) were calculated from the plot of $\ln[a/(a-x)] = \ln[(\varepsilon_1-\varepsilon_2)/(\varepsilon-\varepsilon_2)]$ *versus* time. The extinctions coefficients of the pyridiniums (ε_1) are recorded in SUP 56313, the extinction coefficients of the corresponding pyridines (ε_2) being zero at the kinetic wavelength. First- and second-order rate constants k_1 and k_2 were obtained from the plots of $k_{obs.}$ *versus* nucleophile concentration. For the definition and calculation of errors and for the estimation of the precision of $k_{obs.}$ see ref. 8.

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