The Synthesis of Some Highly Strained Pyrylium and *N*-Benzylpyridinium Salts and Kinetics of their Reactions with Piperidine †

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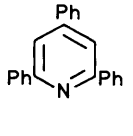
5,8-Dimethyl-1-tetralone (11) yields the hindered pyrylium salts (12)—(14), which give the corresponding pyridines and pyridinium salts with ammonia and amines. Chroman-4-one affords the oxoniaphenanthrene perchlorate (17). The additional steric hindrance from the *C*-methyl groups in (28) and (16) decreases the rate of S_N2 displacement. 2,4-Diphenylbenzo[*h*]chromenylium (7) and 5,6-dihydro-7-phenyldibenzoxanthylium tetrafluoroborates (8) do not give the corresponding pyridinium salts with aliphatic amines.

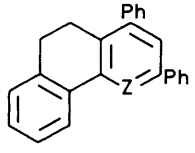
Benzo[*f*]chromanone with αβ-unsaturated ketones yielded tetracyclic pyridinium salts (33) and (34). Acenaphthenone derived pyrylium salts (39), (40), and (46), were prepared from benzylideneacetophenone, styryl t-butyl ketone, and benzo[*f*]chromanone. Kinetic measurements on derived *N*-benzylpyridinium salts demonstrated that the αβ-fusion of an acenaphthene ring *decreased* the tendency of a pyridine to act as a leaving group compared to the corresponding 2-phenylpyridine.

Interest in the development of more highly substituted pyridines as nucleofuges has been stimulated by the discovered advantages of 5,6-dihydro-2,4-diphenylnaphtho-[1,2-*b*]pyridine (3) and 5,6,8,9-tetrahydro-7-phenyldibenz-[*c*,*h*]acridine (6) over 2,4,6-triphenylpyridine (1).[1] The constraining CH_2–CH_2 groups in pyridinium salts derived from compounds (3) and (6) compared with those derived from (1) cause considerably greater reactivity towards nucleophilic displacement at the *N*-substituent: quantitative kinetics indicate that the benzyl derivatives of (1), (3), and (6) react at rates in the approximate ratio 1 : 69 : 900.[2] This has enabled preparative reactions under milder conditions,[3] and also the attainment of reactions not practicable with the triphenyl derivatives.

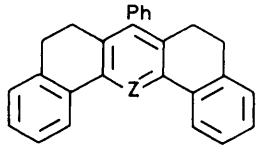
Further elaboration of the pyridines (1), (3), and (6) to increase the non-bonded interaction at the reaction site was envisaged: firstly by forcing atoms into close proximity by bond angle changes, secondly by the introduction of bulky substituents, and thirdly by a fused acenaphthene ring.



(1)



(2) Z = O^+, BF_4^-
(3) Z = N
(4) Z = $\overset{+}{N}Bu^n$, BF_4^-



(5) Z = O^+, BF_4^-
(6) Z = N

Synthesis of Pyrylium Salts.—Aromatisation of tricyclic (3) and pentacyclic compounds containing a pyridine nucleus (6) should increase the non-bonded interaction in the corresponding pyridinium salts. The 2,4-diphenylbenzo[*h*]chromenylium salt (7) was made as previously reported [4] by reaction of 1-naphthol with chalcone and triphenylmethyl tetrafluoroborate. The pentacyclic 5,6-dihydro-7-phenyldibenzo[*c*,*h*]xanthylium tetrafluoroborate (8) was similarly obtained from 1-naphthol and benzylidene-1-tetralone.

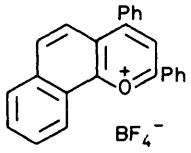
The tricyclic ring system (3) was also modified by replacing the 2-phenyl substituent by a tertiary butyl group: the trifluoromethanesulphonate (9a), perchlorate (9b), and tetrafluoroborate (9c) were all prepared from styryl t-butyl ketone and 1-tetralone.

A substituent R^2 placed at the 1-position of the fixed phenyl ring as in (10) should exert a strong N–R bond-weakening effect, and we therefore prepared such compounds. 5,8-Dimethyl-1-tetralone (11) was obtained by Friedel-Crafts reaction of *p*-xylene with γ-butyrolactone (*cf.* reported [5] preparation of 1-tetralone from benzene and γ-butyrolactone). Condensation of 5,8-dimethyl-1-tetralone (11) with chalcone, styryl t-butyl ketone, and benzylidene-1-tetralone gave the pyrylium salts (12), (13), and (14), respectively. Compound (17) was prepared by reaction of chroman-4-one with benzylideneactophenone and perchloric acid.

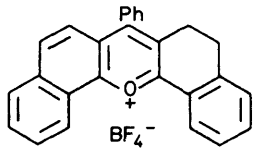
The novel pyrylium systems were treated with ammonium hydroxide and primary amines.

Reactions with 2,4-Diphenylbenzo[h]*chromenylium* (7) *and 5,6-Dihydro-7-phenyldibenzo*[c,h]*xanthylium Tetrafluoroborates* (8).—Although compound (7) is reported [4] to react with ammonium acetate and with *p*-aminophenol to give the corresponding quinoline and *N*-*p*-hydroxyphenylquinolinium tetrafluoroborate respectively, under a variety of conditions benzyl- and n-hexyl-amine with pyrylium salts (7) and (8) failed to give the desired pyridinium tetrafluoroborates: they produced instead the open-chain compounds (20)—(22). Compounds (20)—(22) have low melting points and are

† This is considered as Part 7 of the Series entitled 'Kinetics and Mechanisms of Nucleophilic Displacements with Heterocycles as Leaving Groups'. For Part 6, see A. R. Katritzky, W. H. Basinski, Y. X. Ou, G. Musumarra, and R. C. Patel, *J. Chem. Soc., Perkin Trans 2*, 1982, 1055.



(7)



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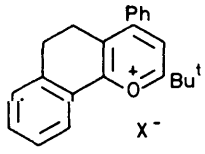
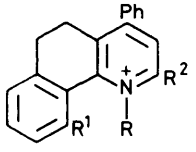


(9)

a; X = CF_3SO_3 b; X = ClO_4
c; X = BF_4



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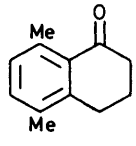
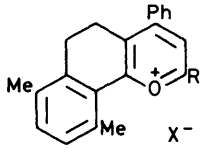
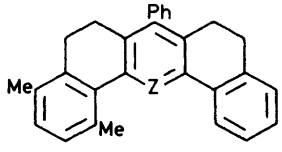


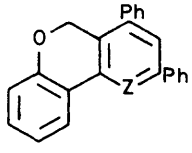
(11)



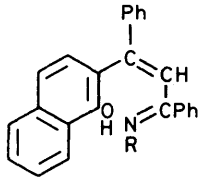
(12) R = Ph
(13) R = Bu^t



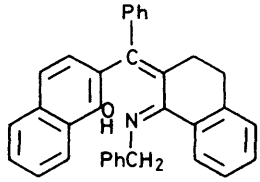
(14) Z = O^+, $CF_3SO_3^-$
(15) Z = N
(16) Z = $\overset{+}{N}CH_2Ph$, $CF_3SO_3^-$



(17) Z = O^+, ClO_4^-
(18) Z = N
(19) Z = $\overset{+}{N}CH_2Ph$, ClO_4^-



(20) R = $PhCH_2$
(21) R = $CH_3(CH_2)_5$



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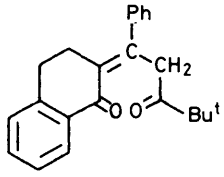

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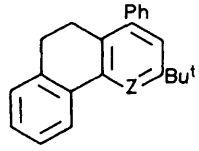
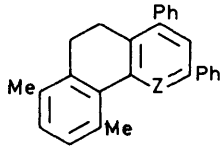
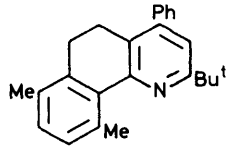


(24) Z = N
(25) Z = $\overset{+}{N}CH_2Ph$ ClO_4^-



(26) Z = N
(27) Z = $\overset{+}{N}Me$, $CF_3SO_3^-$
(28) Z = $\overset{+}{N}CH_2Ph$, $CF_3SO_3^-$



(29)

difficult to crystallise, but can be obtained pure by extraction (see Experimental section). Attempts to ring-close these compounds with acid failed, doubtless due to the phenolic nature of the hydroxy-groups.

Reactions with 5,6-*Dihydro*-4-*phenyl*-2-*t*-*butylbenzo*[h]*chromenylium Salt* (9b).—Reaction of compound (9b) with benzylamine in ethanol gave the ene-1,5-dione (23), also prepared by the action of hydroxide ion on (9a). Acid ($HClO_4$) quantitatively reconverts the pseudobase (23) into the pyrylium system (9). However, benzylamine and (9b) in chloroform when set aside for 3 days gave the pyridinium salt (25). The pyrylium salt (9a) reacted readily with ammonium hydroxide solution in methanol to furnish the corresponding pyridine (24) in high yield.

Aryl and heteroaryl amines failed to react with the pyrylium salt (9) under a variety of conditions: thus (9) was recovered unchanged after being refluxed with *p*-toluidine in dimethylformamide or diglyme.

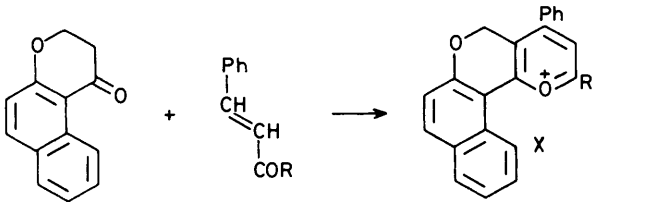
Reactions with 5,6-*Dihydro*-7,10-*dimethyl*-2,4-*diphenylbenzo*[h]*chromenylium* (12), 5,6,8,9-*Tetrahydro*-1,4-*dimethyl*-7-*phenyldibenzo*[c,h]*xanthylium* (14), *and* 2,4-*Diphenyl*-5H-6-*oxabenzo*[h]*chromenylium Salts* (17).—These compounds were readily converted into the corresponding pyridines (15), (18), and (26) and pyridinium salts (16), (19), (27), and (28) by treatment with ammonium hydroxide and primary amines respectively. However, the syntheses of the pyridinium salts must be conducted below 30 °C, otherwise cleavage of the N–C bonds in the products occurs.

The reactions of these systems (12), (14), and (17) were acid-catalysed in the final ring-closure step and base-catalysed in the initial steps [6] (see Experimental section).

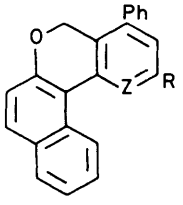
2-*t*-*Butyl*-5,6-*dihydro*-7,10-*dimethyl*-4-*phenylbenzo*[h]*chromenylium Perchlorate* (13; X = ClO_4).—Reaction of (13; X = ClO_4) with ammonium hydroxide gave the corresponding pyridine (29) in good yield.

The substituted pyridines and pyridinium salts were characterised spectrally.

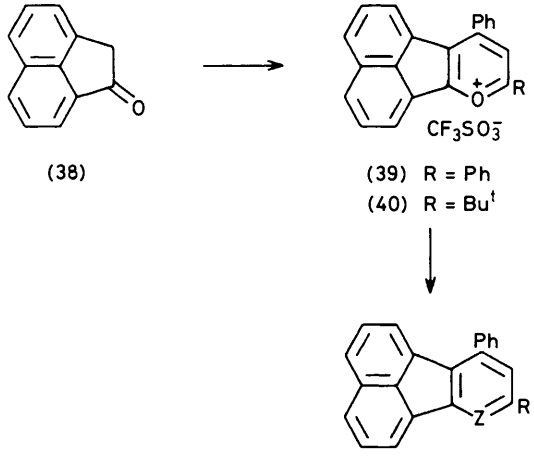
5H-6-*Oxa*-1-*oxoniabenzo*[c]*phenanthrene Series*.—2-Naphthol was converted by cyanoethylation and cyclisation [7] into benzo[*f*]chromanone (30). Condensation of (30) with benzylideneacetophenone (31) failed with $HClO_4$ but yielded



(30) (31) R = Ph (32) R = Bu^t (33) R = Ph, X = BF_4^- (34) R = Bu^t, X = $CF_3SO_3^-$



(35) Z = N, R = Ph
(36) Z = BuN^+, BF_4^-, R = Ph
(37) Z = N, R = Bu^t

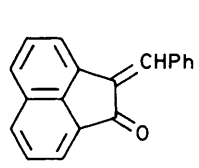


(38) (39) R = Ph (40) R = Bu^t (41) R = Ph, Z = N (42) R = Bu^t, Z = N (43) R = Ph, Z = $\overset{+}{N}CH_2Ph$ (44) R = Bu^t, Z = $\overset{+}{N}CH_2Ph$

2,4-diphenyl-5*H*-6-oxa-1-oxoniabenzo[*c*]phenanthrene fluoroborate (33) with BF_3·Et_2O. The corresponding brilliant orange t-butyl analogue (34) was best prepared from ketones (30) and (32) with CF_3SO_3H.

The pyrylium salt (33) was converted into the pyridine (35) by refluxing ammonium acetate. Synthesis of analogous pyridinium salts was more difficult: eventually the *N*-butyl derivative (36) was prepared under rigorously anhydrous conditions,[8] the reaction being followed by ^{13}C n.m.r. spectroscopy.[9] We also made the pyridine (37), but attempts to prepare the pyridinium salt corresponding to (34) failed.

1-*Oxoniafluoranthene Series*.—Condensation of acenaphthenone (38) [10] with benzylideneacetophenone (31) and styryl t-butyl ketone (32) in the presence of CF_3SO_3H gave the expected pyrylium salts (39) and (40) as triflates (trifluoromethanesulphonates). The perchlorate of compound (39) has previously been reported.[11] The pyrylium salts (39) and (40) were readily converted by ammonia into the pyridines (41) and (42) and by benzylamine into the *N*-benzylpyridinium triflates (43) and (44).



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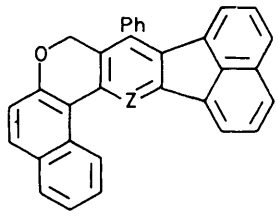
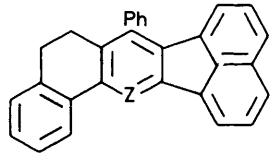


(46) Z = O^+, $CF_3SO_3^-$ (47) Z = N (48) Z = $\overset{+}{N}CH_2Ph$, $CF_3SO_3^-$



(49) Z = O^+ $CF_3SO_3^-$ (50) Z = N (51) Z = $\overset{+}{N}CH_2Ph$, $CF_3SO_3^-$

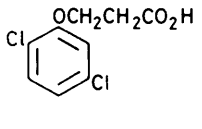
Benzylideneacenaphthenone (45) (prepared by a modification of the published [12] Wittig procedure since the ylide intermediate could not be generated by using ethoxide as recommended) reacted with benzo[*f*]chromanone to give the deep purple pyrylium salt (46), which was converted by ammonia into the pyridine (47) and by benzylamine into the pyridinium salt (48).

Benzylideneacenaphthenone (45) reacted with 1-tetralone to form the brown pyrylium triflate (49) which gave the corresponding pyridine (50) and pyridinium triflate (51).

7,10-*Dichloro*-5H-6-*oxa*-1-*oxoniaphenanthrene Series*—2,5-Dichlorophenol was converted into β-(2,5-dichlorophenoxy)-propionic acid (52) and cyclised *via* the acid chloride to 5,8-dichlorochromanone (53). With benzylideneacetophenone (31) and styryl t-butyl ketone (32), (53) gave the expected pyrylium salts (54) and (57). These were converted into the corresponding pyridines (55) and (58) by ammonia, but attempted preparation of the pyridinium salts [*e.g.* (56)] failed. Both (54) and (57) easily gave pseudo-bases and with benzylamine under rigorously anhydrous conditions, the vinylogous amides (59) and (60) were formed.

Kinetic Rates for Reactions of Pyridinium Salts with Piperidine.—The *N*-benzylpyridinium salts (28), (16), and (19) were treated with piperidine in chlorobenzene under the conditions similar to those reported previously; [13] the results are given in Tables 1 and 2. [Results for compound (25) have been reported elsewhere.[2]] All the compounds react essentially completely by the S_N2 mechanism (*cf.* Table 2).

The oxymethylenepyridinium salt (19) reacts slightly faster by an S_N2 mechanism ($k_2 = 3.03 \times 10^{-2}$ at 60 °C) than the *N*-benzyl analogue derived from (3) ($k_2 = 2.06 \times 10^{-2}$ at 60 °C).[6] However, the two *C*-methyl groups in (28) actually slow down



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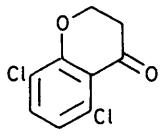

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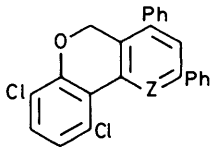
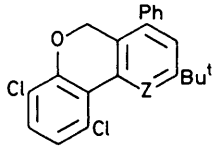
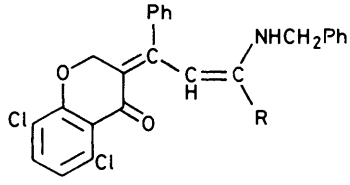


(54) Z = O^+, $CF_3SO_3^-$
(55) Z = N
(56) Z = $\overset{+}{N}CH_2Ph, CF_3SO_3^-$



(57) Z = O^+, $CF_3SO_3^-$
(58) Z = N



(59) R = Ph
(60) R = Bu^t

the reaction ($k_2 = 1.45 \times 10^{-2}$ at 60 °C) compared with the *N*-benzyl derivative of (3) ($k_2 = 2.06 \times 10^{-2}$ at 60 °C).[6] Neither (19) nor (28) react appreciably by the unimolecular mechanism: this is as previously found for the *N*-benzyl derivative of (3).

In the pentacyclic series also, the two *C*-methyl groups again give (16) a somewhat slower S_N2 rate ($k_2 = 5.4 \times 10^{-2}$ at 31 °C) than that previously measured [2] for the *N*-benzyl analogue derived from (6) ($k_2 = 10.5 \times 10^{-2}$ at 30 °C).

The four compounds (43), (44), (48), and (51) contain the αβ-fused acenaphthene ring. Three of these can be compared with the corresponding compounds in which the αβ-acenaphthene ring is replaced by an α-phenyl or an αβ-fused dihydronaphthalene ring (Table 3). The k_2 rate constants for the acenaphthalene derivatives are distinctly less than the α-phenyl analogues—by factors of 5, 3, and 25 in compounds (43), (44), and (51) respectively. Hence, the acenaphtho-fusion has quite the opposite effect to dihydronaphtho-fusion where rates are much faster than for the corresponding α-phenyl derivative.[2] The k_1 rates also appear to be slowed by αβ-acenaphtho-fusion, although the evidence is less clear cut here.

For the 6-oxa-1-azoniabenzo[*c*]phenanthrene series, the available kinetic results refer to (36), an *N*-butyl derivative. Comparison with the tricyclic *N*-butyl analogue (4) [14] gives a k_2 rate ratio (36)/(4) of 15.5, indicating the efficacy of 1-oxa-3,4-phenanthro-fusion.

Compound (48) combines acenaphtho- and 1-oxa-3,4-phenanthro-fusion. The latter structural feature increasing the rate of the second-order reaction is again indicated by the k_2 ratio of 6.4 (at 100 °C) for (48)/(51), however somewhat less than the ratio of 15.5 for (36)/(4).

Conclusions.—Extra steric hindrance in the form of the *C*-methyl groups in compounds (28) and (16), far from having a significant rate accelerating effect, actually slow down the reaction somewhat. This is presumably because the increased release of steric strain in the transition state is outweighed by increased steric hindrance to the approach of the nucleophile. Surprisingly, no significant S_N1 reaction was detected.

Acenaphtho-fusion has a uniformly rate-decreasing effect: the α-phenyl group is evidently pulled away from the *N*-substituent and much less steric acceleration occurs.

The oxygen atom in (19) causes, as compared to the ethano-bridged cyclic analogue, a small rate increase: indicating that

Table 1. Pseudo-first-order rate constants for the reaction of *N*-substituted pyridiniums with piperidine in chlorobenzene

Compound	Temperature (°C)	$10^5 k_{obs}/s^{-1}$	10^3[Nu]/mol l^{-1}
(28) [a,b]	60.0	7.62	5.2
		3.87	2.6
		1.96	1.3
		0.89	0.52
		0.19 [c]	0.052
(16) [d]	31.0 [e]	26.7	4.9
		12.7	2.3
		6.20	1.2
		0.65 [f]	0.047
	60.0 [g]	18.0	4.2
		9.43	2.1
		4.85	1.0
		2.04	0.42
		0.63 [h]	0.042
(19) [i]	60.0	23.2	7.6
		11.9	3.8
		3.03	0.91
		0.49 [j]	0.076
(36) [k]	60.2	0.13	55.6
		0.27	111.3
		0.495	222.5
(43) [l]	100.0	0.24	2.1
		0.45	4.25
		0.865	8.5
(44) [m]	100.0	0.45	1.9
		1.175	18.9
		1.86	37.8
(48) [n]	60.1	0.58	0.93
		1.20	2.3
		2.41	4.7
		4.96	9.3
(48) [n]	100.0	16.85	0.93
		30.6	2.3
		51.5	4.7
		89.0	9.3
(51) [o]	100.0	7.15	3.75
		26.6	18.75
		55.0	37.5
		101.9	75.0

[a] [28] = 5.391×10^{-5} mol l^{-1}. [b] $\varepsilon_1 = 16\,657$, $\varepsilon_2 = 38$, $\lambda = 365$ nm. [c] Estimated from $k_2 = 3.62 \times 10^{-2}$ l mol^{-1} s^{-1}: k_1 negligible. [d] $\varepsilon_1 = 22\,431$, $\varepsilon_2 = 394$, $\lambda = 405$ nm. [e] [16] = 4.753×10^{-5} mol l^{-1}. [f] Estimated from $k_2 = 1.38 \times 10^{-1}$ l mol^{-1} s^{-1}: k_1 negligible. [g] [(16)] = 4.115×10^{-5} mol l^{-1}. [h] Estimated from $k_2 = 1.51$ l mol^{-1} s^{-1}: k_1 negligible. [i] [19] = 7.574×10^{-5} mol l^{-1}; $\varepsilon_1 = 12\,806$, $\varepsilon_2 = 167$, $\lambda = 370$ nm. [j] Estimated from $k_2 = 6.51 \times 10^{-2}$ l mol^{-1} s^{-1}: k_1 negligible. [k] [36] = 11.12×10^{-5} mol l^{-1}; $\varepsilon_1 = 7\,017$, $\varepsilon_2 = 0$, $\lambda = 418$ nm. [l] [43] = 8.134×10^{-5} mol l^{-1}; $\varepsilon_1 = 8\,468$, $\varepsilon_2 = 0$, $\lambda = 370$ nm. [m] [44] = 3.723×10^{-5} mol l^{-1}; $\varepsilon_1 = 25\,096$, $\varepsilon_2 = 7\,042$ $\lambda = 328$ nm. [n] [48] = 4.636×10^{-5} mol l^{-1}; $\varepsilon_1 = 14\,431$, $\varepsilon_2 = 290$, $\lambda = 480$ nm. [o] [51] = 3.768×10^{-5} mol l^{-1}; $\varepsilon_1 = 17\,675$, $\varepsilon_2 = 5\,132$, $\lambda = 342$ nm.

'heterocyclic' analogues, where prepared more easily than 'carbocyclic' compounds, could be advantageous leaving groups. This conclusion is confirmed by work with the 1-oxa-3,4-phenanthro-fused derivatives (36) and (48), where the rate increase caused by the oxa-substituent is larger.

Experimental

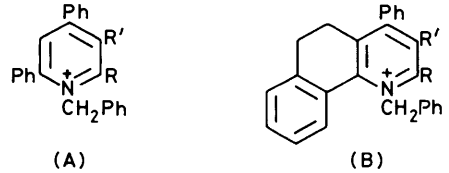
Melting points were determined using a Reichert hot-stage apparatus and are uncorrected. ^1H N.m.r. spectra were recorded on a Varian Associates HA 100 (100 MHz) or a Perkin-Elmer R 12 (60 MHz) spectrometer, using $SiMe_4$ as

Table 2. First- and second-order rate constants for the reactions of *N*-substituted pyridiniums with piperidine in chlorobenzene

Compound no.	t/°C	NR [a]	r [b]	10^2k_2 [c] / l mol^{-1} s^{-1}	10^6k_1/s^{-1} [a]	10^3k_1 [d] / $k_2 + 10k_1$	k_2 relative
(28)	60.0	5	0.999 99	1.45 ± 0.01	1.14 ± 0.34	0.1	0.56 [e]
(16)	31.0	4	0.9998	5.44 ± 0.24	<8	0.1	0.52 [f]
(16)	60.0	5	0.9999	42.5 ± 1.0	41 ± 21	0.1	0.83 [g]
(19)	60.0	4	0.999 99	3.03 ± 0.05	3.1 ± 2.0	0.1	1.17 [e]
(36)	60.2	3	0.9978	0.00216 ± 0.00042	(0.2 ± 0.6)	<30	
(43)	100.0	3	0.9999	0.0978 ± 0.0029	0.35 ± 0.16	0.36	
(44)	100.0	3	0.9989	0.0390 ± 0.0055	4.0 ± 1.6	9.3	
(48)	60.1	4	0.9994	0.526 ± 0.036	(0.2 ± 1.9)	<1	
(48)	100.0	4	0.9992	8.54 ± 0.72	102 ± 39	1.2	
(51)	100.0	4	0.9993	1.34 ± 0.11	(30 ± 50)	<6	

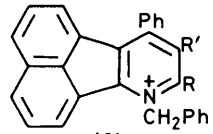
[a] NR = Number of runs. [b] r = Correlation coefficient. [c] 90% Confidence limits. [d] Percentage reaction by S_N1 route at [piperidine] = 10^{-1} mol l^{-1}. [e] Rate relative to *N*-benzyl derivative of (3). [f] Rate relative to *N*-benzyl derivative of (6) at 30 °C. [g] Rate relative to *N*-benzyl derivative of (6).

Table 3. Kinetic rate comparisons for reactions with piperidine in chlorobenzene at 100 °C of *N*-benzyl derivatives for phenyl (A), dihydronaphtho-fused (B), and acenaphthyl-fused series (C)



(A)

(B)



(C)

	10^5k_1/s^{-1}			10^3k_2 / l mol^{-1} s^{-1}		
R'	H	H	CH_2CH_2	H	H	CH_2CH_2
R	Ph	Bu^t	$-(C_6H_4)$	Ph	Bu^t	$-(C_6H_4)$
A	<2 [a]	8·0 [a]	-	4·94 [a]	1·07 [a]	343 [a]
B	-	-	-	343 [a]	608 [a]	4450 [a]
C	*ca.* 0·04 (43) [b]	0·40 (44)	3 (51)	0·98 (43)	0·39 (44)	13·4 (51)

[a] Reference 2. [b] Formulae Nos. given in parentheses.

internal reference. I.r. spectra were obtained on Perkin-Elmer 257 or 297 spectrophotometers.

The following were prepared by the literature procedures cited: 2,4-diphenylbenzo[*h*]chromenylium tetrafluoroborate, m.p. 248—252 °C (lit.,[4] m.p. 240—253 °C); β-(2-napthyloxy) propionitrile, m.p. 102—103 °C (lit.,[7] m.p. 105.5—107 °C; benzo[*f*]chromanone, m.p. 46—48 °C (lit.,[7] m.p. 50—51 °C); benzylideneacetophenone, m.p. 55.5—56.5 °C (lit.,[15] m.p. 58 °C); acenaphthenyl acetate, b.p. 117—118 °C/0.2 mmHg [lit.,[10] b.p. 166—168 °C (5 mmHg)]; acenaphthenol, m.p. 146—149 °C (lit.,[10] m.p. 144.5—145.5 °C); acenaphthenone, m.p. 117—119 °C (lit.,[10] m.p. 121—121.5 °C), styryl t-butyl ketone, m.p. 40—42 °C (lit.,[16] m.p. 43 °C) and benzyltriphenylphosphonium bromide, m.p. 287—288 °C (lit.,[17] m.p. 288 °C).

5,6-Dihydro-7-phenyldibenzo[c,h]*xanthylium Tetrafluoroborate* (8).—1-Naphthol (7.2 g, 0.05 mol), benzylidene-1-tetralone (11.7 g, 0.05 mol), and triphenylmethyl tetrafluoroborate (16.7 g, 0.05 mol) were refluxed in glacial HOAc (100 ml) for 12 h. When the mixture was cooled to 20 °C, Et_2O (400 ml) precipitated the *tetrafluoroborate* (8) which crystallised from glacial HOAc as prisms (7.1 g, 32%), m.p. 279—281 °C (Found: C, 72.7; H, 4.6. $C_{27}H_{19}BF_4O$ requires C, 72.7; H, 4.3%); $\nu_{max.}$ ($CHBr_3$) 1 632s, 1 612ms, 1 602m, and 1 050 cm^{-1}; δ (CF_3CO_2H) 7.7 (15 H, m) and 3.2 (4 H, bs).

2-t-Butyl-5,6-dihydro-4-phenylbenzo[h]*chromenylium Salts* (9).—Styryl t-butyl ketone (12.5 g, 0.067 mol), 1-tetralone (7.5 g, 0.05 mol), and CF_3SO_3H (12.0 g, 0.08 mol) were stirred at 80 °C for 6 h. After the mixture had been cooled to 20 °C, Et_2O (200 ml) was added to give the *pyrylium trifluoromethanesulphonate* (9a) (17 g, 74%) which crystallised from absolute EtOH as prisms, m.p. 239 °C (Found: C, 61.7; H, 5.0; S, 7.0. $C_{24}H_{23}F_3O_4S$ requires C, 62.1; H, 5.0; S, 6.9%); $\nu_{max.}$ (Nujol) 1 623s, 1 600ms, and 1 270vs cm^{-1}; δ (CF_3CO_2H) 8.3 (1 H, m), 7.85 (1 H, s), 7.5 (8 H, bs), 3.28 (4 H, bs), and 1.70 (9 H, s).

A similar procedure but using $HClO_4$ gave the *pyrylium perchlorate* (9b) (78%), as prisms (EtOH), m.p. 215 °C (Found: C, 66.4; H, 5.5. $C_{23}H_{23}ClO_5$ requires C, 66.6; H, 5.6%), $\nu_{max.}$ ($CHBr_3$) 1 623s, 1 603ms, and 1 080vs cm^{-1}.

$BF_3{\cdot}Et_2O$ in 2 molar excess gave the pyrylium tetrafluoroborate (9c) (72%), prisms from EtOH, m.p. 212—214 °C (Found: C, 68.6; H, 6.0. $C_{23}H_{23}BF_4O$ requires C, 68.7; H, 5.8%), $\nu_{max.}$ ($CHBr_3$) 1 620s, 1 600ms, and 1 040 cm^{-1}.

5,8-Dimethyl-1-tetralone (11).—*p*-Xylene (500 ml) and γ-butyrolactone (43 g, 0.5 mol) were stirred while anhydrous $AlCl_3$ (266 g, 2 mol) was added during 1 h. The mixture was heated at 100 °C for 16 h, cooled to 20 °C, and poured onto ice (1.5 kg) and 10M-hydrochloric acid (200 ml). The aqueous layer was separated and extracted with toluene (250 ml).

The organic combined extracts were washed with water and 20% potassium hydroxide, again with water, and then dried ($MgSO_4$). Distillation at reduced pressure gave the tetralone (11) (75 g, 86%), b.p. 160—175 °C at 0.5 mmHg) (Found: C, 82.8; H, 8.2. $C_{12}H_{14}O$ requires C, 82.7; H, 8.1%), $\nu_{max.}$ (film) 2 930 and 1 675 cm^{-1}; δ (neat) 6.75 (2 H, m), 2.8—1.6 (6 H, m), 2.1 (3 H, s), and 2.0 (3 H, s).

5,6-*Dihydro*-7,10-*dimethyl*-2,4-*diphenylbenzo*[h]*chromenylium Salts* (12, X = CF_3SO_3 or ClO_4).—5,8-Dimethyl-1-tetralone (8.7 g, 0.05 mol), benzylideneacetophenone (10.4 g, 0.05 mol), and trifluoromethanesulphonic acid (7.5 g, 0.05 mol) were heated at 90 °C with stirring for 4 h. After the mixture had been cooled to 20 °C, Et_2O (200 ml) was added. The precipitated product was washed with Et_2O (2 × 50 ml) and recrystallised from MeCN–Et_2O to give the *pyrylium trifluoromethanesulphonate* (12) (13.3 g, 52%) as prisms, m.p. 209—211 °C (Found: C, 65.3; H, 4.2; S, 6.5. $C_{28}H_{23}F_3O_4S$ requires C, 65.6; H, 4.5; S, 6.3%), $\nu_{max.}$ ($CHBr_3$) 1 618s, 1 598m, and 1 265vs cm^{-1}; δ (CF_3CO_2H) 8.3 (1 H, m), 7.82 (6 H, s), 7.76 (6 H, m), 3.30 (4 H, m), 2.5 (3 H, s), and 2.42 (3 H, s).

A similar procedure using $HClO_4$ gave the *perchlorate* (12; X = ClO_4) (55%), prisms from MeCN, m.p. 291 °C (Found: C, 69.7; H, 4.7. $C_{27}H_{23}ClO_5$ requires C, 70.1; H, 5.0%), $\nu_{max.}$ ($CHBr_3$) 1 620s and 1 090vs cm^{-1}.

The same procedure with 2 mol equiv. of $BF_3{\cdot}Et_2O$ gave the *pyrylium tetrafluoroborate* (12; X = BF_4) (48%), as prisms (MeCN), m.p. 246—248 °C (Found: C, 71.9; H, 5.1. $C_{27}H_{23}BF_4O$ requires C, 72.0; H, 5.2%); $\nu_{max.}$ ($CHBr_3$) 1 620s, 1 600s, 1 180s, and 1 050vs cm^{-1}.

2-*t-Butyl*-5,6-*dihydro*-7,10-*dimethyl*-4-*phenylbenzo*[h]*chromenylium Perchlorate* (13; X = ClO_4).—5,8-Dimethyl-1-tetralone (8.7 g, 0.05 mol), styryl t-butyl ketone (9.4 g, 0.05 mol), and $HClO_4$ (7.0 g, 0.07 mol) were stirred at 100 °C for 4 h. After the mixture had been cooled to 20 °C Et_2O (200 ml) was added. Filtration gave *pyrylium perchlorate* (13; X = ClO_4) (8.8 g, 40%) which formed prisms from EtOH, m.p. 216—218 °C (Found: C, 67.4; H, 5.9. $C_{25}H_{27}ClO_5$ requires C, 67.8; H, 6.2%), $\nu_{max.}$ ($CHBr_3$) 1 620s, and 1 090vs cm^{-1}; δ (CF_3CO_2H) 7.65 (8 H, bs), 3.15 (4 H, m), 2.5 (3 H, s), 2.9 (3 H, s), and 1.62 (9 H, s).

5,6,8,9-*Tetrahydro*-1,4-*dimethyl*-7-*phenyldibenzo*[c,h]*xanthylium Trifluoromethanesulphonate* (14).—5,8-Dimethyl-1-tetralone (8.7 g, 0.05 mol) and 2-benzylidene-1-tetralone (12 g, 0.05 mol) were stirred at 90 °C with trifluoromethanesulphonic acid (10.5 g, 0.07 mol) for 3 h. When the mixture had been cooled to 20 °C Et_2O (150 ml) was added. The *pyrylium trifluoromethanesulphonate* (14) was washed with Et_2O (2 × 50 ml) and recrystallised from HOAc to give prisms (14 g, 52%), m.p. 292—293 °C (Found: C, 67.0; H, 4.5; S, 5.9. $C_{30}H_{25}F_3O_4S$ requires C, 66.9; H, 4.7; S, 6.0%), $\nu_{max.}$ ($CHBr_3$) 1 620s, 1 600m, and 1 270vs cm^{-1}; δ (CF_3CO_2H) 8.35 (2 H, m), 7.5 (9 H, m), 3.01 (8 H, bs), and 2.49 (6 H, bs).

1,3-*Diphenyl*-10H-9-*oxa*-4-*oxoniaphenanthrene Perchlorate* (17).—Chroman-4-one * (4.2 g, 0.03 mol), benzylideneacetophenone (6.2 g, 0.03 mol), and $HClO_4$ (3 g, 0.03 mol) were heated at 90 °C for 3 h. When the mixture had been cooled, Et_2O (100 ml) was added to give the *pyrylium perchlorate* (17) which was filtered off and washed with Et_2O (8.6 g, 70%). Recrystallisation from HCO_2H gave red prisms, m.p. 291 °C (Found: C, 66.0; H, 3.9. $C_{24}H_{17}ClO_6$ requires C, 65.9; H, 3.9%); $\nu_{max.}$ (Nujol) 1 623s, 1 575ms, and 1 080vs cm^{-1}; δ (CF_3CO_2H) 8.2 (4 H, m), 7.4 (11 H, m), and 5.62 (2 H, s).

Reaction of 2,4-*Diphenylbenzo*[h]*chromenylium Tetrafluoroborate* (7) *with Benzylamine*.—Compound (7) (1.0 g, 0.002 mol), benzylamine (0.4 g, 0.004 mol), and absolute EtOH (10 ml) were kept for 1 h at 20 °C. Et_2O (30 ml) was added and the solution filtered. On removal of the solvent from the mother liquor 2-(1,3-*diphenyl*-3-*benzyliminoprop*-1-*enyl*)-1-*naphthol* (20) was obtained as a gum (0.8 g, 85%). This gum crystallised when warmed with EtOH–light petroleum (b.p. 40—60 °C). This when dried at 0.3 mmHg gave an amorphous solid, m.p. 114 °C (Found: C, 87.3; H, 5.7; N, 2.9. $C_{32}H_{25}NO$ requires C, 87.4; H, 5.8; N, 3.2%); $\nu_{max.}$ ($CHBr_3$) 1 642m, 1 600s, and 745s cm^{-1}.

Reaction of (7) *with Hexylamine*.—A similar procedure to the above gave 2-(1,3-*diphenyl*-3-*hexyliminoprop*-1-*enyl*)-1-*naphthol* (21) (94%) which failed to crystallise, but the analysis for which after it had been dried at 0.5 mmHg overnight was consistent with the proposed structural assignment (Found: C, 85.5; H, 7.3; N, 3.2. $C_{31}H_{31}NO$ requires C, 85.9; H, 7.2; N, 3.2%); $\nu_{max.}$ ($CHBr_3$) 2 920s, 2 845s, 1 642m, 1 615m, and 1 600s cm^{-1}.

Reaction of Compound (7) *with* p-*Toluidine*.—Compound (7) (1.5 g, 0.003 mol) in absolute EtOH (15 ml) when refluxed for 8 h with *p*-toluidine (0.3 g, 0.003 mol) and cooled to 0 °C gave a product which was washed with Et_2O (30 ml) to give 2,4-*diphenyl*-N-(p-*tolyl*)*benzo*[h]*quinolinium tetrafluoroborate* (0.7 g, 41%) prisms from EtOH, m.p. 270—279 °C (Found: N, 3.0. $C_{32}H_{26}BF_4N$ requires N, 2.7%); $\nu_{max.}$ ($CHBr_3$) 1 630s, 1 605w, 1 590s, and 1 050vs cm^{-1}; δ (CF_3CO_2H) 8.2—7.04 (20 H, m) and 2.3 (3 H, s).

Reaction of Compound (8) *with Benzylamine*.—Compound (8) (1.5 g, 0.003 mol) was stirred with benzylamine (0.3 g, 0.003 mol) in Et_2O (20 ml) for 5 min. The solution was washed with dilute Na_2CO_3 solution. The Et_2O layer was dried over $MgSO_4$ and the solvent was removed at 40 °C/20 mmHg to give a brown gum which failed to crystallise but was characterised after drying at 50 °C (2 mmHg) as 2-(1-*hydroxy*-2-*naphthyl*)*phenylmethylene*-1-*benzylimino*-1,2,3,4-*tetrahydronaphthalene* (22) (Found: C, 88.0; H, 5.6; N, 2.7. $C_{34}H_{27}NO$ requires C, 87.7; H, 5.9; N, 3.0%); $\nu_{max.}$ ($CHBr_3$) 1 600m, 805s and 735s cm^{-1}.

The Diketone (23).—The pyrylium salt (9a) (2.5 g, 0.005 mol) in absolute EtOH was treated with conc. NaOH (5 ml). The temperature was raised to 80 °C and the solution stirred for 5 min after which it was cooled to 0 °C. The product was filtered off and on recrystallisation from absolute EtOH the *diketone* (23) was obtained (1.6 g, 90%) as prisms, m.p. 123—124 °C (Found: C, 82.7; H, 7.7. $C_{23}H_{24}O_2$ requires C, 83.1; H, 7.3%); $\nu_{max.}$ ($CHBr_3$) 1 650s and 1 600 cm^{-1}; δ (CCl_4) 7.51 (1 H, m), 7.25 (5 H, s), 7.05 (3 H, s), 3.4 (2 H, bs), 2.6 (2 H, dd); 2.3 (2 H, dd), and 1.05 (9 H, s).

4-*Phenyl*-2-*t-butyl*-5,6-*dihydrobenzo*[h]*quinoline* (24).—The pyrylium salt (9a) (2.5 g, 0.005 mol) was stirred in MeOH (15 ml) with an excess of NH_4OH (40%). The fluorescence disappeared. The solution was warmed to 40 °C for 5 min and then cooled to 0 °C to precipitate the *pyridine* (24) (1.6 g, 95%). It was recrystallised from aqueous EtOH to give prisms, m.p. 97 °C (Found: C, 88.0; H, 7.3; N, 4.3%. $C_{23}H_{23}N$ requires C, 88.1; H, 7.4; N, 4.5%); $\nu_{max.}$ ($CHBr_3$) 1 592s cm^{-1}; δ ($CDCl_3$) 7.6 (1 H, s), 7.4 (9 H, m), 3.3 (4 H, m), and 1.5 (9 H, s).

* From Aldrich Chemical Co.

1-Benzyl-4-phenyl-2-t-butyl-5,6-dihydrobenzo[h]*quinolinium Perchlorate* (25).—The pyrylium perchlorate (9b) (3.0 g, 0.007 mol) was stirred with benzylamine (0.85 g, 0.008 mol) in $CHCl_3$ (20 ml) for 10 min; Et_3N (0.5 ml) was then added. The solution was set aside at room temperature for 3 d after which Et_2O was added at 0 °C; scratching precipitated the *product* (25) (2.1 g, 60%) as prisms ($CHCl_3$–Et_2O), m.p. 166—167 °C (Found: C, 72.0; H, 6.1; N, 2.8. $C_{30}H_{30}ClNO_4$ requires C, 71.5; H, 6.0; N, 2.8%); $\nu_{max.}$ ($CHBr_3$) 1 622s, 1 602s, and 1 060vs cm^{-1}; δ (CF_3CO_2H) 7.8 (1 H, s), 7.72 (8 H, s), 7.5 (6 H, s), 4.45 (2 H, q, *J* 5 Hz), 3.28 (4 H, m), and 1.7 (9 H, s).

5,6-Dihydro-7,10-dimethyl-2,4-diphenylbenzo[h]*quinoline* (26).—The pyrylium salt (12; X = CF_3SO_3) (1.5 g, 0.003 mol) was treated with NH_4OH (40%) at 40 °C for 5 min. The mixture was cooled to 0 °C to give the product which was filtered off. Recrystallisation from aqueous MeOH gave the *pyridine* (26) as prisms (0.9 g, 88%), m.p. 134—135 °C (Found: C, 90.0; H, 6.2; N, 3.8. $C_{27}H_{23}N$ requires C, 89.7; H, 6.4; N, 3.9%), $\nu_{max.}$ ($CHBr_3$) 1 590s, 770vs, and 705s cm^{-1}; δ ($CDCl_3$) 7.6—7.0 (13 H, m), 2.8 (4 H, s), 2.45 (3 H, s), and 2.26 (3 H, s).

5,6,8,9-Tetrahydro-1,4-dimethyl-7-phenyldibenz[c,h]*acridine* (15).—In a similar manner using the pyrylium salt (14) the *acridine* (15) was obtained (94%) as prisms (MeOH), m.p. 89—91 °C (Found: C, 89.9; H, 6.2; N, 3.7. $C_{29}H_{25}N$ requires C, 89.9; H, 6.5; N, 3.6%), $\nu_{max.}$ ($CHBr_3$) 1 550s and 770s cm^{-1}; δ ($CDCl_3$) 7.2 (6 H, s), 7.01 (5 H, m), 3.0 (8 H, bs), 2.45 (3 H, s), and 2.42 (3 H, s).

1,3-Diphenyl-10H-9-oxa-4-azaphenanthrene (18).—The pyrylium salt (17) reacted with an excess of NH_4OH (40%) in refluxing MeOH to give a quantitative yield of the *pyridine* (18) as needles (MeOH), m.p. 140 °C (Found: C, 85.6; H, 5.3; N, 4.0. $C_{24}H_{17}NO$ requires C, 85.9; H, 5.2; N, 4.2%); $\nu_{max.}$ 1 575m, 795s, and 750s cm^{-1}; δ ($CDCl_3$) 8.2 (2 H, m), 7.9—7.4 (13 H, m), and 4.5 (2 H, s).

4-Benzyl-1,3-diphenyl-10H-9-oxa-4-azoniaphenanthrene Perchlorate (19).—The pyrylium salt (17) (1.0 g, 0.002 mol) was stirred in CH_2Cl_2 (10 ml) with benzylamine (0.3 g, 0.003 mol) at 20 °C. After 5 min a catalytic quantity of AcOH (1 drop) was added. The mixture was stirred for a further 10 min during which time the solution turned pale yellow, water (10 ml) was then added. The CH_2Cl_2 layer was separated and the solvent removed at 40 °C (20 mmHg) to leave a residue. The pyrylium salt (19) (1.1 g, 90%), obtained by dissolving the above residue in EtOH (5 ml) and addition of H_2O (1.5 ml) at 0 °C, formed prisms, m.p. 155—157 °C (Found: C, 70.5; H, 4.6; N, 2.5. $C_{31}H_{24}ClNO_5$ requires C, 70.8; H, 4.6; N, 2.7%); $\nu_{max.}$ ($CHBr_3$) 1 620s, 1 610ms, and 1 090vs cm^{-1}; δ (CF_3CO_2H) 8.2—7.0 (18 H, m), 6.6 (2 H, m), 6.1 (2 H, s), and 5.3 (2 H, s).

5,6-Dihydro-7,10-dimethyl-4-phenyl-2-t-butylbenzo[h]*quinoline* (29).—The pyrylium salt (13; X = ClO_4) (1.5 g, 0.003 mol), aqueous ammonia (40%, 5 ml), and MeOH (10 ml) were refluxed for 5 min. The mixture was cooled to 0 °C to give the *pyridine* (29) (1.1 g, 95%) which crystallised from aqueous MeOH as prisms, m.p. 97 °C (Found: C, 85.7; N, 3.9; H, 7.6. $C_{23}H_{27}NO_5$, CH_3OH requires C, 85.7; N, 3.9; H, 7.8%); $\nu_{max.}$ ($CHBr_3$) 1 590s cm^{-1}; δ ($CDCl_3$) 7.9 (1 H, s), 7.6 (7 H, m), 3.3 (4 H, bs), 2.95 (3 H, s), 2.7 (3 H, s), and 1.6 (9 H, s).

Benzylideneacenaphthenone (*see Ref.* 12).—Benzyltriphenylphosphonium bromide (12.2 g, 28 mmol) was stirred under nitrogen at 20 °C in dry THF (70 ml) (consecutively dried by CaH_2 and $LiAlH_4$), n-butyl-lithium (1.4 M; 20 ml, 28 mmol) was injected *via* a septum; an intense orange-red colouration appeared immediately. After 2 h, acenaphthenequinone (5.1 g, 28 mmol) was added and stirring was continued for a further 2 h at 20 °C. Removal of solvent (60 °C/14 mmHg), dissolution of the residue in warm CH_2Cl_2, and chromatography on alumina, with EtOAc as eluant, gave benzylideneacenaphthenone (6.24 g, 87%), m.p. 100—102 °C (lit.,[18] m.p. 107 °C).

3-(2,5-Dichlorophenoxy)acetic Acid.[19]—NaH (3.60 g, 0.15 mol) was added rapidly to 2,5-dichlorophenol (8.15 g, 0.05 mol) and β-chloropropionic acid (6.52 g, 0.06 mol) in DMF (100 ml). The mixture was then heated for 2 h at 100 °C with frequent shaking. When cool, the solution was made up to 500 ml with water, and 15M-aqueous HCl added dropwise until acid to litmus. The precipitate was filtered off, washed with water (1 000 ml), and dried (at 100 °C) to give the acid (4.14 g, 35%), m.p. 144—147 °C, raised by recrystallisation from aqueous EtOH to 148 °C (lit.,[19] m.p. 145—146 °C) (Found: C, 46.1; H, 3.3; Cl, 29.8. Calc. for $C_9H_8Cl_2O_3$: C, 46.0; H, 3.4; Cl, 30.2%).

5,8-Dichlorochromanone (*see Ref.* 19).—3-(2,5-Dichlorophenoxy)propionic acid (2.0 g, 4.24 mmol) and $SOCl_2$ (3.0 ml) were heated at 100 °C for 10 min after which time the excess of $SOCl_2$ was removed under reduced pressure (60 °C/14 mmHg). The residue was dissolved in nitrobenzene (10 ml) and anhydrous $AlCl_3$ (1.2 g, 9.0 mmol) added below 25 °C. After 48 h at 20 °C, the mixture was steam distilled to leave an oil which solidified on cooling. The mixture was extracted with ether (2 × 10 ml) and the extracts washed (aqueous $NaHCO_3$), and dried ($MgSO_4$), and evaporated to give crude 5,8-dichlorochromanone (1.01 g, 55%), m.p. 57—61 °C. Recrystallisation from light petroleum (b.p. 60—80 °C) gave colourless prisms, m.p. 67.5—68 °C (lit.,[19] m.p. 69—70 °C) (Found: C, 49.9; H, 2.7; Cl, 32.4. Calc. for $C_9H_6Cl_2O_2$: C, 49.8; H, 2.8; Cl, 32.7%).

5H-6-*Oxa*-1-*oxoniabenzo*[c]*phenanthrene Series*

2,4-Diphenyl-5H-6-oxa-1-oxoniabenzo[c]*phenanthrene Fluoroborate* (33).—Benzo[*f*]chromanone (6.0 g, 30 mmol), benzylideneacetophenone (9.36 g, 45 mmol), and $BF_3{\cdot}Et_2O$ (90 mmol, 12.0 ml) were heated at 100 °C for 2 h. Ethanol was added (to 75 ml total volume) and the solution reheated to 80 °C. As the mixture cooled, the *pyrylium salt* (33) (4.85 g, 34%) crystallised as deep red prisms, m.p. 255—257 °C (Found: C, 70.7; H, 3.8. $C_{28}H_{19}BF_4O_2$ requires: C, 70.9; H, 4.0%); $\nu_{max.}$ ($CHBr_3$) 1 040 cm^{-1}; δ ($CDCl_3/CF_3CO_2H$) 8.7—7.2 (m, 17 H) and 5.6 (s, 2 H).

4-Phenyl-2-t-butyl-5H-6-oxa-1-oxoniabenzo[c]*phenanthrene Trifluoromethanesulphonate* (34).—Benzo[*f*]chromanone (2.0 g, 10 mmol), styryl t-butyl ketone pinacolone (2.1 g, 11 mmol) and CF_3SO_3H (1.5 g, 10 mmol) were heated for 5 h at 100 °C. The warm melt was triturated with Et_2O (50 ml); the orange precipitate was recrystallised (from light petroleum (b.p. 60—80 °C)–EtOH) to give *pyrylium salt* (34) (0.95 g, 19%) which on further recrystallisation from AcOH–EtOH (9 : 1, v/v) gave brilliant orange prisms, m.p. 290—294 °C (Found: C, 62.6; H, 4.5. $C_{27}H_{23}F_3SO_5$ requires C, 62.8; H, 4.5%); $\nu_{max.}$ ($CHBr_3$) 1 265 cm^{-1}; δ ($CDCl_3$–CF_3CO_2H) 8.8—7.1 (m, 12 H), 5.6 (s, 2 H), and 1.6 (s, 9 H).

2,4-Diphenyl-5H-6-oxa-1-azabenzo[c]*phenanthrene* (35).—The pyrylium salt (33) (0.47 g, 1 mmol) and NH_4OAc (0.39 g, 5 mmol) were refluxed in AcOH (4 ml) for 2 h after which the mixture was poured into water (10 ml); the white precipitate so formed was filtered off and dried at 60 °C. Recrystallisation

gave the *salt* (35) (0.31 g, 79%) as white needles (from AcOH), m.p. 211—212 °C (Found: C, 87.1; H, 5.0; N, 3.6. $C_{28}H_{19}NO$ requires C, 87.3; H, 5.0; N, 3.6%), $\nu_{max.}$ ($CHBr_3$) 1 590 cm^{-1}; δ ($CDCl_3$–TFA) 8.6 (m, 1 H), 8.1—6.5 (m, 16 H) and 5.3 (s, 2 H).

1-*Butyl*-2,4-*diphenyl*-5H-6-*oxa*-1-*azoniabenzo*[c]*phenanthrene Fluoroborate* (36).—Ac_2O (0.82 g, 8 mmol), the pyrylium salt (33) (1.90 g, 4 mmol), CH_2Cl_2 (12 ml), and Et_3N (2.0 g, 20 mmol) were refluxed together for a total of 1.5 h. After 30 min, dry EtOH (0.55 g, 12 mmol) was added and this was followed after 1 h by n-butylamine (0.29 g, 4 mmol). The mixture was then cooled to 20 °C and dry AcOH (1.2 g, 20 mmol) was added; this was followed after 24 h by the addition of Et_2O (10 ml). Further washing with ether (10 ml) and subsequent decantation was continued until the ethereal layer was only faintly yellow. Saturated aqueous $NaHCO_3$ was added to the deep red residue, and the suspension was stirred for 3 d. The mixture was filtered and the product dried (20 °C, *in vacuo*) to give the *pyridinium salt* (36) (1.52 g, 71%) which crystallised from n-pentyl alcohol–di-isopropyl ether as yellow prisms, m.p. 140—144 °C (Found: C, 73.0; H, 5.5; N, 2.7. $C_{32}H_{28}BF_4NO$ requires C, 72.6; H, 5.3; N, 2.7%), $\nu_{max.}$ ($CHBr_3$) 1 050 cm^{-1}; δ ($CDCl_3$) 8.1—6.9 (m, 17 H), 5.4 (d, 1 H, *J* 14 Hz), 4.9 (d, 1 H, *J* 14 Hz), 4.5 (bd, s, 2 H), 4.1 and 3.6 (m, 2 H), and 1.5—1.0 (m, 5 H).

4-*Phenyl*-2-*t*-*butyl*-5H-6-*oxa*-1-*azabenzo*[c]*phenanthrene* (37).—The pyrylium salt (34) (0.20 g, 0.39 mmol) was stirred in Et_2O (5 ml) and aqueous NH_3 (*d* 0.880) (1.7 mmol) added dropwise at 20 °C. After 2 h AcOH (4.0 mmol) was added and the mixture stirred for 16 h. After the solvent had been allowed to evaporate at 25 °C, water (10 ml) was added to the residue to give the *pyridine* (37) (0.11 g, 79%), m.p. 116—117 °C (Found: C, 85.3; H, 6.4; N, 3.8. $C_{26}H_{23}NO$ requires C, 85.5; H, 6.3; N, 3.8%), $\nu_{max.}$ ($CHBr_3$) 1 620, 1 595, and 1 580 cm^{-1}; δ ($CDCl_3$) 7.9—7.0 (m, 12 H), 5.2 (s, 2 H), and 1.6 (s, 9 H).

1-*Oxoniafluoranthene Series*

2,4-*Diphenyl*-1-*oxoniafluoranthene Trifluoromethanesulphonate* (39).—Acenaphthenone (0.84 g, 5 mmol), benzylideneacetophenone (1.56 g, 7.5 mmol), and CF_3SO_3H (0.75 g, 5 mmol) were heated at 100 °C for 4 h. EtOH (5 ml) was added to the hot gum and this was followed by trituration with ether (70 ml). After 1 h the *pyrylium salt* (39) (1.06 g, 42%) separated as brownish yellow prisms, m.p. 251—255 °C (Found: C, 67.0; H, 3.4. $C_{28}H_{17}F_3SO_4$ requires C, 66.4; H, 3.4%), $\nu_{max.}$ ($CHBr_3$) 1 265 cm^{-1}; δ ($CDCl_3$–CF_3CO_2H) 8.8—7.6 (m, 17 H).

4-*Phenyl*-2-*t*-*butyl*-1-*oxoniafluoranthene Trifluoromethanesulphonate* (40).—Acenaphthenone (0.84 g, 5 mmol), styryl t-butyl ketone (1.41 g, 7.5 mmol), and CF_3SO_3H (0.75 g, 5 mmol) were heated for 5 h at 100 °C as described for the pyrylium compound (39). Et_2O (10 ml) was added to the warm melt with trituration, *pyrylium* salt (40) (1.02 g, 83%), separated as green prisms, m.p. 218—222 °C (Found: C, 64.5; H, 4.3. $C_{26}H_{21}F_3SO_4$ requires C, 64.2; H, 4.3%), $\nu_{max.}$ ($CHBr_3$) 1 260 cm^{-1}; δ ($CDCl_3$–CF_3CO_2H) 8.8—7.7 (m, 12 H) and 1.7 (s, 9 H).

2,4-*Diphenyl*-1-*azafluoranthene* (41).[11]—The pyrylium salt (39) (0.35 g, 0.69 mmol) was stirred in Et_2O (5 ml) and aqueous NH_3 (*d* 0.880) (3.4 mmol) was added dropwise followed after 10 min by AcOH (5.7 mmol). The mixture was stirred for 16 h, solvent allowed to evaporate at 25 °C, and water (10 ml) added. Recrystallisation of the precipitate from aqueous Pr^iOH gave azafluoranthene (41) (0.16 g, 69%) as pale brown plates, m.p. 160—166 °C raised by recrystallisation to 169—171 °C (lit.,[11] 168 °C) (Found: C, 91.1; H, 4.7; N, 3.8. Calc. for $C_{27}H_{17}N$: C, 91.2; H, 4.8; N, 3.9%), $\nu_{max.}$ ($CHBr_3$) 1 585, 1 570, and 1 560 cm^{-1}; δ ($CDCl_3$) 8.4 (d, 1 H, *J* 7 Hz), 8.2 (m, 2 H), and 7.5 (m, 14 H).

4-*Phenyl*-2-*t*-*butyl*-1-*azafluoranthene* (42).—The oxoniafluoranthene salt (40) (0.44 g, 0.91 mmol) was stirred in Et_2O (5 ml) and aqueous NH_3 (*d* 0.880) (3.4 mmol) was added dropwise followed after 15 min by AcOH (5.4 mmol); the mixture was then stirred for 16 h. Evaporation of the solvent (25 °C) and addition of water (10 ml) gave a brown powder. Two recrystallisations from aqueous isopropyl alcohol gave the *azafluoranthene* (42) (0.19 g, 63%) as needles, m.p. 125—126 °C (Found: C, 89.1; H, 6.1; N, 4.1. $C_{25}H_{21}N$ requires C, 89.5; H, 6.3; N, 4.2%), $\nu_{max.}$ ($CHBr_3$) 1 565 cm^{-1}; δ ($CDCl_3$) 7.9—7.1 (m, 12 H) and 1.5 (s, 9 H).

1-*Benzyl*-2,4-*diphenyl*-1-*azoniafluoranthene Trifluoromethanesulphonate* (43).—1-Oxoniafluoroanthrene trifluoromethanesulphonate (39) (0.26 g, 0.5 mmol) was stirred in Et_2O (5 ml) and Et_3N (51 mg, 0.5 mmol). Benzylamine (54 mg, 0.5 mmol) was added dropwise at 20 °C, followed after 1 h by AcOH (0.15 g, 2.5 mmol). After being stirred for a further 15 h, the ether had evaporated. Addition of water (5 ml) gave a precipitate which crystallised from boiling toluene to give the *salt* (43) (0.18 g, 60%) as prisms, m.p. 80—81 °C (Found: C, 72.4; H, 4.7; N, 2.0. $C_{35}H_{24}F_3NSO_3$ requires C, 70.6; H, 4.1; N, 2.3%), $\nu_{max.}$ ($CHBr_3$) 1 270 cm^{-1}; δ ($CDCl_3$) 8.1 (s, 1 H), 7.6 (m, 21 H), and 6.9 (s, 2 H).

1-*Benzyl*-4-*phenyl*-2-*t*-*butyl*-1-*azoniafluoranthene Trifluoromethanesulphonate* (44).—1-Oxoniafluoranthene trifluoromethanesulphonate (40) (0.24 g, 0.5 mmol) was treated with benzylamine (54 mg, 0.5 mmol) as described for the salt (43); 10 min after the addition of AcOH, the precipitate was separated. It was dissolved in Pr^iOH–PhMe (1 : 4, v/v); on addition of light petroleum (b.p. 60—80 °C) to the hot solution, 1-*azoniafluoranthene trifluoromethanesulphonate* (44) crystallised as prisms (0.21 g, 71%), m.p. 185—187 °C (Found: C, 68.6; H, 4.9; N, 2.4. $C_{33}H_{28}F_3NSO_3$ requires C, 68.9; H, 4.9; N, 2.4%), $\nu_{max.}$ ($CHBr_3$) 1 270 cm^{-1}; δ ($CDCl_3$) 8.3—7.0 (m, 17 H), 6.8 (s, 2 H), and 1.7 (2, 9 H).

9-*Phenyl*-8H-7-*oxa*-16-*oxoniaphenanthro*[3,4-k]*fluoranthene Trifluoromethanesulphonate* (46)—Benzo[*f*]chromanone (0.26 g, 1.33 mmol) and benzylideneacenaphthenone (0.52 g, 2.0 mmol) were heated with CF_3SO_3H (0.75 g, 5 mmol) at 100 °C for 5 h. EtOH (2.5 ml) was added to the mixture at 80 °C, followed by Et_2O (30 ml) to give the *salt* (46) (0.38 g, 49%) as rich violet prisms, m.p. 232—235 °C (Found: C, 68.1; H, 3.4; S, 5.6. $C_{33}H_{19}F_3SO_5$ requires C, 67.8; H, 3.3; S, 5.5%), $\nu_{max.}$ ($CHBr_3$) 1 270 cm^{-1}; δ ($CDCl_3$/CF_3CO_2H) 8.8—7.0 (m, 17 H) and 6.1 (s, 2 H).

9-*Phenyl*-8H-7-*oxa*-16-*azaphenanthro*[3,4-k]*fluoranthene* (47).—Phenanthro[3,4-*f*]fluoranthene trifluoromethanesulphonate (46) (0.10 g, 0.23 mmol) was stirred in Et_2O (5 ml) and aqueous NH_3 (*d* 0.880) (2.0 mmol) was added dropwise followed by AcOH (2.0 mmol) after 3 h; the mixture was then stirred for 16 h. Evaporation of the solvent (25 °C) and addition of water (10 ml) gave a green powder (60 mg) which was dissolved in CH_2Cl_2 and chromatographed on alumina; elution with EtOAc–light petroleum (b.p. 60—80 °C) (1 : 4, v/v; 60 ml) gave a fraction which deposited 16-*azaphenanthro*[3,4-k]*fluoranthene* (47) (0.046 g, 61%) as bright yellow needles, m.p. 218—221 °C (Found: C, 88.4; H, 4.3; N, 3.2. $C_{32}H_{19}NO$ requires C, 88.7; H, 4.4; N, 3.2%), $\nu_{max.}$ ($CHBr_3$) 1 590 cm^{-1}; δ ($CDCl_3$/CF_3CO_2H) 8.4—7.0 (m, 17 H) and 5.8 (s, 2 H).

16-*Benzyl*-9-*phenyl*-8H-7-*oxa*-16-*azoniaphenanthro*[3,4-k]-*fluoranthene Trifluoromethanesulphonate* (48).—The pyrylium salt (46) (0.10 g, 0.17 mmol) was stirred under Et_2O–CH_2Cl_2 (1 : 1, v/v; 5 ml) and Et_3N (18 mg, 0.17 mmol). Benzylamine (19 mg, 0.17 mmol) was added at 20 °C, followed after 3 h by AcOH (52 mg, 0.43 mmol). After the mixture had been stirred for 16 h water (10 ml) was added; the resulting orange precipitate was stirred for 24 h and then filtered off and dried at 60 °C. The crude product (0.11 g) in CH_2Cl_2 was chromatographed on alumina and eluted with EtOAc to remove a small yellow band; further elution was with AnalaR Me_2CO. Solvent (20 °C, 14 mmHg) was removed from the eluant and the residue stirred with water (10 ml) and dried (80 °C) to give the *pyridinium salt* (48) (70 mg, 61%) as orange prisms, m.p. 152—155 °C (Found: C, 71.3; H, 3.9; N, 1.9. $C_{40}H_{26}F_3NSO_4$ requires C, 71.3; H, 3.9; N, 2.1%), $\nu_{max.}$ ($CHBr_3$) 1 260 cm^{-1}; δ ($CDCl_3$) 8.9 (d, 1 H), 8.5—6.5 (m, 21 H), 6.3 (d, 1 H, *J* 14 Hz), 5.9 (d, 1 H, *J* 7 Hz), and 5.2 (m, 2 H).

5,6-*Dihydro*-7-*phenyl*-14-*oxonianaphtho*[1,2-k]*fluoranthene Trifluoromethanesulphonate* (49).—1-Tetralone (0.15 g, 1 mmol) and benzylideneacenaphthenone (0.26 g, 1 mmol) were heated with CF_3SO_3H (0.75 g, 5 mmol) at 100 °C for 2 h; Et_2O (50 ml) was added, and the mixture triturated to give *pyrylium trifluoromethanesulphonate* (49) (0.22 g, 42%), as orange-brown prisms, m.p. 211—214 °C (Found: C, 67.4; H, 3.5; S, 6.3. $C_{30}H_{19}F_3SO_4$ requires C, 67.7; H, 3.6; S, 6.0%), $\nu_{max.}$ ($CHBr_3$) 1 270 cm^{-1}; δ ($CDCl_3$/CF_3CO_2H) 8.8—7.1 (m, 15 H), 3.8 (t, 2 H, *J* 7 Hz), and 3.3 (t, 2 H, *J* 7 Hz).

5,6-*Dihydro*-7-*phenyl*-14-*azanaphtho*[1,2-k]*fluoranthene* (50) —The pyrylium salt (49) (0.10 g, 0.19 mmol) was suspended in Et_2O (5 ml) at 20 °C and aqueous NH_3 (*d* 0.880) (1.4 mmol) was added dropwise. After the mixture had been stirred for 2 h AcOH (1.4 mmol) was added and the stirring continued until all the solvent had evaporated off (16 h). The residue was treated with water (10 ml), filtered, and dried (60 °C) to give an olive-green powder. This was dissolved in CH_2Cl_2 and eluted with EtOAc–light petroleum (b.p. 60—80 °C) (1 : 9 v/v) on alumina. When kept, the first light yellow fluorescent fraction deposited the *pyridine* (50) (40 mg, 56%), as greenish yellow needles, m.p. 207—208 °C (Found: C, 91.0; H, 5.1; N, 3.6. $C_{29}H_{19}N$ requires C, 91.3; H, 5.0; N, 3.7%), $\nu_{max.}$ ($CHBr_3$) 1 580 cm^{-1}; δ ($CDCl_3$/CF_3CO_2H) 8.4 (s, 1 H), 7.4 (m, 14 H), 3.1 (s, 2 H), and 2.7 (s, 2 H).

14-*Benzyl*-5,6-*dihydro*-7-*phenyl*-14-*azonianaphtho*[1,2-k]-*fluoranthene Trifluoromethanesulphonate* (51).—The pyrylium salt (49) (0.27 g, 0.5 mmol) was stirred in Et_2O–CH_2Cl_2 (1 : 1, v/v; 5 ml) and Et_3N (51 mg, 0.5 mmol). Benzylamine (54 mg, 0.5 mmol) was added dropwise at 20 °C. After 2 h, AcOH (0.15 g, 2.5 mmol) was added and the solution stirred for a further 15 h. Addition of water (10 ml) gave an olive-green powder (0.28 g). This was dissolved in CH_2Cl_2 and chromatographed on alumina by elution with EtOAc to remove impurities as purple and brown bands, and then with AnalaR Me_2CO which gave a bright green fraction. Removal of Me_2CO from the latter (20 °C, 14 mmHg) and treatment of the residue with water (10 ml) gave, after drying (60 °C), the *pyridinium salt* (51) (0.19 g, 60%) as bright yellow prisms, m.p. 160—165 °C (Found: C, 71.2; H, 4.0; N, 2.2. $C_{37}H_{26}F_3NSO_3$ requires C, 71.5; H, 4.2; N, 2.3%), $\nu_{max.}$ ($CHBr_3$) 1 260 cm^{-1}; δ ($CDCl_3$) 8.5—6.4 (m, 20 H), 6.0 (s, 2 H), 3.5 (t, 2 H, *J* 7 Hz), and 3.1 (t, 2 H, *J* 7 Hz).

7,10-*Dichloro*-2,4-*diphenyl*-5H-6-*oxa*-1-*oxoniaphenanthrene Trifluoromethanesulphonate* (54).—5,8-Dichlorochromanone (0.22 g, 1 mmol), benzylideneacetophenone (0.31 g, 1.5 mmol), and CF_3SO_3H (0.75 g, 5 mmol) were heated at 100 °C for 2 h. After the mixture had been cooled Et_2O (50 ml) was added and the whole triturated and kept for 4 h to give the *salt* (54) (0.44 g, 80%) as golden prisms (from Pr^iOH–Pr^i_2O), m.p. 180—183 °C (Found: C, 54.2; H, 2.6; Cl, 12.7. $C_{25}H_{15}Cl_2F_3SO_5$ requires C, 54.1; H, 2.7; Cl, 12.8%), $\nu_{max.}$ ($CHBr_3$) 1 265 cm^{-1}; δ ($CDCl_3$/CF_3CO_2H) 8.3—7.3 (m, 13 H) and 5.6 (s, 2 H).

7,10-*Dichloro*-2,4-*diphenyl*-5H-6-*oxa*-1-*azaphenanthrene* (55).—The pyrylium salt (54) (0.30 g, 0.54 mmol) was suspended in Et_2O (5 ml) at 20 °C and aqueous ammonia (*d* 0.880) (4.1 mmol) was added dropwise. After the mixture had been stirred for 1 h AcOH (6.5 mmol) was added and stirring was continued until all the solvent had evaporated (16 h). The residue was stirred with water for 2 h to give the *pyridine* (55) (0.19 g, 87%), as translucent needles (from aqueous Pr^iOH), m.p. 159—161 °C (Found: C, 71.5; H, 3.4; N, 3.4. $C_{24}H_{15}Cl_2NO$ requires C, 71.3; H, 3.7; N, 3.5%), $\nu_{max.}$ ($CHBr_3$) 1 590 cm^{-1}; δ ($CDCl_3$) 8.1—7.3 (m, 13 H) and 5.1 (s, 2 H)

7,10-*Dichloro*-4-*phenyl*-2-*t*-*butyl*-5H-6-*oxa*-1-*oxoniaphenanthrene Trifluoromethanesulphonate* (57).—5,8-Dichlorochromanone (0.22 g, 1 mmol), styryl t-butyl ketone (0.28 g, 1.5 mmol), and CF_3SO_3H (0.75 g, 5 mmol) were treated as for salt (54), except that the reaction time was 5 h. Trituration of the product gave the *pyrylium salt* (57) (0.37 g, 70%), as bright yellow prisms, m.p. 206—210 °C (Found: C, 51.3; H, 3.4; Cl. 13.1. $C_{23}H_{19}Cl_2F_3SO_5$ requires C, 51.6; H, 3.6; Cl, 13.3%), $\nu_{max.}$ ($CHBr_3$) 1 275 cm^{-1}; δ ($CDCl_3$/CF_3CO_2H) 7.8—7.2 (m, 8 H), 5.6 (s, 2 H), and 1.6 (s, 9 H).

7,10-*Dichloro*-4-*phenyl*-2-*t*-*butyl*-5H-6-*oxa*-1-*azaphenanthrene* (58).—1-Oxoniaphenanthrene salt (57) (0.40 g, 0.75 mmol) was stirred in Et_2O (5 ml) and treated with aqueous NH_3 (*d* 0.880) (3.4 mmol) and subsequently with AcOH as described for the pyridine (55).[1] The product was stirred with water to give the *pyridine* (58) (0.17 g, 60%) as prisms, m.p. 121—123 °C (Found: C, 68.6; H, 5.0; N, 3.6. $C_{22}H_{19}Cl_2NO$ requires C, 68.8; H, 5.0; N, 3.6%), $\nu_{max.}$ ($CHBr_3$) 1 590 cm^{-1}; δ ($CDCl_3$) 7.2 (m, 8 H), 5.0 (s, 2 H), and 1.4 (s, 9 H).

Kinetic Measurements.—Kinetic measurements were carried out under pseudo-first-order conditions, at 'u.v. concentration' (*i.e.* substrate concentration *ca.* 10^{-5} mol l^{-1}, nucleophile concentration *ca.* 10^{-3}—10^{-4} mol l^{-1}) unless otherwise stated. Reactions were followed by u.v. spectrophotometry, the decrease in substrate absorbance with time being monitored at the appropriate analytical wavelength (see Table 1).

Reactions at 100 °C were carried out in thermostatically controlled heating blocks, identical sample tubes being withdrawn at known times, and cooled in ice before measurement. The reaction at 60 °C was followed in the thermostatted cell-compartment of a Pye-Unicam SP8-200 u.v. spectrophotometer. Both devices maintain the temperature within ±0.1 °C.

Pseudo-first-order rate constants were obtained from plots of $\ln \frac{a}{a-x} = \ln\left(\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon - \varepsilon_2}\right)$ *vs.* time. Plots were linear to >60% completion. First- and second-order rate constants k_1 and k_2 were obtained from plots of k_{obs} *vs.* nucleophile concentration.[20]

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