Kinetics and Mechanisms of Nucleophilic Displacements with Heterocycles as Leaving Groups. Part 13.[1] Penta- and Nona-cyclic Derivatives [2]

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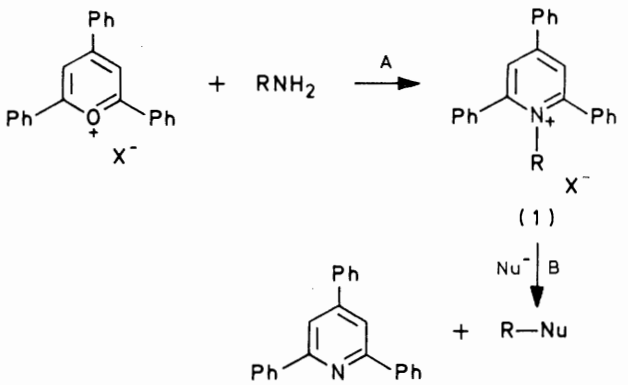
Steric acceleration by α,β-polycyclic fusion in pyridine leaving groups is quantitatively assessed. Constraining phenyl rings in pyridines to near planarity by ethano bridges in phenanthro[2,3-*h*]quinolinium (39) is *less* effective in terms of S_N2 displacement reactions by a factor of *ca.* 20 than in the less sterically hindered benzoquinolinium (2b). However, the corresponding rate for diphenanthro[2,3-*c*;3',2'-*h*]-acridinium (43) is almost the same as that for the dibenzoacridinium (3b) systems. The pendant phenyl groups in systems (12) and (19) decrease S_N2 rates compared with (2a) and (3a) by factors of *ca.* 2 and *ca.* 4, respectively. Neither of these structural modifications significantly increases S_N1 rates.

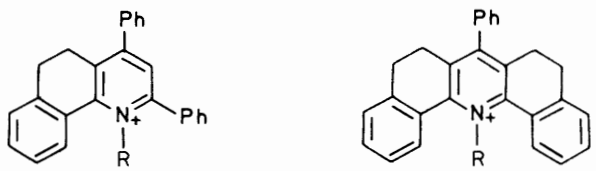
Primary amines have been transformed [3] into a wide range of functionality in a synthetically useful two-step sequence involving nucleophilic attack on isolable pyridinium intermediates.

Whereas [2,3-*a*]acenaphtho-fusion in pyridinium salts uniformly decreases [4] the second-order rate constant k_2, compared with a 2-phenyl substituent for transformation B, on account of steric effects, dihydronaphtho-fusion of the type shown in salts (2) and (3) produces marked increases in k_2 values [4] because of relief of steric strain at the reaction site ($N-C_\alpha$). Thus, constraint of the 2- and 6-phenyl groups in salt (1) to near planarity by the introduction of one (2) or two (3) bridging ethano-groups increases the S_N2 rates for transfer of *N*-benzyl to piperidine by factors of 65 and 900, respectively,[5] and allows preparative work to be carried out under relatively mild conditions.[6,7]

Our continuing search for still better leaving groups has involved the study of various types of monocyclic pyridinium salts [8,9] as well as pyridinium salts fused with heterocyclic rings.[10] In this context, we have now studied the effects of extended benzannelation and pendant phenyl groups on nucleophilic displacement rates.



Scheme 1.



(2a) R = $PhCH_2$
(2b) R = Bu^n

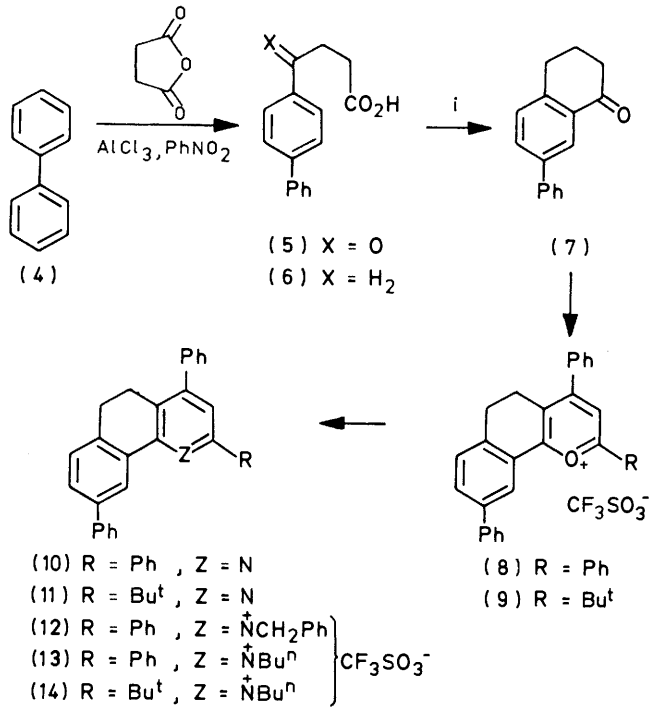
(3a) R = $PhCH_2$
(3b) R = Bu^n

Scheme 2.

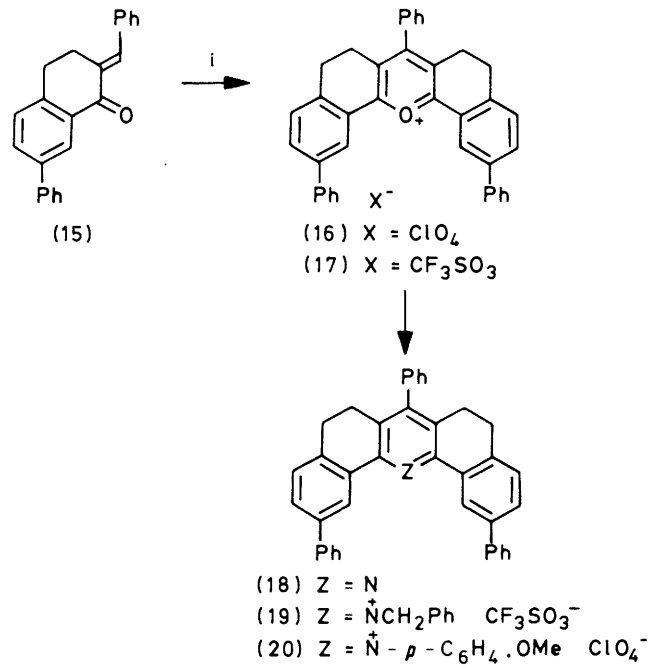
5,6-Dihydro-2,4-diphenylbenzo[h]*quinolinium Series.*—Friedel–Crafts succinoylation of biphenyl (4) afforded, as reported,[11] keto-acid (5). Rather than using a Clemmensen reduction,[11] acid (5) was best reduced to acid (6) by the Huang-Minlon reduction.[12] Ring-closure of acid (6) *via* the acid chloride afforded naphthalenone (7) as reported.[11] The latter and CF_3SO_3H condensed with benzylideneacetophenone and benzylidenepinacolone to afford novel chromenylium salts (8) and (9), respectively; those in turn were converted into the corresponding benzo[*h*]quinolines (10) and (11) upon treatment with ethereal ammonia. Chromenylium salt (8) gave quinolinium salts (12) and (13) upon treatment with benzylamine and n-butylamine respectively, at 20 °C. The large k_1 values induced by an α-t-butyl group [5] made it desirable to prepare pyridinium salt (14); however, treatment of chromenylium salt (9) with n-butylamine afforded only impure samples of salt (14), invariably contaminated with pyridine (11).

Tetrahydro-2,7,12-triphenyldibenz[c,h]*acridinium Series.*—Naphthalenone (7) underwent aldol condensation with benzaldehyde to afford ketone (15), as reported.[13] Condensation of ketones (7) and (15) with $HClO_4$ and CF_3SO_3H led respectively to xanthylium salts (16) and (17), dibenzacridine (18) being prepared from the latter and ammonium hydroxide. Xanthylium salt (17) afforded acridinium salt (19) with benzylamine, and with *p*-anisidine, xanthylium salt (16) gave acridinium salt (20). While 5,6,8,9-tetrahydro-7-phenyldibenz[*c*,*h*]acridinium salts undergo slow stilbene-like photocyclisation,[14] this 2,7,12-triphenyl analogue (20) was recovered unchanged upon irradiation (300 nm) in MeOH at 50 °C.

Synthesis of [7,7'-*Binaphthalene*]-1(2H),1'(2H')-*dione* (25).—Double succinoylation of biphenyl with β-methoxycarbonylpropionyl chloride afforded exclusively diester (21) in a modification of the reported work.[15] The extensive tarring that occurred could not be avoided by conducting the reaction at lower temperatures, since the monosuccinoylated ester (22) was the sole product. Saponification [15] of keto-ester (21) to give keto-acid (23) and Wolff–Kishner reduction [15] (Huang-Minlon modification) of the latter afforded the diacid (24) as reported. While diacid (24) was recovered unchanged upon



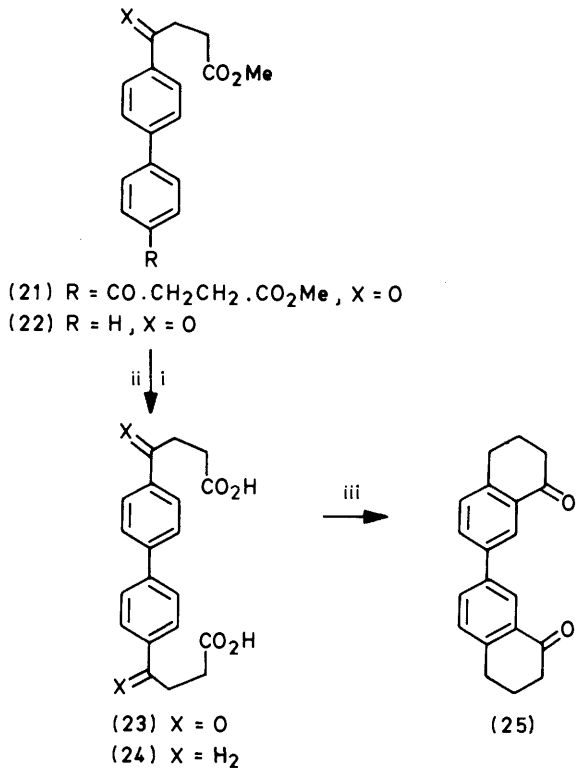
Scheme 3. *Reagents:* i, polyphosphoric acid



Scheme 4. *Reagents:* i, (7); CF_3SO_3H–$HClO_4$

treatment with anhydrous hydrogen fluoride, extensive polymerisation occurred when cyclisation of (24) *via* the acid chloride was attempted. Polyphosphoric acid, often the reagent of choice for ring-closure to tetralones,[16] effected cyclisation of diacid (24) to the novel binaphthalenedione (25); the necessarily unambiguous cyclisation was an important aspect of the synthetic route.

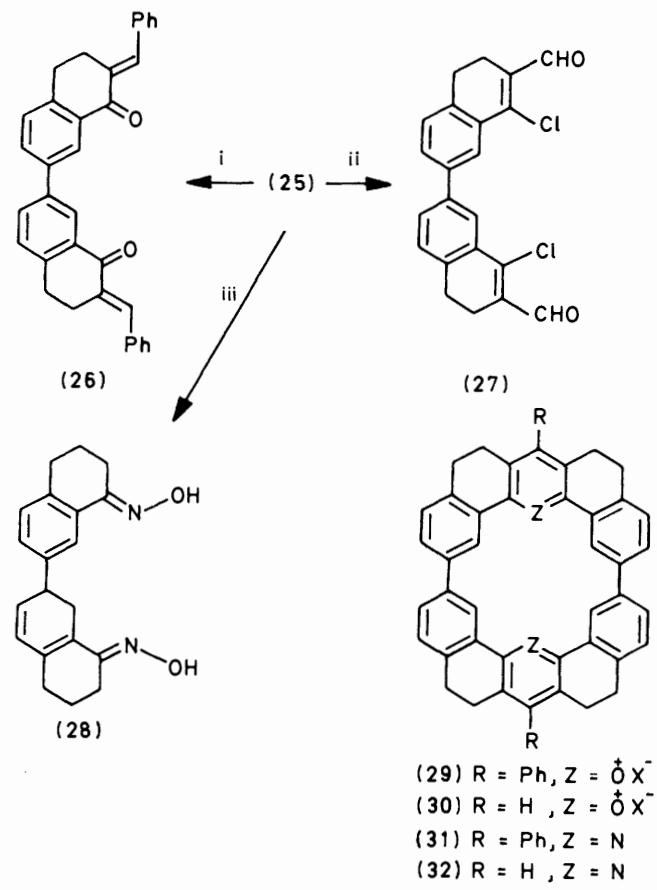
Attempts to prepare Heteromacrocycles.—In connection with work towards a synthesis of heterokekulenes,[17] macro-



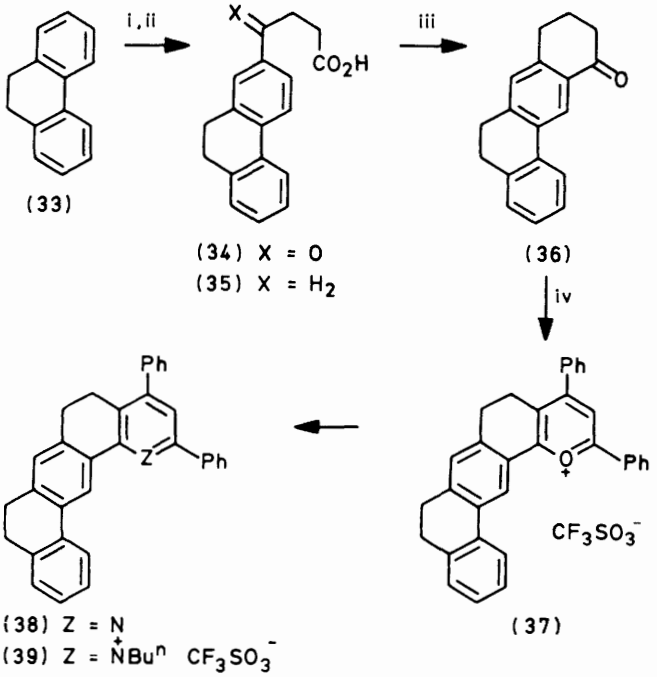
Scheme 5. *Reagents:* i, NaOH; ii, $(HOCH_2)_2$–Na–N_2H_4; iii, polyphosphoric acid

cycles such as (32) were attempted. Key intermediates were synthesised as follows. Condensation of dione (25) with benzaldehyde afforded exclusively the bisbenzylidene derivative (26), but this failed to yield salt (29) with dione (25) and a variety of acids, a carbonyl band being present in the resulting mixtures ($\nu_{max.}$ 1 660 cm^{-1}). The dioxime (28), obtained by treatment of dione (25) with hydroxylamine, failed to give pyridine (31) when treated with dione (26) and NH_4OAc–CH_3CONH_2 in a modified Hantzsch synthesis.[18] Direct fusion also failed. The reactive dialdehyde (27) was prepared by a Vilsmeier–Haack reaction on dione (25), but these two compounds failed to condense to give salt (30) with acids, under a variety of conditions, carbonyl components always remaining ($\nu_{max.}$ 1 670 cm^{-1}). The failure of all the above condensations was attributed to the rotational energy barrier of the biphenyl rings, amounting to *ca.* 18 kcal mol^{-1} of (30), which must be overcome; when held roughly coplanar by ethano-bridges across the 6,6′-positions, those analogues of compounds (25) and (27) condense readily to afford a macrocyclic bispyrylium salt.[17]

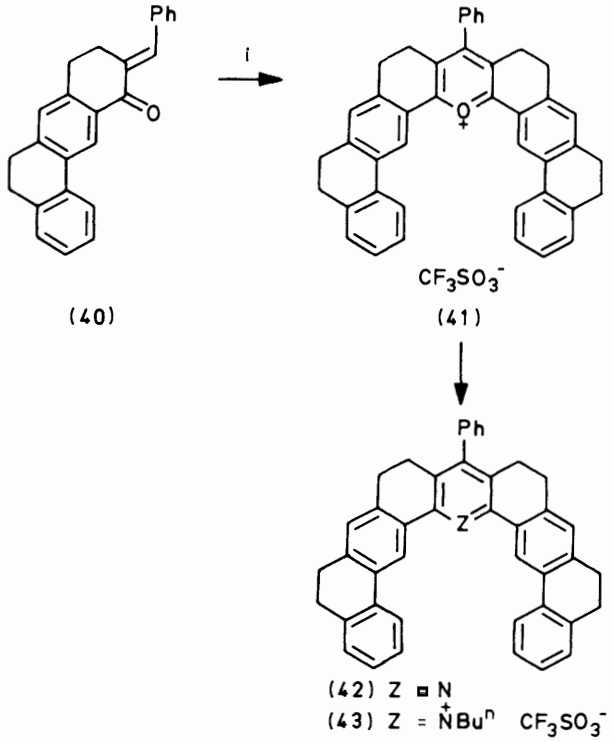
Azoniadibenz[a,j]*anthracene Series.*—The comparison of kinetic results of pyridinium salt (13) with salt (39), in which the 9-phenyl ring in the former is ' fixed ' by an ethano bridge, was of considerable interest. Succinoylation of 9,10-dihydrophenanthrene with succinic anhydride afforded, as reported,[19] keto acid (34); as we have described elsewhere [17] this was best reduced to acid (35) by the Lock modification [20] of the Wolff–Kishner reduction. Cyclisation of acid (35) in HF afforded, as published,[21] benz[*a*]anthracen-11(10*H*)-one (36), which condensed with chalcone, in the presence of CF_3SO_3H, to give azoniadibenz[*a*,*j*]anthracene salt (37). This was converted by ammonium hydroxide into pyridine (38) and by n-butylamine into pyridinium salt (39).



Scheme 6. *Reagents:* i, PhCHO–KOEt; ii, $POCl_3$–DMF; iii, $NH_2OH{\cdot}HCl$–C_5H_5N



Scheme 7. *Reagents:* i, $(CH_2O)_2O$–$AlCl_3$–$PhNO_2$; ii, N_2H_4–KOH; iii, HF; iv, PhCH=CHCOPh–CF_3SO_3H



Scheme 8. *Reagents:* i, (36)–CF_3SO_3H

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

Compound	*t*/°C	$10^5 k_{obs.}$/s^{-1}	10^3[Nu]/ mol l^{-1}
(12) [a]	100.0	49.5	3.20
		82.4	6.40
		109.5	9.60
(19) [b]	60.0	73.3	1.60
		111.0	3.20
		213.0	6.40
		261.0	9.60
		353.0	13.0
(39) [c]	100.0	1.98	320
		2.58	480
		3.15	640
(43) [d]	100.0	4.0	14.4
		7.0	28.8
		13.4	57.6

[a] [(12)] 3.20×10^{-5} mol l^{-1}; ε_1 13 000, ε_2 1 000, λ 360 nm. [b] [(19)] 3.20×10^{-5} mol l^{-1}; ε_1 12 000, ε_2 600, λ 400 nm. [c] [(39)] 1.20×10^{-3} mol l^{-1}; ε_1 12 000, ε_2 0, λ 384 nm. [d] [(43)] 9.60×10^{-5} mol l^{-1}; ε_1 17 000, ε_2 0, λ 421 nm.

Azoniabenzo[a]*phenanthro*[2,3-o]*pentaphene Series.*—A further comparison of the kinetics of pyridinium salts (19) and (43) was desired. Ketone (36) afforded ketone (40) upon treatment with benzaldehyde as previously described.[22] Condensation of ketones (36) and (40) with CF_3SO_3H gave the monocyclic salt (41), which afforded pyridine (42) upon treatment with ammonium hydroxide. Salt (41) was converted into the required pyridinium salt (43) when treated with n-butylamine.

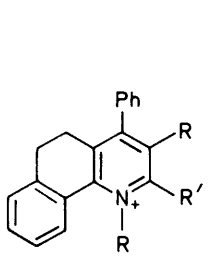
Kinetic Rates for Reactions of Pyridinium Salts with Piperidine.—Kinetic rates were determined by the previously reported method of reaction under pseudo-first-order conditions with piperidine in chlorobenzene solvent (Table 1). In

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

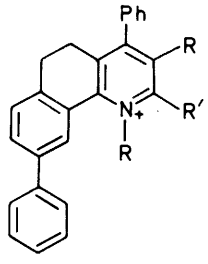
Compound	t/°C	N [a]	r [b]	10^3k_2 [c]/l mol^{-1} s^{-1}	10^6k_1 [a]/s^{-1}	$\frac{10^3k_1}{k_2 + 10k_1}$ [d]
(12)	100.0	3	0.998	93.8 ± 33	(21 ± 23)	<4
(19)	60.0	5	0.995	242 ± 33	38 ± 26	<3
(39)	100.0	3	0.999	0.037 ± 0.004	8 ± 2	68
(43)	100.0	3	0.999	2.2 ± 0.2	(8 ± 7)	<7

[a] Number of runs. [b] Correlation coefficient. [c] 90% Confidence limits. [d] Percentage reaction by S_N1 route at [piperidine] 10^{-1} mol l^{-1}.

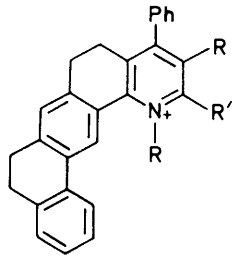
Table 3. Kinetic rate comparisons for reactions with piperidine in chlorobenzene at 100 °C of *N*-benzyl and *N*-n-butyl derivatives for dihydronaphtho-fused (A), 9-phenyldihydronaphtho-fused (B), and tetrahydrobenz[*a*]anthra-fused series (C)



(A)



(B)



(C)

	10^5k_1/s^{-1}				10^3k_2/l mol^{-1} s^{-1}			
	N-n-Butyl		*N*-Benzyl		*N*-n-Butyl		*N*-Benzyl	
R′	Ph		Ph		Ph		Ph	
R	H	Symmetrical system [b]	H	Symmetrical system [b]	H	Symmetrical system [b]	H	Symmetrical system [b]
A	⩽3	⩽10	⩽2	⩽1 [a]	0.69	2.4	341	511*
B			⩽4	⩽6*			94	242*
C	0.8	⩽2			0.037	2.2		

Values starred * at 60 °C; others at 100 °C. [a] Only 30 °C value available; k_2 (0.4 ± 0.8) × 10^{-5} l mol^{-1} s^{-1}. [b] Salts (3), (19), and (43) for A—C, respectively.

all cases plots of $k_{obs.}$ *versus* [piperidine] gave straight lines from the slopes of which the second-order rate constants k_2 were calculated (Table 2). The intercepts represent the first order component k_1: except for (39) these were not significantly different from zero (Table 2).

In Table 3, rate comparisons are made for the presently examined compounds and the tri- and penta-cyclic derivatives (2) and (3). As regards the S_N2 second-order rates, the comparisons of Table 3 show that *both* the simple pendant phenyl group *and* the fused phenanthro-system reduces the rates relative to the simple tri- or penta-cyclic analogues. Curiously the reduction in rate is *less* in the pentacyclic series than in the tricyclic. The reduction is greatest for the phenanthro-system in the tricyclic series and least for the phenanthro-system in the pentacyclic series. Although the detailed rate variations cannot at present be rationalised, it appears that the greater size of the substituent is responsible for hindering the approach of the nucleophile.

As regards the S_N1 rates, for most of the compounds only limiting rates are available. All that can be concluded is that neither the pendant phenyl groups, nor the fused phenanthro-systems greatly increase the S_N1 rates.

Experimental

M.p.s are uncorrected and were measured on a Reichert hot stage microscope. I.r. and mass spectra were recorded using a Perkin-Elmer 238B grating i.r. spectrometer and an RMU-6E Hitachi–Perkin-Elmer spectrometer, respectively. N.m.r. spectra were recorded on Varian EM 360L (^{1}H; 60 MHz) and JNM-FX 100 (^{13}C; 25.05 MHz) instruments, using $SiMe_4$ as internal standard.

The following compounds were prepared using literature methods: 4-oxo-4-biphenyl-4-ylbutanoic acid, m.p. 182—185 °C (lit.,[11] 183 °C); 3,4-dihydro-7-phenylnaphthalen-1(2*H*)-one, m.p. 67—69 °C (lit.,[11] 70 °C); 3,4-dihydro-7-phenyl-2-(phenylmethylene)naphthalen-1(2*H*)-one, m.p. 144—147 °C (lit.,[13] 144 °C); 3-methoxycarbonylpropionyl chloride, b.p. 89—90 °C at 15 mmHg (lit.,[23] 89—90 °C at 15 mmHg); 4,4′-bis-(3-carboxy-1-oxopropyl)biphenyl, m.p. 300—302 °C (lit.,[15] 303 °C); 4,4′-bis-(3-carboxypropyl)biphenyl, m.p. 182—184 °C (lit.,[15] 185 °C); 4-(9,10-dihydrophenanthren-2-yl)-4-oxobutanoic acid, m.p. 157—158 °C (lit.,[19] 157—158 °C); 5,6,7,8-tetrahydrobenz[*a*]anthracen-11(10*H*)-one, m.p. 89.5—90.5 °C, remelting at 96.0—96.5 °C (lit.,[21] 89.5—90.5 °C, remelting at 96.5—97.5 °C); 4-(9,10-dihydrophenanthren-2-yl(butanoic acid,[17] m.p. 91—92 °C (lit.,[24] 92—92.5 °C); 5,6,8,9-tetrahydro-10-(phenylmethylene)benz[*a*]anthracen-11(10*H*)-one, m.p. 159—160 °C (lit.,[22] 161 °C).

4-*Biphenyl*-4-*ylbutanoic Acid* (6).—A Huang-Minlon procedure [25] was adapted as follows. The oxo-acid (5) (16.3 g, 0.068 mol), hydrazine hydrate (7.0 g, 0.14 mol), ethylene glycol (200 ml), and KOH (16.3 g, 0.29 mol) were heated under

reflux for 1 h. After distilling the solution until the temperature rose to 190 °C, the residue was refluxed a further 3 h using an air condenser. Addition of water (600 ml) and neutralisation of the solution with HCl (6N) until just acid to litmus, gave a precipitate which was filtered, and the damp cake dissolved in toluene (200 ml) at 70 °C; extraction with KOH (1.5N; 2 × 100 ml), acidification of the aqueous layer with HCl (6N), filtration and washing with water (500 ml) gave *acid* (6) (13.8 g, 90%), prisms from AcOH, m.p. 116—117 °C (lit.,[11] 118 °C).

5,6-*Dihydro*-2,4,9-*triphenylbenzo*[h]*chromenylium Trifluoromethanesulphonate* (8).—Ketone (7) (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. Trituration of the gum with EtO_2 (50 ml) and standing (1 h) afforded *chromenylium salt* (8) (0.38 g, 68%), orange prisms from anisole–di-isopropyl ether, m.p. 224—226 °C (Found: C, 68.5; H, 4.1. $C_{32}H_{23}F_3O_4S$ requires C, 68.6; H, 4.1%); $\nu_{max.}$ ($CHBr_3$) 1 615, 1 600, and 1 260 cm^{-1}; δ ($CDCl_3$–CF_3CO_2H) 8.3 (1 H, s), 8.2 (3 H, s), 7.6 (15 H, m), and 3.1 (4 H, s).

2-*t*-*Butyl*-5,6-*dihydro*-4,9-*diphenylbenzo*[h]*chromenylium Trifluoromethanesulphonate* (9).—Ketone (7) (0.22 g, 1 mmol), benzylidenepinacolone (0.28 g, 1.5 mmol), and CF_3SO_3H (0.75 g, 5 mmol) were heated at 100 °C for 5 h. Trituration of the gum with Et_2O (50 ml) and standing (1 h) afforded *chromenylium salt* (9) (0.35 g, 65%), yellow prisms from anisole–di-isopropyl ether, m.p. 242—245 °C (Found: C, 66.2; H, 5.0. $C_{30}H_{27}F_3O_4S$ requires C, 66.6; H, 5.0%); $\nu_{max.}$ ($CHBr_3$) 1 620, 1 605, and 1 260 cm^{-1}; δ ($CDCl_3$) 8.2 (1 H, s), 7.6 (13 H, m), 3.1 (4 H, s), and 1.6 (9 H, s).

5,6-*Dihydro*-2,4,9-*triphenylbenzo*[h]*quinoline* (10).—Chromenylium salt (8) (0.30 g, 0.53 mmol) was stirred in Et_2O (5 ml). Aqueous NH_3 (*d* 0.88; 4 mmol) was added dropwise, followed after 2 h by AcOH (0.48 g, 8 mmol). The mixture was stirred for 16 h, solvent allowed to evaporate at 25 °C, and water (10 ml) added. After filtration and drying (80 °C), the residue (0.16 g, 71%) was chromatographed on neutral alumina (15 g; 10% EtOAc–light petroleum) to give, after removal of solvent, *quinoline* (10) as prisms, m.p. 217—219 °C (Found: C, 90.8; H, 5.7; N, 3.4. $C_{31}H_{23}N$ requires C, 90.9; H, 5.7; N, 3.4%); $\nu_{max.}$ ($CHBr_3$) 2 950, 2 930, 1 585, 765, and 760 cm^{-1}; δ ($CDCl_3$–CF_3CO_2H) 8.6 (1 H, s), 7.4 (18 H, m), and 2.8 (4 H, s).

2-*t*-*Butyl*-5,6-*dihydro*-4,9-*diphenylbenzo*[h]*quinoline* (11).—Chromenylium salt (9) (0.40 g, 0.74 mmol) was stirred in Et_2O (5 ml) and aqueous NH_3 (*d* 0.88; 4 mmol) added dropwise followed after 2 h by AcOH (0.48 g, 8 mmol). The mixture was stirred for 16 h, solvent allowed to evaporate at 25 °C, and water (10 ml) added. Filtration and drying (80 °C) gave the product (11) (0.25 g, 88%), which was chromatographed on neutral alumina as for quinoline (10), to give *quinoline* (11), needles, m.p. 163—164 °C (Found: C, 89.3; H, 7.0; N, 3.6. $C_{29}H_{27}N$ requires C, 89.4; H, 7.0; N, 3.6%); $\nu_{max.}$ ($CHBr_3$) 2 960—2 840, 1 585, 770, and 760 cm^{-1}; δ ($CDCl_3$) 8.7 (1 H, s), 7.3 (13 H, m), 2.8 (4 H, s), and 1.4 (9 H, s).

1-*Benzyl*-5,6-*dihydro*-2,4,9-*triphenylbenzo*[h]*quinolinium Trifluoromethanesulphonate* (12).—Chromenylium salt (8) (0.28 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). The mixture was stirred for 16 h, filtered, and the crude product recrystallised to give *quinolinium salt* (12) (0.23 g, 70%), prisms (from ethanol–di-isopropyl ether), m.p. 169—170 °C (Found: C, 71.7; H, 4.7; N, 2.1. $C_{39}H_{30}F_3NO_3S$ requires C, 72.1; H, 4.7; N, 2.2%); $\nu_{max.}$ ($CHBr_3$) 1 610, 1 600, and 1 265 cm^{-1}; δ ($CDCl_3$) 8.3 (1 H, s), 7.4 (20 H, m), 6.5 (3 H, m), 6.1 (2 H, s), and 2.9 (4 H, s).

1-*n*-*Butyl*-5,6-*dihydro*-2,4,9-*triphenylbenzo*[h]*quinolinium Trifluoromethanesulphonate* (13).—Chromenylium salt (8) (0.56 g, 1 mmol) was stirred in Et_2O (5 ml) and Et_3N (0.10 g, 1 mmol). n-Butylamine (73 mg, 1 mmol) was added dropwise at 20 °C, followed after 1 h by AcOH (0.30 g, 5 mmol). The mixture was stirred for 16 h, solvent allowed to evaporate at 25 °C, and water (10 ml) added. After filtration and drying (20 °C and 14 mmHg) the residue was chromatographed on neutral alumina (30 g; EtOAc followed by Me_2CO for pyridinium fraction) to give, after removal of solvent, *quinolinium salt* (13) (0.39 g, 63%), prisms, m.p. 227—228 °C (Found: C, 70.2; H, 5.3; N, 2.3. $C_{36}H_{32}F_3NO_3S$ requires C, 70.2; H, 5.2; N, 2.3%); $\nu_{max.}$ ($CHBr_3$) 2 960, 2 930, 2 870, 1 600, and 1 265 cm^{-1}; δ($CDCl_3$) 8.2 (1 H, s), 7.4 (18 H, m), 4.9 (2 H, t, *J* 7 Hz), 2.9 (4 H, s), 1.4 (2 H, m), 0.8 (2 H, m), and 0.5 (3 H, t, *J* 7 Hz).

5,6,8,9-*Tetrahydro*-2,7,12-*triphenyldibenzo*[c,h]*xanthylium Perchlorate* (16).—Ketone (7) (0.22 g, 1 mmol), benzylidene-ketone (15) (0.31 g, 1 mmol), and $HClO_4$ (70%, 0.20 ml) were heated at 100 °C for 40 min. Trituration of the gum with Et_2O (5 × 10 ml) and filtration afforded *xanthylium perchlorate* (16) (0.23 g, 38%), as orange prisms, m.p. >300 °C (Found: C, 76.3; H, 4.8. $C_{39}H_{29}ClO_5$ requires C, 76.4; H, 4.8%); $\nu_{max.}$ ($CHBr_3$) 1 620 and 1 085 cm^{-1}; δ ($CDCl_3$–CF_3CO_2H) 8.4 (2 H, d, *J* 2 Hz), 7.9 (2 H, dd, *J* 2 and 7 Hz), 7.5 (17 H, m), and 3.1 (8 H, s).

5,6,8,9-*Tetrahydro*-2,7,12-*triphenyldibenzo*[c,h]*xanthylium Trifluoromethanesulphonate* (17).—Ketone (7) (0.11 g, 0.5 mmol), benzylidene-ketone (15) (0.16 g, 0.5 mmol) and CF_3SO_3H (0.75 g, 5 mmol) were heated at 100 °C for 4 h. Trituration of the gum with Et_2O (5 × 10 ml) and filtration afforded *xanthylium trifluoromethanesulphonate* (17) (0.12 g, 33%), orange prisms (from AcOH–$MeNO_2$–Pr^i_2O 4 : 1 : 4), m.p. 292—294 °C (Found: C, 72.2; H, 4.4; S, 4.6. $C_{40}H_{29}F_3O_4S$ requires C, 72.5; H, 4.4; S, 4.8%); $\nu_{max.}$ ($CHBr_3$) 1 620 and 1 270 cm^{-1}; δ ($CDCl_3$–CF_3CO_2H) 8.4 (2 H, d, *J* 2 Hz), 7.5 (19 H, m), and 3.0 (8 H, m).

5,6,8,9-*Tetrahydro*-2,7,12-*triphenyldibenz*[c,h]*acridine* (18).—Xanthylium salt (17) (0.20 g, 0.3 mmol) was stirred in Et_2O–CH_2Cl_2 (5 ml; 1 : 1 v/v) and aqueous NH_3 (*d* 0.88; 2 mmol) added dropwise followed after 2 h by AcOH (0.24 g, 4 mmol). The mixture was stirred for 16 h, solvent allowed to evaporate at 25 °C, and water (10 ml) added. Filtration and drying (80 °C) gave a brown product which was chromatographed on alumina (30 g; EtOAc), and the solvent removed (20 °C and 14 mmHg) to give *acridine* (18) (0.12 g, 80%) as buff plates; m.p. 210—213 °C (Found: C, 91.2; H, 5.7; N, 2.6. $C_{39}H_{29}N$ requires C, 91.5; H, 5.7; N, 2.7%); $\nu_{max.}$ ($CHBr_3$) 2 985—2 840, 1 600, and 760 cm^{-1}; δ($CDCl_3$–CF_3CO_2H) 8.2 (2 H, s), 7.5 (19 H, m), and 2.8 (8 H, s).

14-*Benzyl*-5,6,8,9-*tetrahydro*-2,7,12-*triphenyldibenz*[c,h]*acridinium Trifluoromethanesulphonate* (19).—Xanthylium salt (17) (0.25 g, 0.37 mmol) was stirred in Et_2O (5 ml) and Et_3N (38 mg, 0.37 mmol). n-Benzylamine (40 mg, 0.37 mmol) was added at 20 °C followed after 2 h by AcOH (0.11 g, 1.9 mmol). The mixture was stirred for 16 h, solvent allowed to evaporate at 25 °C, and water (10 ml) added. After stirring for 8 h the solid was filtered and dried (20 °C and 14 mmHg), affording *dibenzacridinium salt* (19) (0.24 g, 87%) as yellow prisms, m.p.

158—161 °C (Found: C, 75.2; H, 5.1; N, 1.6. $C_{47}H_{36}F_3NO_3S$ requires C, 75.1; H, 4.8; N, 1.9%); $\nu_{max.}$ ($CHBr_3$) 1 610, 1 595—1 560, 1 275, and 1 265 cm^{-1}; δ($CDCl_3$–CF_3CO_2H) 8.1 (2 H, s), 7.5 (24 H, m), 6.2 (2 H, s), and 2.6 (8 H, s).

5,6,8,9-*Tetrahydro*-14-(4-*methoxyphenyl*)-2,7,12-*triphenyldibenz*[c,h]*acridinium Perchlorate* (20).—Xanthylium salt (16) (0.31 g, 0.5 mmol) was stirred in CH_2Cl_2 (5 ml) and Et_3N (51 mg, 0.5 mmol). *p*-Anisidine (62 mg, 0.5 mmol) was added at 20 °C followed after 2 h by AcOH (0.15 g, 2.5 mmol). The mixture was stirred for 16 h, solvent allowed to evaporate at 25 °C, and the residue stirred with water (10 ml) for 4 h. Filtration and drying (20 °C and 14 mmHg) gave a solid which was chromatographed in portions of 100 mg (neutral alumina, 15 g per run). Elution with EtOAc (100 ml per run) removed impurities, and subsequent elution with Me_2CO (30 ml per run) and combining of those solutions, afforded on evaporation (20 °C and 20 mmHg) *dibenzacridinium salt* (20) (0.26 g, 72%) as cream prisms, m.p. >300 °C (Found: C, 76.7; H, 5.1; N, 1.9. $C_{46}H_{36}ClNO_5$ requires C, 76.9; H, 5.1; N, 2.0%); $\nu_{max.}$ ($CHBr_3$) 2 970, 1 085, and 760 cm^{-1}; δ($CDCl_3$–CF_3CO_2H) 7.8—6.8 (25 H, m), 3.9 (3 H, s), and 2.9 (8 H, s).

4,4′-*Bis*-(3-*methoxycarbonyl*-1-*oxopropyl*)*biphenyl* (21).—Double succinoylation of biphenyl with 3-methoxycarbonylpropionyl chloride was effected as previously reported,[15] except that $AlCl_3$ was added in portions over 30 min to the mixture of biphenyl, acid chloride, and CS_2; also, the temperature was allowed to rise from 15 to 45 °C over 2 h before refluxing for 4 h. Recrystallisation of the crude product from MeOH afforded a sample of diester (21) suitable for the Wolff–Kishner reduction. The diester (21) crystallised as plates, m.p. 136—137.5 °C (from acetone) (lit.,[15] 136.5—137.5 °C) (Found: C, 69.0; H, 5.7. Calc. for $C_{22}H_{22}O_6$: C, 69.1; H, 5.8%).

Methyl 4-*Biphenyl*-4-*yl*-4-*oxobutanoate* (22).—An attempt to obtain diester (21) by simpler conditions afforded only the product of monosuccinoylation, ester (22). Thus, anhydrous $AlCl_3$ (13.4 g, 0.1 mol) was added in portions over 40 min to biphenyl (3.1 g, 20 mol) and 3-methoxycarbonylpropionyl chloride (7.5 g, 50 mmol) in nitrobenzene (20 ml) at 0 °C. The mixture was stirred for 2 days, hydrolysed with ice (50 g) and HCl (10N, 5 ml), and the nitrobenzene removed by steam distillation. The residue solidified on standing to give *ester* (22) (5.4 g, 100%), m.p. 96—99 °C; recrystallisation afforded ester (22), m.p. 99—100 °C (from MeOH) (lit.,[26] 101 °C) (Found: C, 76.1; H, 6.0. $C_{17}H_{16}O_3$ requires C, 76.1; H, 6.0%); $\nu_{max.}$ ($CHBr_3$) 1 725, 1 675, and 765 cm^{-1}; δ($CDCl_3$) 8.1 (2 H, d, *J* 8 Hz), 7.8—7.4 (7 H, m), 3.7 (3 H, s), 3.3 (2 H, t, *J* 7 Hz), and 2.8 (2 H, t, *J* 7 Hz).

3,3′,4,4′-*Tetrahydro*-[7,7′-*binaphthalene*]-1(2H),1′(2′H)-*dione* (25).—Dicarboxylic acid (24) (0.50 g, 1.53 mmol) was stirred in polyphosphoric acid (5 g) at 75 °C for 45 h. Addition of ice (10 g) and water (20 ml) and extraction with CH_2Cl_2 (3 × 20 ml) gave an organic layer which was washed with Na_2CO_3 (60 ml, 10%) and water (60 ml), and dried (Na_2SO_4). Removal of solvent (70 °C and 20 mmHg) afforded *dione* (25) (0.25 g, 58%), prisms (from HOAc), m.p. 135—140 °C (Found: M^+, 290.1311. $C_{20}H_{18}O_2$ requires *M*, 290.1307); $\nu_{max.}$ ($CHBr_3$) 1 675 cm^{-1}; δ($CDCl_3$) 8.2 (2 H, d, *J* 2 Hz), 7.6 (2 H, dd, *J* 2 and 8 Hz), 7.2 (2 H, d, *J* 8 Hz), 2.9 (4 H, t, *J* 6 Hz), 2.6 (4 H, t, *J* 6 Hz), and 2.1 (4 H, m).

3,3′,4,4′-*Tetrahydro*-2,2′-*bis*(*phenylmethylene*)-[7,7′-*binaphthalene*]-1(2H),1′(2′H)-*dione* (26).—Dione (25) (0.17 g, 0.6 mmol), benzaldehyde (0.13 g, 1.2 mmol), and ethanolic KOH (4% 0.3 ml) were stirred at 20 °C for 3 h. Ethanol (0.5 ml) was added to the residue; filtration afforded the crude product which was chromatographed on alumina (2 × 20 g; $CHCl_3$) to afford *dione* (26) (0.177 g, 63%), prisms, m.p. 235—237 °C (Found: M^+, 466.191. $C_{34}H_{26}O_2$ requires *M*, 466.193); $\nu_{max.}$ ($CHBr_3$) 1 665 cm^{-1}; δ($CDCl_3$–CF_3CO_2H) 8.4 (2 H, s), 7.9—7.4 (16 H, m), and 3.1 (8 H, s).

1,1′-*Dichloro*-3,3′,4,4′-*tetrahydro*-[7,7′-*binaphthalene*]-2,2′-*dicarbaldehyde* (27).—$POCl_3$ (1.60 g, 10.4 mmol) was added over 20 min to a stirred mixture of dimethylformamide (0.76 g, 10.4 mmol) and trichloroethylene (2 ml) at 5 °C in a three-necked flask equipped with a $CaCl_2$ drying tube. A solution of dione (25) (1.0 g, 3.6 mmol) in $CHCl_3$ (2 ml) was then added, and the mixture heated at 80 °C for 14 h. The residue was dissolved in CH_2Cl_2–10% NaOAc (1 : 1 v/v, 100 ml) and the organic layer separated and dried (Na_2SO_4). The solvent was removed (60 °C and 20 mmHg) and the residue dissolved (CH_2Cl_2, 10 ml) to give a solution which was chromatographed on neutral alumina (30 g; $CHCl_3$). After discarding a preliminary small yellow band, the major yellow fraction was collected, and the solvent removed from it (50 °C and 20 mmHg) to give *dicarbaldehyde* (27) (0.44 g, 33%), pale yellow prisms, m.p. 219—221 °C (Found: M^+, 382.0515. $C_{22}H_{16}Cl_2O_2$ requires *M*, 382.0527); $\nu_{max.}$ ($CHBr_3$) 1 665 cm^{-1}; δ($CDCl_3$) 10.3 (2 H, s), 8.0 (2 H, d, *J* 2 Hz), 7.6 (2 H, dd, *J* 2 and 7 Hz), 7.3 (2 H, d, *J* 7 Hz), and 2.8 (8 H, m).

3,3′,4,4′-*Tetrahydro*-[7,7′-*binaphthalene*]-1(2H),1′(2H′)-*dione Dioxime* (28).—Dione (25) (0.24 g, 0.83 mmol), hydroxylamine hydrochloride (0.23 g, 3.3 mmol), pyridine (1.1 ml), and ethanol (1.1 ml) were refluxed for 3 h. The solution was allowed to cool to 20 °C when prisms deposited; filtration and washing with Et_2O (10 ml) gave *dioxime* (28) (0.205 g, 77%), prisms, m.p. 218—221 °C (Found: C, 75.1; H, 6.3; N, 8.7. $C_{20}H_{20}N_2O_2$ requires C, 75.0; H, 6.3; N, 8.7%); $\nu_{max.}$ 3 250 cm^{-1}; δ[$(CD_3)_2SO$] 8.1 (2 H, s), 7.8 (2 H, d, *J* 4 Hz), 7.7 (2 H, d, *J* 4 Hz), 3.5 (2 H, s), 2.7 (8 H, m), and 1.8 (4 H, m).

5,6,8,9-*Tetrahydro*-2,4-*diphenyl*-1-*oxoniadibenz*[a,j]*anthracene Trifluoromethanesulphonate* (37).—Ketone (36) (0.50 g, 2 mmol), chalcone (0.62 g, 3 mmol), and CF_3SO_3H (0.75 g, 5 mmol) were heated at 100 °C for 2 h. Trituration of the gum with Et_2O (5 × 20 ml) and filtration afforded *pyrylium salt* (37) (0.80 g, 68%), orange prisms, m.p. 250—254 °C (Found: M^+, 436.1811. $C_{34}H_{25}F_3SO_4 - CF_3SO_3H = C_{33}H_{24}O$ requires *M*, 436.1827); $\nu_{max.}$ ($CHBr_3$) 1 260 and 1 025 cm^{-1}; δ($CDCl_3$–CF_3CO_2H) 8.4 (1 H, s), 8.0 (3 H, m), 7.7—7.2 (13 H, m), 3.1 (4 H, s), and 2.9 (4 H, s).

5,6,8,9-*Tetrahydro*-2,4-*diphenyl*-1-*azadibenz*[a,j]*anthracene* (38).—Pyrylium salt (37) (0.29 g, 0.5 mmol) was stirred in Et_2O (5 ml) and aqueous NH_3 (*d* 0.88, 3 mmol) added dropwise followed after 2 h by AcOH (0.36 g, 6 mmol). The mixture was stirred for 16 h, solvent allowed to evaporate at 25 °C, and water (10 ml) added. Filtration and drying (50 °C) gave a residue which was chromatographed on alumina (20 g; 10% EtOAc–light petroleum), and the solvent reduced to 3 ml (20 °C and 14 mmHg) to give a precipitate which was filtered and washed (eluant) to give *pyridine* (38) (0.134 g, 62%), prisms, m.p. 200—202 °C (Found: M^+, 435.1990. $C_{33}H_{25}N$ requires *M*, 435.1987); $\nu_{max.}$ ($CHBr_3$) 1 590, 1 570, and 760 cm^{-1}; δ ($CDCl_3$) 8.9 (1 H, s), 8.2—7.7 (3 H, m), 7.5—6.9 (13 H, m), and 2.8 (8 H, s).

1-*n*-*Butyl*-5,6,8,9-*tetrahydro*-2,4-*diphenyl*-1-*azoniadibenz*-[a,j]*anthracene Trifluoromethanesulphonate* (39).—Pyrylium salt (37) (0.29 g, 0.5 mmol) was stirred in CH_2Cl_2 (5 ml) and Et_3N (51 mg, 0.5 mmol). n-Butylamine (37 mg, 0.5 mmol) was

added at 20 °C followed after 2 h by AcOH (0.15 g, 2.5 mmol). The mixture was stirred for 16 h, solvent allowed to evaporate at 25 °C, and water (10 ml) added. After stirring for 8 h the precipitate was filtered, dried, and chromatographed on alumina in two portions (2 × 15 g; EtOAc eluted a golden yellow impurity; then Me_2CO eluted a bright yellow band). Removal of Me_2CO (20 °C and 14 mmHg), treatment of the residue with water, filtration and drying (40 °C and 14 mmHg) gave *pyridinium salt* (39) (0.229 g, 71%) as yellow prisms, m.p. 130—134 °C (Found: C, 71.1; H, 5.4; N, 2.2. $C_{38}H_{34}F_3NO_3S$ requires C, 71.1; H, 5.3; N, 2.2%); $\nu_{max.}$ ($CHBr_3$) 1 260 and 1 025 cm^{-1}; δ($CDCl_3$) 8.3 (1 H, s), 7.9—7.1 (16 H, m), 5.0 (2 H, t, *J* 6 Hz), 2.9 (8 H, s), 1.3 (2 H, m), and 1.0—0.3 (5 H, m).

5,6,8,9,11,12,14,15-*Octahydro*-10-*phenyl*-21-*oxoniabenzo*-[a]*phenanthro*[2,3-o]*pentaphene Trifluoromethanesulphonate* (41).—Ketone (36) (122 mg, 0.5 mmol), ketone (40) (162 mg, 0.5 mmol), and CF_3SO_3H (0.15 g, 1 mmol) were heated at 100 °C for 2.5 h. Trituration of the gum with Et_2O (5 × 10 ml) and filtration afforded *pyrylium salt* (41) (204 mg, 57%) as orange prisms, m.p. >300 °C (Found: C, 73.8; H, 4.7; S, 4.5. $C_{44}H_{33}F_3O_4S$ requires C, 73.9; H, 4.7; S, 4.5%); $\nu_{max.}$ ($CHBr_3$) 1 275 and 1 260 cm^{-1}; δ($CDCl_3$–CF_3CO_2H) 8.5 (2 H, s), 7.9—7.2 (15 H, m), and 3.0 (16 H, m).

5,6,8,9,11,12,14,15-*Octahydro*-10-*phenyl*-21-*azabenzo*[a]-*phenanthro*[2,3-o]*pentaphene* (42).—Pyrylium salt (41) (150 mg, 0.21 mmol) was stirred in CH_2Cl_2 (5 ml) and aqueous NH_3 (*d* 0.88; 1 mmol) added dropwise, followed after 1 h at 20 °C by AcOH (0.12 g, 2 mmol). The mixture was stirred for 16 h, solvent allowed to evaporate at 25 °C, and water (10 ml) added. Filtration and drying (50 °C) gave a residue which was chromatographed on alumina (15 g; 10% EtOAc–light petroleum), and the solvent reduced to 3 ml (20 °C and 14 mmHg) to give, after filtration, *pyridine* (42) (69 mg, 58%), prisms, m.p. 287—290 °C (Found: M^+, 563.2577. $C_{43}H_{33}N$ requires *M*, 563.2613); $\nu_{max.}$ ($CHBr_3$) 3 060—2 830, 1 540, 1 485, 910, and 770 cm^{-1}; δ($CDCl_3$) 9.0 (2 H, s), 8.0 (2 H, dd, *J* 1 and 6 Hz), 7.2 (13 H, m), and 2.9 (16 H, m).

21-*n*-*Butyl*-5,6,8,9,11,12,14,15-*octahydro*-10-*phenyl*-21-*azoniabenzo*[a]*phenanthro*[2,3-o]*pentaphene Trifluoromethanesulphonate* (43).—Ac_2O (56 mg, 0.54 mmol), pyrylium salt (41) (0.20 g, 0.27 mmol), CH_2Cl_2 (1 ml), and Et_3N (0.14 g, 1.4 mmol) were refluxed for 1.5 h. After 30 min, dry EtOH (38 mg, 0.82 mmol), and after 1 h n-butylamine (20 mg, 0.27 mmol) were added. After cooling to 20 °C, dry AcOH (82 mg, 1.4 mmol) was added followed after 1 week by saturated aqueous sodium hydrogencarbonate (10 ml). The precipitate was filtered, dried (40 °C), and chromatographed on alumina (15 g; EtOAc removed impurities and then Me_2CO eluted a yellow band). Removal of Me_2CO (20 °C and 14 mmHg), standing in water, filtration and drying (40 °C and 14 mmHg) gave *pyridinium salt* (43) (0.11 g, 52%) as orange-yellow prisms m.p. 148—152 °C (Found: C, 74.7; H, 5.6; N, 1.9. $C_{48}H_{42}F_3NO_3S$ requires C, 74.9; H, 5.5; N, 1.8%); $\nu_{max.}$ ($CHBr_3$) 1 265 cm^{-1}; δ($CDCl_3$) 8.4 (2 H, s), 8.0—7.2 (15 H, m), 5.4 (2 H, m), 2.9—1.9 (18 H, m), 1.2 (2 H, s), and 0.54 (3 H, t, *J* 4 Hz).

Kinetic Measurements.—Kinetic measurements were carried out under pseudo-first-order conditions, at a substrate concentration of *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, monitoring the decrease in substrate absorbance.

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. Reactions at 60 °C were followed in the 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 $\ln[a/(a-x)] = \ln[(\varepsilon_1 - \varepsilon_2)/(\varepsilon - \varepsilon_2)]$ *versus* time. Plots were linear to >60% completion. First- and second-order rate constants k_1 and k_2 were obtained from plots of $k_{obs.}$ *versus* nucleophile concentration.[27] For definitions and calculation of errors and for estimation of the precision of $k_{obs.}$ see ref. 28.

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