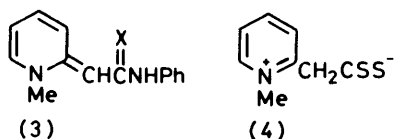
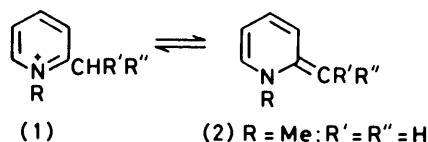


## The Chemistry of Some Bicyclic Pyridinium Anhydrobases

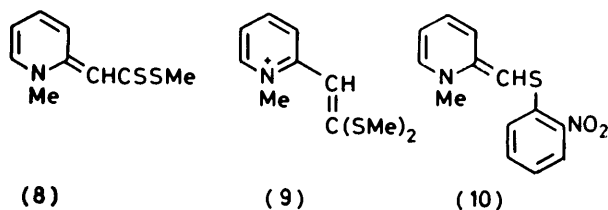
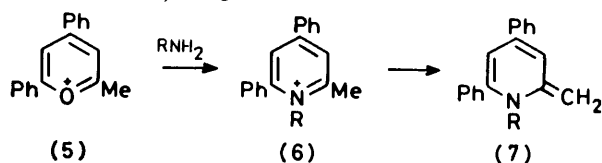
By Alan R. Katritzky,\* † Laszlo Ürögdi,§ and Ranjan C. Patel, School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ

The anhydrobase from 5,6,7,8-tetrahydro-2,4-diphenyl-1-*p*-tolylquinolinium reacts with C-, N-, and S-electrophiles to form adducts and new anhydrobases. The tautomeric structures of the adducts are deduced from spectral evidence.

THE possibility of  $\alpha$ -proton loss from a 2-alkyl group of a quaternary pyridinium cation to yield an anhydrobase [e.g. compound (1)  $\rightarrow$  the anhydro-derivative (2)] was first recognised by Decker.<sup>1</sup> The reactions of the simple anhydrobase (2), from 1,2-dimethylpyridinium (1a), with electrophiles were studied by Schneider *et al.*:<sup>2</sup> treatment with phenyl isocyanate, phenyl isothiocyanate, and carbon disulphide gave the derivatives (3a), (3b), and (4), respectively. The same group also investigated<sup>3</sup> the reactions of a variety of anhydrobases of the type (7)



a; X = O  
b; X = S



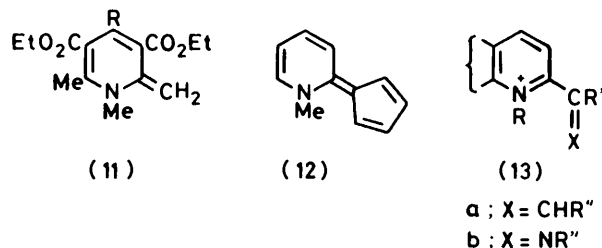
which were prepared *via* the pyridiniums (6) from the pyrilium (5). With the above electrophiles the anhydrobase (7) gave adducts similar to those obtained with its analogue (3) except that with carbon disulphide the product was unidentified. Foye has claimed<sup>4</sup> that the

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reaction of 1,2-dimethylpyridinium iodide with carbon disulphide gives 1-methylpyridinium-2-dithiocarboxylate; however, later Japanese work<sup>5</sup> seems to disprove this and it was possible to prepare the dithiocarboxylate (8) and the disulphide (9). Baker and McEnvoy<sup>6</sup> studied 1-benzylpyridine-2-methanide and particularly its acylation; 1-methylpyridine-2-phenylmethanide reacts similarly.<sup>7</sup> Rumanian authors<sup>8</sup> obtained the sulphide (10).

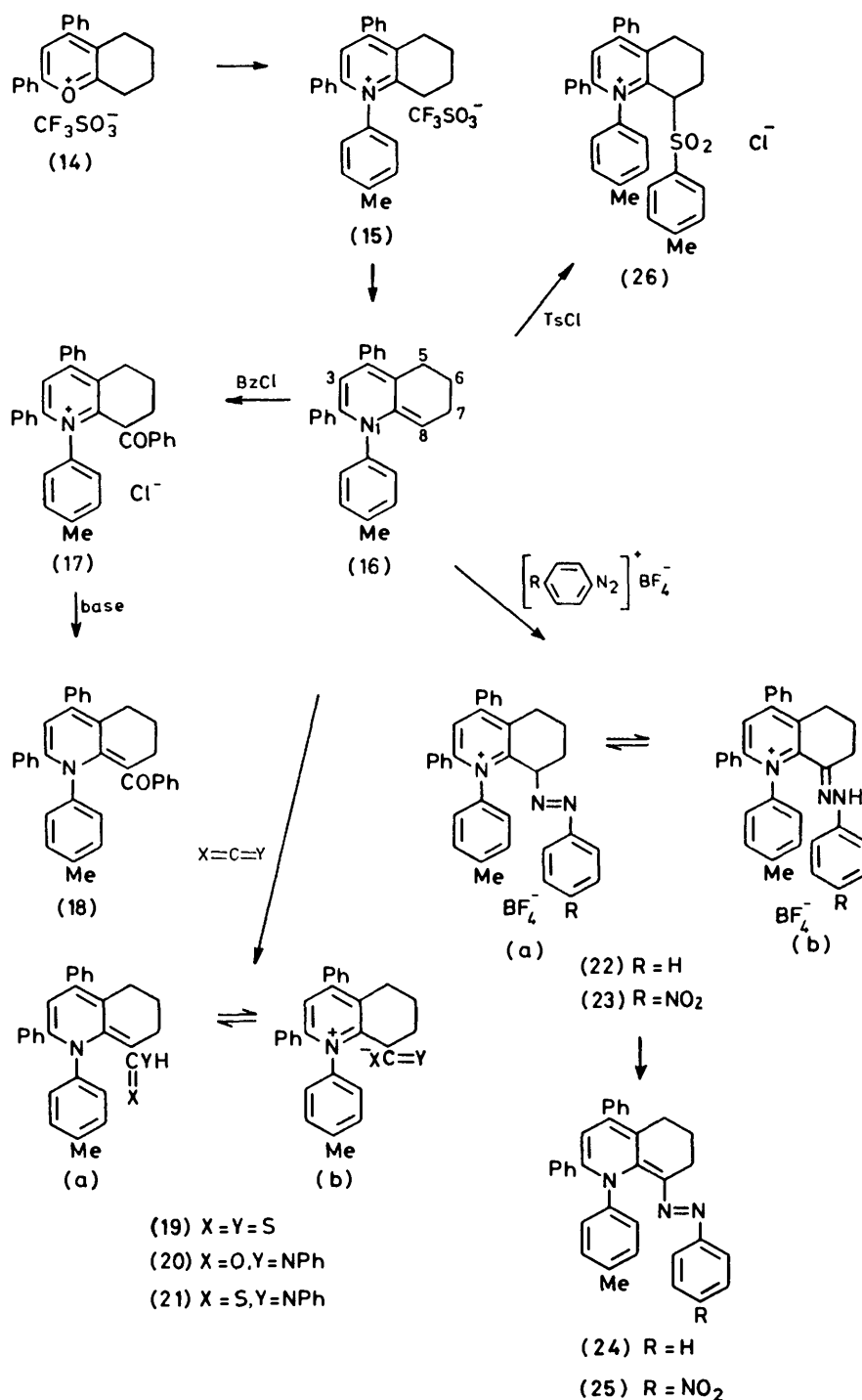
Little further work on the reactions of simple pyridinium anhydrobases has appeared although the reactions of more complex derivatives have been studied, such as the ester (11) [from the Hantsch pyridine synthesis; reactions of compound (11) frequently involve the  $\beta$ -CO<sub>2</sub>Et group]<sup>9</sup> and the cyclopentadiene derivative (12).<sup>10</sup> Furthermore, many reactions of pyridiniums at  $\alpha$ -alkyl groups proceed *via* an anhydrobase which is formed *in situ*.<sup>11</sup> These include the preparation of vinyl derivatives (13a) from aldehydes,<sup>12</sup> of imines (13b) from nitroso-compounds,<sup>13</sup> and of cyanine dyes.<sup>14</sup>



In connection with work on the transformations of amines mediated by pyriliums<sup>15</sup> we have now investigated the anhydrobases (16) and (29); in these the fused alicyclic ring confers rigidity on the molecule and thus could facilitate intramolecular reactions of the N-substituent with groups introduced by electrophilic reactions at the anhydrobase enamine system.

*Preparation of the Anhydrobase (16).*—Chalcone, cyclohexanone, and trifluoromethanesulphonic acid gave 5,6,7,8-tetrahydro-2,4-diphenylchromenylium trifluoromethanesulphonate (14) which was converted by *p*-toluidine in refluxing 1,2-dichloroethane into 5,6,7,8-tetrahydro-1-*p*-tolyl-2,4-diphenylquinolinium trifluoromethanesulphonate (15). This quinolinium, when treated with sodium methoxide in methanol, afforded the orange anhydrobase (16).

The pyrilium (27) was similarly prepared from chalcone

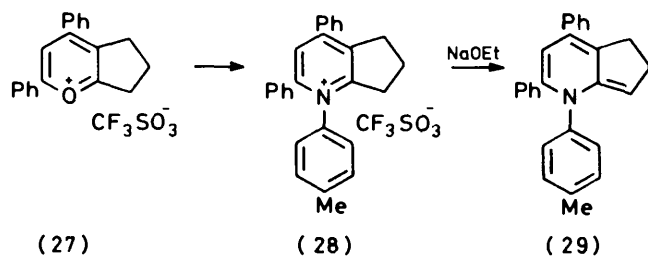


and cyclopentanone, and was treated with *p*-toluidine to give the pyridinium (28). However, attempts to prepare the anhydrosalt (29) using sodium ethoxide-ethanol led to rapid decomposition *in situ*; this was possibly due to the increased ring strain in the anhydrosalt (29).

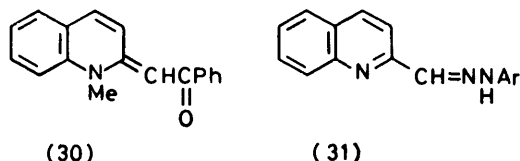
*Reactions of the Anhydrosalt (16) with Carbon Electrophiles.*—Benzoyl chloride reacted readily at 20 °C in

diethyl ether to give the quinolinium adduct (17) (87%) which was subsequently converted by sodium ethoxide into the conjugated, red anhydrosalt (18) (94%). Compounds of a similar type have been previously obtained, *e.g.* 1,2-dimethylquinolinium was treated with benzoyl chloride under Schotten-Baumann conditions and was subsequently converted into the anhydrosalt (30).<sup>16</sup>

Carbon disulphide in toluene gives the adduct (19) (83%) which crystallises with a molecule of toluene (confirmed by analysis and  $^1\text{H}$  n.m.r. spectroscopy). Phenyl isocyanate and isothiocyanate react with the anhydrobase (16) in diethyl ether to give the quinoline (20) (89%) and the thioimidate (21) (98%), respectively. Adduct (20) decomposed on attempted crystallisation but, although the analytical figures were slightly out, the spectral data clearly identified its structure.



Heating in toluene of the adducts (20) and (21) leads to reversion to the starting anhydrobase (16) as does attempted reaction with base (e.g. sodium hydride-toluene or butyl-lithium-tetrahydrofuran (THF) to form the corresponding anion. The mass spectra of the adducts (20) and (21) showed no molecular ion peaks but the characteristic peaks for compound (16) were observed.



*Reactions of the Anhydrobase (16) with N-Electrophiles.*—When compound (16) is added to benzenediazonium at 25 °C in various solvents a transient black colour is observed together with the evolution of gas and a mixture of pyridiniums is obtained. A much cleaner reaction occurs at -20 °C: orange crystals of the crude adduct (22a) were isolated which sodium methoxide converted into the black anhydrobase (24). This anhydrobase (24) on treatment with aqueous tetrafluoroboric acid gives the tautomeric isomer (22b).

Similarly, *p*-nitrobenzenediazonium gives the adduct (23a) at -20 °C, and the black dye (25). König<sup>17</sup> allowed 1-alkyl-2-methylquinoliniums to react with diazonium salts but the adducts dealkylated to give compounds (31). Although 2-picoline methiodide did not couple with benzenediazonium, 2-picoline itself formed the azo-compound with *p*-nitrobenzenediazonium.<sup>18</sup> In common with some of the other compounds prepared it proved to be difficult to obtain satisfactory analytical figures for compound (25) and so it was characterised by mass spectroscopy (Found:  $M^+$  524.2215. Calc. for  $\text{C}_{34}\text{H}_{28}\text{N}_4\text{O}_2$ :  $M$  524.2214). The principal fragment peaks corresponded to loss of NO ( $M - 30$ ),  $\text{CH}_3\text{C}_6\text{H}_4$  ( $M - 91$ ),  $\text{NC}_6\text{H}_4\text{NO}_2$  ( $M - 136$ ), and  $\text{N}_2\text{C}_6\text{H}_4\text{NO}_2$  ( $M - 150$ ), in good agreement with the suggested structure.

Thermolysis of compounds (24) and (25) at their respective m.p.s leads to extensive decomposition with evolution of ammonia: the respective anilines were detected by i.r. spectroscopy and t.l.c. and the residue contained no methylenic protons.

*Reaction of the Anhydrobase (16) with Tosyl Chloride.*—The anhydrobase (16) reacts rapidly with toluene-*p*-sulphonyl chloride in THF to give the pyridinium chloride (26) but attempts to prepare the anhydrobase failed. The anhydrobase of 1-methyl-2-phenylsulphonylpicolinium iodide was obtained using sodium hydroxide.<sup>19</sup>

*Spectral Studies.*— $^1\text{H}$  N.m.r. spectra (Table 1) show a clear distinction between the 'pyridinium salt' structures, typified by compound (15) and including compounds (17), (19b), (21b), (22b), and (26), and the 'anhydrobase' structures, typified by compound (16) and including compounds (18) and (20a). In the anhydrobases 3-CH [for numbering see structure (16)] is a clear singlet at  $\delta$  5.15–6.03 whereas in the salts it is in the aromatic multiplet at  $\geq \delta$  7.0: by contrast the anhydrobases show 5- $\text{CH}_2$  at  $\delta$  2.7–3.0 and 6- $\text{CH}_2$  at  $\delta$  1.8–2.1, in both cases downfield of the 5- $\text{CH}_2$  at  $\delta$  2.4–2.6 and 6- $\text{CH}_2$  at  $\delta$  1.5–1.7 in the salts.

*Tautomeric Structures of the Adducts with Neutral Electrophiles.*—For the carbon disulphide adduct (19) the betaine structure (19b) is predominant. In  $\text{CDCl}_3$  solution, in addition to the general n.m.r. features (above), the 8-CH is observed as a broad triplet at  $\delta$  4.50; this would be absent in the neutral structure (19a). The i.r.

TABLE 1  
 $^1\text{H}$  N.m.r. data <sup>a</sup> from quinoliniums and quinolines

Compound no.	3-H	5- $\text{H}_2$	6- $\text{H}_2$	7- $\text{H}_2$	8- $\text{H}_{1,2}$	4- $\text{CH}_3$	Aromatics
(15)	7.4 <sup>b</sup>	2.82 (m)	1.83 (m)	1.83 (m)	2.82 (2 H, m)	2.30 (s)	7.4 (15 H, m) <sup>c</sup>
(16)	5.15 (s)	2.40 (t)	1.56 (m)	2.04 (m)	3.65 (1 H, t)	2.18 (s)	7.1 (14 H, m)
(17)	7.3 <sup>b</sup>	3.0 (m)	2.1 (m)	2.1 (m)	5.25br (1 H)	2.0 (s)	7.3 (20 H, m) <sup>c</sup>
(18)	6.03 (s)	2.6 (m)	1.73 (m)	2.6 (m)		2.06 (s)	6.9 (19 H, m)
(19b)	7.3 <sup>b</sup>	2.90 (m)	1.9 (m)	1.9 (m)	4.55br	2.23 (s) <sup>d</sup>	7.3 (15 H, m) <sup>c</sup>
(20a)	5.90 (s)	2.56 (m)	1.65 (m)	2.1 (m)		2.06 (s)	7.1 (19 H, m)
(21b)	7.3 <sup>b</sup>	2.95 (m)	1.85 (m)	2.2 (m)	4.25br	2.28 (s)	7.3 (20 H, m) <sup>c</sup>
(22b)	7.1 <sup>b</sup>	2.73 (m)	2.1 (m)	2.1 (m)		2.06 (s)	7.1 (25 H, m) <sup>c</sup>
(26)	7.1 <sup>b</sup>	2.8 (m)	2.1 (m)	2.1 (m)	5.25br	2.25br (6 H, s)	7.1 (19 H, m) <sup>c</sup>

<sup>a</sup> In  $\text{CDCl}_3$ ;  $\delta$  (p.p.m.). <sup>b</sup> Obscured by 2,4-diphenyl signals. <sup>c</sup> Integration containing 3-H. <sup>d</sup> Toluene  $\text{CH}_3$  at 2.33 (3 H, s), see analysis.

spectrum (Table 2) suggests this structure in  $\text{CHBr}_3$  (e.g. pyridinium  $\nu_{\text{C}=\text{O}}$  at  $1\ 620\ \text{cm}^{-1}$ ) but in THF solution the maximum at  $450\ \text{nm}$  indicates the anhydrobase structure (19a).

For the phenyl isocyanate and isothiocyanate adducts, in  $\text{CDCl}_3$  and  $\text{CHBr}_3$  solutions, the oxygen derivative exists predominantly in the neutral form (20a) whereas the sulphur analogue occurs predominantly as the zwitterion (21b), presumably because of the higher acidity of  $\text{COSH}$  than  $\text{CO}_2\text{H}$ .<sup>20</sup> This difference is easily discerned by the i.r. [ $\text{NH}$  for structure (18a) at  $3\ 400\ \text{cm}^{-1}$

washed with  $\text{Et}_2\text{O}$  to give the *trifluoromethanesulphonate* (18.4 g, 35%), m.p.  $187\ ^\circ\text{C}$  (Found: C, 60.4; H, 4.3.  $\text{C}_{22}\text{H}_{19}\text{F}_3\text{O}_4\text{S}$  requires C, 60.5; H, 4.4%).

*6,7-Dihydro-2,4-diphenyl-5H-cyclopenta[b]pyrylium Trifluoromethanesulphonate* (27).—This compound was prepared as above, as pink plates from  $\text{EtOH}$  (21%), m.p.  $169\text{--}172\ ^\circ\text{C}$  (Found: C, 59.4; H, 4.0.  $\text{C}_{21}\text{H}_{17}\text{F}_3\text{O}_4\text{S}$  requires C, 59.7; H, 4.1%).

*5,6,7,8-Tetrahydro-1-p-tolyl-2,4-diphenylquinolinium Trifluoromethanesulphonate* (15).—A solution of the chromenylium salt (14) (20.2 g, 46.4 mmol) and *p*-toluidine (5.4 g, 51 mmol) in  $\text{CH}_2\text{Cl}_2$  (200 ml) was heated with continuous

TABLE 2  
Relevant u.v.<sup>a</sup> and i.r.<sup>b</sup> data for quinoliniums and quinolines

Compound no.	Solvent	U.v. $\lambda_{\text{max.}}/\text{nm}$	$\epsilon$	I.r.
(15)	MeOH			1 620s, 1 270br, 1 030s
(16)	THF	450	3 750	<sup>c</sup> 1 630s
(17)	EtOH			1 670s, 1 618s
(18)	EtOH	514	19 200	1 620w, 1 605w, 1 480s
(19b)	THF	450	2 160	<sup>d</sup> 1 620s
(20a)	THF	422	5 630	3 410s, 1 660s, 1 640s, 1 625s
(21b)	THF	470—495	5 100	<sup>e</sup> 1 612s, 1 520s, 1 010s
(22a)	MeOH	450	5 100	<sup>f</sup> 1 620s, 1 050br and s
(22b)	MeOH	450	19 300	3 285s, 1 630s
(23a)	MeOH	430	19 000	1 620s, 1 530s, 1 350s, 1 050br and s

<sup>a</sup> Visible region only.  $\epsilon$  Values are approximate. <sup>b</sup> Run as solutions in  $\text{CHBr}_3$ , only salient bands given. <sup>c</sup> Loss of  $\text{CF}_3\text{SO}_3$  at  $1\ 270, 1\ 030$ , cf. in compound (15). <sup>d</sup> SH not observed, cf. required for structure (19a). <sup>e</sup> No NH, SH, cf. as required for structure (21a). <sup>f</sup> No NH, cf. as in tautomer (22b).

and  $^1\text{H}$  n.m.r. [triplet at  $\delta\ 4.21$  for 8-CH structure (21b)] spectra. Further evidence is provided by the general  $^1\text{H}$  n.m.r. features (see above and in Table 1) and by the i.r. spectrum (Table 2) [ $\nu_{\text{C}=\text{O}}$   $1\ 640\ \text{cm}^{-1}$  for structure (20a)].

The ketone (17) ( $\nu_{\text{C}=\text{O}}$   $1\ 670\ \text{cm}^{-1}$ ) shows no evidence for enolisation 8-CH occurring at  $\delta\ 5.25$ .

As first obtained, the diazonium adducts (22) and (23) appear to exist mainly in the azo-tautomeric forms (22a) and (23a), the absence of  $\nu_{\text{NH}}$  clearly indicating form (a). The adducts were directly converted by base into the anhydrobase (24) which with acid yields the hydrazone tautomer (22b), as deduced by the appearance of an NH band in the i.r. ( $3\ 295\ \text{cm}^{-1}$ ) and  $^1\text{H}$  n.m.r. ( $\delta\ 8.9$ , disappears with  $\text{D}_2\text{O}$ ) spectra.

## EXPERIMENTAL

M.p.s were obtained on a Kofler hot-stage apparatus and are uncorrected. I.r. spectra were run using NaCl plates on a Perkin-Elmer 257 grating spectrophotometer as solutions in  $\text{CHBr}_3$ .  $^1\text{H}$  n.m.r. spectra were run on a Perkin-Elmer 60 MHz R-12 permanent magnet spectrophotometer in  $\text{CDCl}_3$ , unless otherwise stated, with  $\text{Me}_4\text{Si}$  as internal standard. Visible spectra were obtained on a Perkin-Elmer SP 800 spectrophotometer (air reference). Chalcone was prepared following Vogel (90%), m.p.  $56\ ^\circ\text{C}$  (lit.,<sup>21</sup> m.p.  $56\text{--}57\ ^\circ\text{C}$ ).

*5,6,7,8-Tetrahydro-2,4-diphenylchromenylium Trifluoromethanesulphonate* (14).—To a solution of chalcone (52 g, 0.25 mol) and cyclohexanone 12.2 g, 0.12 mol) in  $\text{Et}_2\text{O}$  (225 ml) was added trifluoromethanesulphonic acid (11.1 ml, 0.12 mol) at  $25\ ^\circ\text{C}$ . The mixture was stirred for 2 h at  $25\ ^\circ\text{C}$  after which the resulting pink plates were filtered off and

removal of solvent for 1 h after which time the solution volume was concentrated to ca. 50 ml. Addition of  $\text{Et}_2\text{O}$  (200 ml) gave a white solid (22.6 g, 93%), m.p.  $140\text{--}141\ ^\circ\text{C}$ . Recrystallisation from  $\text{EtOAc}\text{--}\text{Et}_2\text{O}$  gave colourless prisms (m.p.  $175\ ^\circ\text{C}$ ) of the *trifluoromethanesulphonate* (Found: C, 66.1; H, 5.0; N, 2.7.  $\text{C}_{29}\text{H}_{26}\text{F}_3\text{NO}_3\text{S}$  requires C, 66.3; H, 5.0; N, 2.7%).

*6,7-Dihydro-2,4-diphenyl-1-p-tolyl-5H-cyclopenta[b]pyridinium Trifluoromethanesulphonate* (28).—This was prepared as above as plates (81%) from  $\text{EtOH}$  (95%), m.p.  $151\text{--}152\ ^\circ\text{C}$  (Found: C, 65.4; H, 4.6; N, 2.7.  $\text{C}_{28}\text{H}_{24}\text{F}_3\text{N}_2\text{O}_3\text{S}$  requires C, 65.7; H, 4.7; N, 2.7%).

*1,5,6,7-Tetrahydro-2,4-diphenyl-1-p-tolylquinoline* (16).—To a stirred solution of the quinolinium salt (15) (6.8 g, 13 mmol) in absolute  $\text{EtOH}$  (50 ml), a  $\text{NaOEt}$  solution (1 N; 14 ml) was added dropwise. After the mixture had been stirred for 10 min the resulting orange solid was filtered off and washed with cold  $\text{EtOH}$  to give the orange product (4.1 g, 83.5%). Recrystallisation from  $\text{CH}_2\text{Cl}_2\text{--}\text{EtOH}$  gave the *quinoline* (16) as orange plates, m.p.  $130\text{--}135\ ^\circ\text{C}$  (Found: C, 89.5; H, 6.8; N, 3.7.  $\text{C}_{28}\text{H}_{25}\text{N}$  requires C, 89.6; H, 6.7; N, 3.7%).

*8-Benzoyl-5,6,7,8-tetrahydro-2,4-diphenyl-1-p-tolylquinolinium Chloride* (17).—To a solution of the anhydrobase (16) (0.5 g, 1.3 mmol) in  $\text{Et}_2\text{O}$  (20 ml) was added dropwise benzoyl chloride (0.2 g, 1.4 mmol). The resulting pale yellow prisms (0.6 g, 87%) of the *chloride* (17) were filtered off and dried *in vacuo* (25 mmHg;  $\text{P}_2\text{O}_5$ ), m.p.  $148\text{--}150\ ^\circ\text{C}$  (Found: C, 81.0; H, 5.8; N, 2.4.  $\text{C}_{33}\text{H}_{30}\text{ClNO}$  requires C, 81.5; H, 5.9; N, 2.7%). The compound was very hygroscopic and difficult to recrystallise.

*8-Benzoyl-1,5,6,7-tetrahydro-2,4-diphenyl-1-p-tolylquinoline* (18).— $\text{NaOEt}$  (0.08 g, 1.1 mmol) in absolute  $\text{EtOH}$  (5 ml) was added to a solution of the *chloride* (17) (0.5 g, 1.0 mmol) in  $\text{EtOH}$  (5 ml). The resulting red prisms (0.45 g, 94%) were filtered off, washed with cold  $\text{EtOH}$  (10 ml),

and dried *in vacuo* (25 mmHg; over  $P_2O_5$ ) to give the *quinoline* (18) as red plates (absolute, EtOH), m.p. 159—161 °C (Found: C, 87.5; H, 6.0; N, 2.7.  $C_{35}H_{29}NO$  requires C, 87.7; H, 6.1; N, 2.9%).

5,6,7,8-Tetrahydro-2,4-diphenyl-1-p-tolylquinolinium-8-dithiocarboxylate (19).—Compound (16) (0.38 g, 1 mmol) was stirred at 25 °C in a mixture of toluene (9 ml) and carbon disulphide (1 ml) for 5 h. The resulting brown prisms of the *dithiocarboxylate* were filtered off and washed with toluene (0.37 g, 83%), m.p. 125—130 °C (Found: C, 79.0; H, 6.1; N, 2.5; S, 11.5.  $C_{29}H_{25}NS_2C_7H_8$  requires C, 79.5; H, 6.1; N, 2.6; S, 11.8%).

1,5,6,7-Tetrahydro-2,4-diphenyl-8-phenylcarbamoyl-1-p-tolylquinoline (20).—To a suspension of compound (16) (0.75 g, 2 mmol) in dry  $Et_2O$  (20 ml) was added phenyl isocyanate (0.3 ml, 2.7 mmol) at 25 °C. After 1 h the resulting orange needles were filtered off and washed with dry  $Et_2O$  to give the *quinoline* (20) (0.88 g, 89%), m.p. 123—125 °C (Found: C, 84.3; H, 6.1; N, 5.6.  $C_{35}H_{30}N_2O$  requires C, 85.0; H, 6.1; N, 5.7%). The compound decomposed on attempted recrystallisation.

5,6,7,8-Tetrahydro-2,4-diphenyl-1-p-tolylquinolinium-8-(N-phenylthiocarboximidate) (21).—To a suspension of compound (16) (0.94 g, 2.5 mmol) in dry  $Et_2O$  (25 ml) was added phenyl isothiocyanate (0.35 ml, 2.9 mmol) at 25 °C. The mixture was stirred for 1 h, and then kept at ca. 0 °C for 12 h. The resulting yellow prisms of *compound* (21) were filtered off and washed with dry  $Et_2O$  (1.25 g, 98%), m.p. 133—136 °C (Found: N, 5.3; S, 6.2.  $C_{35}H_{30}N_2S$  requires N, 5.5; S, 6.3%). The compound decomposed on attempted recrystallisation.

1,5,6,7-Tetrahydro-2,4-diphenyl-1-p-tolylquinoline-8-azobenzene (24).—Compound (16) (0.94 g, 2.5 mmol) was added to a well-stirred suspension of phenyldiazonium tetrafluoroborate (0.48 g, 2.5 mmol) in sodium dry THF (10 ml) at -20 °C. After 15 min at -20 °C dry  $Et_2O$  (40 ml) was added, and the mixture kept at 0 °C for 12 h. The orange product was triturated with dry  $Et_2O$  (40 ml) giving orange crystals (1.18 g, 83%). It was dissolved in MeOH (20 ml) and solid NaOMe (0.12 g, 2.2 mmol) was added with stirring. After filtration and washing with MeOH the black *quinoline* (24) resulted (0.50 g, 42%). Recrystallisation from toluene gave the *quinoline* (24) as black prisms, m.p. 210—210.5 °C (Found: C, 85.2; H, 6.2; N, 8.5.  $C_{34}H_{29}N_3$  requires C, 85.1; H, 6.1; N, 8.8%).

1,5,6,7-Tetrahydro-2,4-diphenyl-1-p-tolylquinoline-8-azo-4'-nitrobenzene (25).—Compound (16) (0.94 g, 2.5 mmol) was treated with 4-nitrophenyldiazonium tetrafluoroborate (0.59 g, 2.5 mmol) in sodium dry THF as above. After reaction of the crude orange-brown quinolinium adduct (1.30 g, 85%) with NaOMe (0.12 g, 2.2 mmol) in MeOH the black anhydrobase *quinoline* (25) was obtained as prisms

(0.65 g, 49%), m.p. 223—230 °C (Found: C, 74.9; H, 5.0; N, 10.0.  $C_{34}H_{28}N_4O_2$  requires C, 77.8; H, 5.4; N, 10.7%).

5,6,7,8-Tetrahydro-8-(4-methylphenylsulphonyl)-2,4-diphenyl-1-p-tolylquinolinium Chloride (26).—To toluene-*p*-sulphonyl chloride (0.44 g, 2.3 mmol) dissolved in sodium dry THF (7 ml) was added compound (16) (0.42 g, 1.1 mmol) in small portions at 25 °C (during 2—3 min). After 10 min the solvent was removed under reduced pressure (25 °C, 25 mmHg). The residue was scratched with sodium dry  $Et_2O$  and gave off the white hygroscopic *chloride* (0.51 g, 98%) as colourless plates, m.p. 96—106 °C (Found: N, 2.4; S, 5.3.  $C_{35}H_{32}ClNO_2S$  requires N, 2.5; S, 5.7%).

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