Intermolecular Reactions of *N*-Aryl-pyridinium, -quinolinium, and -acridinium Salts with Nucleophiles

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N-Aryl-mono-, -tri- and -pentacyclic pyridinium cations react with *S*- and *C*-nucleophiles to give: (i) simple addition of hydride at the α-ring position, (ii) nucleophilic addition of thiophenoxide at the γ-ring position, (iii) deprotonation at the 6-position of a 5,6-dihydroquinolinium ring followed by prototropic shift to give a 1,2-dihydroquinoline derivative, (iv) ring contraction of a pyridine to a pyrrole ring, and (v) nucleophilic displacement of the *N*-aryl group.

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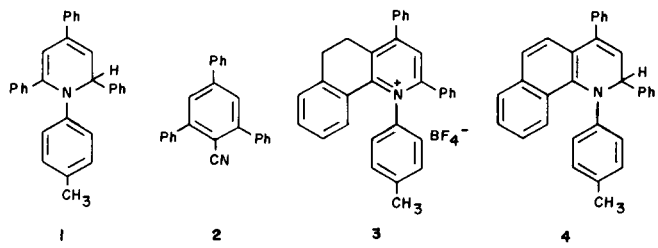
Previous papers in this series have shown that *N*-aryl groups attached to pyridinium rings can be replaced in intramolecular nucleophilic substitutions with the formation of CO, CN and CS bonds [2-4]. In these reactions the orientation of the incoming nucleophile is geometrically favourable. By contrast, this cannot occur for intermolecular displacements of *N*-aryl groups which are rare. The relatively easy formation of aryl iodides [5] is an exception, and we have also shown [6] that, using the more reactive benzo[*h*]quinolinium series, aryl thiocyanates can also be formed. Various attempts with other nucleophiles have been made: fluoride gives the arene corresponding to the original primary arylamine [7]; however, no useful products were obtained using chloride or bromide [8].

It seems likely that in the intermolecular reactions studied, a radical mechanism is involved. We now describe our attempts to uncover further examples of radical displacement of this type, utilizing sulphur and carbon nucleophiles.

2,4,6-Triphenylpyridinium System.

We have shown in related work that 1-phenyl derivatives of this cation form charge-transfer complexes with carbanions, and sigma complexes with other nucleophiles [9]. When the 1-*p*-methylphenyl compound was reacted with sodium hydride in dimethylformamide and in acetonitrile, the products were as shown in structures **1** and **2**, respectively. The asymmetry of the ^{1}H nmr of the dihydropyridine **1** clearly demonstrates that the 1,2-dihydroadduct was formed, rather than the 1,4-dihydroadduct. The formation of dihydropyridine **1** involves simple attack of H^- at the 2-position of the pyridinium ring. Compound **2** results from attack by the acetonitrile anion in the 2-position, followed by a ring-opening-reclosure reaction of a known type [10].

Block 1

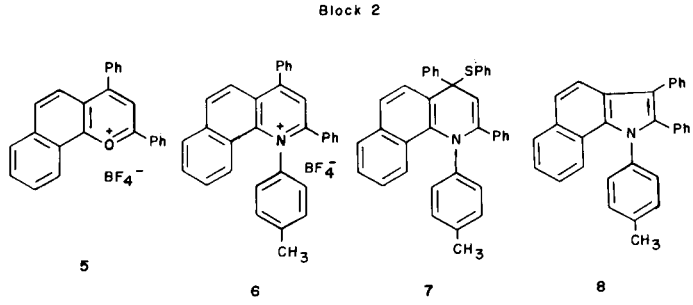


1 2 3 4

2,4-Diphenyl-5,6-dihydrobenzo[*h*]quinolinium System.

Reaction of compound **3** with sodium thiophenoxide gave product **4** by deprotonation and isomerisation. The structure of dihydrobenzo[*h*]quinoline **4** was established as follows: the ^{1}H nmr spectrum showed both the presence of an AB system (doublets at *ca.* 5.85 and 6.45 ppm) and also the absence of an ethylene linkage (no signal at *ca.* 3 ppm). In conjunction with the high resolution mass spectrum, the latter observation implies unsaturation at C-5, C-6. The AB system was assigned to H-2 and H-3. In addition, the line at 63.8 ppm in the ^{13}C nmr spectrum is consistent with C-3 in the 1,2-dihydro structure.

Block 2



5 6 7 8

2,4-Diphenylbenzo[*h*]quinolinium System.

To circumvent the problem of deprotonation as described in the preceding section, we prepared the fully aromatic tricyclic pyrylium salt **5** by a literature method [11]. Pyrylium salts with benzo[*b*] ring fusion usually do not give the corresponding pyridinium cations with primary aliphatic amines [12], owing to the unreactivity of

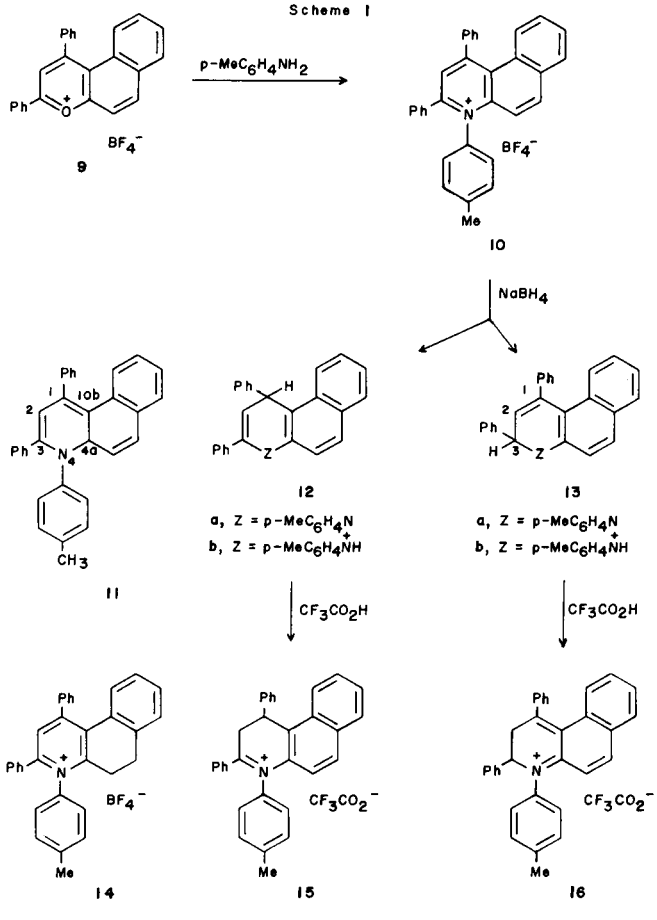
the intermediate phenol. However, with primary arylamines, such reactions do give the *N*-arylpyridinium salts [11], and pyridinium salt **6** was obtained in this way from pyrylium salt **5** with *p*-toluidine.

Reaction of pyridinium salt **6** with sodium thiophenoxide gave, in addition to PhSSPh, products **4** and **7** which were formed, respectively, by the addition of hydride ion to the 2-position and of thiophenolate anion to the 4-position of the pyridinium ring. The products were inseparable by chromatography and their structures were therefore identified by the ^{1}H nmr spectrum of the mixture. Dihydropyridine **4** revealed the expected shifts and coupling constants for H-2 and H-3 (*vide supra*). Compound **7** showed a signal at 4.32 ppm (singlet), assigned to H-3.

It was hoped that di-*t*-butyl peroxide would assist in oxidative cleavage of any 1,4-dihydropyridine intermediates, as has been reported for hydrogen peroxide [13]. However with the 2-propanenitronate anion reaction with pyridinium salt **6** took a completely different course from *C*-alkylation, affording the ring-contracted benzo[*g*]indole **8** in low yield. The structure of **8** was demonstrated by CHN analysis, and by spectroscopy.

The conversion of pyridinium salt **6** into indole **8** is probably caused by the di-*t*-butyl peroxide used as an additive in the reaction. Similar oxidative ring-contractions of quinoline to indole skeletons have been observed using hydrogen peroxide [14] and potassium ferricyanide [15].

Scheme I



2,4-Diphenylbenzo[*f*]quinolinium System.

2,4-Diphenylbenzo[*f*]chromenylium tetrafluoroborate **9** was converted into the corresponding 1-(4-methylphenyl)-2,4-diphenylbenzo[*f*]quinolinium salt **10** by refluxing with *p*-toluidine in acetic acid. Reduction of quinolinium salt **10** with sodium borohydride at $-5°$ gave a mixture of two products which were assigned as the 1,2-dihydroadduct **13a** and the 1,4-dihydroadduct **12a**, through their transformation with acids to iminium salts **16** and **15** respectively, and by the following comparative nmr data.

The absence of lines arising from an ethylene unit in both the ^{1}H and ^{13}C nmr spectra of the above mixture indicates that reduction occurred solely in the pyridinium ring of salt **10**, as expected. The line at 39.9 ppm in the ^{13}C nmr of dihydroquinoline **12a** (C-1) is in excellent agreement with that of 3,5-diethoxycarbonyl-1,4-dihydro-2,6-dimethyl-4-phenylpyridine (C-4) which resonates at 39.7 ppm [16]. The line at 61.9 ppm in the ^{13}C nmr of dihydroquinoline **13a** in deuteriochloroform is assigned as C-3, close to that at 63.8 ppm in the analogous benzo[*h*]quinoline **4**.

On addition of 40% fluoroboric acid to the above mixture, dihydroquinoline **12a** underwent *N*-protonation to give salt **12b** which precipitated from the ethereal solution, while quinoline **13a** remained in the solution unaffected.

The presence of a substantial amount of the alternative dihydroquinoline **11** in the reduction mixture could be ruled out because protonation at the C-10b atom of quinoline **11** would lead to two aliphatic methine carbon atoms (C-4a and C-10b), for which signals are not observed in the ^{13}C nmr spectrum. However, protonation of quinoline **13a** (at C-2) would lead to an ABX system (at C-2 and C-3), which is indeed observed in the product, salt **16** (*vide infra*). Thus, dihydrobenzo[*f*]quinoline **12a** behaves as an enamine, for which reversible *C*-protonation is the norm [17] but isomer **13a** behaves as a naphthylamine, the lower basicity of which explains why quinoline **13a** fails to undergo *N*-protonation to salt **13b**.

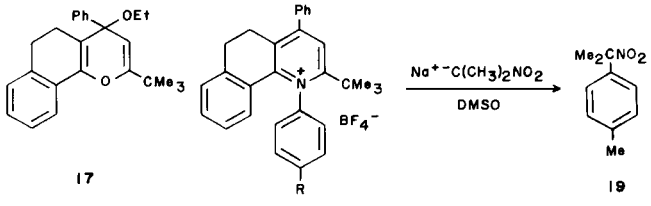
The ^{13}C and ^{1}H nmr spectra of the cations formed in solution on treatment of heterocycles **12a** and **13a** with trifluoroacetic acid imply the presence of a $-CH_2CH-$ unit in both compounds, which leads by logical necessity to the two structures **15** and **16**, respectively.

Enaminic behaviour of quinoline **12a**, in addition to that described above, was observed when quinoline **12a** was treated with anhydrous trifluoroacetic acid; protonation at the carbon atom occurred to give iminium salt **15**, which displayed a singlet at *ca.* 184 ppm in the ^{13}C nmr

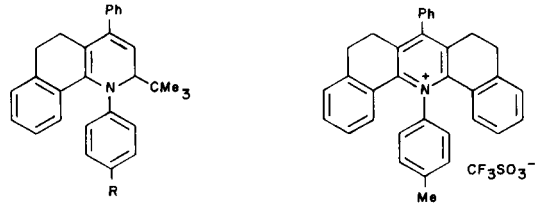
spectrum, characteristic of the α-carbon atom of phenyl-substituted iminium salts [18]. The ^{1}H nmr spectrum, displaying 2H and 1H multiplets centered at *ca.* 4.3 and 5.4 ppm respectively, also confirmed the structure of salt **15**; in the decoupled ^{13}C nmr spectrum a doublet at 34.4 ppm and a triplet at 42.1 ppm were assigned to C-1 and C-2, respectively.

Treatment of quinoline **13a** with trifluoroacetic acid produced an interesting reaction; trifluoroacetic acid proved to be a strong enough acid for quinoline **13a** to undergo protonation at what is formally the δ-carbon atom of a dienaminic residue to give the cross-conjugated iminium salt **16**, in which the aromaticity associated with the naphthalene ring in quinoline **13a** is no longer present. The lines at 164.0 and 164.4 ppm in the ^{13}C nmr spectrum of quinolinium salt **16** are tentatively assigned as C-1 and C-4a, respectively; C-2 and C-3 resonate at 40.7 ppm (t) and 63.8 ppm (d) respectively. The ^{1}H nmr of salt **16** displays an ABX system with the appropriate multiplets centered at 3.83 ppm and 5.53 ppm. Neither of salts **15** and **16** was isolated. The conversion of either dihydropyridine **12a** or **13a** into the desired salt **14**, by bond isomerism and protonation could not be accomplished.

Scheme 2



a, R = Me
b, R = Cl
c, R = OMe



2-*t*-Butyl-4-phenyl-5,6-dihydrobenzo[*h*]quinolinium System.

Preparation of 2-*t*-Butyl-1-(4-chlorophenyl)-4-phenyl-5,6-dihydrobenzo[*h*]quinolinium Tetrafluoroborate **18b**.

Under the conditions used for the preparation of pyridinium salt **18a**, 2-*t*-butyl-4-phenyl-5,6-dihydrobenzo[*h*]chromenylium tetrafluoroborate and *p*-chloroaniline gave **18b** contaminated with the starting pyrylium salt. The latter was removed as the ether-soluble 4-adduct **17** by treating the reaction mixture with triethylamine in ethanol. Pyran **17** was also prepared independently and characterised by CHN analysis and ^{13}C nmr spectroscopy.

Cleavage of 1-Arylpyridinium Salts by 2-Propanenitronate Anion.

Whereas a variety of 1-alkylpyridinium salts react with alkanenitronate anions [19], the corresponding reaction of 1-arylpyridinium salts has not been previously described. Reaction of benzo[*h*]quinolinium tetrafluoroborate **18a** with sodium 2-propanenitronate in dimethylsulfoxide at 100° gave an oil which when purified by column chromatography on neutral silica afforded 2-(4-methylphenyl)-2-nitropropane **19** in 17% yield. However, the highest yield obtained was 23%, the major product always being the tetrahydroquinoline **20a**: numerous attempts [20], including changing the conditions or adding catalysts, failed to increase that yield. When the tricyclic pyridinium system **18** was replaced by the pentacyclic dibenz[*c,h*]acridinium trifluoromethanesulphonate **22**, the yield of nitropropane **19** was only 11%.

Moreover, replacement of the 1-(4-methylphenyl) substituent in benzo[*h*]quinolinium salt **18a** by either a 1-(4-chlorophenyl) **18b** or 1-(4-methoxyphenyl) **18c** substituent directed the reaction course with sodium 2-propanenitronate in dimethylsulfoxide to give complete reduction to the corresponding 1,2,5,6-tetrahydrobenzo[*h*]quinolines **20b** and **21** in respective yields of 62 and 65%. Here, none of the desired 2-(4-substituted phenyl)-2-nitropropanes could be detected. The ^{1}H nmr spectra of both dihydro compounds display an AX system (doublets centered at *ca.* δ 4.1 and 5.6; J = 7 Hz), which indicates *a fortiori* either 1,2- or 1,4-dihydro- adducts; a line (C-1) at *ca.* 70 ppm in the ^{13}C nmr spectra of the above benzo[*h*]quinolines (C-2) strongly suggests the exclusive formation of the respective 1,2-dihydroadducts **20b** and **21**.

We have shown in related work that 1-phenylpyridinium cations form charge-transfer complexes with carbanions in dimethylsulfoxide. We believe that this is a fast first step in the reaction described in the present paper. Apparently, in most cases the escape of [PyAr· + Nu·] from the solvent cage is faster than the heterolysis PyAr· → Py + Ar·; the PyAr· merely abstracts H· from solvent to give the dihydro compound.

EXPERIMENTAL

Melting points were determined with a Reichert hot-stage apparatus and are uncorrected. The ^{1}H nmr spectra were run on a Varian 360L, with TMS as internal standard. The ^{13}C nmr spectra were run on either a JEOL JNM-FX 100 or a Nicolet NT-300 spectrometer with TMS as internal standard. The ir spectra were recorded on a Perkin-Elmer 283 spectrophotometer. Mass spectra at 70 eV were recorded on an A. E. I.

MS30 spectrometer. Microanalyses were performed by Dr. R. W. King of our department. Extractions with ether refer to the use of diethyl ether. Evaporation refers to removal of solvent under reduced pressure.

The following compounds were prepared by the literature procedures cited: 5,6-dihydro-1-(4-methylphenyl)-2,4-diphenylbenzo[*h*]quinolinium tetrafluoroborate, yellow needles (from ethanol) mp 290-292° (prepared by general method of ref [21]).

Anal. Calcd. for $C_{30}H_{30}BF_4N$: C, 73.47; H, 6.12; N, 2.86. Found: C, 73.20; H, 6.30; N, 2.70.

2,4-Diphenylbenzo[*f*]chromenylium tetrafluoroborate, had mp 245-250° (lit [11] mp 240-251°); 2,4-diphenylbenzo[*h*]chromenylium tetrafluoroborate (**5**), mp 256-265° dec (lit [11] mp 240-253°); 2-*t*-butyl-5,6-dihydro-1-(4-methylphenyl)-4-phenylbenzo[*h*]quinolinium tetrafluoroborate, mp 234-236° (lit [22] mp 234-235°); 2-*t*-butyl-5,6-dihydro-4-phenylbenzo[*h*]chromenylium tetrafluoroborate, mp 178-180° (lit [23] mp 175-176°); 5,6,8,9-tetrahydro-1-(4-methylphenyl)-7-phenyldibenz[*c,h*]-acridinium trifluoromethanesulphonate, mp 338-340° (lit [22] mp 338-340°).

1-(4-Methylphenyl)-2,4,6-triphenylpyridinium Tetrafluoroborate.

To a solution of 25 g (63 mmoles) of 2,4,6-triphenylpyrylium tetrafluoroborate in 200 ml of dichloromethane, 6.76 g (63 mmoles) of *p*-toluidine and 6.38 g (63 mmoles) of triethylamine were added at 25°. After 4 hours acetic acid (2.6 g) was added and after further 16 hours the solution was extracted with water, dried over magnesium sulfate and evaporated. The residue was treated with ether and recrystallised from ethanol to give 18 g (59%) of 1-(4-methylphenyl)-2,4,6-triphenylpyridinium tetrafluoroborate as colourless needles, mp 240-244°; pmr (deuteriochloroform): δ 2.10 (s, CH_3, 3H), 6.7-7.7 (m, 19H), 7.8 (s, 2H).

Anal. Calcd. for $C_{30}H_{24}BF_4N$: C, 74.38; H, 4.96; N, 2.89. Found: C, 74.10; H, 5.00; N, 2.70.

Reaction of 1-(4-Methylphenyl)-2,4,6-triphenylpyridinium Tetrafluoroborate: A. With Sodium Borohydride.

To a solution of 1-(4-methylphenyl)-2,4,6-triphenylpyridinium tetrafluoroborate (6.0 g, 13.2 mmoles) in 30 ml of acetonitrile-methanol (1:1 V/V) was added with stirring sodium borohydride (0.5 g, 13.2 mmoles), whereupon hydrogen was evolved and the solution turned deep red. After 2 hours at 5° the solvent was evaporated and water (50 ml) added to the residue. The mixture was extracted with ether (3 x 30 ml), dried over magnesium sulfate and evaporated to yield a dark oil (4.3 g) which was purified by column chromatography (silicagel; dichloromethane: hexanes, 1:1) to yield 2.37 g (45%) of **1** as yellow prisms, mp 141-143°; ir (bromoform): 2920, 2850 and 1600 cm^{-1} (arom); pmr (deuteriochloroform): δ 2.20 (s, CH_3, 3H), 5.65 (d, H-2, 1H, J = 6.5 Hz); 6.10 d, H-3, 1H, J = 6.5 Hz), 6.45 (s, H-5, 1H), 8.00-8.87 (m, 19H).

Anal. Calcd. for $C_{30}H_{25}N$: C, 90.23; H, 6.27; N, 3.51. Found: C, 90.50; H, 6.30; N, 3.50.

B. With Sodium Hydride.

To a suspension of sodium hydride (0.2 g, 8.3 mmoles) in dry acetonitrile (10 ml), 1-(4-methylphenyl)-2,4,6-triphenylpyridinium (2.6 g, 5.36 mmoles) was added, giving a deep red solution, which was warmed to 60-70° whereupon hydrogen was evolved and the solution became dark purple. After 2.5 hours at 60-70° the solvent was removed and the residue treated with water (50 ml). The resulting mixture was extracted with ether (50 ml), and the organic layer dried over magnesium sulfate and evaporated to yield a dark oil (2 g) which was purified by column chromatography (silicagel; dichloromethane:hexanes; 1:4, then 1:2) to give, after evaporation of solvent, 0.4 g (15%) of **2** as colourless needles, mp 166-167° (lit [24] mp 166-167°); ir (bromoform): 2215 cm^{-1} (CN); pmr (deuteriochloroform): δ 8.00-7.50 (m, 5H).

Reaction of 5,6-Dihydro-1-(4-methylphenyl)-2,4-diphenylbenzo[*h*]quinolinium Tetrafluoroborate (**3**) with Sodium Thiophenoxide.

Sodium thiophenoxide (2.27 g, 4.43 mmoles) was added to a solution of the quinolinium salt **3** (2.2 g, 4.3 mmoles) in dry dimethylformamide (30 ml). The solution immediately turned dark blue and was heated at 110-120°; after 2 hours, additional sodium thiophenoxide (1.2 g, 2.2 mmoles) was added. After a further 3 hours the colourless residue was treated with water (40 ml) and cooled to 25°. Extraction with ether (2 x 30 ml), gave an organic layer which was washed with water (4 x 30 ml), dried over magnesium sulfate and the solvent removed to yield an oil (2.4 g), which was purified by column chromatography (silicagel, hexanes:dichloromethane, 2:1) to give 1.1 g (60%) of **4** as prisms, mp 95-97°; pmr (deuteriochloroform): δ 2.30 (s, CH_3, 3H), 5.85 (d, H-2, 1H, J = 6 Hz), 6.45 (d, H-3, 1H, J = 6 Hz), 7.10-8.00 (m, 20H); cmr (deuteriochloroform): δ 24.4 (s, *C*H_3), 63.8 (d, C-2), 120-7-148.8 (C=C).

Anal. Calcd. for $C_{32}H_{25}N$: C, 90.78; H, 5.91; N, 3.31. Found: C, 90.39; H, 6.02; N, 3.20.

1-(4-Methylphenyl)-2,4-diphenylbenzo[*h*]quinolinium Tetrafluoroborate (**6**).

p-Toluidine (1.28 g, 11.9 mmoles) was added to a mixture of pyrylium salt **5** (5 g, 11.9 mmoles) in dichloromethane (30 ml), followed by triethylamine (1.2 g, 11.9 mmoles). The mixture was stirred at 25° for 5 hours and acetic acid (30 ml) added; the dichloromethane was evaporated and the remaining solution heated at 100° for 16 hours. After cooling, water was added (40 ml), the mixture extracted with dichloromethane (2 x 40 ml) and the organic layer washed with water (4 x 40 ml), dried over magnesium sulfate and concentrated to a volume of 30 ml. The product was precipitated with ether (200 ml); recrystallisation from dichloromethane/ethanol afforded 4.25 g (70%) of **6** as yellow plates, mp 314-316°; pmr (deuteriochloroform/trifluoroacetic acid): δ 2.55 (s, CH_3, 3H), 7.95 (s, 6H), 7.00-8.40 (m, 15H).

Anal. Calcd. for $C_{32}H_{24}BF_4N$: C, 75.46; H, 4.75; N, 2.75. Found: C, 75.06; H, 4.88; N, 2.97.

Reaction of 1-(4-Methylphenyl)-2,4-diphenylbenzo[*h*]quinolinium Tetrafluoroborate (**6**). A: With Sodium Thiophenoxide.

Sodium thiophenoxide (0.66 g, 5 mmoles) was added to a solution of pyridinium salt **6** in dry dimethylformamide (25 ml); the solution turned dark red, and was heated at 100° for 24 hours. Addition of water (30 ml) and extraction of the mixture with ether (2 x 40 ml), gave an organic layer which was washed with water (4 x 40 ml), dried over magnesium sulfate and evaporated to yield an oil (2 g). Column chromatography (silicagel; hexanes:dichloromethane, 1:1) afforded a fraction (0.65 g) identified as a mixture of diphenyl disulphide and dihydropyridine **4**.

B: With Sodium 2-Propanenitronate.

A mixture of pyridinium salt **6** (3.0 g, 5.89 mmoles), sodium 2-propanenitronate (2.22 g, 20 mmoles) and dimethyl sulfoxide (25 ml) was heated to 85°. One drop of di-*t*-butylperoxide was added, and the reaction mixture was stirred for 48 hours at 85°. After cooling to 20°, water (30 ml) was added, the mixture extracted with ether (2 x 40 ml) and the organic layer dried over magnesium sulfate. Removal of solvent under reduced pressure gave an oil (2.9 g) which was purified by column chromatography (silicagel, hexanes:dichloromethane, 4:1) to afford 0.40 g (17%) of **8** as colourless needles, mp 197°; pmr (deuteriochloroform): δ 2.45 (s, CH_3, 3H), 7.20-8.30 (m, 20H); cmr (deuteriochloroform): δ 21.3 (*C*H_3), 117.6-138.3 (10 quart C, 14 tert C); ms: 409 (M^+, 100), 317 (4.5), 291 (7.9).

Anal. Calcd. for $C_{31}H_{23}N$: C, 90.92; H, 5.66; N, 3.42. Found: C, 91.23; H, 5.82; N, 3.26.

1-(4-Methylphenyl)-2,4-diphenylbenzo[*f*]quinolinium Tetrafluoroborate **10**.

2,4-Diphenylbenzo[*f*]chromenylium tetrafluoroborate **9** (8.4 g, 20 mmoles) and *p*-toluidine (17.1 g, 0.16 mmoles) in glacial acetic acid (120 ml) were refluxed for 2 hours. After cooling to 25° ether was added and the mixture stirred at ambient temperature for 16 hours. The precipitate was filtered, washed with ether and recrystallized from acetic acid to yield 5.7 g (56%) of **10** as yellow prisms, mp 350°; ir (bromoform): 1610 (arom), 1580 (arom), and 1050 br (BF_4^-) cm^{-1}; pmr (deuteriochloroform/trifluoroacetic acid: δ 2.5 (s, CH_3, 3H), 7.40-8.50 (m, 21H).

Anal. Calcd. for $C_{32}H_{24}BF_4N$: C, 75.59; H, 4.72; N, 2.76. Found: C, 75.90; H, 4.90; N, 2.90.

1,2-Dihydro-2,4-diphenylbenzo[*f*]quinoline (**13a**) and 1,4-Dihydro-2,4-diphenylbenzo[*f*]quinoline (**12a**).

To a mixture of quinolinium tetrafluoroborate **10** (1.5 g, 2.94 mmoles), water (20 ml), methanol (5 ml), diethyl ether (20 ml) and sodium hydroxide (118 mg, 2.94 mmoles) was added dropwise a solution of sodium borohydride (0.22 g, 5.9 mmoles) in water (3 ml) with stirring at −8°. The mixture was stirred at −5° for 1 hour and allowed to warm to room temperature and kept at 25° for another hour. The ethereal layer was decanted, dried over magnesium sulfate and the solvent removed to yield 1.2 g (96%) of an oil; pmr (deuteriochloroform): δ 2.32 (CH_3, 3H), 2.41 (s, CH_3, 3H), 5.30 (d, H-1 in quinoline **12a** 1H, J = 6 Hz) 5.70 (m, C-2*H* in quinolines **12a** and **13a** 2H), 6.30 (d, C-3*H* in (**13a**), 1H, J = 9 Hz)), 7.20-7.90 (m); cmr (dimethylsulphoxide-d_6): δ 20.4 (CH_3), 39.9 (C-1 in **12a**), 60.6 (C-3 in **13a**), 107.3-147.9 (aromatic and olefinic carbons).

Treatment of 1,2- and 1,4-Dihydro-2,4-diphenylbenzo[*f*]quinolines **13a** and **12a** with Acid. A: With Fluoroboric Acid.

Upon addition of fluoroboric acid (40%, 350 mg) to a solution of the above mixture of quinolines **12a** and **13a** in ether (20 ml), 410 mg (27%) of the salt **12b** precipitated, as yellow prisms from ethanol/ethyl acetate, mp 335-340°; pmr (deuteriochloroform): δ 2.32 (3H, s), 5.33 and 5.80 (AB-quartet, 2H, J_{AB} = 6 Hz), 7.1-8.2 (20H, m); ^{13}C nmr (dimethylsulphoxide-d_6): δ 20.1 (CH_3), 39.9 (C-1), 107.0-147.6 (aromatic and olefinic carbons).

Anal. Calcd. for $C_{32}H_{26}BF_4N$: C, 75.16; H, 5.12; N, 2.74. Found: C, 75.63; H, 4.67; N, 2.61.

The ethereal solution was evaporated and the residue recrystallised from ethanol to give 440 mg (35%) of **13a** as orange prisms, mp 169-170°; pmr (deuteriochloroform): δ 2.41 (s, CH_3, 3H), 5.70 (d, H-2, 1H, J = 9 Hz), 6.30 (d, H-3, 1H, J = 9 Hz), 7.0-8.0 (m, 20H); cmr (deuteriochloroform): δ 20.7 (CH_3), 61.9 (C-3), 116.2-144.9 (aromatic and olefinic carbons).

Anal. Calcd. for $C_{32}H_{25}N$: C, 90.74; H, 5.95; N, 3.31. Found: C, 91.10; H, 5.82; N, 3.13.

B: With Trifluoroacetic Acid.

Compound **12b** (80 mg) was dissolved in deuteriochloroform (0.25 ml) and 2 drops of trifluoroacetic acid added to give a solution containing cation **15**; pmr (deuteriochloroform/trifluoroacetic acid): δ 2.46 (s, CH_3, 3H), 4.20-4.40 (m, H-3, 2H), 5.3-5.5 (m, H-4, 1H), 7.00-8.30 (m, 20H); cmr (deuteriochloroform/trifluoroacetic acid): δ 20.9 (q, CH_3), 34.4 (d, C-1), 42.1 (t, C-2), 118.5-142.7 (aromatic and olefinic carbons), 183.6 (s, C-3).

Compound **13a** (80 mg) was dissolved in deuteriochloroform (0.25 ml) and two drops of trifluoroacetic acid added to give a solution containing cation **16**; pmr (deuteriochloroform/trifluoroacetic acid): δ 2.46 (s, CH_3, 3H), 3.83 (d, H-3, 2H, J = 6 Hz), 5.53 (t, H-2, 2H, J = 6 Hz), 6.8 (d, 1H, J = 10 Hz), 7.20-7.70 (m, 18H), 8.80 (d, 1H, J = 10 Hz); cmr (deuteriochloroform/trifluoroacetic acid): δ 20.0 (q, CH_3), 40.7 (t, C-2), 63.8 (d, C-3), 109.3-151.1 (aromatic and olefinic carbons), 164.0 (s, C-1), 164.4 (s, C-4a).

2-*t*-Butyl-4-ethoxy-5,6-dihydro-4-phenyl-4*H*-naphtho[1,2-*b*]pyran (**17**).

A mixture of 2-*t*-butyl-5,6-dihydro-4-phenylbenzo[*h*]chromenylium tetrafluoroborate (1 g, 2.5 mmoles) and triethylamine (0.56 g, 5.5 mmoles) in ethanol (10 ml) was refluxed for 1 hour. On cooling 750 mg (83%) of **17** crystallised as needles, mp 123-125°; pmr (deuteriochloroform): δ 1.1 (s, $(CH_3)_3$, 9H), 2.1-2.8 (m, CH_2CH_2, 4H), 3.2-3.7 (m, CH_2, 2H), 5.40 (s, H-3, 1H), 7.1-7.5 (m, 8H), 7.6-7.9 (m, 1H); cmr (deuteriochloroform): δ 15.9 (q, CH_3CH_2O), 23.2 (t), 24.6 (q, $(CH_3)_3C$), 28.3 (t), 40.9 (s, $(CH_3)_3C$), 58.0 (t, CH_3CH_2O), 105.0 (s), 105.2 (s), 113.5 (d), 121.9 (d), 126.5 (d), 127.0 (d), 127.4 (d), 127.7 (d), 128.1 (d), 131.0 (s), 136.9 (s), 139.4 (s), 141.6 (s), 147.3 (s).

Anal. Calcd. for $C_{25}H_{28}O_2$: C, 83.30; H, 7.83. Found: C, 83.74; H, 8.10.

2-*t*-Butyl-1-(4-chlorophenyl)-5,6-dihydro-4-phenylbenzo[*h*]quinolinium Tetrafluoroborate (**18b**).

A mixture of 2-*t*-butyl-5,6-dihydro-4-phenylbenzo[*h*]chromenylium tetrafluoroborate (6 g, 15 mmoles), *p*-chloroaniline (3.9 g, 30 mmoles), triethylamine (1.5 g, 15 mmoles) and dichloromethane (30 ml) was stirred at 20° for 16 hours; acetic acid (2.0 g, 35 mmoles) was then added. After stirring for a further day, the mixture was washed with water (2 x 50 ml), the organic layer dried over magnesium sulfate and concentrated under reduced pressure to a volume of 15 ml. Ether was then added until no more solid precipitated. Filtration afforded the crude product which was heated under reflux with ethanol (30 ml) and triethylamine (1.0 g, 10 mmoles) for 1 hour. This solution, upon standing at 20° yielded 2.5 g (33%) of **18b** as needles, mp 246-248°; ir (bromoform): 1605 (arom), and 1050 (BF_4^-) cm^{-1}; pmr (deuteriochloroform): δ 1.33 (s, $(CH_3)_3$, 9H, 2.80 (s, CH_2CH_2, 4H), 6.90-7.30 (m, 4H), 7.60-7.80 (m, 9H), 8.06 (s, 1H).

Anal. Calcd. for $C_{29}H_{27}BClF_4N$: C, 68.06; H, 5.32; N, 2.74. Found: C, 67.93; H, 5.38; N, 5.4; N, 2.63.

2-*t*-Butyl-5,6-dihydro-1-(4-methoxyphenyl)-4-phenylbenzo[*h*]quinolinium Tetrafluoroborate **18c**.

A mixture of 2-*t*-butyl-5,6-dihydro-4-phenylbenzo[*h*]chromenylium tetrafluoroborate (6.0 g, 15 mmoles), *p*-toluidine (3.7 g, 30 mmoles), triethylamine (1.5 g, 15 mmoles) and dichloromethane (50 ml) was stirred at 20° for 16 hours; acetic acid (2.0 g, 35 mmoles) was then added. After stirring for a further 16 hours, the mixture was then washed with water (3 x 80 ml), the organic layer dried over magnesium sulfate and the solvent evaporated. The residue was dissolved in ethanol (10 ml) and poured into ether (150 ml). After stirring for 2 hours, the crystals were filtered and recrystallised from ethanol to give 5.3 g (70%) of **18c** as needles, mp 217-218°; ir (bromoform): 3080, 2960, 2880, 2840, 1590 (arom) and 1060 br (BF_4^-) cm^{-1}; pmr (deuteriochloroform): δ 1.33 (s, $(CH_3)_3$, 9H), 2.82 (s, CH_2CH_2, 4H), 3.88 (s, OCH_3, 3H), 6.9-7.7 (m, 13H), 8.05 (s, 1H).

Anal. Calcd. for $C_{30}H_{30}BF_4NO$: C, 71.02; H, 5.96; N, 2.76. Found: C, 70.98; H, 6.09; N, 2.63.

Reaction of Sodium 2-Propanenitronate with Pyridinium Salts **18a-18c**, and **22**. General Procedure.

Sodium 2-propanenitronate (0.5 g, 4.5 mmoles) was added to a solution of the pyridinium salt **18** (3 mmoles) in dimethylsulphoxide (15 ml) under nitrogen. The mixture was then heated at 100° for 6 hours; on allowing to cool to 20°, water (15 ml) was added. Extraction of the mixture with ether (3 x 20 ml) gave an organic layer which was dried over magnesium sulfate and then saturated with gaseous hydrogen chloride. The solution was filtered and the filtrate evaporated to give an oil which was chromatographed on neutral silica (60-80 mesh; *n*-hexane/dichloromethane 1:1). The first 50-100 ml of eluent contained 2-nitropropane and other unidentified products, and was discarded. The subsequent fraction (70 ml) was collected, washed with sodium hydroxide (0.5 *M*, 50 ml) and then water (50 ml), and dried over magnesium sulfate. Removal of solvent gave the product which was purified further either by chromatography (as above) or by distillation below 1 mm Hg.

Accordingly, pyridinium tetrafluoroborate **18a** gave a product which was purified by column chromatography to give 0.09 g (17%) of **19** as an oil; pmr (deuteriochloroform): δ 2.00 (s, $(CH_3)_2$, 6H), 2.37 (s, CH_3, 3H), 7.4 (m, 4H); cmr (deuteriochloroform): δ 22.9 (4-CH_3), 27.0 ($(CH_3)_2$), 89.6 (C-NO_2), 125.0, 129.2, 137.2, 138.7 (arom); ms: 179 (M^+, 0.05), 133 (100), 105 (66).

Anal. Calcd. for $C_{10}H_{13}NO_2$: C, 67.04; H, 7.26; N, 7.82. Found: C, 66.80; H, 7.40; N, 8.00.

Pyridinium tetrafluoroborate **18b** gave an oil which was purified by column chromatography to give 0.8 g (62%) of **20b** as yellow needles; pmr (deuteriochloroform): δ 1.08 (s, $(CH_3)_3$, 9H), 1.60-3.20 (s, CH_2CH_2, 4H) 4.08 (d, H-2, 1H, J = 7 Hz), 5.70 (d, H-3, 1H, J = 7 Hz), 6.90-7.60 (m, 13H); cmr (deuteriochloroform): δ 24.1 (CH_2), 26.2 ($C(CH_3)_3$), 28.4 (CH_2), 37.6 ($C(CH_3)_3$), 69.6 (C-2), 119.3 (d), 121.0 (d), 123.9 (s), 124.9 (d), 125.9 (s), 126.4 (d), 126.7 (d), 127.1 (d), 127.4 (d), 128.1 (d), 128.4 (d), 128.6 (d), 132.2 (s), 134.6 (s), 137.2 (s), 139.3 (s), 140.1 (s), 148.4 (s).

Anal. Calcd. for $C_{29}H_{28}ClN$: C, 81.79; H, 6.58; N, 3.29. Found: C, 81.47; H, 6.70; N, 3.11.

Pyridinium tetrafluoroborate **18c** gave an oil which was purified by column chromatography to give 0.8 g (65%) **21** as yellow needles; pmr (deuteriochloroform): δ 1.07 (s, $(CH_3)_3$, 9H), 1.50-3.20 (m, CH_2CH_2, 9H), 3.73 (s, OMe, 3H), 4.00 (d, H-2, 3H, J = 7 Hz), 5.54 (d, H-3, 3H, J = 7 Hz), 6.70-7.60 (m, 13H); cmr (deuteriochloroform): δ 24.1 (CH_2), 26.2 ($C(CH_3)_3$), 28.6 (CH_2), 37.5 ($C(CH_3)_3$), 55.3 (OCH_3), 70.4 (C-2), 114.0 (d), 118.2 (d), 121.7 (d), 122.7 (s), 125.1 (d), 126.3 (d), 126.4 (d), 126.9 (d), 127.2 (d), 128.0 (d), 128.5 (d), 132.8 (s), 135.5 (s), 137.4 (s), 139.2 (s).

Anal. Calcd. for $C_{30}H_{31}N$: C, 85.51; H, 7.36; N, 3.33. Found: C, 85.97; H, 7.64; N, 3.18.

Pyridinium trifluoromethanesulphonate **22** gave an oil which was purified by chromatography to give 0.06 g (11%) of **19** as an oil with spectral data as quoted above.

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