Identification of the Products of Solvolysis† of *N*-Benzylpyridinium Cations in the Absence of Nucleophiles[1]

Alan R. Katritzky,* Charles M. Marson, Jen-Luan Chen, Franciszek Saczewski, and Roy W. King
Department of Chemistry, University of Florida, Gainesville, FL 32611 U.S.A.

Mono-, tri-, and penta-cyclic *N*-benzylpyridinium tetrafluoroborates undergo thermolysis in chlorobenzene as solvent to give products of benzylation both of the solvent and of the pyridine leaving group. Thermolysis alone, and in nitrobenzene as solvent, yielded mainly products of benzylation of the leaving group. The results support the previously postulated mechanism of unimolecular solvolysis of compounds of these types in non-polar solvents.

Extensive work described in previous papers from our group has shown that *N*-alkyl and *N*-benzyl substituents are transferred smoothly from pyridinium cations to nucleophiles under preparative conditions.[2] Under kinetic conditions we have shown that plots of observed rate constants against nucleophile concentration are generally straight lines, but in many cases these straight lines give a positive intercept when extrapolated to zero nucleophile concentration.[3] This behaviour has been interpreted in terms of a composite reaction proceeding simultaneously through unimolecular S_N1-type as well as bimolecular S_N2-type mechanisms. The question then arises as to the fate of the *N*-alkyl or *N*-benzyl substituent in reactions which proceed in the absence of nucleophile. The present paper is concerned with the identification of such reaction products. We have studied three pyridinium salts under various conditions. Their structures were chosen both to give a variety of types, and to facilitate identification of reaction products.

The work to be described demonstrates that, in such cases, the products formed are those expected for electrophilic attack of a carbocation on either the solvent or the leaving group (other than at the nitrogen atom).

Monocyclic Series.—The decomposition of 1-(*p*-bromobenzyl)-2-t-butyl-4-(*p*-fluorophenyl)-6-phenylpyridinium trifluoromethanesulphonate (**1**) was induced (*a*) by heating under reflux in chlorobenzene, (*b*) similarly in nitrobenzene, and (*c*) by thermolysis at 250 °C. The mixtures so obtained were analysed by g.l.c.—mass spectrometry (using temperatures up to 350 °C to elute components from the column), and by ^1H and ^{13}C n.m.r. spectroscopy.

From the reaction in chlorobenzene, the most volatile components observed by g.l.c.–mass spectrometry were two of the three possible isomers of (*p*-bromophenyl)(chlorophenyl)-methane (**5**). In both cases signals at *m/z* 280 (*M*, $^{81}Br/^{35}Cl$ + $^{79}Br/^{37}Cl$), 280 (*M*, $^{79}Br/^{35}Cl$), 245 (*M* − Cl), and 125 (*M* − PhBr) were observed (the detailed fragmentation patterns were distinct for the different isomers). High-resolution mass spectrometry carried out on the mixture disclosed the signal at *m/z* 280 as a single peak which showed the precise mass expected for $C_{13}H_{11}BrCl$, thereby confirming that this signal originated only from one or more of the (*p*-bromophenyl)-(chlorophenyl)methanes (**5**).

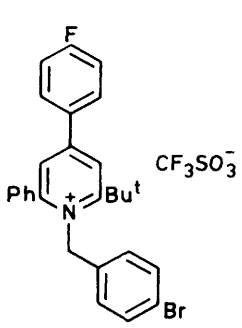
Column chromatography enabled a mixture of the two (*p*-bromophenyl)(chlorophenyl)methanes (**5**) to be separated from the other components; analysis of the ^{13}C n.m.r. spectrum of the mixture (Table 1) showed that the minor component was the *meta*-isomer (**5b**) and the major one the *para*-isomer (**5c**). Whereas the latter assignment is unambiguous, on account of the number of lines in the ^{13}C n.m.r. spectrum, the former assignment is less secure. However, the value of 134.1 p.p.m. for the *ipso*-carbon atom (with respect to chlorine) agrees fairly well with that calculated for (**5b**) (134.8 p.p.m.); the corresponding calculated value for the isomer (**5a**) is 135.3 p.p.m. The other assignments are also consistent with the presence of isomers (**5b**) and (**5c**), and the absence of isomer (**5a**).

After isomers (**5b**) and (**5c**), the trisubstituted pyridine (**2**) was the next most volatile component (*M*, 305); a sample was isolated by preparative column chromatography. The least volatile components detected were three isomers of *p*-bromobenzylated 2-t-butyl-4-(*p*-fluorophenyl)-6-phenylpyridine; in each case a signal at *m/z* 475 (*M*, ^{81}Br) was observed, although the detailed fragmentation patterns were distinct for the different isomers. High-resolution examination of the reaction mixture (without g.l.c.) showed the signals at *m/z* 473 (^{79}Br) and 475 (^{81}Br) to be single peaks, corresponding precisely to $C_{28}H_{25}BrFN$, thereby confirming that this signal originated only from one or more isomeric mono-(*p*-bromobenzyl) derivatives of pyridine (**2**). Column chromatography enabled a mixture of *two* of these isomers to be isolated; analysis of the ^{13}C n.m.r. spectrum (Table 2) showed that this mixture consisted solely of the β-substituted derivative (**3**) and the α-*ortho*-compound (**4a**). The incremental effects of *p*-bromobenzylation determined by comparison of the chemical shifts of the pyridines (**2**) and (**4a**) at C-18, C-20, and C-21 are −2.3, 0.5, and 12.8 p.p.m., respectively; those changes are identical with those calculated‡ for a benzyl group at the *ortho*-position in the pyridine (**4**), and they rule out the presence of isomers (**4b**) and (**4c**) in this fraction. Interestingly, there was no evidence of any appreciable *p*-bromobenzylation at C-3 of the pyridine (**2**). Study of the material balance for the thermolysis of (**1**) in chlorobenzene showed that approximately 20% of the *p*-bromobenzyl group was accounted for in the form of the two isomers of (*p*-bromobenzyl)chlorobenzene (**5b** and **c**), and an additional 5% as the three isomeric *C*-(*p*-bromobenzyl) derivatives of the pyridine (**2**).

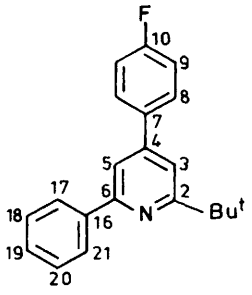
From the decomposition of the pyridinium salt (**1**) in nitrobenzene, the most volatile product detected by g.l.c.–mass spectrometry was one isomer of (*p*-bromophenyl)(nitrophenyl)-methane (**6**) (*M* 293/291). The next most volatile component was the pyridine (**2**). Less volatile still were five mono-(*p*-

† Here and elsewhere the word 'solvolysis' is used to denote a reaction which is induced by the fact that a substrate is dissolved in a solvent. In a solvolysis, a solvent molecule need not be involved in the rate-determining stage.

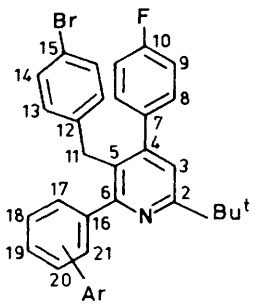
‡ These values for a benzyl substituent on a benzene ring were taken from ref. 4.



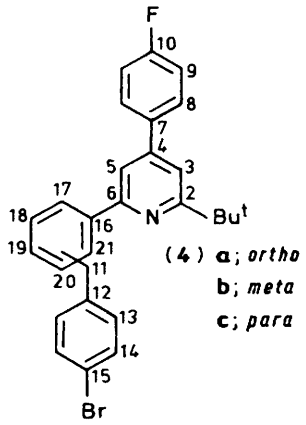
(1)



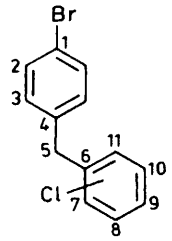
(2)



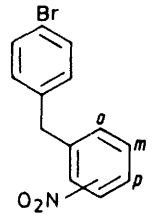
(3)



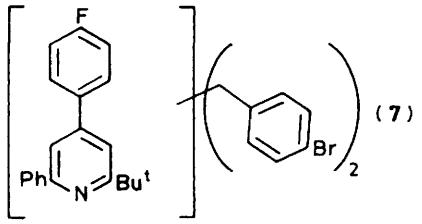
(4) **a**; *ortho*
b; *meta*
c; *para*



(5) **a**; *ortho*
b; *meta*
c; *para*



(6) **a**; *ortho*
b; *meta*
c; *para*



(7)

bromobenzyl) isomers of the pyridine (**2**), each with molecular ions at *m/z* 475 and 473; detailed fragmentation patterns for each isomer are given in the Experimental section. Comparison of retention times obtained in the chlorobenzene run showed that the first and second isomers to be eluted were the pyridines (**3**) and (**4a**), respectively. Since no benzylation of the *p*-fluorophenyl ring had occurred (^{1}H and ^{13}C n.m.r. data for this substituent were essentially unaltered for all five isomeric products) it follows that the three unassigned mono-(*p*-bromobenzyl)pyridines are benzylated C-3, C-9 [pyridine (**4b**)], and C-10 [pyridine (**4c**)]. High-resolution examination of the reaction mixture showed the signals at *m/z* 473 (^{79}Br) and 475 (^{81}Br) to be single peaks corresponding precisely to $C_{28}H_{25}BrFN$, thereby confirming that this signal originated only from the isomeric *p*-bromobenzylpyridines. 1,2-Bis-(*p*-bromophenyl)ethane was also detected (*M* 342/340/338) with a retention time somewhat greater than the third of the foregoing isomers. The least volatile detected component was a trace of a bis-(*p*-bromobenzyl)pyridine (**7**) (*M* 641 ^{79}Br/^{79}Br) of unknown substitution pattern. Study of the material balance for the thermolysis of (**1**) in nitrobenzene showed that approximately 15% of the *p*-bromobenzyl group was accounted for in the form of the (*p*-bromophenyl)(nitrophenyl)methane (**6**), and an additional 20% as the five isomeric *C*-(*p*-bromobenzyl) derivatives (**3**) and (**4**) of the pyridine (**2**).

Thermolysis of the pyridinium salt (**1**) at 250 °C, followed by alkaline work-up, gave an oil which was subjected to g.l.c.–mass spectrometry. Most volatile was the pyridine (**2**); less volatile were four isomeric *p*-bromobenzyl derivatives of the pyridine (**2**); in each of the latter cases, signals at *m/z* 475 and 473 (*M*) were detected. Comparison of retention times with those obtained in the runs carried out in chloro- and nitro-benzene showed that the first and second isomers to be eluted were (**3**) and (**4a**), respectively. The least volatile detected component was again a trace of a bis-(*p*-bromobenzyl)pyridine (**7**) (*M* 641, ^{79}Br/^{79}Br) of unknown substitution pattern. Study of the material balance for the thermolysis of (**1**) neat at 250 °C showed that approximately 30% of the *p*-bromobenzyl group was accounted for in the form of the four isomeric *C*-(*p*-bromobenzyl) derivatives (**3**) and (**4**) of the pyridine (**2**).

Tricyclic Series.—1-Benzyl-2-t-butyl-4-phenyl-5,6-dihydrobenzo[*h*]quinolinium tetrafluoroborate (**9**) on heating for 4 h in chlorobenzene at 100 °C gave the salt (**8**) together with one or more benzylchlorobenzenes, and a mixture of four benzylated 2-t-butyl-5,6-dihydro-4-phenylbenzo[*h*]quinolines (**10**) as shown by g.l.c.–mass spectrometry.

Use of temperatures up to 400 °C to elute components from the column gave first one or more benzylchlorobenzenes (**11**) [*m/z* 204 (*M*, ^{37}Cl), 202 (*M*, ^{35}Cl), 167 (*M* − Cl), and 125 (*M* − Ph)]. Secondly, a considerable quantity of 2-t-butyl-5,6-dihydro-4-phenylbenzo[*h*]quinoline [*m/z* 313 (*M*) and 298 (*M* − Me)] was eluted.

Least volatile were four isomeric benzyl-2-t-butyl-4-phenyl-

Table 1. ^{13}C N.m.r. data for (*p*-bromophenyl)(chlorophenyl)methanes (**5**) (p.p.m. from Me_4Si)

Carbon atom	Calc.[a]			Found	
	(**5a**)	(**5b**)	(**5c**)	(**5b**)	(**5c**)
1	120.4	120.4	120.4	120.0	120.1
2	131.7	131.7	131.7	131.4	131.5
3	130.6	130.6	130.6	130.5	130.5
4	139.7	139.7	139.7	137.9	138.4
5				38.5	40.5
6	141.7	142.7	139.4	138.4	138.8
7	135.3	129.4	130.4	129.5	130.1
8	128.9	134.8	128.9	134.1	128.5
9	127.6	126.6	132.5	126.8	132.0
10	126.6	129.9	128.9	130.8	128.5
11	130.4	127.1	130.4	127.8	130.1

[a] Taking benzene as 128.5 (ref. 4).

benzo[*h*]quinolines, designated (**10a—d**), in order of elution; in each case, signals at *m/z* 403 (*M*), 388 (*M* − Me), and 361 (*M* − C_3H_6) were observed. High-resolution examination of the reaction mixture (without g.l.c.) showed the signal at *m/z* 403 to be a single peak, which corresponded precisely to $C_{30}H_{29}N$, thereby confirming that this signal originated only from isomeric benzylbenzo[*h*]quinolines of type (**10**). The positions of the benzyl groups in the isomers (**10a—d**) were not established; certain signals of the isomer (**10a**) were substantially different from those of the other three, possibly indicating benzylic substitution at the 3-position; also benzylic substitution in the 4-phenyl ring cannot be ruled out.

Pentacyclic Series.—The decomposition of 14-benzyl-5,6,8,9-tetrahydro-7-phenyldibenz[*c,h*]acridinium trifluoromethanesulphonate (**13**) was induced (*a*) by heating under reflux in chlorobenzene, (*b*) similarly in nitrobenzene, and (*c*) by thermolysis at 250 °C. The mixtures obtained were analysed by g.l.c.–mass spectrometry, by use of temperatures up to 300 °C to elute components from the column.

From the reaction with chlorobenzene the most volatile components were the *ortho-*, *meta-*, and *para*-isomers of benzylchlorobenzene, designated (**11a—c**), in order of elution from the column. In each case signals at *m/z* 204 (*M*, ^{37}Cl), 202 (*M*, ^{35}Cl), 167 (*M* − Cl), and 125 (*M* − Ph) were observed, although the detailed fragmentation patterns were distinct for the different isomers. High resolution carried out on the mixture showed the signal at *m/z* 202 as a single peak which corresponded precisely to $C_{13}H_{11}Cl$, thereby confirming that this signal orginated only from the benzylchlorobenzenes (**11**). Less volatile were the five detected isomers of benzyl(chlorobenzyl)benzene (**15a—e**) each with parent ions at *m/z* 294 and 292 ($^{37}Cl/^{35}Cl$); detailed fragmentation patterns for all these are given in the Experimental section. While alternative structures involving a methyl group cannot be ruled out, the general formula (**15**) is likely to be correct; for example, fragmentation with loss of a methyl group was not observed. The least volatile component detected was a benzylated dibenz[*c,h*]acridine (**14**), in which the benzyl substituent could be located in one of the four different sites of the fused benzene rings or, less likely, on the 7-phenyl substituent. Signals at *m/z* 449 (M^+) and 91 (C_7H_7) were among those detected.

From the decomposition of dibenz[*c,h*]acridinium trifluoromethanesulphonate (**13**) in nitrobenzene three isomers of the benzylated dibenz[*c,h*]acridine (**14**) were obtained; the g.l.c.–mass spectra were distinct but all gave signals at *m/z* 450 (*M* + 1), 449 (*M*), and 91 (C_7H_7). No products were detected derived from nitrobenzene, which evidently acted only as a solvent.

Table 2. ^{13}C N.m.r. data of 2-t-butyl-4-(*p*-fluorophenyl)-6-phenylpyridines (**2**), (**3**), and (**4a**) (p.p.m. from Me_4Si)

Carbon atom	(**2**)	(**3**)	(**4**)
2	169.6	166.5	168.7
3	115.3	114.4	114.4
4	148.4	150.0	147.5
5	115.5	126.7	118.8
6	156.1	158.2	158.7
7[a]	130.4	136.3	135.2
8[b]	130.7	128.0	128.4
9[c]	117.1	114.7	115.5
10[d]	165.3	162.4	163.2
11		34.0	37.9
12		138.3	140.3
13		130.3	130.2
14		130.5	130.6
15		119.0	119.0
16	139.8	140.0	140.9
17	127.0	127.1	127.1
18	128.6	128.7	126.4
19	128.8	129.0	129.0
20	128.6	128.7	129.2
21	127.0	127.1	139.9

[a] J_{CF} 3 Hz. [b] J_{CF} 8 Hz. [c] J_{CF} 22 Hz. [d] J_{CF} 240—260 Hz.

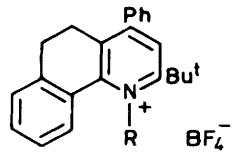
Thermolysis of dibenz[*c,h*]acridinium trifluoromethanesulphonate (**13**) at 250 °C and alkaline work-up gave a solid which contained four isomers of dibenz[*c,h*]acridine (**14**), as shown by g.l.c.–mass spectrometry. In each case signals at *m/z* 450 (*M* + 1), 449 (*M*), and 91 (C_7H_7) were observed.

Kinetic evidence indicates that the *N*-benzyl tricyclic pyridinium tetrafluoroborate (**9**) undergoes unimolecular reaction in chlorobenzene;[5] it is now apparent that, in the absence of other nucleophiles, after dissociation into an ion–molecule pair, the benzyl cations are captured, partly by the solvent to form chlorodiphenylmethanes (**11**), and partly by the leaving group to form four isomeric benzylated benzo[*h*]-quinolines (**10**).

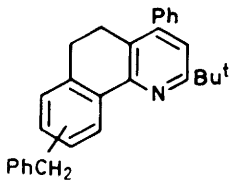
Conclusions.—We have now demonstrated that the monocyclic *N*-benzyl cation (**1**) behaves similarly to the cation (**9**) in chlorobenzene as solvent in the absence of other nucleophiles; it gives two products [(**5b**) and (**5c**)] of benzylation of the solvent and three *p*-bromobenzylated pyridines [(**3**), (**4a**), and another isomer in which the position of the *p*-bromobenzyl group was not established]. The pyridinium salt (**1**) on thermolysis in nitrobenzene behaves similarly; *C*-(*p*-bromobenzylation) of nitrobenzene was observed (*O*-benzylation would lead to products unstable under the g.l.c. separation conditions); the *p*-bromobenzylpyridines (**3**) and (**4a**) were found, and also three more *p*-bromobenzylated isomers. Some 1,2-bis-(*p*-bromophenyl)ethane and a trace of a bis-(*p*-bromobenzyl) pyridine (**7**) were also detected.

Thermolysis of the pyridinium salt (**1**) neat gave compounds (**3**) and (**4a**), two *p*-bromobenzylated isomers, and a trace of a bis-(*p*-bromobenzyl)pyridine (**7**).

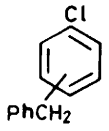
The pentacyclic *N*-benzyl cation (**13**) behaves similarly to the cation (**9**) in chlorobenzene as solvent in that it gives (**11**) and a benzylated base (**14**). However, five isomeric products (**15a—e**) of the reaction of two benzyl cations with one solvent molecule were also found. Those probably arise from the reaction of ion conglomerates; although at the concentrations used for kinetics (less than 10^{-2}M) these pyridinium salts exist in chlorobenzene predominantly as ion pairs, the present experiment was carried out at concentrations where, as we have shown in other work, considerable ion conglomeration occurs; such conglomeration



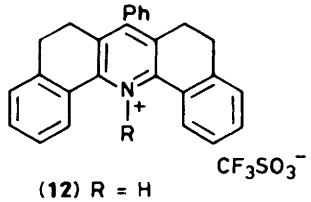
(8) R = H
(9) R = CH_2Ph



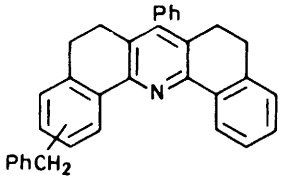
(10)



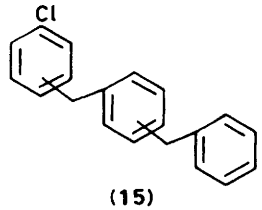
(11)



(12) R = H
(13) R = CH_2Ph



(14)



(15)

is expected to be considerably greater than that in the monocyclic series because of greater planarity in the former.

Thermolysis of the pyridinium salt (**13**) in nitrobenzene *and* without solvent in each case gave isomers of (**11**).

The work reported in this paper supports the previous interpretation[3] of the kinetic behaviour of *N*-substituent displacements, in particular the occurrence of distinct unimolecular and bimolecular reaction modes.

Experimental

M.p.s were determined with a Hoover Uni-melt capillary apparatus. I.r. spectra were recorded with a Perkin-Elmer 283B spectrophotometer, u.v. spectra with a Perkin-Elmer 330 instrument, ^1H n.m.r. spectra with a Varian EM 360L spectrometer, and ^{13}C n.m.r. spectra with a JEOL FX-100 spectrometer. Mass spectra were measured with an A.E.I. MS30 instrument, coupled with a Pye 104 gas chromatograph with a glass column. 'Ether' refers to diethyl ether; 'evaporation' refers to removal of solvent under reduced pressure. Anhydrous magnesium sulphate was used as a drying agent.

The following compounds were prepared by literature procedures: *p*-fluorobenzylidenepinacolone, m.p. 38—39 °C (lit.,[6] 37—39 °C); 1-benzyl-2-t-butyl-5,6-dihydro-4-phenylbenzo[*h*]-quinolinium tetrafluoroborate (**9**), m.p. 136—137 °C (lit.,[7] 136—137 °C); 5,6,8,9-tetrahydro-7-phenyldibenz[*c*,*h*]acridinium trifluoromethanesulphonate (**12**), m.p. 285—287 °C (lit.,[8] 280—285 °C); 14-benzyl-5,6,8,9-tetrahydro-7-phenyldibenz[*c*,*h*]acridinium trifluoromethanesulphonate (**13**), m.p. 169—171 °C (decomp.) (lit.,[9] 170—171 °C).

2-t-Butyl-4-(p-fluorophenyl)-6-phenylpyrylium Trifluoromethanesulphonate.—A mixture of *p*-fluorobenzylidenepinacolone (3.0 g, 14.6 mmol), acetophenone (0.90 g, 7.5 mmol), and CF_3SO_3H (8.0 g, 53.3 mmol) was heated at 100 °C for 6 h. Trituration of the residue with ether (100 ml) afforded *2-t-butyl-4-(p-fluorophenyl)-6-phenylpyrylium trifluoromethanesulphonate* (6.0 g, 90%) as prisms, m.p. 232—233 °C (Found: C, 57.6; H, 4.4. $C_{22}H_{20}F_4O_4S$ requires C, 57.9; H, 4.3%); δ(^1H) ($CDCl_3$) 1.70 (9 H, s) and 7.2—8.6 (11 H, m); $\nu_{max.}$($CHBr_3$) 1 600, 1 590, 1 500, 1 275, 1 020, 950, 835, and 780 cm^{-1}.

1-(p-Bromobenzyl)-2-t-butyl-4-(p-fluorophenyl)-6-phenylpyridinium Trifluoromethanesulphonate (**1**).—To a solution of 2-t-butyl-4-(*p*-fluorophenyl)-6-phenylpyrylium trifluoromethanesulphonate (3.0 g, 6.6 mmol) in EtOH (20 ml) were added *p*-bromobenzylamine hydrochloride (1.5 g, 6.7 mmol) and Et_3N (1.3 g, 12.9 mmol). The mixture was stirred at 25 °C for 16 h, then evaporated, and water (30 ml) was added to the residue. Extraction with CH_2Cl_2 (3 × 30 ml) and drying of the combined organic layers ($MgSO_4$) gave a solution which was evaporated; the residue was triturated with ether (20 ml) to afford the *pyridinium trifluoromethanesulphonate* (**1**) (3.1 g, 75%) as needles, m.p. 167—168 °C (Found: C, 55.6; H, 4.2; N, 2.1. $C_{29}H_{26}F_4NO_3S$ requires C, 55.8; H, 4.2; N, 2.2%); δ(^1H) ($CDCl_3$) 1.80 (9 H, s), 6.15 (2 H, s), and 6.4—8.5 (15 H, m); δ(^{13}C) ($CDCl_3$) 31.2 (q), 39.0 (s), 57.9 (t), 117.1 (d, *J* 22 Hz), 122.2 (s), 123.6 (d), 126.5 (d), 127.7 (d), 128.5 (d), 128.8 (d), 130.4 (d, *J* 3 Hz), 130.6 (d, *J* 8 Hz), 132.9 (s), 133.6 (s), 156.0 (s), 159.3 (s), and 166.0 (s); $\nu_{max.}$($CHBr_3$) 1 620, 1 600, 1 555, 1 255 (s), 1 030, 830, 785, and 740 cm^{-1}.

2-t-Butyl-4-(p-fluorophenyl)-6-phenylpyridine (**2**).—2-t-Butyl-4-(*p*-fluorophenyl)-6-phenylpyrylium trifluoromethanesulphonate (0.40 g, 0.90 mmol) was stirred with aqueous ammonia (20 ml; 20M) at 100 °C for 10 min. The solution was allowed to cool to 25 °C and extracted with Et_2O (3 × 30 ml); the combined organic layers were dried ($MgSO_4$) and evaporated. The residue was recrystallised from aqueous EtOH to give the *pyridine* (**2**) (0.24 g, 95%) as needles, m.p. 90—92 °C (Found: C, 82.3; H, 7.0; N, 4.5. $C_{21}H_{21}N{\cdot}H_2O$ requires C, 82.6; H, 6.9; N,

4.6%); δ(^{1}H) ($CDCl_3$) 1.50 (9 H, s), 7.1—8.0 (9 H, m), and 8.2—8.5 (2 H, m).

Thermolysis of 1-(p-*Bromobenzyl*)-2-*t*-*butyl*-4-(p-*fluorophenyl*)-6-*phenylpyridinium Trifluoromethanesulphonate* (**1**).—(a) *In chlorobenzene*. 1-(*p*-Bromobenzyl)-2-t-butyl-4-(*p*-fluorophenyl)-6-phenylpyridinium trifluoromethanesulphonate (**1**) (1.0 g, 1.6 mmol) in chlorobenzene (15 ml) was heated at 120 °C for 4 h. The mixture was evaporated, the residue shaken with aqueous ammonia (20 ml; 5M), and the mixture extracted with ether (3 × 20 ml). The extracts were combined, dried ($MgSO_4$), and evaporated to give an *oil* (0.70 g) [δ(^{1}H) ($CDCl_3$) 1.50 (s), 3.85 (s), 4.05 (s), and 6.9—8.4 (m); δ(^{13}C) ($CDCl_3$) 30.3 (q), 37.8 (t), 38.6 (t), 40.5 (s), and 115.2—169.9 (25 lines)], which on chromatography on a Dexsil-300 g.l.c. column (temperature 50—350 °C) afforded (i) an isomer of (bromophenyl)(chlorophenyl)methane (**5**); *m*/*z* 282 (M^+, $^{81}Br/^{35}Cl$ + $^{79}Br/^{37}Cl$; 48%), 281 (6), 280 (M^+, $^{79}Br/^{35}Cl$; 37), 247 (24), 201 (55), 171 (5), 165 (100), 127 (4), and 90 (12); (ii) a second isomer of (**5**): *m*/*z* 282 (M^+, $^{81}Br/^{35}Cl$ + $^{79}Br/^{37}Cl$; 47%), 281 (7), 280 (M^+, $^{79}Br^{35}Cl$; 36), 247 (34), 203 (18), 201 (59), 171 (4), 165 (100), 127 (4), and 90 (10); (iii) 2-t-butyl-4-(*p*-fluorophenyl)-6-phenylpyridine (**2**); *m*/*z* 305 (M^+; 53%), 304 (50), 290 (100), 263 (45), 248 (18), and 145 (16); (iv) a *p*-bromobenzyl derivative of the pyridine (**2**); *m*/*z* 475 (M^+, ^{81}Br; 91%), 474 (94), 473 (M^+, ^{79}Br; 94), 472 (72), 458 (100), 431 (84), 417 (13), 302 (14), 290 (11), 248 (25), 171 (11), and 151 (29); (v) a second *p*-bromobenzyl derivative of the pyridine (**2**); *m*/*z* 475 (M^+, ^{81}Br; 55%), 472 (28), 458 (11), 197 (10), and 189 (9); and (vi) a third *p*-bromobenzyl derivative of the pyridine (**2**); *m*/*z* 475 (M^+, ^{81}Br; 94%), 474 (100), 473 (M^+, ^{79}Br; 98), 472 (82), 460 (61), 432 (43), 304 (44), 290 (19), and 82 (20). High-resolution mass spectrometry on the mixture showed for the *m*/*z* signal at 475 a single peak of *m*/*z* 475.1129 (Calc. for $C_{28}H_{25}{}^{81}BrFN$: *M*, 475.1133) and for the *m*/*z* 473 signal a single peak at 473.1160 (Calc for $C_{28}H_{25}{}^{79}BrFN$: *M*, 473.1154).

The oil was chromatographed (SiO_2; n-hexane) to give (in order of elution): (i) a mixture of diphenylmethanes (**5b**) and (**5c**), the latter being the major component; δ(^{1}H) ($CDCl_3$) (mixture) 3.9 (s), 4.1 (s), and 6.9—7.6 (m); [major component (**5c**)] δ(^{13}C) ($CDCl_3$) 40.5 (t), 120.1 (s), 128.5 (d), 130.1 (d), 130.5 (d), 131.5 (d), 132.0 (d), 138.8 (s), and 139.4 (s); [minor component (**5b**)] δ(^{13}C) ($CDCl_3$) 38.5 (t), 120.0 (s), 126.8 (d), 127.8 (d), 129.5 (d), 130.5 (d), 130.8 (d), 131.4 (d) 134.1 (s), 137.9 (s), and 138.4 (s); (ii) (eluted by 1:9 v/v CH_2Cl_2–n-hexane) the pyridine (**2**); and (iii) a 3:1 mixture of *p*-bromobenzylpyridines (**4a**) and (**3**); see Table for ^{13}C n.m.r. data.

(b) *In nitrobenzene*. 1-(*p*-Bromobenzyl)-2-t-butyl-4-(*p*-fluorophenyl)-6-phenylpyridinium trifluoromethanesulphonate (**1**) (1.0 g, 1.6 mmol) was heated under reflux in nitrobenzene for 1 h. The solution was evaporated, the residue shaken with aqueous ammonia (20 ml; 5M), and the mixture extracted with ether (3 × 20 ml). The extracts were combined, dried ($MgSO_4$), and evaporated to give an *oil* (0.80 g) [δ(^{1}H) ($CDCl_3$) 1.50 (s), 3.95 (s), 4.20 (s), 4.40 (s), and 6.80—8.35 (m); δ(^{13}C) ($CDCl_3$) 30.2 (q), 31.1 (q), 34.2 (t), 38.2 (t), 40.6 (t), 71.1 (t), and 115.4—165.9 (29 lines], which on chromatography on a Dexsil-300 g.l.c. column (temperature 50—350 °C) afforded (i) an isomer of (*p*-bromophenyl)(nitrophenyl)methane (**6**); *m*/*z* 293 (M^+, ^{81}Br; 1%), 291 (M^+, ^{79}Br; 1), 187 (10), 172 (26), 157 (10), and 91 (100); (ii) the 6-phenylpyridine (**2**); (iii) a *p*-bromobenzyl derivative of the pyridine (**2**); *m*/*z* 475 (M^+, ^{81}Br; 65%), 474 (64), 473 (M^+, ^{79}Br; 67), 472 (52), 458 (100), 433 (61), 431 (63), 302 (13), 248 (20), 171 (11), and 169 (11); (iv) a second *p*-bromobenzyl derivative of the pyridine (**2**); *m*/*z* 475 (M^+, ^{81}Br; 96%), 474 (67), 473 (M^+, ^{79}Br; 100), 472 (48), 460 (16), 458 (21), 197 (20), 189 (41), 171 (25), and 169 (26); (v) a third *p*-bromobenzyl derivative of the pyridine (**2**); *m*/*z* 476 (7), 473 (M^+, ^{79}Br; 100%), 460 (17), 458 (18), 432 (9), 430 (9), and 304 (8); (vi) 1,2-bis-(*p*-bromophenyl)ethane; *m*/*z* 342 (M^+, $^{81}Br/^{81}Br$; 14%), 341 (7), 340 (M^+, $^{81}Br/^{79}Br$; 31), 338 (M^+, $^{79}Br/^{79}Br$; 18), 261 (24), 259 (40), 257 (16), 171 (99), and 169 (100); (vii) a fourth *p*-bromobenzyl derivative of the pyridine (**2**); *m*/*z* 475 (M^+, ^{81}Br; 94%), 474 (82), 473 (M^+, ^{79}Br; 100), 472 (61), 461 (28), 460 (83), 458 (98), 433 (66), 431 (63), 248 (26), 178 (20), 171 (95), 169 (94), 165 (29), 159 (27), 91 (56), and 89 (25); (viii) a fifth *p*-bromobenzyl derivative of the pyridine (**2**); *m*/*z* 475 (M^+, ^{81}Br; 97%), 474 (88), 473 (M^+, ^{79}Br; 100), 472 (62), 461 (29), 460 (97), 459 (32), 458 (95), 434 (21), 433 (76), 432 (22), 431 (75), 419 (17), 417 (17), 248 (35), 190 (25), 189 (22), 176 (29), 171 (77), 169 (76), 165 (21), 91 (29), 90 (30), and 73 (56); and (ix) a bis-(*p*-bromobenzyl)pyridine (**7**); *m*/*z* 645 (M^+, $^{81}Br/^{81}Br$; 75%), 644 (32), 643 (100), 642 (74), 641 (66), 565 (27), 563 (36), 178 (15), 177 (18), 176 (16), 144 (21), 142 (27), 91 (18), and 82 (18).

(c) *Thermolysis at* 250 °C. 1-(*p*-Bromobenzyl)-2-t-butyl-4-(*p*-fluorophenyl)-6-phenylpyridinium trifluoromethanesulphonate (**1**) (1.0 g, 1.6 mmol) was heated in a sealed tube at 250 °C for 5 min. The residue was shaken with aqueous ammonia (20 ml; 5M) and the mixture extracted with ether (3 × 20 ml). The extracts were combined, dried ($MgSO_4$), and evaporated to give an *oil* (0.80 g) [δ(^{1}H) ($CDCl_3$) 1.55 (s), 4.4—4.6 (m), and 7.2—8.4 (m); δ(^{13}C) ($CDCl_3$) 30.2 (q), 30.3 (q), 34.4 (t), 34.5 (t), 37.3 (t), 37.7—38.3 (m), 40.8—41.2 (m), and 114.7—169.1 (50 lines)], which on chromatography on a Dexsil-300 g.l.c. column (temperature 50—350 °C) afforded (i) the pyridine (**2**); (ii) a *p*-bromobenzyl derivative of the pyridine (**2**); *m*/*z* 473—5 (100), 472 (25), 461 (10), 460 (34), 459 (12), 458 (37), 433 (29), and 431 (30); (iii) a second *p*-bromobenzyl derivative of the pyridine (**2**); *m*/*z* 475 (M^+, ^{81}Br; 81%), 474 (44), 473 (M^+, ^{79}Br; 100), 460 (12), 458 (14), 197 (12), 171 (12), and 169 (12); (iv) a third *p*-bromobenzyl derivative of the pyridine (**2**); *m*/*z* 475 (M^+, ^{81}Br; 51%), 473—4 (100), 472 (35), 461 (16), 460 (53), 459 (18), 458 (54), 433 (36), 432 (11), 431 (34), 171 (23), 169 (23), 91 (13), and 73 (24); (v) a fourth *p*-bromobenzyl derivative of the pyridine (**2**); *m*/*z* 475 (M^+, ^{79}Br; 97%), 474 (87), 473 (M^+, ^{79}Br; 99) 472 (65), 461 (33), 460 (95), 459 (30), 458 (100), 433 (71), 431 (73), 248 (32), 171 (58), 169 (62), 91 (31), and 73 (131); and (vi) a trace of a bis-(*p*-bromobenzyl)pyridine (**7**); *m*/*z* 645 (M^+, $^{81}Br/^{81}Br$; 45%), 644 (50), 643 (100), 642 (60), 641 (40), 628 (60), 601 (25), 563 (35), 276 (20), 208 (25), 141 (18), 96 (15), and 73 (55).

Thermolysis of 1-*Benzyl*-2-*t*-*butyl*-5,6-*dihydro*-4-*phenylbenzo*[h]*quinolinium Tetrafluoroborate* (**9**) *in Chlorobenzene*.—1-Benzyl-2-t-butyl-5,6-dihydro-4-phenylbenzo[*h*]quinolinium tetrafluoroborate (0.5 g, 1.0 mmol) dissolved in chlorobenzene (10 ml) was heated at 100 °C for 4 h. The mixture was evaporated to dryness, the residue shaken with aqueous ammonia (10 ml; 10%), and the aqueous mixture extracted with ether (3 × 10 ml). The extracts were combined, dried, and evaporated to give an *oil* (0.5 g), which on chromatography on a Dexsil-300 g.l.c. column (temperature 200—400 °C) afforded (i) an isomer of benzylchlorobenzene (**11**); *m*/*z* 204 (M^+, ^{37}Cl; 12%), 202 (M^+, ^{35}Cl; 35), 167 (100), 165 (38), 125 (7), and 91 (14); (ii) 2-t-butyl-5,6-dihydro-4-phenylbenzo[*h*]quinoline; *m*/*z* 313 (M^+, 42%) and 298 (100); (iii) a benzylated 2-t-butyl-5,6-dihydro-4-phenylbenzo[*h*]quinoline (**10**); *m*/*z* 403 (M^+, 100%), 388 (7), 361 (2), 346 (4), 310 (4), and 91 (24); (iv) a second isomer of (**10**); *m*/*z* 403 (M^+, 60%), 388 (58), 361 (82), 346 (15), 194 (8), and 91 (100); (v) a third isomer of (**10**); *m*/*z* 403 (M^+, 29%), 388 (29), 361 (53), 281 (14), 143 (16), and 91 (100); and (vi) a fourth isomer of (**10**); *m*/*z* 403 (M^+, 73%), 388 (39), 361 (94), 347 (19), 281 (8), and 91 (100). High-resolution mass spectrometry on the mixture gave *m*/*z* 202.0566/204.0526 (M^+; $^{35}Cl/^{37}Cl$) [Calc. for $C_{13}H_{11}Cl$: *M*, 202.0549 (^{35}Cl)/204.0520 (^{37}Cl)] and 403.2278 (Calc. for $C_{30}H_{29}N$: *M*, 403.2300).

Thermolysis of 14-*Benzyl*-5,6,8,9-*tetrahydro*-7-*phenyldibenz*[c,h]*acridinium Trifluoromethanesulphonate* (**13**).—(a) *In chlorobenzene.* 14-Benzyl-5,6,8,9-tetrahydro-7-phenyldibenz[*c*,*h*]acridinium trifluoromethanesulphonate (1.0 g, 1.67 mmol) was heated under reflux in chlorobenzene (100 ml) for 4 h. After cooling to 20 °C the mixture was filtered to remove 5,6,8,9-*tetrahydro*-7-*phenyldibenz*[c,h]*acridinium trifluoromethanesulphonate* (**12**) (0.26 g, 30%), as prisms, m.p. 285—287 °C (lit.,[7] 280—285 °C); δ(^{1}H) ($CDCl_3$) 2.77 (8 H, s), 7.1—7.8 (16 H, m, arom.), and 8.7—8.85 (2 H, m, arom.)], and the filtrate was evaporated to dryness. The residue was shaken with aqueous ammonia (10 ml; 10%) and the aqueous mixture extracted with ether (3 × 10 ml). The extracts were combined, dried, and evaporated to give an *oil* (0.1 g) [δ(^{1}H) ($CDCl_3$) 3.93 (s), 4.20 (s), 4.60 (s), and 7.0—7.5 (m); δ(^{13}C) ($CDCl_3$) 39.0 (t), 41.0 (s), and 126—140 (23 lines; arom.)], separated by g.l.c. on a Dexsil-300 column (temperature 50—300 °C) into (i) an isomer of benzylchlorobenzene (**11**); *m*/*z* 204 (M^+, ^{37}Cl; 14%), 202 (M^+, ^{35}Cl; 43), 167 (100), 165 (54), 125 (4), and 91 (7); (ii) a second isomer of (**11**); *m*/*z* 204 (M^+, ^{37}Cl; 15%), 202 (M^+, ^{35}Cl; 45), 167 (100), 165 (51), 125 (6), and 91 (6); (iii) a third isomer of (**11**): *m*/*z* 204 (M^+, ^{37}Cl; 15%), 202 (M^+, ^{35}Cl; 47), 167 (100), 165 (36), 125 (5), and 91 (77); (iv) an isomer of benzyl(chlorobenzyl)benzene (**15**): *m*/*z* 294 (M^+, ^{37}Cl; 5%), 292 (M^+, ^{35}Cl; 15), 207 (12), 180 (54), 179 (100), 167 (41), 166 (19), 165 (36), and 91 (15); (v) a second isomer of (**15**); *m z* 294 (M^+, ^{37}Cl; 22%), 292 (M^+, ^{35}Cl; 64), 201 (54), 179 (19), 167 (100), 166 (25), 165 (48), 125 (14), and 91 (43); (vi) a third isomer of (**15**): *m*/*z* 294 (M^+, ^{37}Cl; 8%), 292 (M^+, ^{35}Cl; 29), 257 (3), 201 (14), 180 (64), 179 (100), 167 (28), 165 (31), and 91 (23); (vii) a fourth isomer of (**15**); *m*/*z* 294 (M^+, ^{37}Cl; 10%), 292 (M^+, ^{35}Cl; 32), 201 (20), 180 (3), 179 (6), 167 (100), 165 (31), and 91 (27); (viii) a fifth isomer of (**15**); *m*/*z* 294 (M^+, ^{37}Cl; 17%), 292 (M^+, ^{35}Cl; 48), 257 (8), 201 (48), 180 (2), 179 (7), 167 (100), 165 (36), 125 (12), and 91 (25); and (ix) a benzyl-5,6,8,9-tetrahydro-7-phenyldibenz[*c*,*h*]acridine (**14**); *m*/*z* 450 (M^+ + 1, 35%), 449 (M^+, 100), 224 (3), 207 (9), 177 (3), 143 (6), 91 (8), and 73 (57). High-resolution mass spectrometry on the mixture gave *m*/*z* 202.0535/204.0518 (M^+; ^{35}Cl/^{37}Cl) [Calc. for $C_{13}H_{11}Cl$: *M*, 202.0549 (^{35}Cl)/204.0520 (^{37}Cl)] and 449.2138 (M^+) (Calc. for $C_{34}H_{27}N$: *M*, 449.2144).

(b) *In nitrobenzene.* 14-Benzyl-5,6,8,9-tetrahydro-7-phenyldibenz[*c*,*h*]acridinium trifluoromethanesulphonate (0.5 g, 0.83 mmol) was heated under reflux in nitrobenzene (5 ml) for 30 min. The mixture was filtered to give 5,6,8,9-*tetrahydro*-7-*phenyldibenz*[c,h]*acridinium trifluoromethanesulphonate* (**5**) (0.11 g, 25%), as prisms, m.p. 285—287 °C (lit.,[7] 280—285 °C), and the filtrate was evaporated to dryness. The solid residue, m.p. 70—77 °C, was subjected to g.l.c. (column temperature 100—300 °C) to give (i) a benzylated 5,6,8,9-tetrahydro-7-phenyldibenz[*c*,*h*]acridine (**14**); *m*/*z* 450 (M^+ + 1, 35%), 449 (M^+, 100), 370 (4), 356 (3), 225 (3), 177 (2), and 91 (5); (ii) a second isomer of (**14**): *m*/*z* 450 (M^+ + 1, 37%), 449 (M^+, 100), 448 (72), and 91 (21); and (iii) a third isomer of (**14**): *m*/*z* 450 (M^+ + 1, 33%), 449 (M^+, 100), 448 (52), 224 (10), and 91 (18).

(c) *Thermolysis at* 250 °C. 14-Benzyl-5,6,8,9-tetrahydro-7-phenyldibenz[*c*,*h*]acridinium trifluoromethanesulphonate (0.5 g, 0.83 mmol) was heated in a sealed tube at 250 °C, in an oil-bath, for 5 min. The residue was shaken with aqueous ammonia (20 ml; 10%) and the aqueous mixture extracted with ether (3 × 15 ml). The extracts were combined, dried, and evaporated to give a solid residue (0.35 g), m.p. 72—80 °C [δ(^{1}H) ($CDCl_3$) 2.90 (8 H, s), 3.9—4.5 (2 H, br, s), 6.8—7.9 (16 H, m, arom.), and 8.15—8.5 (2 H, m, arom.)], which was subjected to g.l.c. (column temperature 50—300 °C) to give (i) a benzyl-5,6,8,9-tetrahydro-7-phenyldibenz[*c*,*h*]acridine (**14**); *m*/*z* 450 (M^+ + 1, 35%), 449 (M^+, 100), 448 (34), 418 (2), 367 (6), 356 (3), 225 (4), 177 (3), and 91 (5); (ii) a second isomer of (**14**); *m*/*z* 450 (M^+ + 1, 21%), 449 (M^+, 53), 448 (33), 359 (3), 91 (10), and 73 (16); (iii) a third isomer of (**14**); *m*/*z* 450 (M^+ + 1, 9%), 449 (M^+, 27), 447 (24), 358 (3), 91 (5), and 73 (13); and (iv) a fourth isomer of (**14**); *m*/*z* 450 (M^+ + 1, 9%), 449 (M^+, 25), 448 (10), 447 (16), 359 (2), 91 (5), and 73 (11).

References

1 This paper is considered as Part 21 of 'Kinetics and Mechanisms of Nucleophilic Displacement with Heterocycles as Leaving Groups;' Part 20, Z. Dega-Szafran, M. Szafran, and A. R. Katritzky, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1895.

2 For reviews see (*a*) A. R. Katritzky, *Tetrahedron*, 1980, **36**, 679; (*b*) A. R. Katritzky and C. M. Marson, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 420.

3 For reviews see (*a*) A. R. Katritzky and G. Musumarra, *Chem. Soc. Rev.*, 1984, **13**, 47; (*b*) A. R. Katritzky, G. Musumarra, and K. Sakizadeh, *Heterocycles*, 1985, **23**, 1765.

4 D. F. Ewing, *Org. Magn. Reson.*, 1979, **12**, 499.

5 A. R. Katritzky, A. M. El-Mowafy, G. Musumarra, K. Sakizadeh, C. S. Ullah, S. M. M. El-Shafie, and S. S. Thind, *J. Org. Chem.*, 1981, **46**, 3823.

6 B. Unterhalt, H. Koehler, and H. J. Reinhold, *Arch. Pharm. (Weinheim, Ger.)*, 1978, **311**, 604.

7 A. R. Katritzky, W. H. Basinski, Y. X. Ou, G. Musumarra, and R. C. Patel, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1055.

8 A. M. El-Mowafy, Ph.D. Thesis, University of East Anglia, 1980.

9 S. S. Thind, Ph.D. Thesis, University of East Anglia, 1979.

Received 9th October 1985; *Paper* 5/1760