S_N2' Type Substitution Reactions of 1-Diphenylamino- and 1-Carbazol-9-yl-pyridinium Cations

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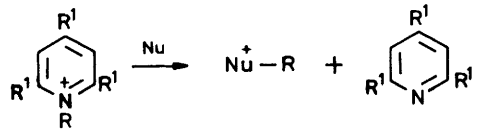
The title compounds react with pyridine and substituted- and benzopyridines to give S_N2' type substitution products by nucleophilic attack at the *para*-position of the benzene rings.

We have described[1] numerous examples of the transfer of *N*-substituents from pyridinium cations to nucleophiles (Scheme). However, in all cases the nucleophilic substitutions occurred at



Scheme.

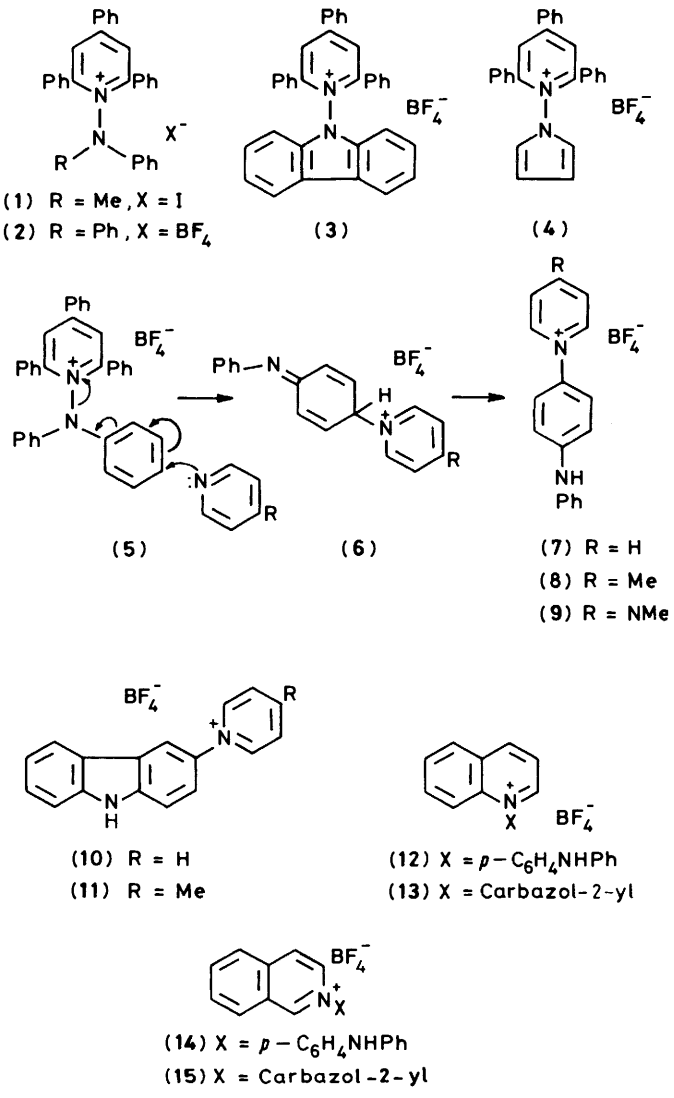
a carbon atom: attempts to transfer an NMe_2 substituent failed, probably because of elimination to $MeN{=}CH_2$.[2] We now report that, in compounds which do not contain β-hydrogen (and thus cannot undergo simple elimination), substitution can indeed occur, but by an S_N2' type mechanism (*cf.* ref. 3).

Pyridinium Salts.—2,4,6-Triphenyl-1-methylphenylamino-pyridinium iodide (**1**) was obtained by methylation of 2,4,6-triphenylpyridine 1-phenylimine as described by Schneider.[4] The pentaphenyl derivative (**2**) was synthesized[5] from the 2,4,6-triphenylpyrylium salt and 1,1-diphenylhydrazine hydrochloride, and 1-pyrrol-1-ylpyridinium salt (**4**) was obtained from 1-aminopyrrole.[6] An analogous procedure gave 1-carbazol-9-yl pyridinium salt (**3**) from 9-aminocarbazole.

Reaction with Nucleophiles.—The pyridinium salt (**2**) reacted smoothly at 120 °C with pyridine, substituted pyridines, quinoline, and isoquinoline to yield products (**7**)—(**9**), (**12**), and (**14**) (Table). Similarly the carbazol-9-ylpyridinium (**3**) gave the products (**10**), (**11**), (**13**), and (**15**) (Table). However, attempted reaction of (**1**) with pyridine gave a complex mixture of products from which only 2,4,6-triphenylpyridine could be isolated; it appears likely that elimination occurred to give methylene aniline which then reacted further.

We had previously attempted the reaction of (**4**) with nucleophiles, but although 2,4,6-triphenylpyridine was formed, no other product could be isolated.[6] In agreement with this we now find that (**4**) does not react with pyridine, substituted pyridines, or isoquinoline under the conditions found successful for the other compounds.

We believe that products (**7**)—(**15**) are formed by nucleophilic attack as shown in (**5**) with intermediates of type (**6**) which rapidly isomerize to the observed products. Thus the reaction is of the S_N2' type,[3] a reaction type not previously found in the displacement of *N*-substituents from pyridinium cations.[1] An alternative mechanism would involve initial dissociation of the substituents to yield species of type Ph_2N^+, but as the compounds are stable in the absence of nucleophile we do not favour this mechanism. No evidence was found for the formation of *ortho* isomers: reactions were followed by t.l.c. and the only distinct product spots which appeared were due to the *para*-isomer isolated and to 2,4,6-triphenylpyridine.



Proof of Structure.—Products were characterized by elemental and spectral analysis. The ^1H n.m.r. spectral data for the products (Experimental section) showed all the expected signals as follows:

(i) Compounds (**7**), (**9**), (**12**), and (**14**) containing the *N*-(4-anilinophenyl) group showed the nine aromatic protons as a multiplet centred at 7.4—8.1 together with the NH singlet near 8.8 p.p.m.

(ii) Compounds (**10**), (**11**), (**13**), and (**15**) containing the carbazol-3-yl group showed signals for 8 H as one or more broad multiplets in the region δ 7.6—8.8, sometimes overlapped by other aromatic protons.

Table. Preparation and physical properties of products derived from 1-(substituted amino) pyridinium salts with nucleophiles.

Product No.	1-Aminopyridinium No.	1-Aminopyridinium Wt (g)	Nucleophiles Vol. (ml)	Nucleophiles Method	Reaction time (min)	Yield (%)	Solvent for crystal.	Crystal form	M.p. (°C)	Molecular Formula	Found (%) (Required) C	Found (%) (Required) H	Found (%) (Required) N
(7)	(2)	0.7	5	A	60	42	EtOH	Plates	162—163 (decomp.)	$C_{17}H_{15}BF_4N_2$	61.0 (61.1)	4.5 (4.5)	8.1 (8.4)
(8)	(2)	2.9	15	A	15	49	H_2O	Micro-crystals	153—156 (decomp.)	$C_{18}H_{17}BF_4N_2$	61.6 (62.1)	4.8 (4.9)	7.8 (8.1)
(9)	(2)	4.0	2.6[a]	B	60	50	EtOH	Prisms	215 (decomp.)	$C_{19}H_{20}BF_4N_3$	60.7 (60.5)	5.5 (5.3)	10.9 (11.1)
(10)	(3)	3.0	20	A	960	45	H_2O	Needles	185—186 (decomp.)	$C_{17}H_{13}BF_4N_2$	61.2 (61.5)	3.7 (3.9)	8.2 (8.4)
(11)	(3)	3.0	20	C	180	6.5	H_2O	Needles	200—201 (decomp.)	$C_{18}H_{15}BF_4N_2$	62.3 (62.5)	4.3 (4.4)	8.0 (8.1)
(12)	(2)	3.1	15	A	10	51	H_2O	Prisms	218—219 (decomp.)	$C_{21}H_{17}BF_4N_2$	65.9 (65.7)	4.4 (4.5)	7.3 (7.3)
(13)	(3)	1.6	10	C	120	23	H_2O	Prisms	278—280 (decomp.)	$C_{21}H_{15}BF_4N_2$	65.6 (66.0)	3.7 (4.0)	7.1 (7.3)
(14)	(2)	2.1	15	A	10	44	H_2O	Plates	198—199 (decomp.)	$C_{21}H_{17}BF_4N_2$	65.4 (65.7)	4.3 (4.5)	7.1 (7.3)
(15)	(3)	0.91	8	D	960	40	EtOH	Needles	285—290 (decomp.)	$C_{21}H_{15}BF_4N_2$	65.7 (66.0)	3.7 (4.0)	7.1 (7.3)

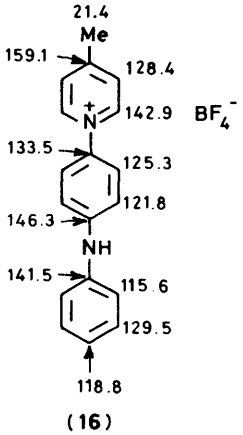
[a] In g.

(iii) The pyridinium compounds showed the expected ring CH signals: 2,6-CH as a doublet (*J* 6—7 Hz) at 9.4—9.6 for (**7**), (**8**), (**10**), and (**11**), but at 8.6 for (**9**). The 3,5-CH appears as a multiplet near 8.2—8.4 for (**7**), (**8**), and (**10**); it is merged with other peaks for (**9**) and (**11**). The 4-CH is found near 8.9 p.p.m. for (**7**) and (**10**). The 4-methyl groups of (**8**) and (**11**) gave signals near 2.7 p.p.m. and the NMe_2 for (**9**) at 3.30.

(iv) The quinolinium derivatives (**12**) and (**13**) show 2 H multiplets at 9.6—9.7: the remaining five proton signals overlap with other aromatic absorption.

(v) The isoquinoline derivatives (**14**) and (**15**) show the 1-position proton signal as a singlet near 10.5 p.p.m. and a doublet (*J* 7 Hz) for the 3-position proton near 9.2 p.p.m., with the other protons merged into the general aromatic signals.

The ^{13}C spectra of compounds (**8**) and (**11**) were studied in detail. Assignments are given in formulae (**16**) and (**17**),



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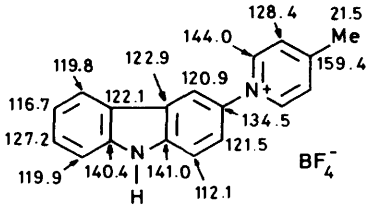

(17)

respectively. Spectra obtained using the 'INEPT' pulse sequence[7] allow the differentiation of CH from quaternary C and of CH_2 from Me. Each of the compounds showed precisely the number of lines of each type expected. This demonstrates the *para* orientation of compound (**8**). Chemical shifts are in line with other work; ^{13}C spectra of carbazoles have been discussed in detail recently.[8]

Experimental

M.p.s were determined with a hot-stage microscope and are uncorrected. ^1H N.m.r. spectra were recorded with a Varian EM 360L spectrometer using $SiMe_4$ as internal standard, and ^{13}C n.m.r. spectra (25.0 MHz) were obtained on a JEOL JNM FX 100 spectrometer.

The following compounds were prepared by literature methods: *N*-aminocarbazole, m.p. 149—151 °C (lit.,[9] 151—152.5 °C); 2,4,6-triphenylpyrylium tetrafluoroborate, m.p. 243—246 °C (lit.,[10] 245—247 °C); 1-(*N*-methylanilino)-2,4,6-triphenylpyridinium iodide (**1**), m.p. 142 °C (lit.,[4] m.p. 136 °C) (Found: C, 66.6; H, 4.7; N, 4.8. Calc. for $C_{30}H_{25}IN_2$: C, 66.7; H, 4.6; N, 5.2%); 1-diphenylamino-2,4,6-triphenylpyridinium tetrafluoroborate (**2**) m.p. 154—157 °C (lit.,[5] 150 °C) (Found: C, 75.0; H, 5.1; N, 5.0. Calc. for $C_{35}H_{27}BF_4N_2$: C, 74.8; H, 4.8; N, 5.0%); and 1-pyrrol-1-yl-2,4,6-triphenylpyridinium tetrafluoroborate (**4**) m.p. 244—245 °C (decomp.) (lit.,[6] 231—232 °C) (Found: C, 70.5; H, 4.7; N, 6.1. Calc. for $C_{27}H_{21}BF_4N_2$: C, 70.5; H, 4.8; N, 6.1).

1-*Carbazol-9-yl*-2,4,6-*triphenylpyridinium Tetrafluoroborate*.—2,4,6-Triphenylpyrylium tetrafluoroborate (0.91 g, 2 mmol) and 9-aminocarbazole (0.42 g, 2 mmol) were heated under reflux for 4 h in ethanol (30 ml). The product precipitated on cooling; it crystallized from ethanol as yellow *plates* (0.90 g, 67%), m.p. 210—212 °C (decomp.) (Found: C, 75.0; H, 4.5; N, 4.9. $C_{35}H_{25}BF_4N_2$ requires C, 75.0; H, 4.5; N, 5.0%); δ[$(CD_3)_2SO$; 60 MHz] 9.13 (2 H, s), 8.63 (2 H, m), 7.90 (6 H, m), and 7.30 (15 H, m).

General Procedure for Nucleophilic Substitution of Pyridinium Derivatives (**2**) *and* (**3**).—*Method A*. The 1-aminopyridinium salt (**2**) or (**3**) and the respective nucleophilic reagent were heated at 120 °C (amounts and reaction times are given in the Table). After cooling, the reaction mixture was added dropwise with stirring to Et_2O (200 ml). The gum was triturated with $CHCl_3$ (5 × 10 ml), dissolved in Me_2CO (5 ml), and again added to Et_2O (150 ml). The product was filtered off and recrystallized.

This method was used to prepare the following. 1-(4-Anilinophenyl)pyridinium tetrafluoroborate (**7**), δ[$(CD_3)_2SO$; 60 MHz] 9.43 (2 H, d, *J* 6 Hz), 8.90 (1 H, s), 8.86 (1 H, m), 8.43 (2 H, m) and 7.50 (9 H, m). 1-(4-Anilinophenyl)-4-methylpyri-

dinium tetrafluoroborate (**8**), δ[$(CD_3)_2SO$; 60 MHz] 9.42 (2 H, d, *J* 7 Hz), 8.85 (1 H, s), 8.17 (2 H, d, *J* 7 Hz), 7.50 (9 H, m), and 2.73 (3 H, s). 1-(4-Anilinophenyl)quinolinium tetrafluoroborate (**12**), δ[$(CD_3)_2SO$; 60 MHz] 9.60 (2 H, m), 8.86 (1 H, s), and 7.96 (14 H, m). 2-(4-Anilinophenyl)isoquinolinium tetrafluoroborate (**14**), δ[$(CD_3)_2SO$; 60 MHz] 10.40 (1 H, s), 9.10 (1 H, d, *J* 7 Hz) and 8.13 (15 H, m). 1-Carbazol-3-ylpyridinium tetrafluoroborate (**10**), δ[$(CD_3)_2SO$; 60 MHz] 9.57 (2 H, d, *J* 6 Hz), 8.93 (2 H, m), 8.40 (3 H, m), and 7.60 (6 H, m).

Method B. A mixture of (**2**) (4 g) and 4-dimethylaminopyridine (2.6 g) in ethanol (130 ml) was refluxed for 1 h and left overnight. The solid 2,4,6-triphenylpyridine was filtered off and the filtrate was concentrated to 5 ml and treated with Et_2O (100 ml). The gum was triturated with $CHCl_3$ (3 × 5 ml) and the 1-(4-diphenylamino)-4-dimethylaminopyridinium tetrafluoroborate (**9**) was recrystallized (Table): δ[$(CD_3)_2SO$; 60 MHz] 8.79 (1 H, s), 8.63 (2 H, d, *J* 7 Hz), 7.40 (11 H, m), and 3.30 (6 H, s).

Method C. The respective nucleophilic reagent was added to the *N*-aminopyridinium salt (**3**) and heated at 120 °C. After cooling, the reaction mixture was added dropwise with stirring to Et_2O (200 ml). The precipitate was heated with water (3 × 100 ml), filtered, and the water was evaporated. The product was purified by crystallization (for details see the Table).

The following were prepared by this method. 1-Carbazol-3-yl-4-methylpyridinium tetrafluoroborate (**11**), δ[$(CD_3)_2SO$; 60 MHz] 9.4 (2 H, d, *J* 6 Hz) 8.8 (1 H, s), 8.33 (3 H, m), 7.60 (6 H, m), and 2.76 (3 H, s). 1-Carbazol-3-ylquinolinium tetrafluoroborate (**13**), δ[$(CD_3)SO$; 60 MHz] 9.76 (2 H m) and 7.96 (13 H, m).

Method D. A mixture of (**3**) (0.91 g) and isoquinoline (8 ml) was heated at 120 °C for 16 h. After cooling, the solid which precipitated from the reaction mixture was filtered off, washed with $CHCl_3$ (3 × 20 ml), and the 1-carbazol-3-ylisoquinolinium tetrafluoroborate (**15**) was recrystallized (Table); δ[$(CD_3)_2SO$; 60 MHz] 10.60 (1 H, s), 9.30 (1 H, d, *J* 7 Hz), and 8.13 (13 H, m).

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