

Thermolysis and Photolysis of 1-Anilino-2-methyl-4,6-diphenylpyridinium Tetrafluoroborate in Arene-Trifluoroacetic Acid Mixtures: a Novel Route to Singlet and Triplet Phenylnitrenium Ions

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Thermolysis of 1-anilino-2-methyl-4,6-diphenylpyridinium tetrafluoroborate (**1**) in trifluoroacetic acid-benzene or -toluene yielded 2-methyl-4,6-diphenylpyridine (**2**) and the *N*-substitution products 2-(2-anilinophenyl)-6-methyl-4-phenylpyridine (**3**) and diphenylamine (**4a**) [or 2- and 4-methyldiphenylamine (**4b**) and (**5b**)], *via* a singlet phenylnitrenium ion formed in the unimolecular decomposition of the salt (**1**). The mechanism was inferred from the kinetics of decomposition of the salt (**1**), the *o*-/*p*-direction in the formation of (**4b**) and (**5b**), the large partial rate factors for *ortho*- and *para*-substitution of toluene, and analysis of the products of the reaction of (**1**) with diethyl sulphide. The preferred production of the 2-anilinophenyl derivative (**3**) rather than the corresponding 4-anilinophenyl compounds, and the relative formation rates of (**2**) and (**3**) suggest that the product (**3**) is formed by an intimate contact reaction between pyridine and phenylnitrenium ion formed initially; the results give relative reactivities of the nitrenium ion with benzene, toluene, naphthalene, and dimethyl sulphide. Photolysis of the salt (**1**), however, gave the pyridine (**2**), aniline (**9**), and hydrogen abstraction products [biphenyl (**10**) or the bitolyls (**11**)] *via* a triplet phenylnitrenium ion, without contamination by compounds (**3**)–(**5**). The triplet mechanism was proved by observation of inter- and intra-molecular heavy atom effects.

Arylnitrenium ions have been extensively studied in recent years: they are reactive metabolites of carcinogenic amines and useful intermediates in organic synthesis.¹ We have reported that arylnitrenium ions² or their complexes with AlCl₃,³ generated from aryl azides in the presence of protic acids like trifluoroacetic (TFA) or trifluoromethanesulphonic acid or in the presence of AlCl₃ undergo aromatic *N*-substitution.

The photolysis of phenyl azide in the presence of TFA has not been studied because phenyl azide decomposes at room temperature under these conditions. However, we considered that it should be possible to carry out both thermal and photochemical reactions of the pyridinium salt (**1**), a potential new precursor of phenylnitrenium ion, in the presence of TFA. Indeed, we found that these reactions provided a novel route to singlet or triplet phenylnitrenium ions.

Results and Discussion

Thermolysis and Photolysis of 1-Anilino-2-methyl-4,6-diphenylpyridinium Tetrafluoroborate (1) in Arene-Trifluoroacetic Acid Mixtures.—A solution of the pyridinium salt (**1**) in a TFA-arene mixture was heated or irradiated under the conditions described in Table 1. After work-up with aqueous Na₂CO₃, products were isolated by chromatography. Thermolysis with benzene or toluene as the arene gave 2-methyl-4,6-diphenylpyridine (**2**), 2-(2-anilinophenyl)-6-methyl-4-phenylpyridine (**3**), and diphenylamine (**4a**) [or 2- and 4-methyldiphenylamine (**4b**) and (**5b**)] together with small amounts of *N*-trifluoroacetanilide (**8**) and 2-aminophenol (**6**). Thermolysis in TFA alone gave compounds (**2**), (**3**), and (**6**), 4-aminophenol (**7**), and the anilide (**8**). Yields are indicated in Table 1.

Photolysis of the salt (**1**) gave the pyridine (**2**), aniline (**9**), and biphenyl (**10**) or the bitolyls (**11**), but none of compounds (**3**)–(**5**). The yields of (**9**) and (**11**) were increased by addition of the heavy atom solvent bromobenzene, and the addition also gave

rise to the formation of small amounts of compounds (**3**)–(**5**) (see Table 1).

Photolysis of the bromo analogue of (**1**) 1-(4-bromoanilino)-2-methyl-4,6-diphenylpyridinium tetrafluoroborate in toluene-TFA produced 4-bromoaniline and bitolyls (**11**) in higher yields than those of (**9**) and (**11**) in the photolysis of (**1**) in toluene-TFA (Table 1).

The difference in the products of photolysis and thermolysis may be ascribable to a difference in mechanism. In the photolysis, the bromine atom in bromobenzene or in the bromo analogue of (**1**) catalyses the singlet → triplet more than the triplet → singlet conversion, to enhance the yield of the triplet products 4-bromoaniline and (**9**)–(**11**); the triplet → singlet conversion is responsible for the formation of (**3**)–(**5**). Thus, we may infer that the thermolysis gives *N*-substitution products (**3**)–(**5**) *via* a singlet intermediate, whereas the photolysis produces (**9**)–(**11**) *via* hydrogen atom abstraction by a triplet intermediate (Scheme 1).

Unimolecular Thermolytic Decomposition of the Salt (1).—Pseudo-first-order rate constants k_{obs} for the thermolysis were evaluated by using the equation $\log[a_0/(a_0 - x_t)] = k_{\text{obs}}t$, where a_0 and $(a_0 - x_t)$ are the concentrations of (**1**) at times zero and t , respectively. If we regard x_t as the total concentration of (**2**) and (**3**) at time t , the correlation between $\log[a_0/(a_0 - x_t)]$ and t gives a straight line with slope (k_{obs}) $1.3 \times 10^{-4} \text{ s}^{-1}$, at 152 °C for reaction in TFA (5.5M)–toluene (5.0M) for decomposition times up to 1 h. Assumption of a steady state for the phenylnitrenium ion gives equation (1) (rate constants are defined in Scheme 1).

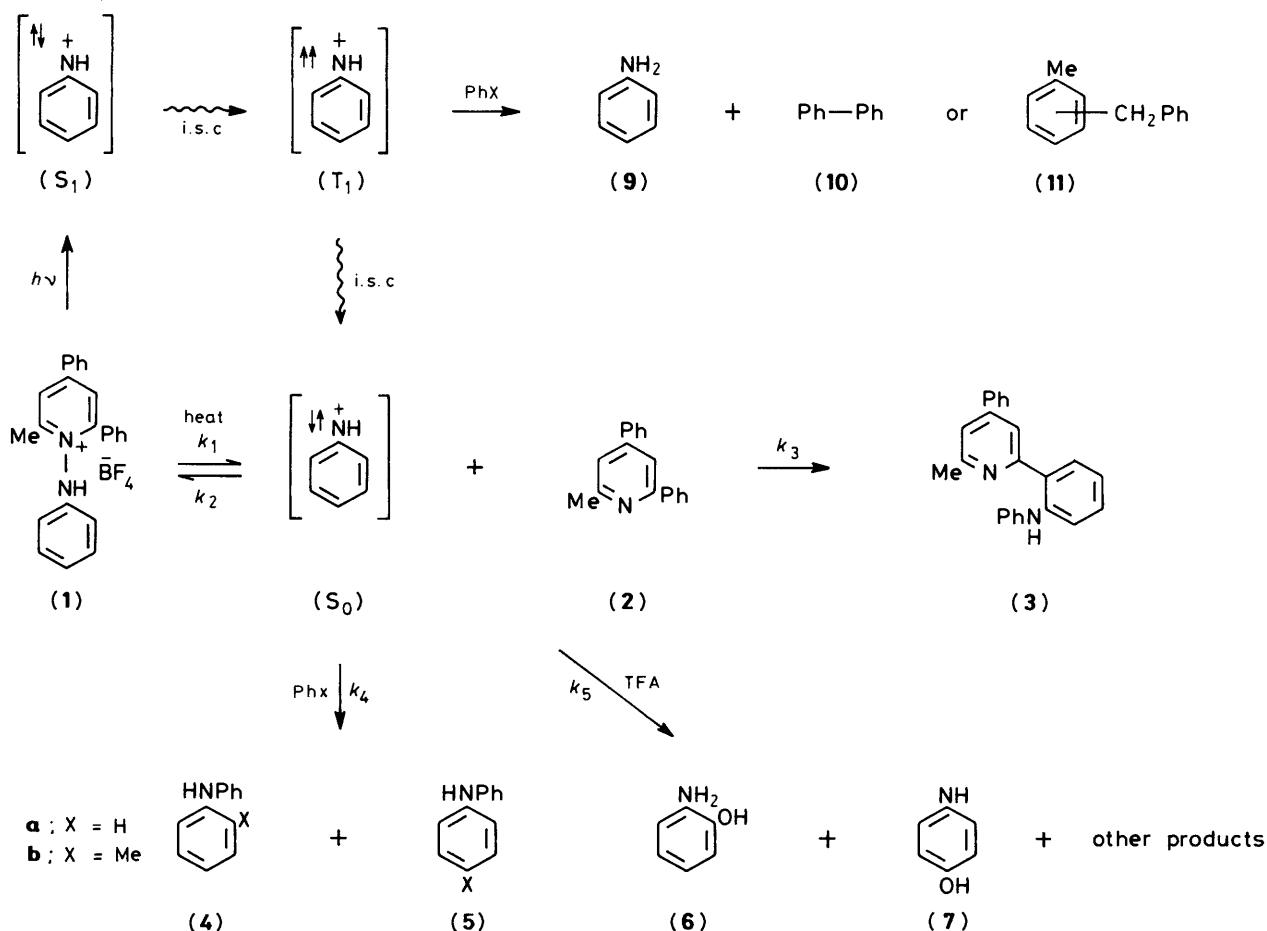
$$k_1[(\mathbf{1})] = (k_2[(\mathbf{2})] + k_3 + k_4[\text{PhX}] + k_5[\text{TFA}]) [S_0] \quad (1)$$

Hence the concentration of phenylnitrenium ion $[S_0]$ is given by equation (2), and the rate of decomposition of (**1**)

Table 1. Thermolysis and photolysis of the pyridinium salt (1) in TFA-arene (PhX)

[(1)]/M	[TFA]/M	[PhX]/M	X in PhX	Yield ^a (%)										
				(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	
0.21 ^b	6.5	4.7	H	36	31	33		5	0	3	0	0		
0.21 ^b	5.2	4.6	Me	50	23	18	28	4	0	6	0		1	
0.43 ^b	10.6			39	22			22	6	10	0			
0.051 ^c	6.4	5.5	H	72	0	0				0	22	Trace		
0.051 ^c	6.4	4.6	Me	84	0	0	0			0	20		5	
0.044 ^{c,d}	5.4	3.9	Me	34	4	3	5			0	32		9	
0.026 ^{c,e}	6.4	4.6	Me	85						0	43 ^f		45	
0.057 ^c	0 ^g	5.6	H	66	0	0				0	39	10		

^a The yield of (2) is based on initial (1), but yields of (3)—(11) are based on (1) consumed [the percentage of (1) consumed is equal to the total yield of (2) and (3), which is based on initial (1)]. The yields of (2), (4), (5), and (9)—(11) were determined by g.l.c. analysis, whereas the yields of (3) and (6)—(8) were obtained by h.p.l.c. ^b Thermolysis at 152 °C for 7 h. ^c Photolysis at room temperature for 1 day. ^d Bromobenzene (1.7M) was added to the system. ^e The bromo analogue of (1) was used instead of (1). ^f Yield of 4-bromoaniline. ^g HFP (50% v/v) was added in place of TFA.



by equation (3). Combining equations (2) and (3), we obtain equation (4). Thus, k_{obs} is given by equation (5).³

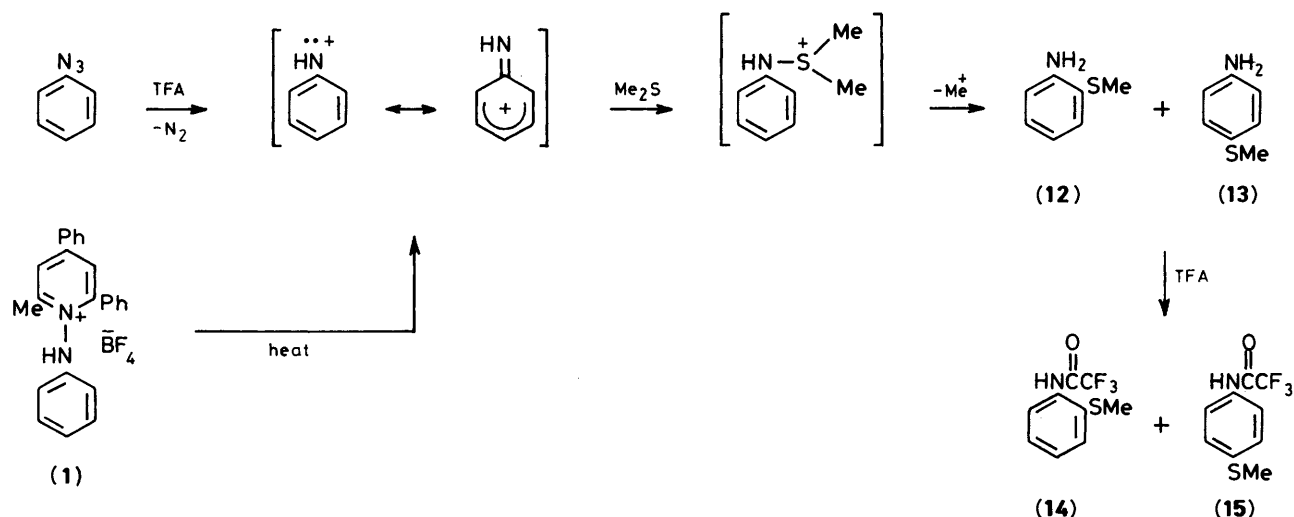
$$[S_0] = k_1[(1)]/(k_2[(2)] + k_3 + k_4[\text{PhX}] + k_5[\text{TFA}]) \quad (2)$$

$$-d[(1)]/dt = (k_3 + k_4[\text{PhX}] + k_5[\text{TFA}])[S_0] \quad (3)$$

$$\frac{-d[(1)]}{dt} = \frac{k_1(k_3 + k_4[\text{PhX}] + k_5[\text{TFA}])(1)}{k_2[(2)] + k_3 + k_4[\text{PhX}] + k_5[\text{TFA}]} \quad (4)$$

$$k_{\text{obs.}} = k_1(k_3 + k_4[\text{PhX}] + k_5[\text{TFA}]) / (k_2[(2)] + k_3 + k_4[\text{PhX}] + k_5[\text{TFA}]) \quad (5)$$

In the initial decomposition (up to ca. 1 h), $k_2[(2)]$ (for the reverse reaction) is negligibly small as compared with $k_3 + k_4[\text{PhX}] + k_5[\text{TFA}]$ (for the forward reactions); thus $k_{\text{obs.}}$ is equal to k_1 . In the thermolysis in TFA (5.5M)—benzene (6.0M), this relationship does not hold, and the corresponding correlation did not provide a straight line; this is because the k_4



Scheme 2.

value is less for the reaction with benzene than for that with toluene. The initial slope at time zero in this case is, however, the same as that in the presence of toluene; the equality holds for the initial decomposition since $[(2)] = 0$. For the thermolysis in TFA (9.4M)–toluene (2.4M) or TFA (9.4M)–benzene (2.8M) a k_{obs} value of $1.1 \times 10^{-4} \text{ s}^{-1}$ was obtained by an analogous method. The slight difference between these k_{obs} values is probably ascribable to the usual solvent effect on the decomposition of (1); the reaction bringing about dissipation of charge upon passing from the initial to the transition state is generally weakly retarded by a more polar solvent because the solvation of the initial state is greater than that of the transition state. Thus, the decomposition of (1) might well be retarded in the presence of a higher concentration of TFA, which is a more polar solvent than benzene or toluene.

When the thermolysis was carried out in dimethyl sulphide–1,1,1,3,3,3-hexafluoropropan-2-ol (HFP), k_{obs} values at 152 °C were 1.6×10^{-4} and $1.5 \times 10^{-4} \text{ s}^{-1}$ in HFP (7.1M)–Me₂S (3.2M) and HFP (8.3M)–Me₂S (1.9M), respectively. The slight difference between k_{obs} in TFA–arene and that in HFP–Me₂S cannot be readily explained, but may involve solvation of (1) or interaction between solvents.

The observation that the initial decomposition rate is almost insensitive to the difference between the aromatic substrates and to the concentration of the arene or the dimethyl sulphide indicates that the thermal decomposition of (1) is unimolecular.

Formation of Phenylnitrenium Ion.—The reaction of phenyl azide with Me₂S in the presence of TFA or trifluoromethanesulphonic acid gave 2- and 4-aminophenyl methyl sulphides, (12) and (13).⁴ The thermolysis of (1) in TFA–Me₂S at 152 °C afforded methyl 2- and 4-(trifluoroacetyl)aminophenyl sulphides (14) and (15),⁴ identical with the products formed by trifluoroacetylation of (12) and (13), respectively. The ratio of (12) to (13) is nearly equal to the ratio of (14) to (15). Thus, these two reactions may be considered to proceed through a common intermediate, a phenylnitrenium ion. The formation of products of C-attack (12) and (13) has been explained in terms of a rearrangement of an aminosulphonium ion intermediate, formed *via* the nitrenium ion⁴ (Scheme 2).

The observed *o*-/*p*-direction in the thermolysis in TFA–toluene and the large partial rate factors for *ortho*- and *para*-substitution of toluene ($p_f = 37$ and $o_f = 12$; if the p_f value satisfies the Hammett equation, $\rho = -5.0$) support the idea

that aromatic *N*-substitution takes place *via* a positively charged intermediate, which must be the phenylnitrenium ion.

The nitrenium ion generated thermally is probably in the singlet state (S_0), in view of the aforementioned mechanistic difference between thermolysis and photolysis. We did not detect 2- and 4-aminobiphenyls, which would be formed by C-attack of the nitrenium ion on benzene, although these products have been observed in the reaction between benzene and the nitrenium ion generated from phenyl azide in the presence of TFA.² This difference can be explained by the idea that the reactivity of the nitrenium ion is affected by a change in gegenanion.² In the photolysis, an excited singlet nitrenium ion (S_1), which does not undergo intersystem crossing (i.s.c.), produces a tar, g.l.c. analysis of which shows negligibly low peaks except those for (2) and (9)–(11) in the absence of a heavy atom.

On the other hand, the triplet phenylnitrenium ion formed in the photolysis performs hydrogen abstraction from benzene or toluene to give compounds (9)–(11). The triplet mechanism is well supported by the heavy atom effect already described. We cannot rule out the possibility that heavy atom catalyses intersystem crossing of (1) (or its bromo analogue) to form the triplet nitrenium ion from the triplet state.

The yields of (9) and (10) for the photolysis in HFP–benzene were higher than those in TFA–benzene. The high yield of (9) can be explained by favourable hydrogen abstraction by the triplet nitrenium ion from HFP (a good hydrogen atom donor). The high yield of (10) presumably results from preferred hydrogen abstraction from benzene by triplet 1,1,1,3,3,3-hexafluoropropan-2-one formed by hydrogen abstraction from HFP.

For the photolysis, we considered the alternative possibility that compounds (9)–(11) were formed by hydrogen abstraction from phenylaminy radical or phenylaminylium radical; the former is predicted to be generated by N–N scission of 1-aminopyridyl radical, formed by photochemical one-electron transfer to the pyridinium cation from the gegenanion⁵ or from the arene,⁶ and the latter to be formed by N–N scission⁷ of a 1-phenylammonio-pyridinium salt [protonated (1)]. However, this possibility can be ruled out since we cannot explain the heavy atom effect [*e.g.* the formation of (3)–(5) in the presence of bromobenzene] by such a mechanism.

The electronic spectrum of (1) in TFA–arene indicates that pyridinium ylide is not present. This excludes the possibility that

Table 2. Relative reactivities ($k_{rel.}$) of phenylnitrenium ion towards substrates

Substrate	$k_{rel.}$
Benzene	1.0 ^a
Toluene	2.2
Naphthalene	16.0
Dimethyl sulphide	11.1

^a Arbitrary standard.

the reaction proceeds *via* a phenylnitrene (usually generated from the ylide).⁸

Intramolecular Aromatic N-Substitution in the Formation of the Pyridine Derivative (3), and Relative Reactivities of the Nitrenium Ion towards Various Substrates.—The formation of the 2-anilinophenyl compound (3) without the corresponding 4-anilinophenyl derivative allows us to assume that (3) is formed by an intimate contact reaction between pyridine and phenylnitrenium ion, generated initially from (1). If this is correct, the rate for the formation of (3) should be independent of the concentration of pyridine, because the concentration of the latter is constant in the proximity of the nitrenium ion. Thus, we can write equation (6), where *S* represents the substrate

$$d[(2)]/d[(3)] = (k_4/k_3) [S] + (k_5/k_3) [HFP] \quad (6)$$

(benzene, toluene, naphthalene, or dimethyl sulphide) and k_3 , k_4 , and k_5 refer to the rate constants for the formation of (3), for the reaction of the nitrenium ion with substrate, and for that with HFP, respectively. The value of $d[(2)]/d[(3)]$ is identical with the yield ratio (2)/(3). When k_5/k_3 is 1.04, a plot of $\{d[(2)]/d[(3)]\} - (k_5/k_3) [HFP]$ against $[S]$ is linear. This implies that the foregoing assumption is reasonable. However, with TFA instead of HFP, the corresponding correlation does not show a linear plot. This can be explained if we consider that the reactivity of the nitrenium ion towards the substrate is changed by a TFA-substrate interaction. The relative slopes of the straight lines with HFP give relative rate constants ($k_{rel.}$) for reactions of the nitrenium ion with the various substrates (Table 2). The high $k_{rel.}$ values for naphthalene and dimethyl sulphide⁴ reflect the high electrophilicity of the nitrenium in reaction with these substrates.

Experimental

I.r. spectra were obtained with a Hitachi EPI-G3 spectrometer. N.m.r. spectra (¹H and ¹³C) were taken with a Nippondenshi JNM-FX-60Q instrument. Mass spectra were recorded with a Hitachi M-80B spectrometer. G.l.c. was performed with a Shimadzu GC-6A chromatograph [glass column (1 m × 3 mm) packed with polyethylene glycol (20 M) on Uniport KS (60–80 mesh)]. H.p.l.c. was performed with a Shimadzu LC-6A system [column of Zorbax ODS (25 cm × 4.6 mm)]. Replicate analyses of products by g.l.c. and h.p.l.c. agreed to within ±3%.

Benzene, toluene, bromobenzene, naphthalene, and dimethyl sulphide were purified by standard methods before use. Trifluoroacetic acid (TFA), diphenylamine (4a), 2- and 4-aminophenols (6) and (7), aniline (9), 4-bromoaniline, biphenyl (10), and 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) were reagent grade (Wako), and used without further purification. 1-Anilino-2-methyl-4,6-diphenylpyridinium tetrafluoroborate (1) (m.p. 178–180 °C) and 1-(4-bromoanilino)-2-methyl-4,6-diphenylpyridinium tetrafluoroborate (m.p. 193–195 °C) were prepared by the method of Katritzky *et al.*⁹ 2-Methyl-4,6-diphenylpyridine (3),¹⁰ 2- and 4-methyldiphenylamines (4b) and (5b),² and

N-trifluoroacetanilide (8)² were synthesized by literature methods.

Thermolysis of 1-Anilino-2-methyl-4,6-diphenylpyridinium Tetrafluoroborate (1) in TFA-Benzene, TFA-Toluene, or TFA.—The thermolysis of the pyridinium salt (1) was carried out in a sealed tube at 152 °C. Detailed conditions are shown in Table 1. After the reaction, aqueous Na₂CO₃ was added to the mixture until the pH of the solution exceeded 7. The organic layer was extracted with benzene, and the products were isolated by column chromatography on silica gel (Wakogel C-300), and identified by comparison (i.r. and ¹H n.m.r. spectra) with authentic specimens. Yields were determined by g.l.c. or h.p.l.c. analysis. The following compounds were not prepared by literature methods, and structures were confirmed by spectroscopic data.

2-(2-Anilinophenyl)-6-methyl-4-phenylpyridine (3) formed white crystals, m.p. 191 °C; $\nu_{max.}$ (Nujol) 3 220 (NH), 1 605 and 1 490 (aromatic C=C), 1 375 (C–N), 770 (*o*-subst. benzene), and 745 and 700 cm⁻¹ (monosubst. benzene); δ_H (CCl₄–CDCl₃) 2.45 (3 H, s, Me), 5.1–5.6 (1 H, br, NH), and 6.5–8.6 (16 H, m, benzene and pyridine protons); δ_C (CCl₄–CDCl₃) 22.1 (Me), 115.0 (C-2 of PhNH and C-3 of 2-C₆H₄ group), 119.3 and/or 119.6 (C-4 of PhNH and/or C-5 of 2-C₆H₄), 126.6 (C-6 of 2-C₆H₄ and C-2 of 4-Ph), 128.3 and/or 128.6 (C-4 of 2-C₆H₄, C-3 and -4 of 4-Ph, and/or C-3 and -5 of pyridine), and 129.1 (C-3 of PhNH); m/z 336 (*M*⁺), 335, 106, and 18 (Found: C, 85.75; H, 5.9; N, 8.5. C₁₈H₁₅N requires C, 85.7; H, 6.0; N, 8.35%).

The bitolyls (11) were obtained as a liquid, $\nu_{max.}$ (neat) 3 045, 3 005, 2 930, 2 900, and 2 850 (CH), 1 600, 1 510, and 1 490 (aromatic C=C), 1 450 (CH₂), 1 380 (Me), and 810, 750, 730, and 700 cm⁻¹ (*o*-, *m*-, and *p*-subst. benzene); δ_H (CCl₄–CDCl₃) 1.8–2.4 (3 H, br d, Me), 3.6–4.1 (2 H, br d, CH₂), and 6.6–7.7 (9 H, m, ArH); m/z 182 (*M*⁺), 181, 167, 166, 165, 104, and 91. G.l.c. showed three peaks attributed to *o*-, *m*-, and *p*-benzyltoluenes.

Pseudo-first-order Rate Constants for the Decomposition of the Pyridinium Salt (1).—The pyridinium salt (1) (0.10M) was dissolved in TFA (5.5M)–toluene (5.0M) or in TFA (5.5M)–benzene (6.0M). A number of identical solutions were made up, and the individual mixtures (0.5 ml) in sealed tubes were examined one by one at fixed times during the reaction at 152 °C. Diethylamine was added to the reaction mixture so as to convert the salts of (2) and (3) into free (2) and (3). The total amount of (2) and (3) (x_t) was determined by h.p.l.c. analysis. The correlation between $\log [a_0/(a_0 - x_t)]$ and t gave a straight line with slope ($k_{obs.}$) $1.3 \times 10^{-4} \text{ s}^{-1}$ for the decomposition in TFA–toluene up to 1 h. The corresponding correlation in TFA–benzene did not give a straight line, but the initial slope at time zero was the same. Similarly, we obtained $k_{obs.} = 1.1 \times 10^{-4} \text{ s}^{-1}$ in TFA (9.4M)–toluene (2.4M) and in TFA (9.4M)–benzene (2.8M), respectively. Values of $k_{obs.}$ in HFP (7.1M)–Me₂S (3.2M) and in HFP (8.3M)–Me₂S (1.9M) were 1.6×10^{-4} and $1.5 \times 10^{-4} \text{ s}^{-1}$, respectively.

Relative Reactivities of Phenylnitrenium Ion towards Substrates.—The pyridinium salt (1) (0.12M) was dissolved in HFP–benzene, HFP–toluene, HFP–naphthalene, or HFP–Me₂S. Thermolysis and determination of the amount of (2) and (3) were performed as before. The ratio (2)/(3) [equal to $d[(2)]/d[(3)]$ in equation (6)] was unchanged in the decomposition up to 1 h. The slope represents $k_{rel.}$ (Table 2).

Photolyses of the Pyridinium Salts (1) and 1-(4-Bromoanilino)-2-methyl-4,6-diphenylpyridinium Tetrafluoroborate.—Photolyses were conducted externally in a quartz tube (25 × 1.8 cm) with a 300 W high-pressure mercury lamp (Halos PIH-300)

after purging with dry nitrogen for 15 min. Detailed conditions are shown in Table 1. Analysis and characterization of the products were performed as for the thermal reaction.

ortho- and para-Attack Partial Rate Factors for Toluene.—A mixture of the salt (**1**) (220 mg), TFA (1.00 ml), benzene (0.871 g), and toluene (0.428 g) was heated under thermal conditions for 2 or 4 h. Yields of (**4a**), (**4b**), and (**5b**) were determined as before. Values o_f and p_f were calculated as described in a previous report.² The values were independent of difference in reaction time.

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