Novel Generation of Parent, Alkyl, Dialkyl and Alicyclic Nitrenium Ions in Photolyses of Pyridinium, Quinolinium, Bipyridinium and Phenanthrolinium Salts and Aromatic *N*-Substitution by Nitrenium Ions†

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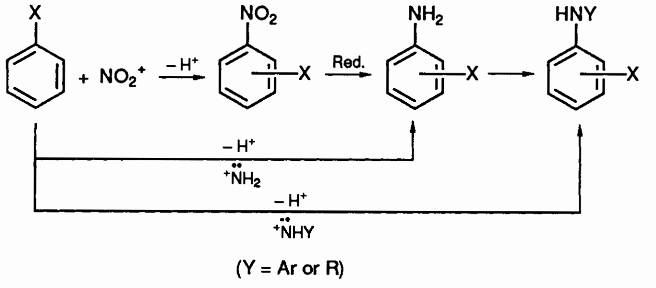
The photolyses of 1-aminopyridinium, 1-aminoquinolinium, 1-amino-2,2′-bipyridinium, 1,1′-diamino-2,2′-bipyridinium and 1-amino-1,10-phenanthrolinium salts **1** and **10–13** in arene–trifluoroacetic acid (TFA) mixtures gave aromatic *N*-substitution products such as anilines and toluidines, and radical products such as benzyltoluene and (dimethylbenzyl)mesitylene. The effect of heavy atoms and O_2 indicates that the *N*-substitution and radical products are characteristic of a singlet and a triplet species, respectively. The intermediacy of a nitrenium ion species was suggested by a Hammett plot with $\rho - 1.9$ and by the exclusion of other mechanisms. Selectivity factors (S_f), log[2 × (%*para*)/(%*meta*)], for the formation of toluidines are influenced by both the substituent on the pyridine ring of the substrate **1** and the nature of the counter-ion. This demonstrates that the parent nitrenium ion is not free but interacts intimately with both the heterocyclic nitrogen atom and the counter-ion. The interaction with the heterocyclic nitrogen stabilises selectively the singlet state rather than the triplet to favour aromatic amination. Similarly the photolyses of 1-(amino, methylamino, dimethylamino and piperidino)-2-methyl-4,6-diphenylpyridinium tetrafluoroborates **1m–p** in benzene–TFA gave the corresponding anilines. Photolyses of substrates **1m** and **1n** in toluene–TFA yielded the toluidine derivatives. However, photolyses of substrates **1o** and **1p** in TFA–toluene or –mesitylene did not produce the toluidine derivatives, but instead gave benzyltoluene and (dimethylbenzyl)mesitylene. These allowed us to propose that the singlet reaction giving the aromatic amines is prevented by a fast triplet reaction with toluene or mesitylene according to Le Chatelier's principle when the nitrenium ion has a very small S–T energy gap; the singlet state of the dialkyl or alicyclic nitrenium ion (having a smaller energy gap than the parent or alkyl nitrenium ion) is selectively stabilised by interaction with the heterocyclic nitrogen, resulting in a very low S–T energy gap. The proposal is well supported by the fact that a very low S–T energy gap of a five-membered intermediate gives an unusually low yield of toluidines and a relatively high yield of benzyltoluene in the photolysis of compound **13** in toluene–TFA.

It would be much simpler if aromatic amines could be obtained by direct amination, and not *via* hydrogenation of the corresponding nitro compounds (Scheme 1). Direct aromatic aminations can occur *via* an ethoxycarbonylnitrenium ion,[1] arylnitrenium ion,[2,3] and arylnitrenium–$AlCl_3$ complex.[4]



Scheme 1

However, it is believed that parent, alkyl and dialkyl nitrenium ions cannot bring about aromatic amination because the singlet nitrenium ions initially generated are quickly converted into the triplet ground states[5] which are inert to amination, or react with the substrate to give a complex mixture of products. In this paper we report direct aromatic amination by singlet nitrenium ions which are stabilised by interaction with both the heterocyclic nitrogen and the counter-anion in the photolyses of 1-(amino, alkylamino and dialkylamino)pyridinium salts, 1-aminoquinolinium salts, *etc.*

Results and Discussion

Photolyses of 1-*Aminopyridinium Salts* **1** *in TFA–Benzene or –Toluene*.—(a) *Effect of heavy atoms and oxygen.* The photolysis of 1-aminopyridinium mesitylsulphonate **1a** in TFA–benzene or –toluene gave aniline **2a** and biphenyl **6** or 2-, 3- and 4-toluidines **3a–5a** and benzyltoluene **7**, respectively, along with pyridine (Table 1 and Scheme 2). Similarly, **3a–5a** and **7** were produced in the photolysis of 1-aminopyridinium perchlorate, bromide and iodide **1b**, **1c** and **1d** in toluene–TFA (Table 1 and Scheme 2). The total yield of compounds **3a–5a** from substrates **1c** and **1d** was lower than that from substrates **1a** and **1b** whereas the yield of compound **7** from substrates **1c** and **1d** was higher than that from the salts **1a** and **1b** (Table 1). The yield of aniline **2a** from substrate **1a** was depressed in the presence of CH_2Br_2 or oxygen (Table 1).

Heavy atoms such as bromine and iodine catalyse an S ⟶ T conversion *via* intersystem crossing (ISC), and oxygen also promotes S ⟶ T conversion by its paramagnetic character.[6] Therefore *N*-substitution products **2a–5a** and the hydrogen-abstraction products **6** and **7** can be formed *via* a singlet and a triplet species, respectively.

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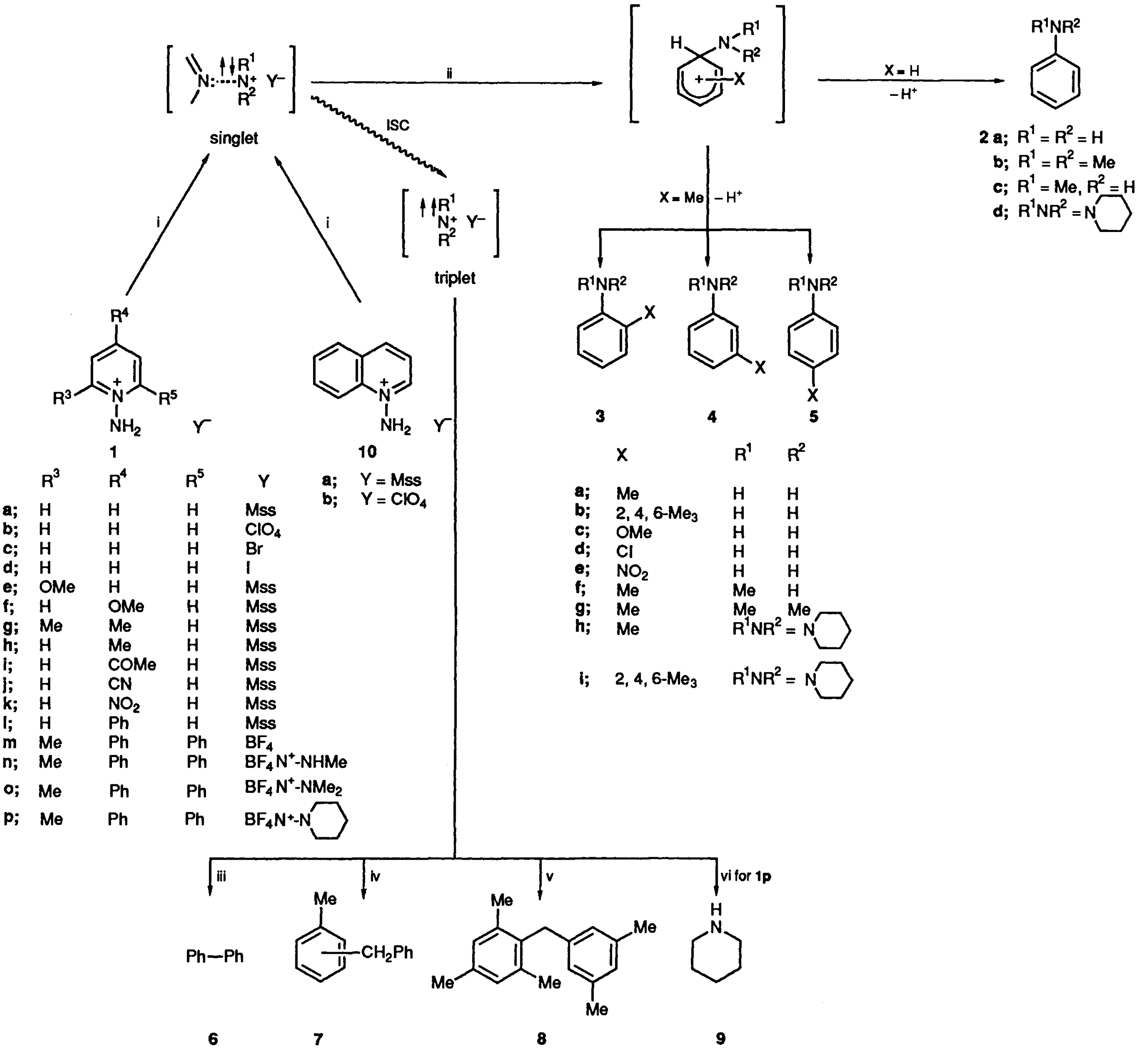
† Preliminary report, H. Takeuchi, *J. Chem. Soc., Chem. Commun.*, 1987, 961; H. Takeuchi, S. Hayakawa and H. Mural, *J. Chem. Soc., Chem. Commun.*, 1988, 1287.

Table 1 Photolyses[a] of 1-aminopyridinium salts **1** in TFA–benzene or –toluene

				Yield[b] (%)						
				from PhH		from PhMe				
Salt	Counter-ion	[1]/mol dm^{-3}	TFA (% v/v)	**2a**	**6**	**3a**	**4a**	**5a**	**7**	S_f
1a	Mss^{-c}	0.058	47	30	trace	20	9.5	14	11	0.47
1b	ClO_4^-	0.058	47			16	10	14	4.5	0.45
1c	Br^-	0.058	47			13	6.4	12	25	0.57
1d	I^-	0.058	47			17	7.9	4.0	19	0.00
1a	Mss$^-$	0.062	33	31						
1a[d]	Mss$^-$	0.062	33	18						
1a[e]	Mss$^-$	0.068	33	14						

[a] The photolyses were carried out in the presence of benzene or toluene for 4 or 8 h, respectively. [b] The yields are based on substrate **1** used. [c] Mss = mesitylenesulphonate. [d] The photolysis was performed in the presence of CH_2Br_2 (6.2% v/v). [e] The photolysis was carried out under atmospheric O_2.



Scheme 2 *Reagents and conditions:* i, *hv*; ii, PhX; iii, PhH; iv, PhMe; v, mesitylene; vi, H˙. Mss = mesitylenesulphonate.

(b) *Formation of a parent nitrenium ion.* As shown in Fig. 1, a plot of log k_f against σ^+ gives a good linear plot, with ρ −1.9, where k_f is the *para-* or *meta*-attacking partial rate factor. The negative ρ-value shows that the aromatic amination giving species **2a**–**5a** occurs *via* a positive intermediate, *e.g.* a parent nitrenium ion. In this Hammett plot, we selected only alkylbenzenes as substrates because the reactivity of aromatic substrates containing a heteroatom such as oxygen, nitrogen or halogen was depressed by a preferred interaction of TFA with the heteroatom as shown later.

Both the low positional selectivity (*ortho-*, *meta-* and *para-*direction) and a low substrate selectivity (the small negative ρ)

Table 2 Photolyses[a] of 1-aminopyridinium mesitylenesulphonates **1a**, **1e-k** (0.058 mol dm^{-3}) and compound **10b** in TFA (47% v/v)-benzene (53% v/v) or -toluene (53% v/v)

		Yield[b] (%)						
		from PhH		from PhMe				
Salt	Substituent	**2a**	**b**	**3a**	**4a**	**5a**	**7**	S_f
1a	None	30	trace	20	9.5	14	11	0.47
1e	2-OMe	37		17	10	12	11	0.38
1f	4-OMe	28		21	9.5	9.8	7.8	0.31
1g	2,4-Me$_2$	39		21	4.8	5.0	9.0	0.32
1h	4-Me	36		22	13	18	9.2	0.44
1i	4-COMe	21		24	8.6	15	16	0.54
1j	4-CN	29		17	8.8	32	5.8	0.86
1k	4-NO$_2$	0.6		2.5	4.4	1.6	26	−0.14
10b[c]		0	4.8					
10b[d]		0	0.7					

[a] The photoreaction with benzene or toluene was carried out for 4 or 8 h, respectively. [b] The yields are based on substrate **1** used. [c] The photolysis of 1-aminoquinolinium perchlorate (**10b**) was carried out using 2,2,2-trifluoroethanol (TFE) instead of TFA. [d] The photolysis of compound **10b** was carried out using acetonitrile instead of TFA.

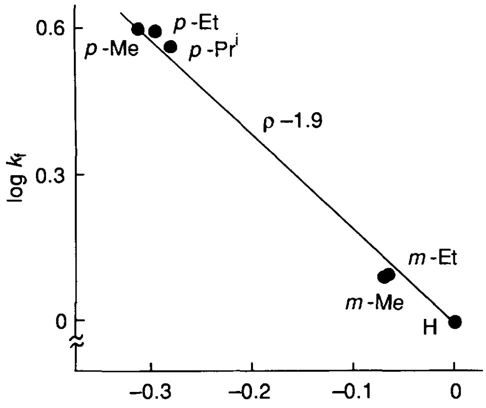
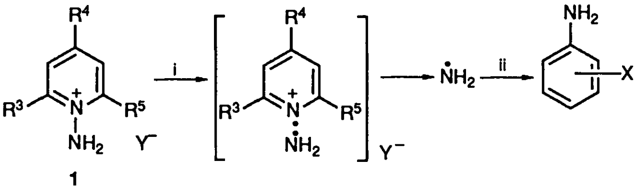


Fig. 1 Hammett plot of σ$^+$ against log k_f for the formation of anilines in the reaction of 1-aminoquinolinium perchlorate **10b** with alkylbenzenes



Scheme 3 *Reagents and conditions:* i, *hv*; ii, PhX

contrast with the high selectivities (formation of only *ortho*- and *para*-isomers and ρ *ca.* −5) for the singlet phenylnitrenium ion from phenyl azide[2] or pyridinium salt.[3] From the reactivity–selectivity principle, these indicate that the positive intermediate might be the singlet parent nitrenium ion which is more reactive than the singlet phenylnitrenium ion. This is expected because the nitrenium ion conjugates with a phenyl using its vacant orbital, leading to stabilisation and enhanced selectivity.

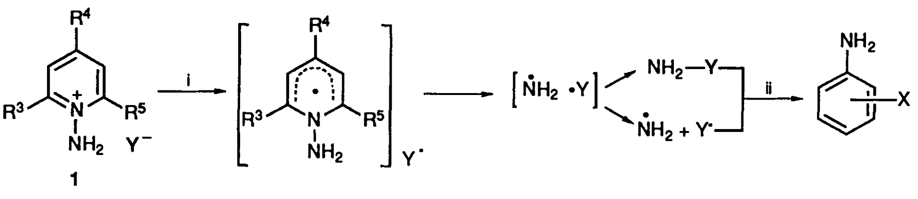
The following discussions will exclude mechanisms other than the nitrenium ion mechanism. The ρ-value (−1.9) is more negative than that assumed for aromatic amination by an amino radical. Reaction of amino radical with benzene or toluene gives an unstable amine, which is decomposed to biphenyl and aniline (1.3%) or benzyltoluene and 4-toluidine (1.0%) by distillation.[7,8] Therefore our observations rule out amination *via* the amino radical by homolysis of substrate **1** as shown in Scheme 3.

We did not observe aniline **2a** in the photolysis of compound **10b** in benzene–2,2,2-trifluoroethanol (TFE) (Table 2), and *N*,*N*-dimethylaniline **2b** was not formed in the photolysis of substrate **1o** in benzene-1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) (see Table 5). These facts indicate that a reaction of excited species **1** with aromatics seems to be impossible; such a reaction should give an aniline **2a** or **2b** in the photolysis in benzene–TFE or –HFP as well as in benzene–TFA. A possible reason for the lack of the formation of a product **2a** or **2b** is that the singlet nitrenium ion reacts with TFE or HFP, giving some unidentified product, or is changed to the triplet state by a fast S ⟶ T conversion.

Photochemical one-electron transfer[9] from the counter-ion to the positive nitrogen atom of the pyridinium cation (Scheme 4) is not possible, considering that the aromatic amination occurs using pyridinium salts **1** with BF_4^- and ClO_4^- which are non-electron-donating counter-anions.[10]

Intermolecular one-electron transfer[11] as shown in Scheme 5 is unlikely because the photolysis of 1-aminoquinolinium perchlorate **10b** in acetonitrile–benzene does not produce aniline **2a** (Table 2) although a reaction by intermolecular electron-transfer is usually accelerated by a more polar solvent such as acetonitrile. Hence, the reaction would not be subject to aromatic amination.

The aminium radical mechanism[12] (Scheme 6) is not plausible since the counter-ion affects the amination (Table 1). This mechanism is also excluded since the amination of toluene by aminium radical gives large proportions of *meta*-product,[12] whereas our amination usually yields much more of the *ortho*- and *para*-toluidines rather than the *meta*-isomer, and that



Scheme 4 *Reagents and conditions:* i, *hv*; ii, PhX

Table 3 Photoreactions of 1-aminopyridinium mesitylenesulphonates **1** and 1-aminoquinolium salts **10** with mesitylene, anisole, chlorobenzene or nitrobenzene in the presence of TFA (33% v/v)

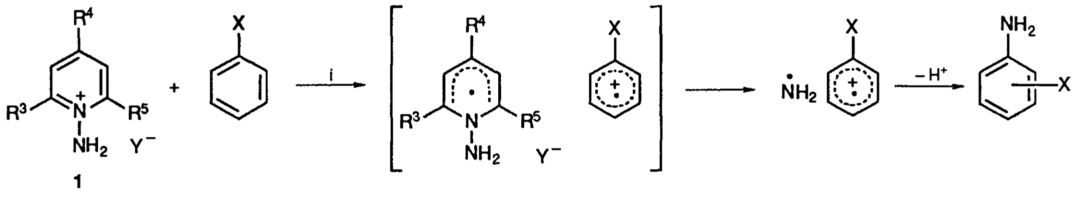
Salt	Substituent	Arene	[**1**]/mol dm^{-3}	t/h	Yield[a] (%) **3**	**4**	**5**
1a	None	Mesitylene	0.058	8	45[b]		
10a	None	Mesitylene	0.058	4	79[b]		
1a	None	Anisole	0.058	5	31	0	3
1l	4-Ph	Anisole	0.072	5	18	0	7
1i	4-COMe	Anisole	0.040	8	11	0	trace
1j	4-CN	Anisole	0.042	8	16	0	0
1a[c]	None	Chlorobenzene	0.13	4	4.4	0	9.7
10b[d]	None	Nitrobenzene	0.058	4	0	0	0

[a] The yields are based on substrate **1** used. [b] This indicates the yield of 2,4,6-trimethylaniline **3b**. [c] The photolysis was carried out in chlorobenzene (26% v/v)–TFA (74% v/v). [d] After the photolysis, quinoline (~20% yield) was detected by GLC analysis.

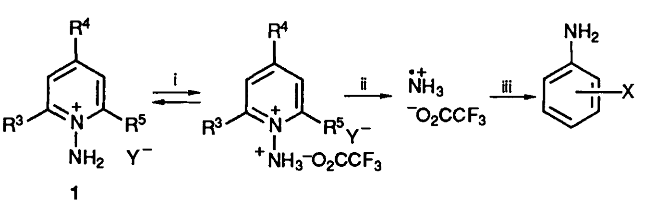
Table 4 Photolyses[a] of 1-aminoquinolinium, 1-amino-2,2′-bipyridinium, 1,1′-diamino-2,2′-bipyridinium and 1-amino-1,10-phenanthrolinium salts **10**–**13** in TFA–benzene or –toluene

Salt	[Salt]/mol dm^{-3}	TFA (% v/v)	Yield[b] (%) from PhH **2a**	from PhMe **3a**	**4a**	**5a**	**7**	S_f
10a	0.058	47	54	26	15	28	14	0.57
10b	0.058	47	63	32	20	19	trace	0.46
11	0.040	33	26.4					
11[c]	0.040	31	9.6					
11[d]	0.040	33	11.3					
12	0.040	33	16.2					
12[c]	0.040	31	10.9					
12[d]	0.040	33	12.1					
13	0.040	31	25.0	3.5	2.3	8.6	12	0.87
13[c]	0.040	33	9.8					
13[d]	0.040	33	8.4					

[a] The photolyses were carried out in the presence of benzene or toluene for 4 or 8 h, respectively. [b] The yields are based on the amount of salt used. [c] The photolysis was performed in the presence of CH_2Br_2 (7.4% v/v). [d] The photolysis was conducted under atmospheric O_2.



Scheme 5 *Conditions:* i, *hν*



Scheme 6 *Reagents and conditions:* i, TFA; ii, *hν*; iii, PhX

dimethylaminium radical undergoes a reaction with toluene efficiently to give *N*,*N*-dimethyl-2-, -3- and -4-toluidine **3g**–**5g**[12] although the photolysis of the 1-dimethylamino-2-methyl-4,6-diphenylpyridinium salt **1o** in toluene–TFA did not give **3g**–**5g** (see Table 5).

(c) *Interaction of the nitrenium ion with both the heterocyclic nitrogen atom and the counter-ion.* Selectivity factors, $S_f = \log [2 \times (\%para)/(\%meta)]$, for the formation of toluidines for S_N1 and S_N2 Friedel–Crafts alkylations are 0.5–0.6 and *ca.* 0.8, respectively,[13,14] and the relatively high *meta*-content suggests attacking species to be considerably active.[15] This means that the nitrenium ion strongly interacting with the counter-ion has high S_f because of the low activity. The S_f-values increase with an increase in localised charge (*i.e.*, no increase in polarisable charge) of the counter-ion ($Br^- > Mss^- > ClO_4^- > I^-$); **1c** > **1a** > **1b** > **1d** (Table 1). The counter-ion with the higher localised charge may intimately interact more strongly with the nitrenium ion; formation of an intimate nitrenium ion–counter-ion pair is suggested.

The influence of the substituent on the pyridine ring of substrates **1** on the S_f-value was examined for the photolyses of the 1-aminopyridinium mesitylenesulphonates **1a** and **1e**–**k** (Table 2). The S_f-values increased with a decrease in nucleophilicity (by an electron-withdrawing group such as COMe or CN) of the pyridine, and decreased with an increase in nucleophilicity (by an electron-donating group such as Me or OMe) (Table 2). The result cannot be explained completely unequivocally. However, at the present time, we believe that the positive charge of the nitrenium ion becomes greater in the presence of a less nucleophilic pyridine because of lowered electron transfer of the unshared electron of the pyridine to the nitrenium ion, so that ionic interaction of the nitrenium ion with the counter-ion is facilitated, resulting in the greater S_f-value by the lowered reactivity; the reactivity (or selectivity) depends upon the ionic interaction affected by the nitrenium ion–heterocyclic nitrogen interaction, not directly upon the latter interaction, except for the example that a very weak or a strong latter interaction directly gives an unusually low or high S_f-value in the photolysis of compound **1k** or **13**, respectively (Tables 2 and 4).

Considering that the S_f-value is influenced by the substituent on the pyridine ring of substrate **1** and by the nature of the counter-ion, the parent nitrenium ion generated in the first step is not free but is stabilised by the interactions with both the heterocyclic nitrogen and the counter-ion (Scheme 2). The heterocyclic compound formed in the reaction does not interact intermolecularly with the nitrenium ion because the compound forms the conjugate acid in the presence of TFA; we suggest formation of an intimate nitrenium ion–heterocyclic compound pair. Nucleophilic substitution of *N*-alkylpyridines has been proposed to involve an intimate carbocation–pyridine pair.[16] It is possible that the bonding interaction is only with the heterocyclic nitrogen since it has been claimed that a 3-centre bond is generally unstable with respect to a 2-centre bond.[17] Thus the nitrenium ion–counter-ion interaction would be ionic, not covalent bonding.

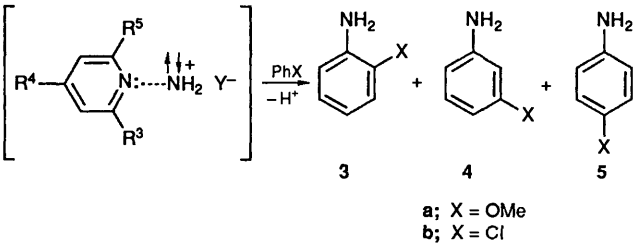
The interaction with the heterocyclic nitrogen results in the selective stabilisation of the singlet species relative to the triplet to favour (usually) the singlet reaction. A similar interaction with the unshared electron pair of the heteroatom has been predicted in nitrene chemistry.[17–21]

(d) *Effect on the yield of aromatic amination of the substituent on the pyridine ring of* 1-*aminopyridinium mesitylenesulphonates* **1**. The photolyses of substituted 1-aminopyridinium salts **1e–k** in TFA–benzene or –toluene also afforded aniline **2a** or toluidine **3a–5a** and compound **7**, respectively (Table 2 and Scheme 2). In the photolysis of 1-amino-4-nitropyridinium salt **1k**, the very poor nucleophile 4-nitropyridine shows hardly any interaction with the nitrenium ion, so that the photolysis may show a very low yield of singlet products **2a–5a** and a high yield of the triplet product **7** (Table 2). The photolysis of 1-amino-4-acetylpyridinium salt **1i** compared with 1-amino-4-cyanopyridinium salt **1j** showed a low yield of the singlet products **2a** and **3a–5a** and a high yield of the triplet product **7** (Table 2). This implies an enhanced involvement of the triplet nitrenium ion *via* a triplet excited substrate **1i**.

As for the yield of compounds **2a** and **3a–5a** in the photolyses of compounds **1a**, **1f**, **1h** and **1j**, there is no monotonic variation with the electron ability of the 4-substituent at first sight (Table 2). However, this can reasonably be explained by consideration of the competing S ⟶ T conversion against the aromatic amination: The singlet stabilisation increases the singlet concentration to enhance the yield of the singlet product, but at the same time facilitates the competing S ⟶ T conversion to lower the yield because of the lowered S–T energy gap caused by the selective stabilisation of the singlet relative to the triplet. The competing rate of reaction of the nitrenium ion from **1** with 4-OMe or 4-Me is too high to ignore because of the high singlet stabilisation. We observed a relatively high yield of the triplet product **7** for the photolysis of salts **1f** or **1h** in spite of the high reactivity (*i.e.*, the low S_f) (Table 2). On the other hand, the competing rate for the nitrenium ion interacting with 4-cyanopyridine is significantly slower as compared with the slow rate for the aromatic amination because of the high S–T energy gap; the yield of compound **7** from substrate **1j** is actually low, and the rate for the amination is slow (*i.e.*, has high S_f) (Table 2). Hence the yields of the amination shown in Table 2 are lowered by the participation of the competing S ⟶ T conversion, so that the yields from substrates **1** with electron-donating groups would be more enhanced than those from substrates **1** with electron-withdrawing groups if the competing reaction is completely ignored. Therefore we would expect the rates and yields for the reaction with both benzene and toluene to be similarly affected if no competing reaction pathways are available.

Photolyses of 1-*Aminopyridinium Mesitylenesulphonates* **1** *or Quinolinium Salts* **10** *with Mesitylene, Anisole, Chlorobenzene and Nitrobenzene in the Presence of TFA.*—The photolysis of compound **1a** in mesitylene–TFA produced 2,4,6-trimethylaniline **3b** (Table 3 and Scheme 7). The product **3b** was formed in high yield (79%) in the photolysis of 1-aminoquinolinium mesitylenesulphonate **10a** (Table 3). This is of especial interest from a synthetic point of view.

This preferred formation of 2-anisidine **3c** rather than 3- and 4-anisidine **4c** and **5c** in the reaction with anisole (Table 3 and Scheme 7) indicates that the reaction proceeds *via* an interaction of the nitrenium ion with the lone-pair electrons of the oxygen atom of anisole. Such an interaction would be more favourable when the nitrenium ion initially generated interacts more weakly with the heterocyclic nitrogen since the preferable formation of 2-anisidine **3c** needs a favourable transformation of the interaction with pyridine into that with anisole. Thus compound **3c** was formed preferably when we used a pyridinium salt which generates a less nucleophilic pyridine which is more difficult to interact with the nitrenium ion (Table 3): The preference was in the following order; **1j** > **1i** > **1a** > **1l**. The low amination efficiency for the reaction with anisole or chlorobenzene (Table 3) implies that the interaction of TFA with the heteroatom of the substrate results in the low reactivity of the substrate.

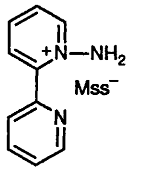


Scheme 7 Using mesitylene instead of PhX, only 2,4,6-trimethylaniline **3b** was formed

No aromatic amination was observed in the photolysis of 1-aminoquinolinium perchlorate **10b** in nitrobenzene–TFA (Table 3). In the photolysis, quinoline was formed in only ~20% yield because the preferential absorption of light by nitrobenzene prevents the photoreaction. This result suggests that the nitrenium ion is less reactive toward the very weak nucleophile nitrobenzene, so that the preferable, competing S ⟶ T conversion takes place.

Photolyses of 1-*Aminoquinolinium,* 1-*Amino*-2,2′-*bipyridinium,* 1,1′-*Diamino*-2,2′-*bipyridinium and* 1-*Amino*-1,10-*phenanthrolinium Salts* **10–13** *in TFA–Benzene or –Toluene.*—The photolyses of 1-aminoquinolinium mesitylenesulphonate and perchlorate **10a** and **10b** gave high yields of products **2a** and **3a–5a** compared with the photolyses of the other salts (Table 4 and Scheme 2); in particular, compound **10b** afforded the highest yields. Thus the Hammett plot was examined using compound **10b** as mentioned above. We will give full details of the efficient amination of compounds **10** in the near future.

The yield of aniline **2a** in the photolyses of 1-amino-2,2′-bipyridinium, 1,1′-diamino-2,2′-bipyridinium and 1-amino-1,10-phenanthrolinium salts **11–13** was low as compared with that in the photolysis of compound **1a** (Tables 1 and 4). We expected the high yield from enhanced singlet stabilisation of a five-membered intermediate which is formed by the interaction of the singlet nitrenium ion with bipyridyl nitrogens (Scheme 8).



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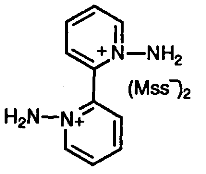

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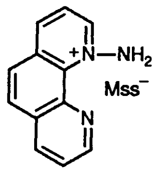

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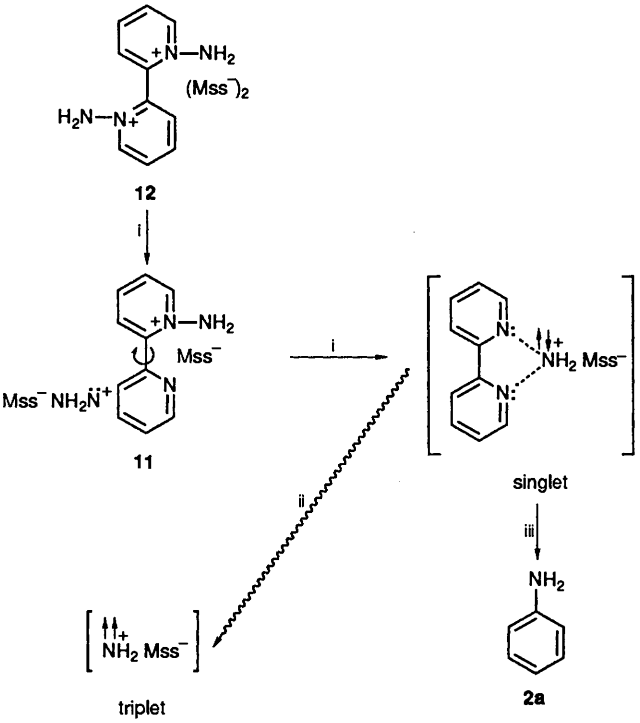
The unexpectedly low yield is explained by the evidence that the high singlet stabilisation of the intermediate enhances the singlet concentration to increase the yield of singlet product whereas the highly selective singlet stabilisation causes a very small S–T energy gap to lead to a favourable S ⟶ T conversion, resulting in the decreased yield.

The yield of the singlet product **2a** in the photolyses of **11** and **13** is greatly depressed in the presence of the heavy-atom solvent CH_2Br_2 and under atmospheric oxygen as compared with that in the photolysis of compound **1a** (see Tables 1 and 4). Considering the probability of collision for the S ⟶ T conversion, the longer lifetime (*i.e.*, the higher stability) of the singlet state, the greater the decrease in the singlet product by the effect of heavy-atoms or oxygen. Hence the lifetime for the singlet state from substrates **11** or **13** may be longer than that from salt **1a**; the longer lifetime suggests the formation of the more stabilised five-membered intermediate from substrates **11** and **13** (Scheme 8).



Scheme 8 *Reagents and conditions:* i, *hν*; ii, O_2, heavy atom; iii, benzene

The effects of heavy atoms and oxygen in the photolysis of compound **12** was lower than that in the photolysis of substrate **1a**, **11** and **13** (Tables 1 and 4). This was expected, because the photolysis of compound **12** involves a free singlet nitrenium ion which does not interact with the heterocyclic nitrogen, as shown below. The free nitrenium ion may show less heavy-atom or O_2 effect due to its very short lifetime.

The yield of aniline **2a**, 16.2%, in the photolysis of 1,1′-diamino-2,2′-bipyridinium salt **12** was lower than that (26.4%) in the photolysis of 1-amino-2,2′-bipyridinium salt **11** (Table 4). This suggests that the free nitrenium ion generated in the first step from compound **11** is converted into aniline in very low yield. This yield can be estimated to be 6% (from 2 × 16.2% − 26.4%). This low yield results from a lack of singlet stabilisation of the free nitrenium ion not interacting with the heterocyclic nitrogen; the rotation about C(2)–C(2′) in the pyridinium salt **11** occurs because of an ionic repulsion between the initially formed nitrenium ion and the positive nitrogen atom of salt **11** formed from compound **12**, and prevents the interaction between the nitrenium ion and the heterocyclic nitrogen (Scheme 8). The occurrence of the ionic repulsion is supported by the fact that mass spectral analysis of the reaction mixture from the photolysis of compound **12** does not show the hydrazinium ion but it does show the ammonium ion.

Photolyses of 1-(*Amino, Methylamino, Dimethylamino and Piperidino*)-2-*methyl*-4,6-*diphenylpyridinium Tetrafluoroborates* **1m–p** *in Arene–TFA*.—The photolyses of 1-(amino and methylamino)-2-methyl-4,6-diphenylpyridinium salts **1m** and **1n** in benzene–TFA gave the singlet products aniline **2a** and *N*-methylaniline **2c**, respectively (Table 5 and Scheme 2). The photolysis of compounds **1m** and **1n** in toluene–TFA afforded products **3a–5a** and *N*-methyl-2-, -3- and -4-toluidine **3f**, **4f** and **5f**, respectively (Table 5 and Scheme 2). *N*,*N*-Dimethylaniline **2b** and *N*-phenylpiperidine **2d** were formed in the photolyses of 1-(dimethylamino and piperidino)-2-methyl-4,6-diphenylpyridinium salts **1o** and **1p**, respectively, in benzene–TFA (Table 5 and Scheme 2). However, the photolyses of compounds **1o** and **1p** in TFA–toluene and –mesitylene did not yield singlet products such as *N*,*N*-dimethyltoluidines **3g–5g**, 2-, 3- and 4-piperidinotoluenes **3h**, **4h** and **5h**, and *N*-mesitylpiperidine **3i**, but only triplet products such as **6**, **7**, (dimethylbenzyl)mesitylene **8** and piperidine **9** (Table 5 and Scheme 2).

It appears contradictory that, at first sight, the singlet product is not formed in spite of the presence of aromatics more nucleophilic than benzene. However, we can explain the fact by the following proposal: When the singlet state is highly stabilised, a fast triplet reaction in the presence of a good H-atom donor (*e.g.*, toluene or mesitylene) prevents the singlet reaction giving the aromatic amines according to Le Chatelier's principle; such prevention may occur very rapidly in the case of an extremely low S–T energy gap (< *ca.* 5 kcal mol^{-1})* due to an already fast S–T equilibration. The energy gap of a free dialkyl or alicyclic nitrenium ion is predicted to be much smaller than that of the free parent nitrenium ion.[1,22] The gap of a dialkyl or alicyclic nitrenium ion which interacts with the heterocyclic nitrogen would be extremely small since the singlet stabilisation depresses selectively the singlet state relative to the triplet state; there is also the possibility that the interacting nitrenium ion is in the triplet ground state. This proposal is well supported by the fact that the photolysis of compound **13** gives unusually low yields of products **3a–5a** and a relatively high yield of compound **7** (Table 4); the singlet nitrenium ion from species **13** is highly stabilised by the formation of the five-membered intermediate as shown above.

Experimental

IR spectra were obtained on a Hitachi EPI-G3 spectrometer. NMR spectra (^1H and ^{13}C) were taken with a Nippondensi JNM-FX-60Q instrument. Mass spectra were recorded with a Hitachi M-80B spectrometer. GLC was performed with a Shimazu GC-6A chromatograph [column A, a glass column (2 m × 3 mm) packed with 10% polyethylene glycol (20 M) on 80–100 Chromosorb W; column B, a glass column (1 m × 3 mm) packed 10% silicone SE-30 on 80–100 Chromosorb W]. HPLC was carried out with a Shimazu LC-6A system [column of

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* 1 cal = 4.184 J.

Table 5 Photolyses[a] of 1-(amino, methylamino, dimethylamino and piperidino)-2-methyl-4,6-diphenylpyridinium tetrafluoroborates **1m–p** in PhX–TFA

				Yield[b] (%)							
				from PhH		from PhMe					from MsH
Salt	[1] mol dm^{-3}	PhX	t/h	**2**	**6**	**3**	**4**	**5**	**7**	**9**	**8**
1m	0.025	X = H	20	35	0						
1m	0.025	X = Me	18			24	11	21	19		
1n	0.024	X = H	16	55	0						
1n	0.036	X = Me	17			6	11	37	11		
1o	0.023	X = H	20	15	0						
1o	0.023	X = Me	19			0	0	0	84		
1o[c]	0.023	X = H	23	0	4						
1p	0.080	X = H	5	25	0					10	
1p	0.080	X = Me	5			0	0	0	36	16	
1p	0.080	*c*	5	0[d]						8.7	42

[a] Photolyses of substrates **1m–o** were carried out in PhX (71% v/v)–TFA (29%) using a 300 W high-pressure Hg lamp (Halos PIH-300), but the photolysis of substrate **1p** in PhX (67% v/v)–TFA (33% v/v) used a 500 W high-pressure Hg lamp. [b] The yields are based on substrate **1** used. [c] 1,1,1,3,3,3-Hexafluoropropan-2-ol (HFP) was used instead of TFA. [c] Mesitylene (MsH) was used instead of PhX. [d] This yield means that of *N*-mesitylpiperidine **3i**.

Zorbax ODS (25 cm × 4.6 mm). Two runs agreed within ±2% for the yields of the products which were determined by replicate GLC or HPLC analyses. Photolyses were performed using a 500 W high-pressure Hg lamp (Eikosha EHB-W-500) unless indicated otherwise when the 500 W high-pressure Hg lamp was used, the reactant salts were sufficiently consumed in photolyses in the presence of benzene (mesitylene, anisole or chlorobenzene) or toluene after 4 or 8 h, respectively. When using a 300 W high-pressure Hg lamp (Halos PIH 300), an irradiation time (16–23 h) was needed for almost complete decomposition of substrates **1m–o**.

Benzene, toluene, ethylbenzene, cumene, mesitylene, anisole, nitrobenzene, chlorobenzene, pyridine, quinoline, CH_2Br_2 and acetonitrile were purified by standard methods before use. TFA and HFP were purified by distillation.

The following compounds were reagent grade (Wako), and used without further purification: Aniline **2a**, *N*-methylaniline **2c**, *N*,*N*-dimethylaniline **2b**, *N*-phenylpiperidine **2d**, 2-, 3- and 4-toluidine **3a**, **4a** and **5a**, 2,4,6-trimethylaniline **3b**, 2-, 3- and 4-anisidine **3c**, **4c** and **5c**, 2-, 3- and 4-chloroaniline **3d**, **4d** and **5d**, 2-, 3- and 4-nitroanilines **3e**, **4e** and **5e**, *N*-methyl-2-, -3- and -4-toluidine **3f**, **4f** and **5f**, *N*,*N*-dimethyl-2-, -3- and -4-toluidine **3g**, **4g** and **5g**, 2- and 4-ethylaniline, 4-isopropylaniline, biphenyl **6**, piperidine **9**, 2- and 4-methoxypyridine, 2,4-dimethylpyridine, 4-phenylpyridine, 4-methylpyridine, 4-acetylpyridine, 4-cyanopyridine, 4-nitropyridine, 2,2′-bipyridyl and 1,10-phenanthroline.

The following compounds were prepared by the methods described in the literature: 1-Aminopyridinium mesitylenesulphonate **1a**,[23] 1-aminopyridinium iodide **1d**,[24] 1-amino-2,4-dimethylpyridinium mesitylenesulphonate **1g**,[23] 1-amino-4-methylpyridinium mesitylenesulphonate **1h**,[25] 1-amino-4-acetylpyridinium mesitylenesulphonate **1i**,[25] 1-amino-4-cyanopyridinium mesitylenesulphonate **1j**,[23] 1-amino-4-phenylpyridinium mesitylenesulphonate **1l**,[23] 2-methyl-4,6-diphenylpyridine,[26] benzyltoluene **7**,[3] (dimethylbenzyl)mesitylene **8**,[27] 1-aminoquinolinium mesitylenesulphonate **10a**,[23] and 1,1′-diamino-2,2′-bipyridinium mesitylenesulphonate **12**.[25]

The following new compounds were synthesized by methods similar to those described in the literature.[23,29]

1-*Aminopyridinium Perchlorate* **1b**.—A solution of the mesitylenesulphonate **1a** in ethanol was treated with 60% aq. $HClO_4$, and the product **1b** was obtained by addition of diethyl ether to the reaction mixture.[28] The crystalline *product* **1b** had m.p. 214–215 °C; ν_{max}(Nujol)/cm^{-1} 3320, 3190, 3060, 1635, 1505, 1480, 1320, 1040, 890, 770, 675 and 625 (Found: C, 31.1; H, 3.45; N, 14.1. $C_5H_7ClN_2O_4$ requires C, 30.85; H, 3.65; N, 14.4%).

1-*Aminopyridinium Bromide* **1c**.—A concentrated solution of the mesitylenesulphonate **1a** in ethanol was treated with 48% aq. HBr,[28] and compound **1c** (m.p. 153–154 °C) was precipitated by addition of diethyl ether, ν_{max}(Nujol)/cm^{-1} 3170, 3100, 1620, 1590, 1510, 1240, 1205, 1195, 1140, 1085, 1055, 1030, 945, 930, 790, 765, 670 and 645 (Found: C, 34.25; H, 3.95; N, 15.75. $C_5H_7BrN_2$ requires C, 34.3; H, 4.05; N, 16.0%).

1-*Amino*-2-*methoxypyridinium Mesitylenesulphonate* **1e**.[23]—Crystals, m.p. 129–130 °C; ν_{max}(Nujol)/cm^{-1} 3230, 3130, 1660, 1630, 1605, 1570, 1510, 1330, 1210, 1085, 1010, 850, 800, 780, 735 and 675; $\delta_H(D_2O)$ 2.1 (3 H, s, 4-Me of Mss), 2.4 (6 H, 2- and 6-Me of Mss), 4.2 (3 H, s, OMe), 4.4–4.8 (2 H, br, NH_2), 6.9 (2 H, s, ArH of Mss) and 7.2–8.4 (4 H, m, pyridinyl H); $\delta_C(D_2O)$ 19.7 (4-Me of Mss), 21.8 (2- and 6-Me of Mss), 59.0 (OMe), 110.5 (C-5), 118.3 (C-3), 130.7 (C-3 and -5 of Mss), 136.9 (C-6), 139.6 (C-2 and -6 of Mss), 140.7 (C-4 of Mss), 144.8 (C-4) and 170.2 (C-2) (Found: C, 55.3; H, 6.1; N, 8.3. $C_{15}H_{20}N_2O_4S$ requires C, 55.55; H, 6.2; N, 8.65%).

1-*Amino*-4-*methoxypyridinium Mesitylenesulphonate* **1f**.[23]—M.p. 122–123 °C; ν_{max}(Nujol)/cm^{-1} 3220, 3150, 1665, 1620, 1600, 1560, 1510, 1405, 1335, 1315, 1210, 1085, 1015, 855, 825, 750 and 675; $\delta_H(CDCl_3)$ 2.25 (3 H, s, 4-Me of Mss), 2.6 (6 H, s, 2- and 6-Me of Mss), 6.9 (2 H, s, ArH of Mss), 7.0–7.6 (4 H, m, pyridinyl H) and 8.75–9.1 (2 H, br, NH_2); $\delta_C(CDCl_3)$ 20.7 (4-Me of Mss), 23.0 (2- and 6-Me of Mss), 57.4 (OMe), 130.6 (C-3 and -5 of Mss), 136.9 (C-2 and -6), 138.4 (C-2 and -6 of Mss), 139.8 (C-4 of Mss), 143.5 (C-3 and -5) and 167.6 (C-4) (Found: C, 55.3; H, 6.1; N, 8.4%).

1-*Amino*-4-*nitropyridinium Mesitylenesulphonate* **1k**.[23]—This yellow compound had m.p. 151–152 °C; ν_{max}(Nujol)/cm^{-1} 3270, 3060, 1600, 1545, 1350, 1250, 1210, 1175, 1085, 1010, 860, 745, 685 and 640; $\delta_H(D_2O)$ 2.1 (3 H, s, 4-Me of Mss), 2.4 (6 H, s, 2- and 6-Me of Mss), 4.4–5.2 (2 H, br, NH_2), 6.9 (2 H, s, ArH of Mss) and 8.8 (4 H, ABq, pyridinyl H); $\delta_C(D_2O)$ 19.7 (4-Me of Mss), 21.8 (2- and 6-Me of Mss), 121.9 (C-3 and -5), 130.7 (C-3 and -5 of Mss), 136.9 (C-2 and -6), 137.1 (C-4), 139.7 (C-2 and -6 of Mss) and 140.7 (C-4 of Mss) (Found: C, 49.7; H, 5.15; N, 12.15. $C_{14}H_{17}N_3O_5S$ requires C, 49.55; H, 5.05; N, 12.4%).

1-*Amino*-2-*methyl*-4,6-*diphenylpyridinium Tetrafluoroborate* **1m**.[29]—This compound had m.p. 185–187 °C (from $CHCl_3$–Et_2O); ν_{max}(Nujol)/cm^{-1} 3360, 3280, 1630, 1600, 1355, 1060, 870, 770 and 700; δ_H($CDCl_3$) 3.0 (3 H, s, Me), 6.3–6.6 (2 H, br, NH_2) and 7.2–8.2 (12 H, m, ArH and pyridinyl H): δ_C($CDCl_3$) 20.1 (Me), 124.1, 125.1, 127.6, 129.2, 129.7, 130.0, 130.2 and 133.9 (C-4, -4, -2/6, -2/6, -3/5, -3/5, -1 and -1 of phenyl group, 131.6 and 131.8 (C-3 or -5 and -5 or -3) and 151.9, 152.4 and 153.3 (each corresponds to C-2, -4 or -6) (Found: C, 61.7; H, 5.1; N, 8.3. $C_{18}H_{17}N_2BF_4$ requires C, 62.1; H, 4.9; N, 8.05%).

2-*Methyl*-1-*methylamino*-4,6-*diphenylpyridinium Tetrafluoroborate* **1n**.[29]—This pale yellow compound had m.p. 126–128 °C (from $CHCl_3$–Et_2O); ν_{max}(Nujol)/cm^{-1} 3330, 1630, 1580, 1415, 1350, 1300, 1050, 890, 775 and 695; δ_H($CDCl_3$) 2.6 (3 H, d, NMe), 3.0 (3 H, s, 2-Me), 6.2–6.8 (1 H, br, NH) and 7.3–8.2 (12 H, m, ArH and pyridinyl H); δ_C($CDCl_3$) 19.7 (2-Me), 38.2 (NMe), 125.1, 126.2, 128.0, 129.2, 129.2, 129.7, 130.8 and 133.9 (C-4, -4, -2/6, -2/6, -3/5, -3/5, -1 and -1 of phenyl groups), 131.2 and 131.9 (C-3 or -5 and -5 or -3) and 154.9, 155.8 and 157.2 (each corresponds to C-2, -4 or -6) (Found: C, 63.0; H, 5.2; N, 7.85. $C_{19}H_{19}BF_4N_2$ requires C, 63.0; H, 5.3; N, 7.75%).

1-*Dimethylamino*-2-*methyl*-4,6-*diphenylpyridinium Tetrafluoroborate* **1o**.[29]—This pale yellow compound had m.p. 178–181 °C (from $CHCl_3$–Et_2O); ν_{max}(Nujol)/cm^{-1} 1625, 1565, 1350, 1100, 1060, 890, 775 and 710; δ_H($CDCl_3$) 2.4–3.2 (9 H, br, NMe_2 and 2-Me) and 7.2–8.2 (12 H, m, ArH and pyridinyl H); δ_C($CDCl_3$) 20.7 (2-Me), 44.9 (NMe_2), 126.2, 127.2, 128.2, 128.5, 129.0, 129.6, 130.6 and 132.4 (C-4, -4, -2/6, -2/6, -3/5, -3/5, -1 and -1 of phenyl groups), 130.6 and 131.9 (C-3 or -5 and -5 or -3) and 155.8, 159.0 and 159.8 (each corresponds to C-2, -4 or -6) (Found: C, 63.55; H, 5.5; N, 7.85. $C_{20}H_{21}BF_4N_2$ requires C, 63.85; H, 5.65; N, 7.5%).

2-*Methyl*-4,6-*diphenyl*-1-*piperidinopyridinium Tetrafluoroborate* **1p**.[29]—This crystalline compound had m.p. 210–214 °C (from CH_2Cl_2–Et_2O); ν_{max}(Nujol)/cm^{-1} 1630, 1570, 1420, 1350, 1250, 1050, 930, 890, 780, 770, 705 and 690; δ_H($CDCl_3$) 0.8–2.0 (6 H, br, 3-, 4- and 5-H_2 of piperidino group), 2.3–3.7 (4 H, br, 2- and 6-H_2 of piperidino group), 3.0 (3 H, s, Me) and 7.3–8.4 (12 H, m, ArH and pyridinyl H); δ_C($CDCl_3$) 21.1 (Me), 22.9, 25.9 and 54.3 (C-4, -3/5 and -2/6 of piperidino group), 126.1, 127.2, 128.2, 128.4, 128.9, 129.6, 130.5 and 133.9 (C-4, -4, -2/6, -2/6, -3/5, -3/5, -1 and -1 of phenyl groups), 131.9 and 132.7 (C-3 or -5 and -5 or -3) and 155.5, 158.9 and 159.7 (each corresponds to C-2, -4 or -6) (Found: C, 66.3; H, 6.05; N, 6.85. $C_{23}H_{25}BF_4N_2$ requires C, 66.35, H, 6.05; N, 6.75%).

1-*Aminoquinolinium Perchlorate* **10b**.—This was prepared from compound **10a** by a method similar to that mentioned above.[28] The crystalline compound **10b** had m.p. 132–134 °C; ν_{max}(Nujol)/cm^{-1} 3330, 3250, 3080, 1640, 1590, 1570, 1510, 1400, 1345, 1285, 1245, 1220, 1180, 1150, 1060–1100, 970, 815, 770, 720, 625, 610, 535, 520 and 470 (Found: C, 44.55; H, 3.8; N, 11.45. $C_9H_9ClN_2O_4$ requires C, 44.2; H, 3.7; N, 11.45%).

1-*Amino*-2,2′-*bipyridinium Mesitylenesulphonate* **11**.[23]—A solution containing *O*-mesitylenesulphonylhydroxylamine (12.7 mmol) in CH_2Cl_2 (15 cm^3) was slowly added dropwise to a stirred solution of 2,2′-bipyridyl (25.4 mmol) in CH_2Cl_2 (15 cm^3). After addition of diethyl ether (30 cm^3) to the reaction mixture, the liquid product **11** was separated from the organic layer, and washed with diethyl ether; ν_{max}(neat)/cm^{-1} 3250, 3080, 2970, 2920, 1600, 1585, 1470, 1450, 1430, 1405, 1380, 1210, 1180, 1090, 1015, 855, 775, 745, 720 and 680; δ_H($CDCl_3$) 2.2 (3 H, s, 4-Me of Mss), 2.7 (6 H, s, 2- and 6-Me of Mss), 6.9 (2 H, s, ArH of Mss), 7.4–9.0 (8 H, m, bipyridinyl H) and 9.3–9.6 (2 H, br, NH_2); δ_C($CDCl_3$) 20.8 (4-Me of Mss), 23.0 (2- and 6-Me of Mss), 126.1, 126.2, 127.1 and 129.0 (C-3′, -5′, -6′ and -4′), 130.5 (C-3 and -5 of Mss) and 136.9, 138.1, 138.8, 139.0, 140.1, 140.3, 143.2, 148.7 and 148.9 (C-6, -2′, -4 or -5, -5 or -4, -2/6 of Mss, -1 of Mss, -4 of Mss, -3 and -2) (Found: C, 61.65; H, 5.8; N, 11.0. $C_{19}H_{21}N_3O_3S$ requires C, 61.45; H, 5.7; N, 11.3%).

1-*Amino*-1,10-*phenanthrolinium Mesitylenesulphonate* **13**.[23]—This was prepared by the reaction of *O*-mesitylenesulphonylhydroxylamine with 1,10-phenanthroline by a method similar to that mentioned above. The product **13** had m.p. 174–176 °C; ν_{max}(Nujol)/cm^{-1} 3180, 3140, 1590, 1530, 1400, 1260, 1215, 1170, 1080, 1015, 855, 710 and 675; δ_H(D_2O) 2.25 (3 H, s, 4-Me of Mss), 2.7 (6 H, s, 2- and 6-Me of Mss), 4.7–5.3 (2 H, br, NH_2), 6.9 (2 H, s, ArH of Mss) and 7.7–9.4 (8 H, m, ArH); δ_C(D_2O) 20.0 (4-Me of Mss), 22.2 (2- and 6-Me of Mss), 124.0, 125.7 and 126.5 (C-9, -7 and -8), 130.3, 130.7, 131.9, 136.9, 137.4, 138.1, 139.7, 140.4, 146.8, 148.4 and 150.0 (C-6, -3/5 of Mss, -6a, -5, -4a, -3, -2/6 of Mss, -4, -4 of Mss, -10a, -2 and -10b) (Found: C, 64.1; H, 5.55; N, 10.45. $C_{21}H_{19}N_3O_3S$ requires C, 63.8; H, 5.35; N, 10.6%).

Photolyses of 1-*Aminopyridinium Mesitylenesulphonates* **1a**, **1e–k** *in TFA–Benzene or –Toluene*.—Photolyses of the sulphonates **1a**, **1e–k** were carried out externally in a quartz tube (25 cm × 1.8 cm) at room temperature after purging with dry nitrogen for 15 min. Detailed conditions are indicated in Table 2. After the reaction, aq. Na_2CO_3 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 (Wako C-300), and identified by comparison (IR and ^1H and ^{13}C NMR spectra) with authentic specimens. Pyridine derivatives (~70–80% yield) were isolated besides the products shown in Table 2, and decomposed gradually under the photoreaction conditions. The yields of products **2a–5a**, **6** and **7** were obtained by GLC analysis using column A. The yields and S_f-values for the formation of toluidines are shown in Table 2. The photolysis of compound **1a** in the presence of CH_2Br_2 or under atmospheric O_2 was carried out similarly, and the results are shown in Table 1.

Photoreactions of 1-*Aminopyridinium Mesitylenesulphonates* **1** *with Nitrobenzene, Anisole, Chlorobenzene or Mesitylene in the Presence of TFA*.—Photoreactions of substrates **1** with nitrobenzene, anisole, chlorobenzene and mesitylene were carried out in the presence of TFA under the conditions mentioned in Table 3. Isolation and characterisation of the products **3–5** were carried out by methods similar to those described above, and the yields of the products by GLC analysis using column A are shown in Table 3. However, the yield of 2-, 3- and 4-nitroaniline **3e**, **4e** and **5e** was determined by GLC analysis using column B.

Photolyses of 1-*Aminoquinolinium*, 1-*Amino*-2,2′-*bipyridinium*, 1,1′-*Diamino*-2,2′-*bipyridinium and* 1-*Amino*-1,10-*phenanthrolinium, Salts* **10–13** *in TFA–Benzene or –Toluene*.—Photolyses of compounds **10–13** were performed in arene–TFA under the conditions indicated in Table 4. Yields of the products **2–7** were determined as described above, and are shown in Table 4. Besides the products, quinoline, bipyridyl and 1,10-phenanthroline were isolated (~70–80% yield) and decomposed slowly under the photoreaction conditions. Hydrazinium ion (*m*/*z* 33) was not detected [but ammonium ion (*m*/*z* 18) *was* detected] by mass spectral analysis of the reaction mixture from the photolysis of bipyridinium salt **12**. Photolyses of compounds **11**, **12** and **13** were carried out similarly in the presence of CH_2Br_2 or under atmospheric O_2, and the results are shown in Table 4. Photolysis of compound **10b** in benzene–TFE or benzene–acetonitrile was also performed similarly, and the results are indicated in Table 2.

Photolyses of 1-(*Amino, Methylamino, Dimethylamino and Piperidino*)-2-*methyl*-4,6-*diphenylpyridinium Tetrafluoroborates* **1m**, **1n**, **1o** *and* **1p** *in PhX–TFA.*—Photolyses of substrates **1m–p** were performed under the conditions shown in Table 1. Isolation and characterisation of the products **2–9** were carried out as in the above photolyses. The yield (~70–95%) of 2-methyl-4,6-diphenylpyridine was determined by HPLC analysis. Yields of products **2–9** were obtained by GLC analysis using column A, and the results are summarised in Table 5. Photolysis of compound **1n** in benzene–HFP was also carried out similarly, and the results are shown in Table 5. We did not confirm the formation of 2-, 3-, 4-piperidinotoluene **3h**, **4h** and **5h** or *N*-mesityltoluidine **3i** by comparisons with standard materials, but there are no special GLC peaks except those of 2-methyl-4,6-diphenylpyridine, piperidine **9**, compound **7** or **8** in the reaction mixture from the photolysis of compound **1p** in TFA–toluene or –mesitylene. The results mean no formation of compounds **3h**–**5h** and **3i**.

Hammett Plot.—A solution (8.0 cm^3) containing compound **10b** (0.87 mmol) and an aromatic substrate (benzene and toluene, benzene and ethylbenzene or benzene and cumene) in the presence of TFA (47% v/v) was irradiated using a 500 W high-pressure Hg lamp for 4 h under conditions similar to those mentioned above after purging with dry N_2. The molar ratio of substrate **10b** to aromatic substrate was less than 1:100. After the reaction mixture had been treated as mentioned above, the ratios **2a**:**4a**, **2a**:**5a**, **2a**:3-ethylaniline, **2a**:4-ethylaniline and **2a**:4-isopropylaniline, were determined by HPLC analysis. The *para*-and *meta*-attacking partial rate factors (k_f) for toluene, ethylbenzene and cumene were calculated on the basis of the above product ratios, the initial concentration of the aromatic compound, the number of C–H bonds of benzene and of *para*- and *meta*-C–H bonds of the substituted aromatics. The product ratios did not vary upon treatment of a mixture of these products under the reaction conditions. The results are indicated in Fig. 1. The k_f-value for 3-isopropylaniline was not obtained because the compound was not commercially available.

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