Efficient Direct Aromatic Amination by Parent Nitrenium Ion. Photolyses of 1-Aminopyridinium and 1-Aminoquinolinium Salts and Effect of Crown Ethers

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Photolyses of 1-aminopyridinium salts 1a–f, 2-aminoisoquinolinium salt 2 and 1-aminoquinolinium salts 3a–f gave aniline 4 or a mixture of 2-, 3- and 4-toluidines 5a–7a in benzene–trifluoroacetic acid (TFA) or in toluene–TFA, respectively. The use of 1-aminoquinolinium perchlorate 3a showed the highest yield in these photolyses. Irradiation of 3a in the presence of ethylbenzene, *p*-xylene, mesitylene, anisole and chlorobenzene similarly yielded arylamines. The yields of arylamines were generally increased in the presence of a small amount of crown ether. The aromatic amination is discussed in terms of the intermediacy of a parent nitrenium ion.

We have reported the direct aromatic amination by ethoxycarbonylnitrenium ions,[1] arylnitrenium ions[2] and aryl-nitrenium–AlCl₃ complexes.[3] It has been assumed that a free parent nitrenium ion cannot bring about aromatic aminations because its singlet state, which is capable of undergoing this reaction, is immediately converted into the inert triplet ground state.[4]

By contrast, if the parent singlet nitrenium ion could interact with both an unshared electron pair on the heterocyclic nitrogen atom and the counter ion, it would be sufficiently stabilised to allow aromatic aminination, as a high enough singlet concentration would result from the increased singlet lifetime. A similar singlet stabilisation by its interaction with the unshared electron pair of the heteroatom has been reported in nitrene chemistry.[5] Thus we have found direct aromatic aminations by the parent nitrenium ion (interacting with the above both heterocyclic nitrogen and counterion) generated photochemically from 1-aminopyridinium, 1-amino-quinolinium, 1-amino-2,2'-bipyridinium, 1,1'-diamino-2,2'-bipyridinium, 1-amino-1,10-phenanthrolinium and S-amino-sulphonium mesitylenesulphonates in arene–TFA (trifluoro-acetic acid).[6–8] However the yields for these aminations were not high. The increase in the yields were not attained by the high stabilisation of the singlet nitrenium ion interacting with 2,2'-bipyridine, 1,10-phenanthroline, or a pyridine having an electron-donating group; such a high stabilisation increases the concentration of the singlet state of the nitrenium ion due to the long lifetime, but at the same time decreases the yield by a favourable competing S ⟶ T conversion.

Interestingly, as described in this paper, the usage of 1-amino-quinolinium perchlorate 3a provides a high yield for the aromatic amination and effective amination in the presence of 18-crown-6.

Results and Discussion

Photolyses of 1-Aminopyridinium, 2-Aminoisoquinolinium and 1-Aminoquinolinium Salts 1–3 in Benzene–TFA or in Toluene–TFA.—Photolyses of 1–3 in benzene–TFA and in toluene–TFA produced aniline 4 and 2-, 3- and 4-toluidines 5a–7a, respectively, as the aromatic amination compounds (Table 1 and Scheme 1). The compounds have been recognized as the products formed *via* the singlet nitreniumoid ion (see Scheme 1) which interacts with both the counter ion and the unshared electron pair of the heterocyclic nitrogen.[7,8] Biphenyl (a trace) and bitolyl 8 (a low yield) were formed as the triplet-derived products.[6–8] Obviously pyridines, isoquinoline and quinolines

Table 1 Photolyses[a] of 1-aminopyridinium, 2-aminoisoquinolinium and 1-aminoquinolinium salts 1–3 in benzene–TFA or in toluene–TFA

Salts	Substituent	Counter ion	Yield[b] (%) from PhH 4	from PhMe 5a	6a	7a	8	S_f
1a	None	ClO₄⁻	17	16	10	14	4.5	0.45
1b	2-OMe	ClO₄⁻	41	21	13	16	—	0.39
1c	4-CN	ClO₄⁻	16	25	14	44	2.3	0.80
2	None	ClO₄⁻	58	28	18	25	—	0.44
3a	None	ClO₄⁻	63	32	20	29	Trace	0.46
3a[c]	None	ClO₄⁻	68	33	21	31	—	0.47
3a[d]	None	ClO₄⁻	59	—	—	—	—	—
3b	4-Me	ClO₄⁻	61	31	18	32	—	0.55
3c	4-Cl	ClO₄⁻	45	21	14	24	—	0.54
3d	None	Mss⁻[e]	54	26	15	28	14	0.57
3e	4-Me	Mss⁻	54	21	11	25	—	0.66
3f	4-Cl	Mss⁻	44	20	9.4	16	—	0.53

[a] The photolyses of the salts (0.058 mol dm⁻³) were carried out in ArH (53% v/v)–TFA (47% v/v) for 4 h. [b] The yields are based on the initial salts 1–3 used. [c] The photolysis was done in a Pyrex tube instead of a quartz tube. [d] The photolysis was carried out using a 75 W low pressure Hg lamp (Toshiba GL lamp) for 24 h, the yield of 4 was not changed by irradiation for 48 h. [e] Mss = Mesitylenesulphonate.

(*ca.* 70–80% yield) were formed in the photolyses, but decomposed gradually under the photoconditions.

(a) Efficient Amination using 1-Aminoquinolinium Perchlorate 3a.—The photolyses of quinolinium and isoquinolinium per-chlorates 3a–c and 2 gave a high yield of 4 and 5a–7a compared with those from the pyridinium perchlorates 1a–c (Table 1). The trace yield of the triplet-derived product 8 from the quinolinium perchlorate 3a was lower than that from the other salts (Table 1). This indicates that the singlet nitrenium ion is formed, without contamination by the triplet nitrenium ion, in the photolysis of 3a. The quinolinium and isoquinolinium salts have absorption bands at longer wavelengths than the pyridinium salts. The photolysis of 3a in a Pyrex tube which transmits only wavelengths above λ *ca.* 300 nm gave somewhat high yields of 4 and 5a–7a as compared with those in the photolysis in a quartz tube (Table 1). Further the photolysis of 3a using a low pressure lamp (λ 244 nm irradiation) resulted in a slightly lower yield of 4 (Table 1). These results imply that the absorption-energy on photolysis plays an important role in the aromatic efficiency.
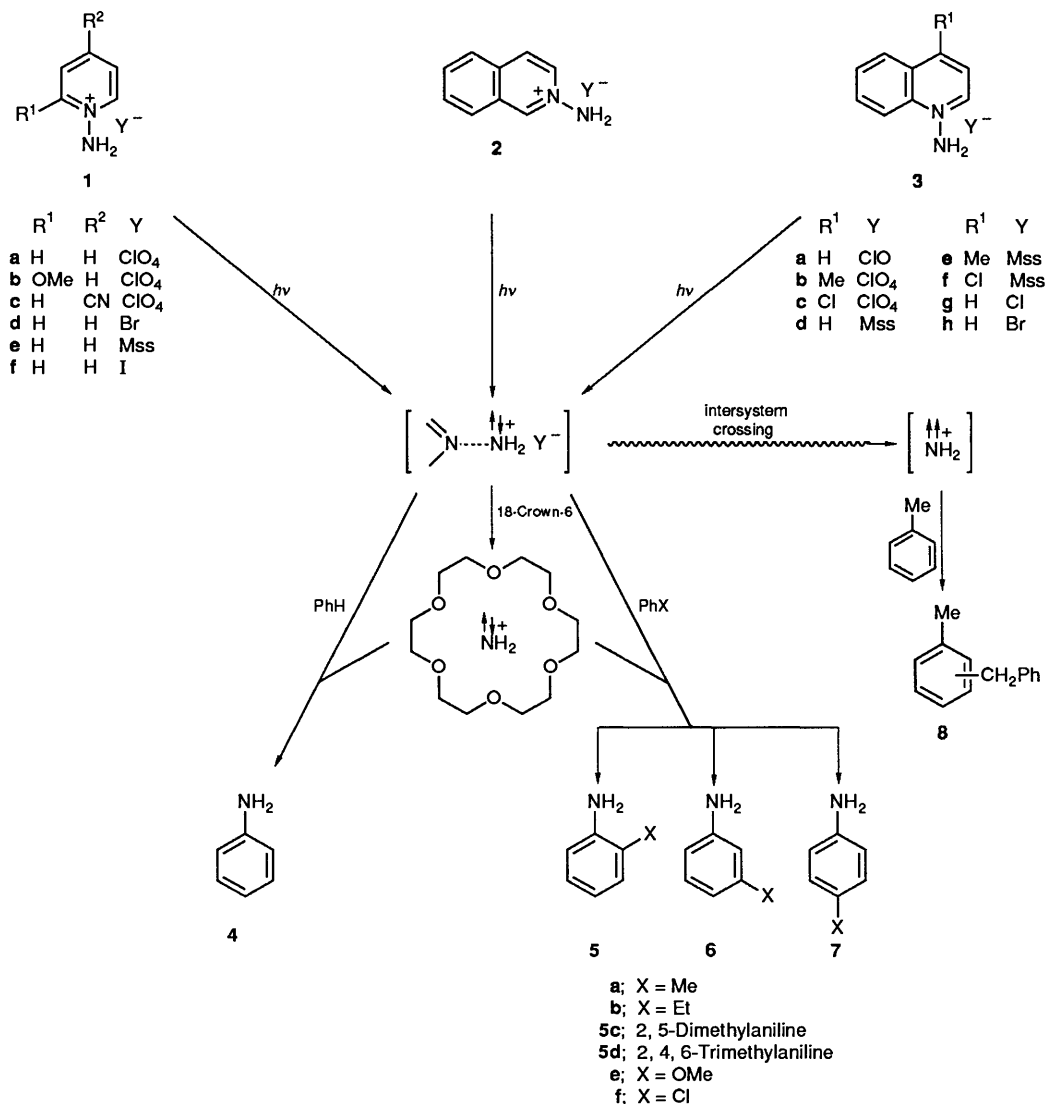
Scheme 1

The excess of energy of the singlet nitrenium ion or heterocyclic compounds generated on the irradiation seems to affect the efficiency of the interaction of the nitrenium ion with heterocyclic nitrogen or counter ion, but the details of this are now under investigation.

(*b*) *Effect of Interactions with the Heterocyclic Nitrogen on* S_f.—The selectivity factors S_f, $\log[(2 \times \%para)/(\%meta)]$, for the formation of toluidines vary in a similar manner to those for the photolysis of pyridinium perchlorates 1a–c; *i.e.* increasing with a decreased basicity (by electron-withdrawing groups such as CN) of pyridines, and decreasing with an increased basicity (by methoxy groups) of pyridines; 1c > 1a > 1b (Table 1). The results agree well with those for the photolyses of 1-aminopyridinium mesitylenesulphonates.[8] However the S_f for the photolysis of quinolinium salts 3a–f was less sensitive to the basicity of quinolines, and tended to increase slightly with the enhanced basicity (Table 1).

We assumed that for the substituent-effect for the pyridinium salts a smaller charge-transfer from a less basic pyridine to the nitrenium ion gives the nitrenium ion possessing a more positive charge, resulting in a higher S_f by the stronger interaction between the nitrenium ion and the counter ion.[8] We have no evidence to explain the S_f of quinolinium salts at the present, but it seems to derive from the weaker quinoline–nitrenium ion

interaction compared to the pyridine–nitrenium ion interaction (the weaker interaction is described later); the weaker interaction would not greatly perturb the nitrenium ion–counter ion interaction.

(*c*) *Effect of Substituent at Pyridine or Quinoline Ring on the Amination Yield.*—The variation in the yields of 4 and 5a–7a in the photolysis of substituted 1-aminopyridinium perchlorates 1a–c follows no regular pattern (Table 1).
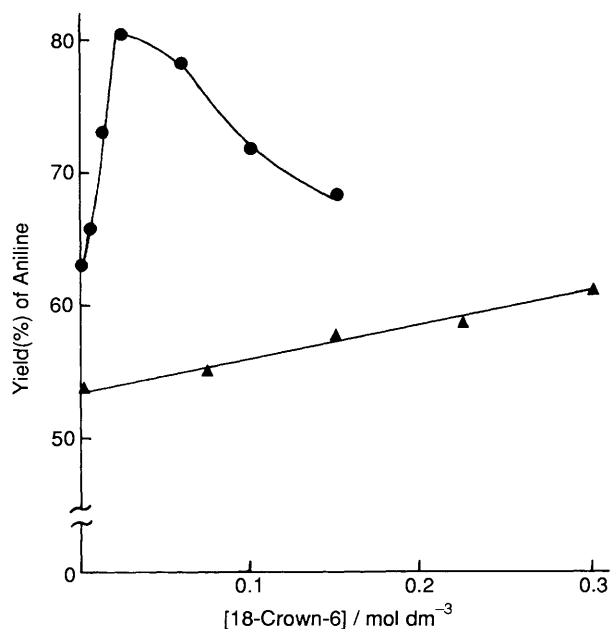
In the photolyses of quinolinium perchlorates 3, the substituent-effect on the amination yields was smaller than that for the photolyses of the pyridinium perchlorates (Table 1) because the interaction of the nitrenium ion with quinoline is weaker than that with pyridine as described below; the perturbation of the weaker interaction by subsituents may give a weaker effect. In the photolyses of quinolinium mesitylene-sulphonates 3d–f, the substituent effect on the yields is similar to that in the photolyses of quinolinium perchlorates 3a–c.

Effect of Counter Ions.—Since the usage of the quinolinium salt 3a gave very high aromatic amination as described above, we investigated the effect of counter ions on the amination using various quinolinium salts. The yield of 4 or the total yield of 5a–7a tends to increase with a decrease in a localized charge of the counter ion; the order for the magnitude of yields is 3a >

Table 2 Effect of counter ion on the photolyses of 1-aminopyridinium and 1-aminoquinolinium salts 1 and 3 (0.058 mol dm⁻³) in benzene (67% v/v)–TFA (33%) or in toluene (53% v/v)–TFA (47% v/v) for 4 h

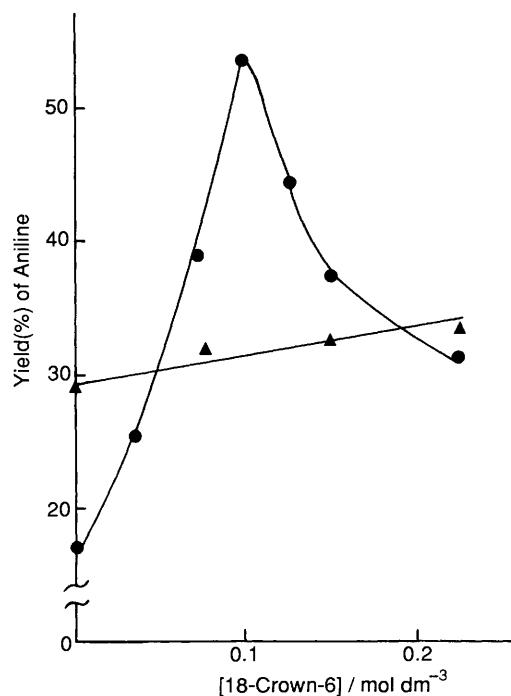| | | Yield[a] (%) | | | | |
| | | from PhH | from PhMe | | | |
Salts	Counter ion	4	5a	6a	7a	S_f
1d	Br⁻	—	13	6.4	12	0.57
1e	Mss⁻	30	20	9.5	14	0.47
1a	ClO₄⁻	17	16	10	14	0.45
1f	I⁻	—	17	7.9	4.0	0.00
3g	Cl⁻	39	18	9.8	23	0.67
3h	Br⁻	45	12	8.4	18	0.63
3d	Mss⁻	54	26	15	28	0.57
3a	ClO₄⁻	61	32	20	29	0.46

[a] The yields are based on the salts 1 and 3 which are used.

Fig. 1 Effect of 18-crown-6 on the yield of aniline 4 in the photolysis of 1-aminoquinolinium perchlorate 3a (●) or 1-aminoquinolinium mesitylenesulphonate 3d (▲) in benzene (53% v/v)–TFA (47% v/v)

Fig. 2 Effect of 18-crown-6 on the yield of aniline 4 in the photolysis of 1-aminopyridinium perchlorate 1a (●) or 1-aminopyridinium mesitylenesulphonate 1e (▲) in benzene (53% v/v)–TFA (47% v/v)

3d > 3g (Table 2), and the order of the charge is Cl⁻ > Mss⁻ > ClO₄⁻. In this case, we did not consider the photolysis of 3h which has Br⁻ because of the heavy-atom effect. The effect of the counter ion suggests that the weaker the interaction of the nitrenium ion with the counter ion, the higher the reactivity (i.e. the lower S_f); of course, a counter ion such as ClO₄⁻ with a low localized charge has a high reactivity (i.e. a low S_f) and gives high yields for the amination. In fact, the S_f values decreased with the decreased localized charge; Cl⁻ > Br⁻ > Mss⁻ > ClO₄⁻ (Table 2).

In the photolyses of 1-aminopyridinium salts 1a, and 1d–f, the S_f values also decreased with decreasing localized charge of the counter ion; Br⁻ > Mss⁻ > ClO₄⁻ > I⁻, but, at the present time, we cannot explain the lower yields of 4 and 5a–7a from 1a compared to those from 1e.

Effect of Crown Ether.—The effect of 18-crown-6 on the yield of aniline 4 was examined in the photolysis of 1-aminoquinolinium mesitylenesulphonate 3d and perchlorate 3a. In the photolysis of 3d, the yield increased very gradually with an increased concentration of the crown ether (Fig. 1). However, in

the photolysis of 3a, the yield of 4 increased from 63 to 81% by the addition of a very small amount of the crown ether (0.025 mol dm⁻³). Further addition decreased the yield (Fig. 1). The effect of the crown ether in the photolyses of pyridinium perchlorate and mesitylenesulphonate 1a and 1e was similar to that in the photolyses of 3a and 3d, respectively (Fig. 2). However, the photolysis of 3a compared with that of 1a showed that the former gave the higher maximum yield of 4 and the maximum yield by the smaller addition of the crown ether (Figs. 1 and 2). The results mean that the greatest effect of crown ether appears using ClO₄⁻ instead of Mss⁻ or using quinolinium salt in place of pyridinium salt. The formation of a complex between the singlet nitrenium ion and the crown ether may occur favourably when the singlet nitrenium ion interacts weakly with both the counter ion and the heterocyclic nitrogen. Therefore the results indicate that ClO₄⁻ should interact with the nitrenium ion more weakly than should Mss⁻, and that the nitrenium ion would interact weakly with quinoline compared with pyridine. The weaker interaction of ClO₄⁻ is also described above. Quinoline is only slightly weaker as a base than is pyridine in solution. We assume that quinoline would be a much weaker base than pyridine under the conditions where the interaction occurs intimately without participation of solvent.

Any addition of the crown ether greater than that showing the maximum yield, lowered the yield of 4 (Figs. 1 and 2). This indicates that a sandwich complex of one nitrenium ion with two crown ether is less reactive due to steric crowding.

The photolysis of 3a in the presence of crown ether showed the following maximum yield of 4: 18-crown-6 (0.025 mol dm⁻³); 81%, 15-crown-5 (0.025 mol dm⁻³); 91%, and 12-crown-4 (0.010 mol dm⁻³); 75%. This shows that the inclusion size of 15-crown-5 is suitable for the formation of the complex with the singlet nitrenium ion.

In the photolysis of 3a, the yield of 4 was decreased from 63% to 40% in the presence of O₂ (Table 3). This can be interpreted by the S→T conversion by the oxygen catalyst.[8] The effect of O₂ was much greater in the presence of 18-crown-6; the yield was lowered from 78 to 27% in the presence of O₂ (Table 3). If O₂

Table 3 Effect of 18-crown-6 on the photolysis of 1-aminoquinolinium perchlorate **3a** (0.058 mol dm^{-3}) in ArH (53% v/v)–TFA (47% v/v) for 4 h

ArH	[18-Crown-6]/ mol dm^{-3}	Yield[a] (%) from PhH 4	from Arene 5	6	7	S_f
Benzene	0.0	63				
Benzene	0.050	78				
Benzene	0.025	81				
Benzene	0.0	40[b]				
Benzene	0.050	27[b]				
Toluene	0.0		32	20	29	0.46
Toluene	0.050		31	21	21	0.38
Ethylbenzene	0.0		29	20	32	0.51
Ethylbenzene	0.050		29	22	31	0.45
p-Xylene	0.0		60			
p-Xylene	0.050		62			
Mesitylene	0.0		77			
Mesitylene	0.050		80			
Ansole	0.0		28	1.6	15	1.3
Anisole	0.050		31	5.3	19	0.86
Chlorobenzene	0.0		30	12	30	0.70
Chlorobenzene	0.030		28	13	29	0.65

[a] The yields are based on **3a** used. [b] The yield means that in the photolysis under atmospheric O_2.

catalyses more favourably the S→T conversion of more stabilised singlet nitrenium ions,[8] the larger decrease in yield in the presence of both O_2 and the crown ether suggests that the complex should be highly stabilized with a long lifetime as compared with the singlet intermediate before complexing with crown ether; this also supports the formation of the complex of the singlet nitrenium ion with the crown ether.

Aromatic aminations of toluene, ethylbenzene, p-xylene, mesitylene, anisole and chlorobenzene were carried out in the photolysis of **3a** in the absence or presence of 18-crown-6 (0.03–0.05 mol dm^{-3}) (Table 3). 2-, 3- and 4-Ethylanilines **5b–7b**, 2,5-dimethylaniline **5c**, 2,4,6-trimethylaniline **5d**, 2-, 3- and 4-anisidines **5e–7e** and 2-, 3- and 4-chloroanilines **5f–7f** were formed from toluene, ethylbenzene, p-xylene, mesitylene, anisole and chlorobenzene, respectively (Table 3 and Scheme 1). With the substrates such as alkylbenzenes, anisole and chlorobenzene, the reaction showed a slightly enhanced yield and somewhat lowered S_f in the presence of the crown ether (Table 3). The lowered S_f presumably arises from the higher reactivity of the complex compared to the singlet intermediate before complexing because the complex does not have the counter ion. The great effect of the crown ether on the reaction with benzene compared to the other aromatics is not ambiguous at the present time.

The high yield for the reaction with chlorobenzene relative to benzene is interesting, and the mechanistic detail is now under investigation.

Experimental

IR spectra were recorded using a Hitachi EPI-G3 spectrometer. GLC analyses were performed with a Shimazu GC-6A chromatograph using a glass column (2 m × 3 mm) packed with 10% polyethylene glycol (20M) on Chromosorb WAW DMCS (60–80 mesh). Replicate GLC analysis (within ±2%) was used to determine product yields. Photolyses were carried out for 4 h at room temp. externally in a quartz tube (25 × 1.8 cm) with a 500 W high pressure Hg lamp (Eikosha EHB-W-500) after purging with dry nitrogen gas for 15 min.

Benzene, toluene, ethylbenzene, p-xylene, mesitylene, anisole,

chlorobenzene, pyridine and quinoline were purified by standard methods before use. 2-Methoxypyridine, 4-cyanopyridine, isoquinoline, 4-methylquinoline, 4-chloroquinoline, o-, m- and p-toluidines **5a–7a**, 2-, 3- and 4-ethylanilines **5b–7b**, 2,5-dimethylaniline **5c**, 2,4,6-trimethylaniline **5d**, 2-, 3- and 4-anisidines **5e–7e**, 2-, 3- and 4-chloroanilines **5f–7f**, 18-crown-6, 15-crown-5 and 12-crown-4 were reagent grade (Wako), and used without further purification. Trifluoroacetic acid (TFA) was purified by distillation before use.

The following compounds were prepared by the methods described in the literature: 1-aminopyridinium perchlorate **1a**,[8] 1-amino-4-cyanopyridinium perchlorate **1c**,[8] 1-aminopyridinium bromide **1d**,[8] 1-aminopyridinium mesitylenesulphonate **1e**,[10] 1-aminopyridinium iodide **1f**,[11] 1-aminoquinolinium perchlorate **3a**[8] and 1-aminoquinolinium mesitylenesulphonate **3d**.[10]

The following new compounds were synthesized by the methods similar to those described in the literature.

1-Amino-2-methoxypyridinium perchlorate **1b**. A concentrated solution of 1-amino-2-methoxypyridinium mesitylenesulphonate[8] in ethanol was treated with 60% $HClO_4$,[8] and the white product **1b** (m.p. 54–55 °C) was precipitated by addition of ether; v_{max}(Nujol)/cm^{-1} 3310, 3270, 3070, 1600, 1510, 1320, 1230, 1050–1090, 770, 730, 625, 540, 505 and 440 (Found: C, 32.4; H, 3.9; N, 12.25. $C_6H_9ClN_2O_5$ requires C, 32.1; H, 4.05; N, 12.45%).

2-Aminoisoquinolinium perchlorate **2**. The title compound was synthesized from 2-aminoisoquinolinium mesitylenesulphonate by a method similar to that above. The white crystalline *product* **2** (m.p. 162–163 °C) obtained had v_{max}(Nujol)/cm^{-1} 3310, 3230, 3150, 1665, 1550, 1500, 1390, 1350, 1280, 1190, 1185, 1155, 1135, 1070–1090, 970, 935, 890, 870, 815, 620 and 470 (Found: C, 44.1; H, 3.8; N, 11.35. $C_9H_9ClN_2O_4$ requires C, 44.2; H, 3.7; N, 11.45%).

1-Amino-4-methylquinolinium perchlorate **3b**. The title compound was prepared from 1-amino-4-methylquinolinium mesitylenesulphonate **3e** (see below) by a method similar to that above. The white crystalline *product* **3b** had m.p. 222–223 °C; v_{max}(Nujol)/cm^{-1} 3310, 3230, 3070, 1610, 1580, 1515, 1400, 1370, 1290, 1260, 1240, 1185, 1155, 1070–1090, 990, 950, 840, 770 and 625 (Found: C, 46.3; H, 4.35; N, 10.7. $C_{10}H_{11}ClN_2O_4$ requires C, 46.45; H, 4.3; N, 10.85%).

1-Amino-4-chloroquinolinium perchlorate **3c**. The title compound was synthesized from 1-amino-4-chloroquinolinium mesitylenesulphonate **3f** (see below) by a method similar to that above, and the white crystalline *compound* **3c** (m.p. 199–200 °C) was obtained; v_{max}(Nujol)/cm^{-1} 3320, 3230, 3070, 1610, 1565, 1510, 1270, 1250, 1215, 1180, 1155, 1070–1090, 1030, 980, 930, 840, 775, 725, 670 and 630 (Found: C, 39.0; H, 2.75; N, 9.95. $C_9H_8ClN_2O_4$ requires C, 38.75; H, 2.9; N, 10.05%).

1-Amino-4-methylquinolinium mesitylenesulphonate **3e**. This compound was prepared by a method similar to a literature method.[9] White crystals, m.p. 149–150 °C; v_{max}(Nujol)/cm^{-1} 3220, 3110, 3090, 1630, 1615, 1600, 1520, 1400, 1310, 1245, 1175, 1150, 1080, 1010, 850, 825, 780, 765, 675, 580 and 550 (Found: C, 63.8; H, 6.4; N, 7.45. $C_{19}H_{22}N_2O_3S$ requires C, 63.65; H, 6.2; N, 7.8%).

1-Amino-4-chloroquinolinium mesitylenesulphonate **3f**. The title compound was prepared by a method similar to a literature method.[9] The white crystalline compound has m.p. 158–159 °C; v_{max}(Nujol)/cm^{-1} 3370, 3200, 3070, 1635, 1605, 1580, 1520, 1400, 1250, 1220, 1170, 1085, 1010, 940, 850, 830, 765, 720, 680, 660, 580, 550 and 530 (Found: C, 56.9; H, 5.4; N, 7.2. $C_{18}H_{19}ClN_2O_3S$ requires C, 57.05; H, 5.05; N, 7.4%).

1-Aminoquinolinium chloride **3g**. A concentrated solution of 1-aminoquinolinium mesitylenesulphonate **3d** in ethanol was treated with 36% HCl, and the white crystalline *compound* **3g** which contains one molecule of water of crystallization had m.p. 181–182 °C; v_{max}(Nujol)/cm^{-1} 3190, 3080, 1635, 1590, 1530, 1405,

1265, 1205, 1190, 1145, 1065, 960, 940, 855, 815, 780, 710 and 530 (Found: C, 54.3; H, 5.6; N, 14.2. $C_9H_9ClN_2$ + H_2O requires C, 54.4; H, 5.6; N, 14.1%).

1-*Aminoquinolinium bromide* **3h**. A solution of the corresponding mesitylenesulphonate **3d** in ethanol was treated with 48% HBr, and the white crystalline *product* **3h** had m.p. 180–182 °C; v_{max}(Nujol)/cm^{-1} 3350, 3060, 1630, 1580, 1510, 1400, 1285, 1210, 1180, 1150, 1140, 1100, 1065, 950, 920, 855, 805, 770, 710, 580, 540 and 525 (Found: C, 47.9; H, 3.9; N, 12.45. $C_9H_9BrN_2$ required C, 48.05; H, 4.05; N, 12.45%).

Photolyses of 1-*Aminopyridinium*, 2-*Aminoisoquinolinium and* 1-*Aminoquinolinium Salts* **1–3** *in Benzene–TFA or in Toluene–TFA.*—A solution containing TFA (7.0 cm^3) and arene (8.0 cm^3) was irradiated under the photochemical conditions shown in Table 1. After the reaction, aqueous 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, **4**, **5a–7a** and **8** were isolated by column chromatography on silica gel (Wakogel C-300), and identified by comparison (IR and ^{1}H and ^{13}C NMR spectra) with authentic specimens. The yield of the products was determined by GLC analysis. The irradiation for 4 h results in decomposition of almost all of the starting salt, and the products did not decompose under the photochemical conditions. The yields of the products and S_f values are summarized in Table 1.

Effect of Counter Ion on the Photolyses of 1-*Aminopyridinium and* 1-*Aminoquinolinium Salts* **1** *and* **3** *in Benzene–TFA or in Toluene–TFA.*—The photolyses of **1** and **3** which contained various counter ions were performed under conditions similar to those described above. The detailed conditions are shown in Table 2. The procedure of the isolation and characterization of the products **4** and **5a–7a** were performed as indicated above, and the yields of the products and S_f values are shown in Table 2.

Effect of Crown Ethers on the Photolyses of 1-*Aminopyridinium and* 1-*Aminoquinolinium Salts* **1** *and* **3** *in ArH–TFA.*—The photolyses of 1-aminoquinolinium perchlorate and mesitylenesulphonate **3a** and **3d** in benzene (8.0 cm^3)–TFA (7.0 cm^3) were carried out in the presence of various amounts of 18-crown-6 as shown in Fig. 1. Each reaction mixture was worked up as above and the yield of aniline **4** was determined by GLC analysis; the results are given in Fig. 1. The effects of 18-crown-6 on the photolysis of 1-aminopyridinium perchlorate and mesitylenesulphonate **1a** and **1e** were obtained by a method similar to that described above, and the results are shown in Fig. 2. The photolysis of 1-aminoquinolinium perchlorate **3a** in benzene

(8.0 cm^3)–TFA (7.0 cm^3) containing 18-crown-6 (0.050 mol dm^{-3}), 15-crown-5 (0.025 mol dm^{-3}) or 12-crown-4 (0.010 mol dm^{-3}) was performed as described above, and the yields of **4** obtained were 78, 91 or 75%, respectively. The photolysis of **3a** was carried out in arene–TFA both in the presence and absence of 18-crown-6 by a method similar to that described above. The detailed conditions are as shown in Table 3. The yields of the products **4** and **5–7** were obtained by a method similar to that shown above. The yields and S_f values are summarized in Table 3.

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