Direct Amination of Aromatic Compounds by Nitrenium and Alkylnitrenium Ions. Photolysis of 1-(Amino and alkylamino)-2-methyl-4,6-diphenylpyridinium Tetrafluoroborates in Aromatic Solvent–Trifluoroacetic Acid

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Photolyses of 1-(amino, methylamino, and dimethylamino)-2-methyl-4,6-diphenylpyridinium tetrafluoroborates in benzene or toluene in the presence of trifluoroacetic acid gave anilines or toluidines by an electrophilic aromatic substitution of the parent nitrenium ion and alkylnitrenium ions in singlet states.

It would be much simpler if aromatic amines could be produced by direct amination, and not *via* hydrogenation of the corresponding nitro compounds. Since the parent nitrenium ion $\overset{\cdot\cdot +}{N}H_2$ and alkylnitrenium ions have triplet ground states,[1] nitrenium ions cannot bring about an aromatic amination, but usually undergo deprotonation (or 1,2-alkyl or 1,2-aryl migration) and hydrogen atom abstraction to give imines (or iminium ions) and amines, respectively.[1] The use of singlet alkylnitrenium ions for aromatic amination has not been reported presumably because they are converted into triplet nitrenium ions by intersystem crossing (ISC), or react with the substrate to give a complex mixture of products.

It has been reported that the aromatic amination can occur *via* a singlet phenylnitrenium ion generated thermally from phenyl azide[2] or 1-phenylamino-2-methyl-4,6-diphenylpyridinium salt[3] in the presence of trifluoroacetic acid (TFA). It has been proposed that a singlet ground state (S_0) of the phenylnitrenium ion is lower in energy than the triplet state (T_1), but the S_0 of the alkylnitrenium ion is generally higher in energy than its T_1.[1] Thus, it should be possible to form the S_0 of $\overset{\cdot\cdot +}{N}H_2$ and the alkylnitrenium ion by photolysis of 1-(amino and alkylamino)-2-methyl-4,6-diphenylpyridinium salts in the presence of TFA. The title photolysis reaction is the first direct amination by a singlet nitrenium ion.

1-(Amino, methylamino, and dimethylamino)-2-methyl-4,6-diphenylpyridinium tetrafluoroborates (**1a**—**c**), prepared using the method of Katritzky *et al.*,[4] were dissolved in benzene (71% v/v)–TFA (29% v/v), and the solution was irradiated externally in a quartz vessel at room temperature with a high-pressure Hg lamp after purging with dry N_2. After work-up with aqueous Na_2CO_3, aniline (**3a**), *N*-methylaniline (**3b**), and *N*,*N*-dimethylaniline (**3c**) were isolated along with 2-methyl-4,6-diphenylpyridine (**2**) (Table 1, Scheme 1). Similar photolyses of (**1a**) and (**1b**) in toluene (71% v/v)–TFA (29% v/v) produced 2-, 3-, and 4-toluidines (**4a**), (**5a**), and (**6a**) and *N*-methyl-2-, 3-, and 4-toluidines (**4b**), (**5b**), and (**6b**), respectively, together with (**2**) and toluene dimers (**8**) (Table 1, Scheme 1).†‡

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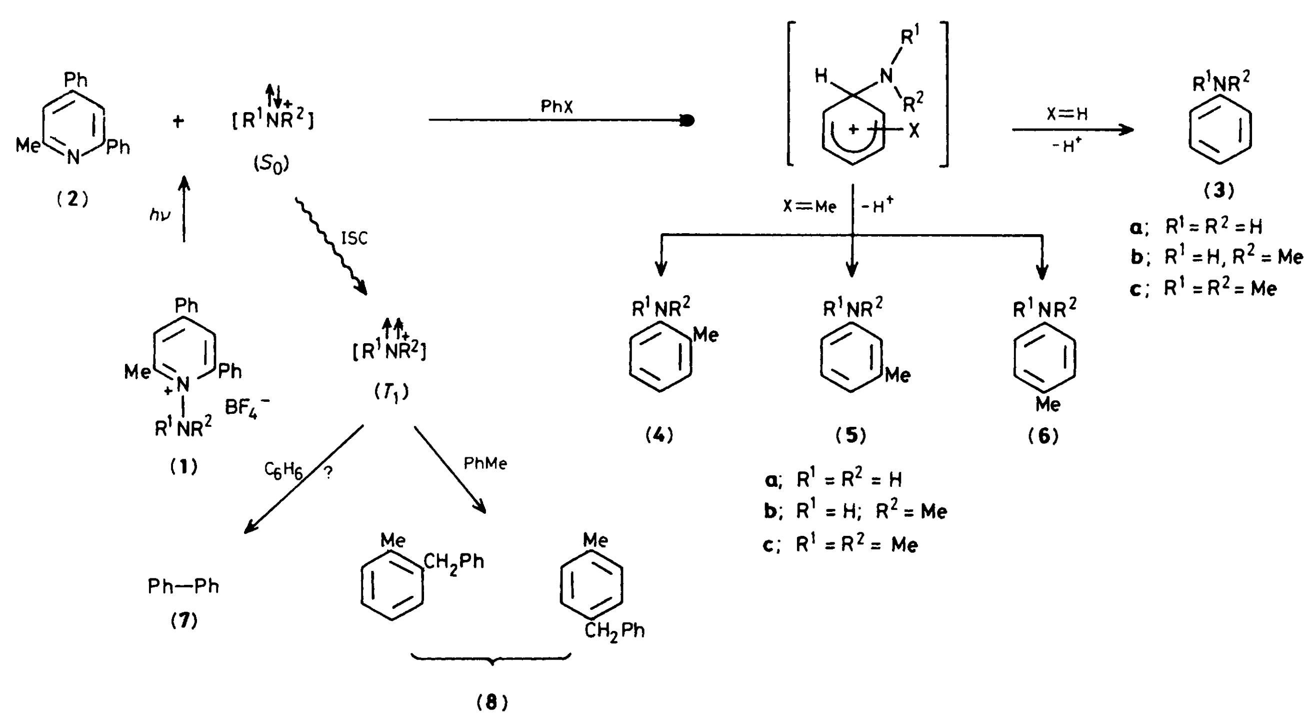
† Product (**8**) is a mixture of 2- and 4-benzyltoluenes. Because (**8**) is also formed in the reaction of triplet phenylnitrenium ion with toluene (see ref. 3), (**8**) may be regarded as a triplet product, although detection of the triplet products, ammonia, methylamine, and dimethylamine, was not attempted in the photolysis.

‡ The products were confirmed by i.r., ^1H and ^{13}C n.m.r., and mass spectroscopy, and the yields determined by g.l.c. or h.p.l.c. analysis.



Scheme 1

Table 1. Photolyses of (**1**) in aromatic solvents (PhX)–TFA.

Pyridinium salts	[(1)]/M	t/h	X in PhX	Yield^a (%) (2)	(3)	(4)	(5)	(6)	(7)	(8)
(**1a**)	0.025	20	H	59	60	—	—	—	0	—
(**1a**)	0.025	18	Me	82	—	29	13	25	—	23
(**1b**)	0.024	16	H	71	78	—	—	—	0	—
(**1b**)	0.036	17	Me	81	—	7	13	46	—	14
(**1c**)	0.023	20	H	62	24	—	—	—	0	—
(**1c**)	0.023	19	Me	99	—	0	0	Trace	—	85
(**1c**)^b	0.023	23	H	74	0	—	—	—	6	—

[a] The yield of (**2**) is based on (**1**) used, but yields of (**3**)—(**8**) are based on decomposed (**1**); this is nearly equal to the yield of (**2**). [b] HFP (33% v/v) was employed instead of TFA.

The yield of (3) and the total yield of (**4**—**6**) are lower from the photolysis of (**1c**) than in that of (**1a**) and (**1b**), but the yield of (**8**) is higher for (**1c**) (Table 1). Since (**8**)† is formed by hydrogen abstraction from toluene by the triplet nitrenium ion, the result provides evidence that (**3**—**6**) are formed *via* the singlet nitrenium ion, not the triplet one (see Scheme 1); a favourable $S \rightarrow T$ conversion§ of $\mathrm{Me_2\overset{\cdot\cdot+}{N}}$ rather than $\mathrm{\overset{\cdot\cdot+}{N}H_2}$ and $\mathrm{Me\overset{\cdot\cdot+}{N}H}$ results in the low yield of singlet products (**3c**—**6c**) and the high yield of the triplet product (**8**). A higher yield of (**3c**) than (**4c**—**6c**) is unexpected. One possibility is that the $S \rightarrow T$ conversion is promoted in toluene rather than in benzene because the triplet nitrenium ion is more reactive to toluene compared with benzene.

Partial rate factors (k_f), p_f and m_f for *para-* and *meta-*positions of both toluene and ethylbenzene and p_f of cumene were determined for the formation of aniline derivatives from (**1a**) under similar conditions to those mentioned above. The correlation between log k_f and σ^+ gives a good linear plot with ρ -2.1. The ρ value indicates that the aromatic amination giving (**3**—**6**) takes place *via* a nitrenium ion intermediate.

Both the low positional selectivity (*ortho-*, *meta-*, and *para-*direction shown above) and a low substrate selectivity (a smaller negative ρ value) suggest that the singlet $\mathrm{\overset{\cdot\cdot+}{N}H_2}$ or $\mathrm{Me\overset{\cdot\cdot+}{N}H}$ is highly reactive. The results contrast with those (selective formation of only *ortho-* and *para-*isomers and ρ *ca.* -5) for the singlet phenylnitrenium ion generated from phenyl azide[2] or pyridinium salt.[3] The contrasting result indicates that the singlet alkylnitrenium ion is of higher energy than the singlet phenylnitrenium ion. In view of the prediction[1] that S_0 of the former is energetically higher than the T_1 whereas S_0 of the latter is lower than the T_1, the singlet alkylnitrenium ion giving the amination products may be in S_0, not an excited singlet state S_1.

The value of ρ as -2.1 is more negative than that expected for aromatic amination by an amino radical. The photolysis of (**1c**) in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP)–benzene gave (**2**) in high yield along with biphenyl (**7**)¶ without work-up with aqueous Na_2CO_3 (Table 1). The formation of (**2**) excludes the homolysis of (**1**); if the homolysis occurs, a salt from a radical cation of (**2**) would be formed without contamination by (**2**). No formation of (**3c**) in the above

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§ The favourable $S \rightarrow T$ conversion presumably results from a low triplet–singlet energy gap or from an unfavourable formation of a σ-complex of $\mathrm{Me_2\overset{\cdot\cdot+}{N}}$ with the aromatic compound.

¶ A higher yield of (**7**) in the photolysis in HFP–benzene compared with that in TFA–benzene was also observed in the photolysis of 1-phenylamino-2-methyl-4,6-diphenylpyridinium salt (see ref. 3). The formation mechanism in HFP–benzene is ambiguous at present.

photolysis indicates a reaction of excited (**1**) with aromatic species to be impossible; such a reaction should produce (**3c**) in the photolysis in HFP–benzene as well as in TFA–benzene. Possible reasons for the lack of formation of (**3c**) are that the singlet nitrenium ion reacts with HFP to give some unidentified products, or is changed to the triplet nitrenium ion by a favourable *S* → *T* conversion.

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References

1 R. A. Abramovitch and R. Jeyaraman, 'Azides and Nitrenes,' ed. R. E. V. Scriven, Academic Press Inc., New York, 1984, p. 297—357.
2 H. Takeuchi, K. Takano, and K. Koyama, *J. Chem. Soc., Chem. Commun.*, 1982, 1254; H. Takeuchi and K. Takano, *ibid.*, 1983, 447; *J. Chem. Soc., Perkin Trans. 1*, 1986, 611.
3 H. Takeuchi, unpublished results.
4 A. R. Katritzky, P. Ballesteros, and A. T. Tomas, *J. Chem. Soc., Perkin Trans. 1*, 1981, 1495; A. R. Katritzky, R. C. Patel, and M. Shanta, *ibid.*, 1980, 1888.