Singlet Stabilisation of Parent Nitrenium Ion

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The parent nitrenium ion generated from *N*-aminopyridinium, *S*-aminosulphonium, or *N*-aminobipyridinium salts interacts with both the unshared electron pair of the heteroatom of pyridine, sulphide, or bipyridyl and the gegen anion by hydrogen bonding; the singlet nitrenium ion is stabilised by this interaction, and the stabilised singlet state undergoes fast singlet → triplet conversion in the presence of molecular oxygen or chlorine.

The metabolically activated forms of some carcinogens such as arylamines, *N*-arylhydroxylamines, and arylnitroso and arylnitro compounds are thought to have arylnitrenium ion structures,[1—3] and so studies on the reactivity of nitrenium ions are of great interest biochemically.

It has been reported that aromatic amination can occur *via* singlet phenyl- and parent-nitrenium ions, generated from phenyl azide[4] or 1-anilino-2-methyl-4,6-diphenylpyridinium salt[5] and 1-amino-2-methyl-4,6-diphenylpyridinium salt,[6] respectively, in the presence of trifluoroacetic acid (TFA). Such a direct aromatic amination is also the simplest method for obtaining aromatic amines which does not involve the corresponding nitro compounds.

The reactivity of the parent nitrenium ion generated from the *N*-aminopyridinium salts (**1**) in arene–TFA mixtures is influenced by the substituent on the pyridine ring of the salts (**1**) and by the nature of the gegen anion (Table 1). Electron-withdrawing groups (*e.g.* CN) on the pyridine ring and gegen anions capable of hydrogen bonding with the nitrenium ion increased the selectivity factor S_f [log (2 × % *para*/% *meta*)] for the formation of toluidines. It has been proposed that S_f values for S_N1 and S_N2 Friedel–Crafts alkylations are nearly 0.5 and 0.8, respectively.[7] The yields of β- and α-naphthylamines, and their relative proportions, are controlled by steric hindrance of the gegen anion and the pyridiyl unit. These data imply that the parent nitrenium ion generated in the first step is not free but interacts with both the unshared electron pair of pyridine and the gegen anion (Figure 1). This type of interaction retards the singlet–triplet (S → T) conversion to favour the singlet reaction. A similar interaction with the unshared electron pair of the heteroatom has been predicted in nitrene chemistry.[8]

The photolysis of the *S*-aminosulphonium salts (**2a**) and (**2b**) instead of the *N*-aminopyridinium salts (**1**) was carried out (Scheme 1). Compared with the photolysis of (**1**),[6] this gave low yields of the aromatic amination products, aniline (**3**) or 2-, 3-, 4-toluidines (**4a—c**), high yields of hydrogen-abstraction product such as biphenyl (**5**) or bitolyls (**6**), and low S_f values (Table 2). The sulphide unshared electron pair interacts more weakly with the nitrenium ion than that of

Table 1. Effects of the substituent on the pyridine ring and the gegen anion in the photolysis of pyridinium salts (**1**) in arene–TFA (30% v/v).

	Pyridinium salt (**1**)							
	R^1	R^2	R^3	R^4	R^5	X	S_f	β/α
a	Me	H	Ph	H	Ph	BF_4	0.60	2.1
b	H	H	H	H	H	I	0.49	
c	Me	H	H	H	H	I	0.42	
d	H	Me	H	Me	H	Mss[a]	0.49	2.8
e	H	H	CN	H	H	Br	0.69	0.8
f	H	H	CN	H	H	Mss	0.77	1.7
g	H	H	CO_2Me	H	H	Mss	0.77	

[a] Mss = mesitylenesulphonate ($2,4,6\text{-}Me_3C_6H_2SO_3^-$).

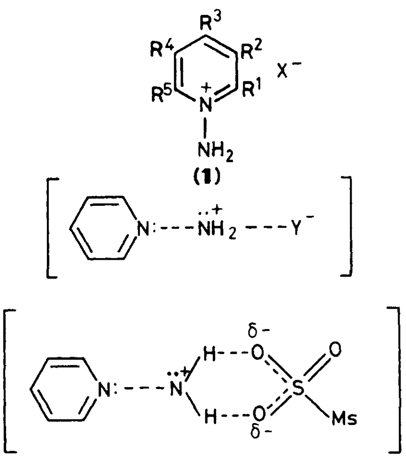
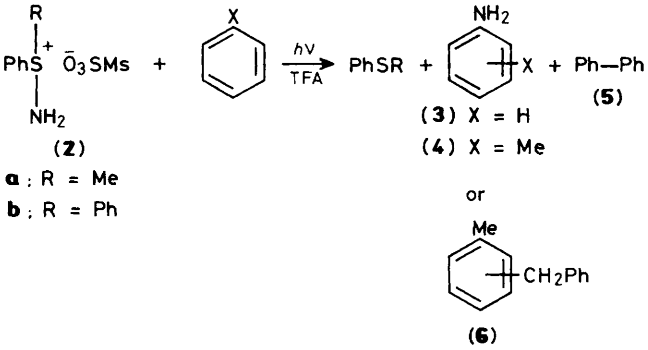


Figure 1. The interaction of the parent nitrenium ion with an unshared electron pair and hydrogen bonding. (Ms = mesityl).



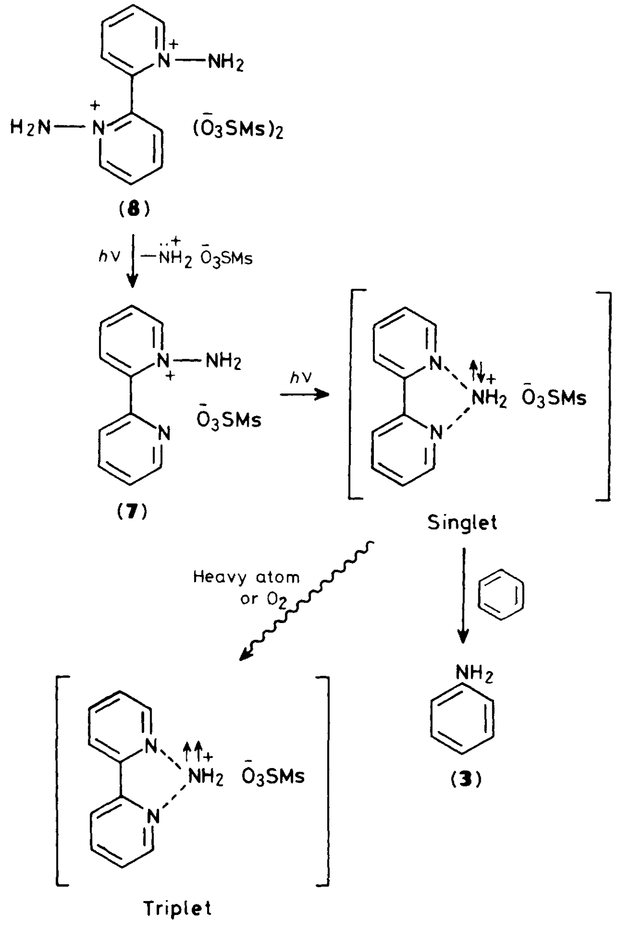
Scheme 1

Table 2. Photolysis of sulphonium salts (2) in arene(PhX)–TFA (30% v/v).

		Yield (%)							
(2)	X in PhX	(3)	(4a)	(4b)	(4c)	(5)	(6)	S_f	β/α
(2a)	H	10	—	—	—	1	—		
(2a)	Me	—	3.5	1.8	1.7	—	12	0.28	
(2b)	H	18	—	—	—	12	—		
(2b)	Me	—	7.8	4.1	5.3	—	14	0.41	6.8

pyridine because sulphides are less nucleophilic than pyridine. Therefore, the nitrenium ion from (**2**) may be subject to a more favourable S → T conversion than that from (**1**).

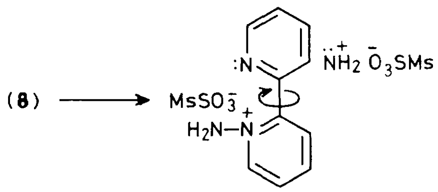
Singlet stabilisation by this type of interaction with an unshared electron pair was proved by the following experiment. The photolysis of the *N*-aminobipyridinium salt (**7**) in benzene–TFA produced (**3**) and (**5**). The yield of the singlet product, aniline (**3**), is markedly decreased in the presence of the heavy atom solvents dichloromethane or methyl iodide, and under atmospheric oxygen (Table 3). In the photolysis of *N*-aminopyridinium mesitylenesulphonate (**1h**), the yield of the singlet products, the toluidines (**4**), is greatly decreased in



Scheme 2

Table 3. Effects of heavy-atom solvent and oxygen on S → T conversion of parent nitrenium ion.

								Yield (%)			
Precursor	Atmosphere	Benzene /ml	Toluene /ml	TFA /ml	CH_2Cl_2 /ml	MeI /ml	CH_2Br_2 /ml	(3)	(4)	(5)	(6)
(**7**)	N_2	10	0	5	0	0	0	34	—	trace	—
(**7**)	N_2	10	0	5	1.8	0	0	3	—	trace	—
(**7**)	N_2	10	0	5	0	1.8	0	0	—	0.5	—
(**7**)	O_2	10	0	5	0	0	0	3	—	0	—
(**1h**)	N_2	0	10	5	0	0	0	—	50	—	20
(**1h**)	N_2	0	10	5	0	0	3	—	<1	—	58
(**1h**)	N_2	0	10	5	3	0	0	—	41	—	26
(**1h**)	O_2	0	10	5	0	0	0	—	13	—	25
(**2b**)	N_2	0	10	5	0	0	0	—	17	—	16
(**2b**)	N_2	0	10	5	0	0	3	—	<1	—	23
(**2b**)	N_2	0	10	5	3	0	0	—	11	—	23
(**2b**)	O_2	0	10	5	0	0	0	—	11	—	21



Scheme 3

the presence of dibromomethane, slightly decreased in the presence of dichloromethane, and considerably decreased in the presence of molecular oxygen (Table 3). In the photolysis of the *S*-aminosulphonium salt (**2b**), the yield of singlet products (**4**) is also greatly decreased in the presence of dibromomethane, and slightly decreased in the presence of dichloromethane or molecular oxygen (Table 3). The promotion of S → T conversion by molecular oxygen[9] and by dichloromethane, which contains a less 'heavy' atom than iodine or bromine atom indicates that the singlet nitrenium ion has a comparatively long lifetime. Considering the probability of collision for S → T conversion, and the longer lifetime of the singlet intermediate, the greater decrease in the singlet product occurs in the presence of chlorine or oxygen. Thus, the order of the lifetimes for the singlet nitrenium ion (S_0) is as follows: S_0 from (**7**) >> S_0 from (**1h**) > S_0 from (**2b**).

The longer lifetime of the nitrenium ion generated from (**7**) can be explained as follows. The interaction between the nitrenium ion and the unshared electron pairs of bipyridyl leads to a five-membered ring intermediate which stabilises the singlet state (Scheme 2). Singlet intermediates with a long lifetime may undergo fast S → T conversion even in the presence of chlorine or oxygen.

The yield of aniline, 20%, in the photolysis of *N,N'*-diaminobipyridinium salt (**8**) was lower than that (34%) in the photolysis of (**7**). This suggests that the nitrenium ion generated in the first step from (**8**) is converted into aniline in very low yield. This yield can be estimated to be 6% from: 2 × 20% − 34%. This low yield results from a lack of singlet stabilisation because of free rotation about C(2)—C(2') in the bipyridinium salt, and ionic repulsion between the nitrenium ion generated in the first step and the positive nitrogen atom of (**7**) formed from (**8**) decreases the extent of interaction between the nitrenium ion and the unshared electron pair to undergo a rapid S → T conversion (see Scheme 3). This also suggests the idea that interaction of the nitrenium ion with unshared electron pairs plays an important role in singlet stabilisation. Such an ionic repulsion is supported by the fact that the mass spectral analysis does not show the hydrazinium ion but it does show the ammonium ion. The singlet stabilisation by hydrogen bonding between the nitrenium ion and the gegen anion is under investigation.

There is no great increase in the triplet product in the presence of a heavy atom solvent or molecular oxygen. This means that the triplet nitrenium ion is converted into products besides (**5**) and (**6**) whose structure is not yet clear.

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