Pyridine *N*-Sulphides. Some Simple *N*-Arylthiopyridinium Salts and a Possible Source of Arylsulphenium Ions

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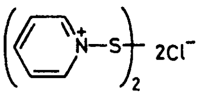
Summary *NN'*-Dipyridinium disulphide dichloride (**1**) and 1-(4-nitrophenylthio)pyridinium chloride (**5**) and its 4-NMe$_2$ derivative (**2**) have been synthesized and their structures established unambiguously; they undergo nucleophilic attack at sulphur rather than in the pyridine ring and the tetrafluoroborate from (**5**) serves as a possible source of 4-nitrophenylsulphenium ion which can attack anisole readily to give (**7**).

As we pointed out in an earlier paper,[1] virtually nothing is known about pyridine *N*-sulphides and *N*-thiopyridinium salts. Though the intermediacy of such compounds has been postulated a number of times[2] they have been isolated and characterised definitively in only a very few cases, such as in the case of isothiazolo[2,3-*a*]pyridinium salts.[1,3] Two other possible pyridine *N*-sulphide derivatives have been reportedly isolated but not formulated as such. The reaction of pyridine with sulphur monochloride was said to give a compound $S_2Cl_2.2C_5H_5N$ which was ionic.[4] Similarly, pyridine and sulphur dichloride in carbon tetrachloride have been said to give a crystalline product $SCl_2.2C_5H_5N$.[5] We have established (n.m.r. spectroscopy, microanalysis) that the former has structure (**1**) and is attacked by water at sulphur to give pyridine (89%), sulphur (19%), and SO_2.[6] We also report the synthesis and properties of the first fully isolated and characterised simple *N*-arylthiopyridinium salts.

Reaction of 4-dimethylaminopyridine with *p*-nitrobenzenesulphenyl chloride in dry CCl_4 and work-up of the precipitate formed under N_2 and anhydrous conditions (dry box) gave colourless 4-dimethylamino-1-(4-nitrophenylthio)pyridinium chloride (**2**) (72%) which still contained one molecule of water of crystallisation! On drying *in vacuo* at 60 °C it lost half a molecule of water of crystallisation, and at 80 °C it was obtained anhydrous.‡§ On exposure to air the compound turned yellow, probably owing to some hydrolysis to 4,4'-dinitrodiphenyl disulphide (**3**).

Similar reaction of *p*-nitrobenzenesulphenyl chloride with an excess of dry pyridine (dried over CaH_2 and distilled under N_2 in a dry box) under conditions as anhydrous as we could achieve gave 1-(4-nitrophenylthio)pyridinium chloride (**5**) (82%), m.p. 62—64 °C (decomp.),‡¶ as yellow-brownish crystals containing one molecule of water of crystallisation. When the compound was dried further in a nitrogen stream at room temperature it analysed for 3/4 H_2O of crystallisation. It could not be dried at higher temperatures because it underwent thermolysis readily. Indeed, sublimation of (**5**) *in vacuo* at 120 °C gave pyridine (62%), (**3**) (37%), and *p*-nitrobenzenesulphenyl chloride (**4**) (65%) [contaminated with sublimed (**5**)]. Compound (**4**) was recovered unchanged under similar conditions so that (**3**) must result from the thermolysis of (**5**) and not from (**4**).

Treatment of (**5**) with water led to the formation of pyridine hydrochloride (88%), (**3**) (47%), and (**6**) (49%).[7] Attempted nitration of (**5**) led only to the isolation of (**6**)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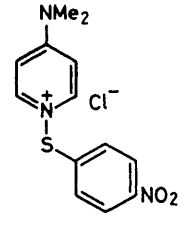
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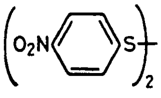
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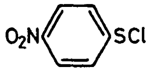
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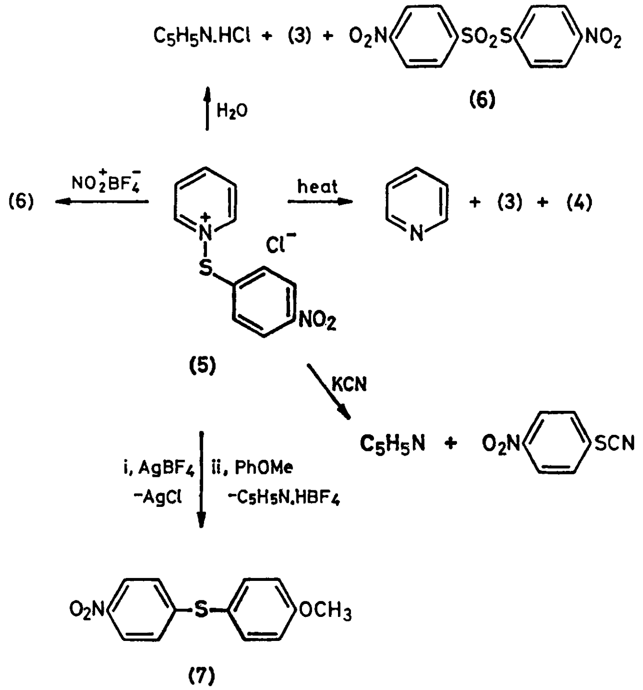

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‡ All new compounds gave microanalytical and spectral data consistent with their proposed structures.

§ ^{1}H N.m.r. ($CDCl_3$) δ 8·15 (d, 2H, $J_{\alpha,\beta}$ 8 Hz, H$_\alpha$), 8·09 (d, 2H, $J_{o,m}$ 6·5 Hz, H$_o$), 7·57 (d, 2H, $J_{\alpha,\beta}$ 8 Hz, H$_\beta$), 6·78 (d, 2H, $J_{o,m}$ 6·5 Hz, H$_m$), 3·25 (s, 6H, CH$_3$).

¶ ^{1}H N.m.r. ($CDCl_3$) δ 8·65 (d, 2H, $J_{\alpha,\beta}$ 4 Hz, H$_\alpha$), 8·25 (d, 2H, $J_{o,m}$ 8·3 Hz, H$_o$), 7·7—7·2 (m, 5H, H$_\gamma$, H$_\beta$, H$_m$). The spectrum was different from the sum of those of the starting materials.

(91%). Reaction of (**5**) with sodium azide, or with triethylamine in dry acetonitrile, or attempted photolysis in the presence of anisole gave only (**3**), some of which at least could have arisen from (**5**) or other products during work-up. Reaction of (**5**) with KCN in acetonitrile at room temperature gave *p*-nitrophenylthiocyanate (85%). Anion exchange with tetrafluoroborate or 2,4,6-trinitrobenzenesulphonate occurred readily but the products hydrolysed too easily to be isolated in pure form. The above results confirm that both proton bases and carbon nucleophiles prefer to attack the sulphur atom in (**5**) rather than the pyridine ring.

It was hoped that (**5**), like *p*-nitrophenoxypyridinium tetrafluoroborate which undergoes unimolecular thermolysis to generate the *p*-nitrophenyloxenium ion,[8] would undergo heterolysis to pyridine and the *p*-nitrophenylsulphenium ion, $O_2NC_6H_4S^+$. When (**5**) was heated in anisole at 180—200 °C for 2 h only (**3**) could be isolated on work-up. On the other hand, when (**5**) in MeCN was first treated with $AgBF_4$ and then with anisole at room temperature, 4-nitrophenyl 4′-methoxyphenyl sulphide (**7**)[9] (85%) and pyridinium tetrafluoroborate (89%) were isolated. It would appear, therefore, as though (**5**) (as the tetrafluoroborate) might indeed serve as a source of the sulphenium ion. Since, however, a more convenient and unambiguous source of this ion was found[10] no further applications of (**5**) were sought.

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