Nitration of pyridine by dinitrogen pentaoxide in sulfur dioxide: investigation of the reaction mechanism

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The nitration of pyridines with dinitrogen pentaoxide (DNP) in liquid sulfur dioxide has been investigated. ^1H NMR spectroscopy showed that a pyridinium–SO_2–DNP complex (**1**) was formed in SO_2. On reaction of the SO_2 solution with water, **1** reacted with nucleophiles present to give a 1,4-dihydropyridine complex (**2**). This reacted by a first-order reaction to give 3-nitropyridine or substituted nitropyridines. The reaction of **2** was unaffected by addition of sodium nitrate to the water solution and addition of $H^{15}NO_3$ did not result in any incorporation of $^{15}NO_2$ into 3-nitropyridine. The reaction showed no primary deuterium isotope effect. From this it was proposed that the reaction proceeded either by a tight ion pair or by a six-electron six-membered transition state (**3**).

We have reported the nitration of pyridine and substituted pyridines by dinitrogen pentaoxide (DNP) in liquid sulfur dioxide.[1] By this method, pyridine, methyl- and phenyl-substituted pyridines, quinoline and isoquinoline were nitrated in the pyridine ring with good yields. This represents the only method for direct nitration of the electron-deficient pyridine system. Other direct nitration methods give only traces of nitrated products.[2] We now describe some experiments pertinent to the mechanism of the nitration reaction.

We have earlier reported a few observations which suggested that the nitration by DNP–SO_2 was not a normal electrophilic aromatic substitution by NO_2^+: the reaction with 4-phenylpyridine gave 3-nitro-4-phenylpyridine and no nitration of the phenyl ring as obtained by HNO_3–H_2SO_4.[3] The 2,5-, 2,6- and 3,5-dimethylpyridines were not nitrated by DNP–SO_2, despite the fact that these compounds are activated towards electrophilic nitration by HNO_3–H_2SO_4.[4] Furthermore, *N*-nitropyridinium tetrafluoroborate did not react with pyridine to give 3-nitropyridine.[5]

We also presented evidence which indicated that a complex was formed between DNP–SO_2 and pyridine and that this complex reacted in the water phase used for quenching the reaction to give 3-nitropyridine eqn. (1).[1]

$$\mathrm{PyrH} + SO_2 + N_2O_5 \longrightarrow [\mathrm{PyrH}\cdot SO_2\cdot N_2O_5] \xrightarrow{H_2O} 3\text{-}NO_2\text{-}\mathrm{Pyr} + HNO_3 \qquad (1)$$

We now present further evidence for the structure of the complex in liquid SO_2 and also for the reaction of this complex in the water phase.

Results

Reaction in SO_2

The ^1H NMR spectral parameters for pyridine, 4-methylpyridine and 2,6-dimethylpyridine in CCl_4 and in SO_2 before and after addition of DNP are given in Table 1 together with those for some substrate hydrochlorides and *N*-methyl iodides. For convenience, the induced chemical shifts on dissolution of the substrates in SO_2 and on reaction with N_2O_5 are given in Table 2.

It is well known that pyridine forms a complex with SO_2. The geometrical parameters of this have been determined by microwave spectroscopy. The complex has been found to be weaker than those formed from SO_2 and aliphatic amines.[6] From Tables 1 and 2 the induced downfield shifts on dissolution of the pyridines in liquid SO_2 were not as large as those between the signals from pyridines and the corresponding pyridinium salts (Table 1).

On reaction of the pyridines with DNP in SO_2 solution, two points were observed in the ^1H NMR spectra. First, the signal pattern clearly showed that the reaction had taken place on the ring nitrogen atom alone. The number of signals and the coupling constants were all in agreement with *N*-substituted pyridinium complexes. Second, the induced shifts were much larger than those from the reaction with SO_2 alone and the shifts were significantly further downfield than those of simple pyridinium salts, both points in accordance with the formation of a complex of the pyridines with DNP–SO_2. When the SO_2 solution in the NMR tube was poured into water and the water phase worked up, the expected yield of 3-nitropyridine was obtained. The spectra in the SO_2 phase were therefore those of an intermediate in the nitration reaction, not of an artifact, *e.g.*, due to hydrolysis during the manipulation of the SO_2 solution.

The complexes formed were not the *N*-nitropyridinium salts as those would have shifts comparable to those of the pyridinium salts in Table 1: *N*-nitropyridinium tetrafluoroborate in SO_2 at -40 °C showed shifts at $\delta = 8.3$, 7.5 and 7.8 for H2, H3 and H4 respectively,[5] smaller than those observed for the complex of the pyridines and DNP in SO_2. From this it appears reasonable to assume that SO_2 was part of the complex and that it may be formulated as **1** in Scheme 1.

The complex **1** was formed in a rapid reaction. When pyridine was reacted with DNP–SO_2 for 10 min and 4-methylpyridine added to the solution, only 3-nitropyridine and unchanged 4-methylpyridine were isolated.[1] Furthermore, on reaction of 1,2-bis(4-pyridyl)ethane with DNP in SO_2 in a ratio 1,2-bis-(4-pyridyl)ethane/DNP = 2/1, a ratio of 1-(3-nitro-4-pyridyl)-2-(4-pyridyl)ethane/1,2-bis(3-nitro-4-pyridyl)ethane, that is mononitrated/dinitrated product, = 1.5 was obtained. This ratio was considerably lower than that expected from a statistical distribution (6.3), indicating the rate of reaction to be fast on the macroscopic mixing timescale.[7]

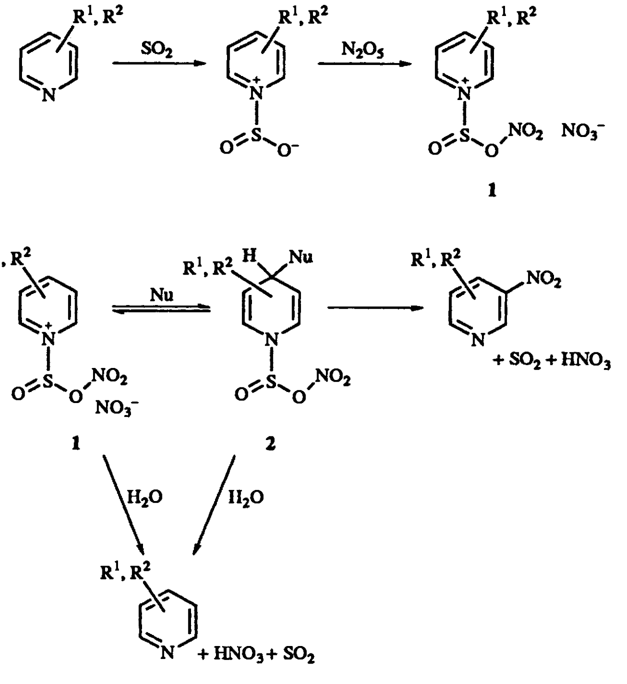
In conclusion on this point, on reaction of the pyridines with DNP in SO_2 an *N*-substituted complex was rapidly formed. No *C*-nitrated products were formed.

Table 1 ^1H NMR data for pyridine and methyl-substituted pyridines

	Chemical shift (ppm from TMS)						Coupling constants (Hz)	
Compound	H2	H3	H4	H5	H6	CH_3	$J_{2,3}$	$J_{3,4}$
PyrH–CCl_4	8.53	7.18	7.57	7.18	8.53		5.86	7.82
PyrH–SO_2	8.57	7.77	8.19	7.77	8.57		5.86	7.82
PyrH·HCl–SO_2	8.71	8.12	8.67	8.12	8.71		6.34	7.33
PyrH·MeI–SO_2	8.68	8.11	8.58	8.11	8.68	4.46		
PyrH·SO_3–SO_2	8.75	8.05	8.58	8.05	8.75			
PyrH–N_2O_5–SO_2	9.77	8.47	9.07	8.47	9.77		6.35	7.33
4-MePyr–CCl_4	8.35	6.98		6.98	8.35	2.32	5.86	
4-MePyr–SO_2	8.24	7.42		7.42	8.24	2.35	6.34	
4-MePyr·MeI–SO_2	9.16	7.89		7.89	9.16	2.69, 4.46		
4-MePyr–N_2O_5–SO_2	9.21	7.85		7.85	9.21	2.77	6.84	
2,6-diMePyr–CCl_4		6.81	7.32	6.81		2.44		7.81
2,6-diMePyr–SO_2		7.31	7.90	7.31		2.72		7.32
2,6-diMePyr–N_2O_5–SO_2		7.97	8.54	7.97		2.98		7.81

Table 2 Induced chemical shifts (ICS) for pyridine and methyl substituted pyridines ($\Delta\delta$ in ppm from spectra in CCl_4) in SO_2 solution and in SO_2-solution with added N_2O_5

	ICS, SO_2					ICS, N_2O_5–SO_2				
Compound	H2	H3	H4	H5	H6	H2	H3	H4	H5	H6
Pyridine	0.04	0.59	0.62	0.59	0.04	1.24	1.29	1.50	1.29	1.24
4-Methylpyridine	−0.11	0.44		0.44	−0.11	0.86	0.87		0.87	0.86
2,6-Dimethylpyridine		0.50	0.58	0.50			1.16	1.22	1.16	



1a, 2a: $R^1 = R^2 = H$
1b, 2b: R^1 = 4-Me, $R^2 = H$
1c, 2c: R^1 = 2-Me, R^2 = 6-Me

Scheme 1

Reaction in water

Pyridine. At the end of the reaction in SO_2, the pyridine–DNP–SO_2 mixture was poured into water. In Fig. 1 the ^1H NMR spectrum of such a solution in D_2O is shown. The spectrum was obtained *ca.* 15 min after the SO_2–D_2O mixing and at 20 °C. Several features are present in the spectrum. The pyridine–DNP–SO_2 complex from the SO_2 solution had disappeared almost completely, only traces were left as shown by the small signal at 9.96 ppm. This signal disappeared rapidly. In the region 8 ppm to 10 ppm, the signals were assigned to those of pyridinium and 3-nitropyridinium salts.

However, the strongest signals appeared as a doublet (J = 7.8 Hz) at 7.76 ppm, a doublet of doublets (J = 4.4 and 7.8 Hz) at 5.51 ppm and a triplet (J = 4.4 Hz) at 4.46 ppm. This set of signals could be assigned to a 1,4-dihydropyridine derivative (**2a**, Scheme 1). The triplet at 4.46 ppm was assigned to the proton at C4, the doublet of doublets at 5.51 ppm to those at C3 and C5 and the doublet at 7.76 ppm to the protons at C2 and C6. The chemical shifts and coupling constants are comparable to those of 1,4-dihydropyridine and *N*-alkyl or -aryl substituted 1,4-dihydropyridines except for a downfield shift indicating an electronegative substituent on the ring nitrogen atom.[8] We will return to the nature of the nucleophile Nu in Scheme 1.

The signals from the 1,4-dihydropyridine derivative **2** decreased and those from pyridine and 3-nitropyridine increased with time. No other signals appeared in the spectrum, compound **2** was transformed quantitatively into 3-nitropyridine and pyridine in a 1.3 : 1 ratio. By using the signal from Me_4Si as an internal standard it was possible to monitor the reaction of **2**. The signal at 7.76 ppm was used for this. The reaction followed a first-order rate law over three half-lives, $k_{obs} = 2.00(1) \times 10^{-2}$ min^{-1} at 22 °C; $0.28(2) \times 10^{-2}$ min^{-1} at 2 °C. The observed first-order rate constant for the reaction of **2a** was composed of two rate constants, one for the formation of 3-nitropyridine and one for the formation of pyridine. From this NMR experiment the ratio of these two constants was 57/43, close to the ratio 63/37 from the preparative run.[1]

4-Methylpyridine. On reaction of the 4-methylpyridine–DNP–SO_2 complex (**1b**) with D_2O, only the spectrum of **1b** together with the signals from traces of 4-methyl-3-nitropyridine and 4-methylpyridine were observed after 8 min reaction. Over *ca.* 3 h, the complex reacted to give a mixture of 4-methyl-3-nitropyridine and 4-methylpyridine in a 4 : 1 ratio. The reaction of the complex **1b** followed a first-order rate law, k_{obs} = $1.7(1) \times 10^{-2}$ min^{-1} at 25 °C; $1.0(1) \times 10^{-2}$ min^{-1} at 2 °C.

2,6-Dimethylpyridine. On quenching of the reaction mixture

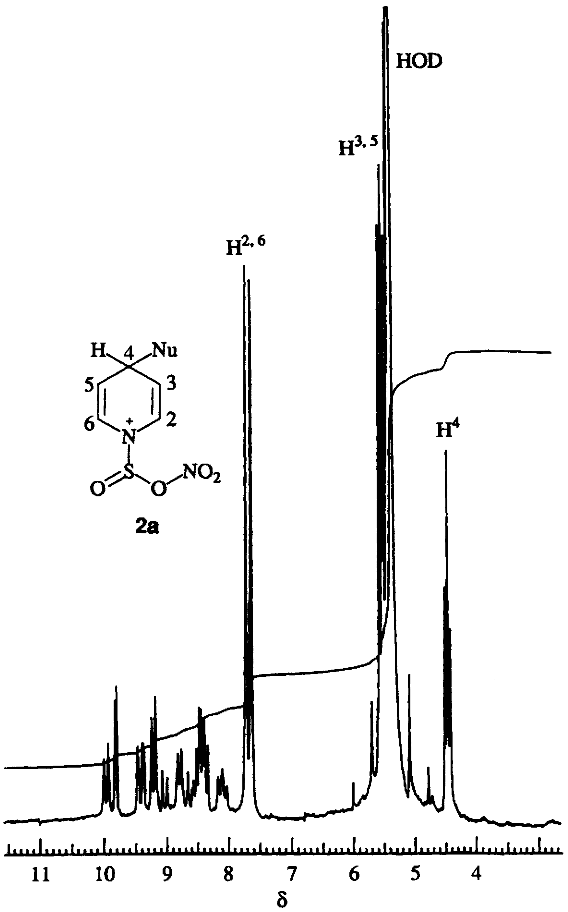


Fig. 1 ^1H NMR spectrum (100 MHz) of a pyridine–DNP–SO_2 complex (**1a**) poured into D_2O, 15 min after mixing

of 2,6-dimethylpyridine–DNP–SO_2 with D_2O, only signals from the complex **1c** (*ca.* 13%) and from 2,6-dimethylpyridinium nitrate (87%) were observed after 35 min in the water solution. After an additional 10 min, only the signals from 2,6-dimethylpyridinium nitrate were observed.

Deuterium isotope effect

The ^1H NMR experiments showed the nitration reaction to be a two-step process: formation of an *N*-substituted pyridinium complex in the SO_2 solution (**1a**) and reaction of this in water to give 3-nitropyridine. A primary kinetic deuterium isotope effect would only be possible for the reaction in the water phase.

Accordingly, the *N*-complex was formed in SO_2 from an equimolecular mixture of pyridine and [$^2H_5$]pyridine. Any isotope effect on the formation of the complex would be a secondary one and accordingly small. On the other hand, a primary kinetic isotope effect on the nitration step (**2a** to 3-nitropyridine) would be possible. This would slow down the rate of formation of [$^2H_4$]-3-nitropyridine relative to that of the formation of 3-nitropyridine and relative to the rate of the competing hydrolysis of **2a** back to the starting materials pyridine and [$^2H_5$]pyridine. Therefore, under identical reaction conditions, the yield of [$^2H_4$]-3-nitropyridine would be lower than that of 3-nitropyridine.

The product mixture from the nitration of the equimolecular mixture of pyridine and [$^2H_5$]pyridine was analysed by GC–MS. The MS of the 3-nitropyridine/[$^2H_4$]-3-nitropyridine peak was identical with that of an equimolecular mixture of 3-pyridine/[$^2H_4$]-3-nitropyridine. The MS thus showed the product from the reaction to consist of equimolecular amounts of deuteriated and non-deuteriated 3-nitropyridine. From this, no primary deuterium kinetic isotope effect was observed for the formation of 3-nitropyridine from the pyridinium complex **1a**.

Discussion

From the evidence available at that time we proposed the nitration of pyridines to be a two-stage reaction, with the formation of a pyridine–DNP–SO_2 complex in the SO_2 solution and a reaction of this complex in water to give 3-nitropyridine.[1] From the NMR investigation it is clear that two complexes were formed, an *N*-substituted pyridinium complex in SO_2 and a 1,4-dihydropyridine complex in water (Scheme 1).

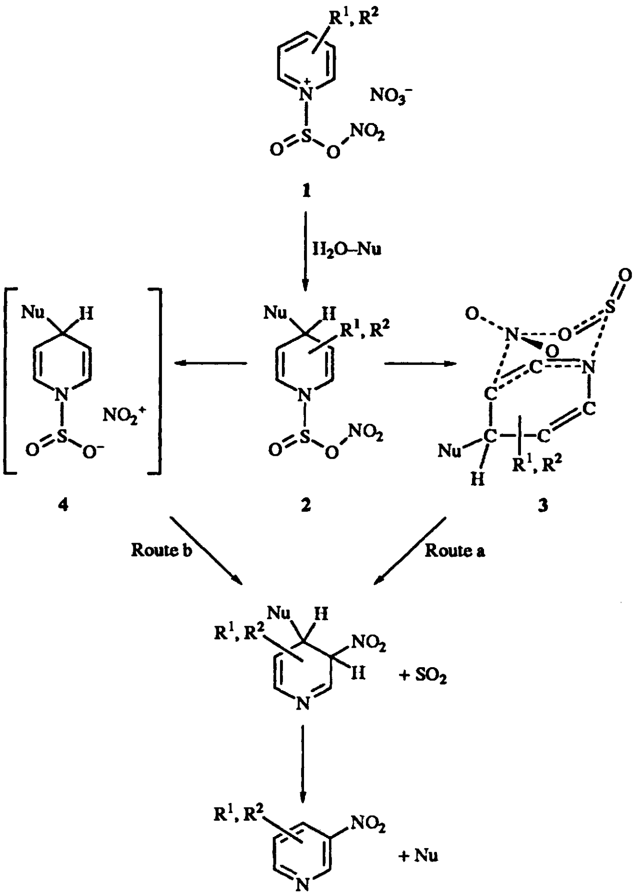
The nucleophile Nu in Schemes 1 and 2 could be H_2O, HSO_3^-/SO_3^{2-} or NO_3^-. However, addition of $NaNO_3$ to the water solution before the addition of the pyridine–DNP–SO_2 complex did not affect the yield of 3-nitropyridine. This would have been expected if NO_3^- was the nucleophile. At present we do not have enough evidence to make a choice between water and HSO_3^-/SO_3^{2-} as the nucleophile. Water was present in a far higher concentration than HSO_3^-/SO_3^{2-}. We have not been able to find data on the nucleophilicity of HSO_3^-. However, SO_3^{2-} is very reactive, *ca.* 10^8 times more reactive than CH_3OH in S_N2 reactions.[9] The HSO_3^-–SO_3^{2-} pair could therefore have acted as the nucleophile.

The results from the reactions of the three DNP–SO_2 complexes **1a–c** in water demonstrate the importance of the individual rates of the consecutive steps in the water solution. The pyridine–DNP–SO_2 complex (**1a**) reacted so rapidly with the nucleophile that only traces were left after 15 min. On the other hand, the 4-methylpyridinium–DNP–SO_2 complex **1b** reacted at a much lower rate and its reaction could be monitored and the first-order rate constant be determined. However, the 1,4-dihydropyridine complex **2b** was not observed, presumably because its further reaction was faster than its formation. The reason for the slow reaction of the 4-methylpyridinium complex **1b** might have been the electron-donating property of the methyl group which made the γ-pyridine carbon less electrophilic.

For 2,6-dimethylpyridine, the complex **1c** was formed (Tables 1 and 2). However, the induced chemical shifts (ICS) for the protons of this complex were smaller than those of pyridine and 4-methylpyridine. This was particularly the case for the proton at C4 with ICS = 1.22 ppm as compared with 1.50 for that in the pyridinium complex **1a** and 1.46 ppm for that in the 4-methylpyridinium complex **1b**. This may indicate a larger electron density at C4 in **1c** than in **1a** and **1b**, making this carbon less electrophilic in **1c** than in the other two complexes. This would make the reaction with the nucleophile less competitive and could explain why the hydrolysis of **1c** back to the 2,6-dimethylpyridinium salt was the only reaction observed. The reason for this was not an electronic effect as *e.g.*, 2,4-dimethylpyridine was nitrated with good yields.[1]

The reaction of the complex **2** in water could have been either inter- or intra-molecular. We have shown that the complex **2a** did not react with 4-methylpyridine added to the water solution.[1] Thus, the reaction appeared to involve only the complex. However, the reaction could nevertheless be intermolecular: in analogy with enamines, the complex **2a** would be activated for electrophilic substitution in the 3/5-positions. It was therefore possible that the nitration of **2a** took place by the excess DNP usually present in the reaction mixture. However, nitration of pyridine also took place when excess pyridine was reacted with DNP. In that case, all the DNP was consumed in the SO_2 solution. From this, DNP was not the nitration agent in the water solution. Nitric acid would be another possible nitration agent, formed for instance by hydrolyses of the pyridine–DNP–SO_2 complex. To test this, we reacted the complex **1a** with water containing $H^{15}NO_3$. The product 3-nitropyridine contained no incorporated ^{15}N and nitric acid was therefore not reacting with the 1,4-dihydro complex **2a** in the water solution. Finally, one could imagine one complex of **2a** nitrating a second complex. However, the reaction of **2a** followed a first-order kinetic rate law. Attempts to fit the data to a second-order rate law failed.

We have thus established that the reaction of the 1,4-dihydropyridine complex **2a** was intramolecular, either as a concerted reaction or as a reaction in a solvent cage. In Scheme 2, we have shown two possible reaction paths for **2**. One is a concerted reaction *via* the transition state **3** (route a), the other is a reaction in a solvent cage, exemplified as an ionic pair in **4** (route b).



1a, 2a: $R^1 = R^2 = H$
1b, 2b: R^1 = 4-Me, $R^2 = H$
1c, 2c: R^1 = 2-Me, R^2 = 6-Me

Scheme 2

Route b could also have been by a radical pair with nitrogen dioxide as the nitration agent. The last possibility has been proposed for the rearrangement of nitramines.[10] As a probe for NO_2 radicals we performed the reaction of the pyridine–DNP–SO_2 complex in water with hydroquinone added. This compound would scavenge any NO_2 radicals leaving the solvent cage and by doing so influence the yield of 3-nitropyridine. This was the case when this test was used in the nitramine rearrangement.[10] In our case no change in the yield of 3-nitropyridine was observed. If NO_2 was the nitration reagent it therefore reacted totally inside the solvent case. From the results of the nitramine rearrangement, we find this less likely. The yield of 3-nitropyridine was also unaffected when the reaction was performed in total darkness to exclude any photochemical formation of radicals.

In the concerted reaction (route a), a six-membered, six-electron chair-shaped transition state (**3**) would be formed by an electrophilic attack of the nitro group at the nucleophilic β-carbon of **2**. This attack would be perpendicular to the ring system. This transition state would be analogous to those proposed for the Cope and the Claisen rearrangement.

Both these mechanisms would be in agreement with the observation that the reaction showed no deuterium isotope effect.

We do not have enough evidence at present to distinguish between routes a and b, although the results from the nitrations of methyl- and dimethyl-pyridines seem to be better explained by the mechanism of route b. These results indicated that neighbouring α- and β-positions of the pyridine ring needed to be unsubstituted for the nitration to be successful. This was not an electronic effect but rather a steric one as indicated by the results from the reaction of 2,6-dimethylpyridine. In that case, the DNP–SO_2 complex formed in SO_2 was weaker than those from pyridine and 4-methylpyridine, probably because of the steric hindrance by the two α-methyl groups. However, 2,5-dimethylpyridine was also unreactive and nitration of 2-methylpyridine gave predominantly nitration in the 5-position.[1] The 2-methyl group thus acted as a shield for reaction in the 3-position. For the two reaction paths in Scheme 2, the concerted mechanism (route a) would be susceptible to steric hindrance by a 2-methyl group as one of the nitro group oxygen atoms would be close to the methyl group in the transition state (**3**). For route b, by a nitronium ion intermediate, the influence of the 2-methyl group would be less, as the nitronium ion would move by the π-electron system of the enamine part of the complex **2**.

A mechanism by which the nitration agent makes an N–α–β two-step migration appears less likely. This migration could proceed either by expulsion of the substituent already present in the α-position or without such an expulsion in analogy with *ipso*-nitration. The first of these possibilities is excluded as no deuterium was incorporated into the α-positions on reaction of **2a** (see Fig. 1) or **2b** in D_2O. An N–α–β migration without expulsion of the substituent in the α-position would be analogous to an *ipso*-nitration. The nitrating agent would approach perpendicular to the ring system with only marginal steric hindrance. Therefore, the α-methyl groups in 2-methylpyridine would not have hindered the nitration of the 3-position as was observed.[1] From these points, we do not believe that the nitration of pyridine in the β-position takes place by an N–α–β migration but rather by a migration as exemplified in Scheme 2.

Conclusions

The nitration of pyridines in liquid SO_2 with N_2O_5 proceeded by the formation of an *N*-substituted SO_2–DNP complex **1**. On reaction with water, this complex reacted with a nucleophile (water or HSO_3^-/SO_3^{2-}) to form a 1,4-dihydropyridine compound **2**. The nitropyridines were formed from **2** either by a concerted reaction *via* a six-membered six-electron cyclic transition state **3** or by the formation of a nitronium ion **4** which reacted in a solvent cage.

Experimental

The reaction conditions and work-up procedures have been reported.[1] The NMR spectra were recorded on a Jeol JNM-FX 100 FT-NMR or a Jeol EX-400 spectrometer. The GC instruments were a Carlo Erba HRGC Fractovap Series 4160 (CP-Wax 52 CB) and a Carlo Erba GC 6000 Vega Series (CP-Sil 5 CB). The mass spectra were recorded on a Hewlett Packard 5989A GC/MS or AEI MS 902 mass spectrometer. From the mass spectra, only peaks larger than 9% (except for M^+) and with m/z > 75 are reported. For the NMR investigations, the SO_2 solution was transferred from the reaction vessel to an

NMR tube which had been cooled to -75 °C and filled with Ar. For the transfer a Pasteur pipette was used which had been cooled to -75 °C in a reaction tube filled with Ar. The NMR tube was sealed before the NMR investigation. For the spectra of the D_2O solutions, the SO_2 solutions were poured into D_2O (25 cm^3) and the first spectrum run as soon as the D_2O sludge had melted. In one experiment the SO_2 solution from the sealed NMR tube (*ca.* 1 cm^3) was poured into D_2O. The ^{1}H NMR spectrum of this solution showed only 3-nitropyridinium and pyridinium salts to be present.

Nitration of 1,2-bis(4-pyridyl)ethane

1,2-bis(4-pyridyl)ethane (2.3 g, 12.5 mmol) and DNP (0.68 g, 6.3 mmol) in SO_2 (25 ml) were stirred at -30 °C for 4 h, poured over ice (100 g) and worked up to give 1.38 g of product. GC–MS analyses of this mixture showed it to consist of starting material (87%) and three compounds 6%, < 1% and 4% of the GC area.

The first of these [6% from GC area, 1-(3-nitro-4-pyridyl)-2-(4-pyridyl)ethane] had MS (GC–MS, BP-1), *m/z* (% rel. int.) 229 (4, M$^+$), 213 (14), 212 (100), 195 (15), 184 (14), 183 (15), 182 (36), 181 (27), 154 (18), 128 (12), 127 (16), 108 (20), 107 (11), 106 (17), 105 (10), 93 (58), 92 (80), 91 (14), 80 (17), 79 (20), 78 (26) and 77 (27).

The third compound [4% from GC area, 1,2-bis(3-nitro-4-pyridyl)ethane] had *m/z* (% rel. int.) 274 (6, M$^+$), 257 (11), 197 (10), 184 (14), 183 (12), 182 (24), 181 (49), 180 (19), 179 (13), 169 (11), 155 (22), 154 (25), 153 (30), 147 (10), 142 (12), 138 (12), 137 (45), 136 (14), 135 (24), 128 (13), 127 (19), 126 (11), 122 (34), 121 (100), 120 (34), 119 (33), 115 (14), 110 (13), 109 (13), 108 (16), 107 (14), 106 (18), 105 (22), 104 (13), 101 (13), 94 (23), 93 (87), 92 (36), 91 (19), 81 (12), 80 (20), 79 (44), 78 (50), 77 (53) and 76 (14). This compound crystallized from the mixture and showed δ_H(400 MHz; $CDCl_3$) 3.33 (4 H, s, CH_2), 7.41 (2 H, d, *J* 4.88 Hz, H5), 8.77 (2 H, d, *J* 4.88, H6) and 9.23 (2 H, s, H2).

Deuterium isotope effect

A mixture of pyridine (488 mg, 6.18 mmol) and [$^2H_5$]pyridine (524 mg, 6.24 mmol) was added to DNP (25 mmol) in SO_2 (25 cm^3) at -30 °C and the reaction mixture was stirred for 2 h. After reaction with ice (100 g) and work-up, 0.79 g of product was obtained. This showed *m/z* (rel. int.) 129 (5), 128 (78), 125 (5), 124 (74), 82 (100), 78 (97). This was identical with that of a 6.18 mmol 3-nitropyridine : 6.24 mmol [$^2H_4$]-3-nitropyridine mixture.

Effect of added $NaNO_3$ to the water phase

The pyridine–DNP–SO_2 solution (25 cm^3) was poured onto ice (100 g) containing sodium nitrate (10 g). The yield was 60% of 3-nitropyridine.

Reaction with $H^{15}NO_3$

A solution of pyridine (0.5 cm^3, 6.20 mmol) and DNP (1.35 g, 12.5 mmol) in SO_2 (13 cm^3) was kept at -30 °C for 4 h and then poured into D_2O containing $H^{15}NO_3$ (98% ^{15}N; 0.2 mol dm^{-3} solution in D_2O). A sample of this solution was used for ^{15}N NMR spectroscopy (40 MHz for ^{15}N). The only signal observed was that of $H^{15}NO_3$. This was constant in intensity for 3 h. The product had MS [GC–MS, *m/z* (rel. int.)] 125 (5), 124 (57), 108 (1), 94 (1), 79 (6), 78 (100) and 76 (2). The mass spectrum of 3-nitropyridine (natural ^{15}N/^{14}N ratio) was [GC–MS, *m/z* (rel. int)] 125 (4), 124 (54), 108 (1), 94 (1), 79 (6), 78 (100) and 76 (2).

Acknowledgements

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