

Nucleophilic Additions to *N*-Nitro- and *N*-(2,4-Dinitrophenyl)-pyridinium Salts

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The reactive *N*-nitropyridinium nitrate (**2**) and the stable *N*-(2,4-dinitrophenyl)-pyridinium chloride (**5**) have been reacted with nucleophiles. *N*-Nitropyridinium nitrate and pyridine gave 4-pyridino-1-nitro-1,4-dihydropyridine (**3**) in an equilibrium reaction. With hydroxide ions, a ring-opening reaction took place to give 5-nitroaminopenta-2,4-dienal (**4**) which gave back **2** upon acidification. *N*-(2,4-Dinitrophenyl)pyridinium chloride reacted with sodium sulfite to give a mixture of two products, one from attack of two sulfite ions on the dinitrophenyl ring (**7**) and one from attack in the 4-position of the pyridinium ring (**6**). The ratio **7/6** increased with increasing polarity of the reaction medium. *N*-(2,4-Dinitrophenyl)pyridinium chloride also reacted with nitromethanide ion to give *N*-(2,4-dinitrophenyl)-4-nitromethyl-1,4-dihydropyridine (**9**). This compound reacted with NO_2BF_4 to give the *N*-(2,4-dinitrophenyl)-4-nitromethylpyridinium ion (**10**).

We have recently reported the successful nitration of pyridine (**1**) and substituted pyridines to yield β -nitropyridine compounds. The synthesis was performed by the reaction of pyridine with dinitrogen pentoxide (DNP) and subsequent reaction of the resulting *N*-nitropyridinium nitrate (**2**) with a nucleophile in water.¹ The nature of the added nucleophile was important, both for the yield of the 3-nitropyridine compound and for the intermediates formed in the reaction. We therefore wished to conduct a wider investigation of the reaction of pyridinium salts with nucleophiles in order better to understand the nitration reaction.

The reactions of pyridinium salts with nucleophiles have been studied in some detail and extensive review articles are available.^{2–4} The reactions reported here are either new or gave significantly different results from those reported earlier.

Results

We have performed the nucleophilic reactions with two pyridinium ions: the relatively unstable *N*-nitropyridinium ion (**2**) and the stable *N*-(2,4-dinitrophenyl)pyridinium ion (**5**).

1. Reactions of N-nitropyridinium nitrate. In the nitration reaction this ion was reacted with SO_2 or HSO_3^- in

water. One nucleophile that might also react with **2** would be pyridine (**1**) itself. It has been reported that *N*-nitropyridinium tetrafluoroborate reacted with excess pyridine to give ring-opened products. The same type of reaction took place on reaction with aqueous sodium hydroxide.^{4,5}

(a) *Reaction with pyridine.* In an exploratory experiment, pyridine reacted with 1 mol equiv. of DNP in $^2\text{H}_3\text{CNO}_2$. A precipitate formed. An ^1H NMR spectrum of the mixture showed broad signals with shifts between those of pyridine and of the *N*-nitropyridinium ion. After addition of one more equivalent of DNP sharp signals at the shifts of the *N*-nitropyridinium ion were observed. However, it was also clear that the bulk of the material was present in the precipitate ($^2\text{H}_2\text{HCNO}_2$ as internal standard). As we have performed the DNP-nitration of pyridine in liquid SO_2 without the formation of a precipitate, we added SO_2 to the $^2\text{H}_3\text{CNO}_2$ solution. The precipitate dissolved but the ^1H NMR spectrum showed the same signals as that before the addition of the SO_2 and the intensities were now approximately the same as those in the spectrum of the starting pyridine solution.

We then added ca. 0.5 mol equiv. of DNP to a pyridine solution in $^2\text{H}_3\text{CNO}_2$ containing 4 equiv. of SO_2 . The ^1H NMR spectrum showed signals from *N*-nitropyridinium nitrate and from pyridine, and six signals at 8.95, 8.6, 8.15, 8.05, 6.45 and 5.65 ppm with a ratio of 2:1:2:2:1:2. From ^1H , ^{13}C and ^1H - ^1H COSY spectra

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it was clear that the signals at 8.95, 8.6 and 8.15 ppm came from one spin system and those at 8.05, 6.45 and 5.65 ppm from another. These data and the observed coupling constants (see Experimental) would fit 4-pyridino-1-nitro-1,4-dihydropyridine (**3**).

A saturation transfer experiment showed **3** to be in rapid equilibrium with **1** and **2**: irradiation of the signal at 9.95 ppm ($H^{2,6}$ in **2**) resulted in a ca. 80% loss in the intensities of the signal at 8.05 ppm ($H^{2,6}$ in **3**) and conversely, irradiation of the signal at 8.05 ppm gave an almost 100% decrease in the intensity of the signal at 9.95 ppm.

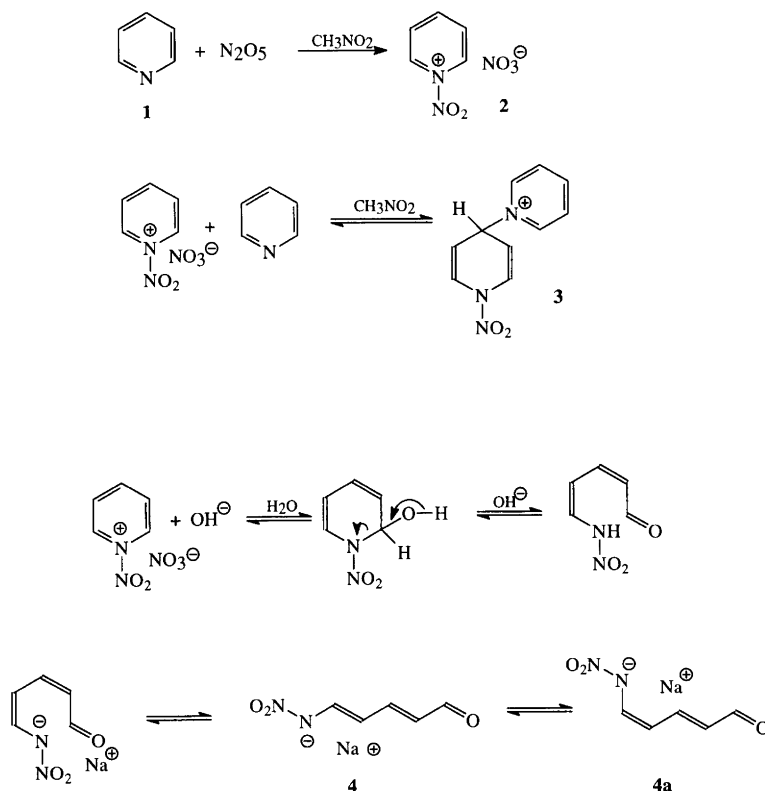
(b) *Reaction with sodium bicarbonate.* When *N*-nitropyridinium nitrate (**2**) was reacted with an aqueous solution of sodium bicarbonate (pH ca. 7) a deep red solution was obtained. Evaporation and extraction of the residue with ethanol followed by evaporation of the ethanol solution produced a red solid which decomposed at 200 °C without melting. The 1H and ^{13}C NMR spectra (Experimental) showed four protons attached to carbons in a diene, all-*trans* configuration, one proton at an aldehyde carbon but no proton at the nitrogen atom. The IR spectrum showed absorptions at 1667 cm^{-1} (aldehyde) and at 1609, 1324 cm^{-1} (nitro group⁶). These data fit the structure **4**, and are analogous to those reported for similar reactions with other pyridinium salts.^{3,4}

The compound was stable in the solid state. In an

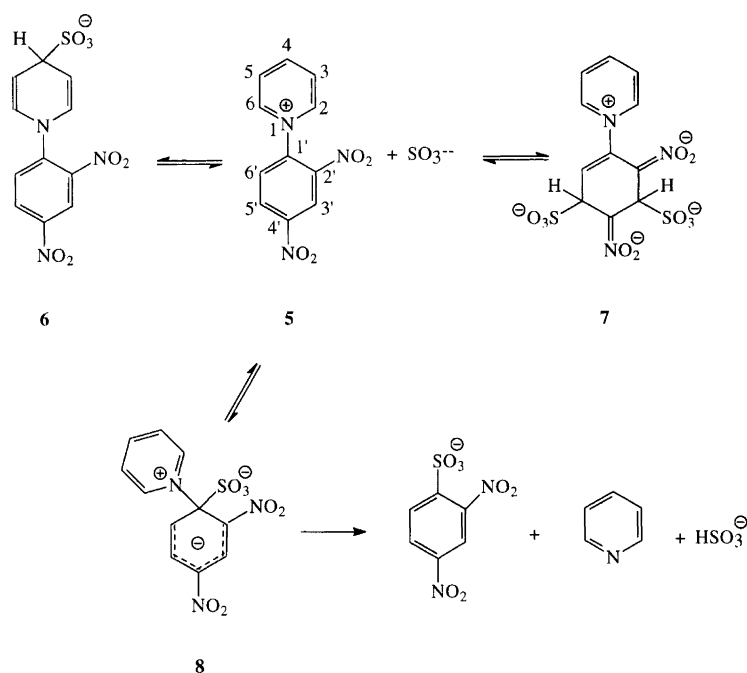
acidic aqueous solution it gave back the *N*-nitropyridinium ion **2** (1H NMR spectroscopy), which on reaction with NaHSO_3 gave 3-nitropyridine. The 1H NMR spectra also showed a minor component to be present. This showed almost the same chemical shifts and vicinal coupling constants as **4** except for $^3J_{4,5}$. This was 8.4 Hz as compared with 13.4 Hz for **4**, showing the C^4-C^5 double bond to have a *Z* configuration. These points strongly suggest the minor component to be the stereoisomer **4a** (Scheme 1). The ratio $[4]/[4a]$ was temperature dependent (Table 2, Experimental section) with $\Delta G_o = -1.31(7)\text{ kcal mol}^{-1}$.

2. *Reactions of N-(2,4-dinitrophenyl)pyridinium chloride (5).* To study the reactions of a more stable pyridinium salt we treated *N*-(2,4-dinitrophenyl)pyridinium chloride (**5**) with several nucleophiles: pyridine, halogenide ions, $\text{SO}_2 \cdot (\text{H}_2\text{O})_n$, HSO_3^- , SO_3^{2-} and $[\text{H}_2\text{CNO}_2]^-$. Of these, only sulfite ions and $[\text{CH}_2\text{NO}_2]^-$ reacted.

(a) *With sodium sulfite.* Two compounds were formed from **5** and SO_3^{2-} . The concentrations of both these decreased with time and the end products were pyridine and the sodium salt of 2,4-dinitrobenzenesulfonic acid. 1H , ^{13}C and correlation NMR spectroscopy showed that one of the intermediates (**6**) was formed from attack of SO_3^{2-} in the 4-position of the pyridinium ring, the other (**7**) from reaction between two SO_3^{2-} ions and the dinitrophenyl ring (Scheme 2).



Scheme 1.



Scheme 2.

Only one set of NMR signals was observed from the diadduct 7, indicating only one diastereomer to have been formed. The ratio 6/7 was dependent on the composition of the reaction medium: in pure water the ratio was close to one but in DMSO–water 2:5 (v/v) this ratio increased to 12 (Table 1).

(b) *With nitromethanide anion.* The nitromethanide anion was formed from nitromethane by the use of fluoride ion. The ^1H and ^{13}C NMR spectra showed that $[\text{CH}_2\text{NO}_2]^-$ had reacted in the 4-position of the pyridinium ring to give the 1,4-dihydropyridine derivative 9, a deep red compound in 75% yield. This was stable under the reaction conditions, in contrast with compounds 6 and 7 formed by the reaction with the sulfite ion.

In an exploratory experiment we reacted 9 with NO_2BF_4 . Owing to the enamine structure of C^3 , an attack of $[\text{NO}_2]^+$ at C^3 was expected. However, the product from the reaction was the *N*-(2,4-dinitrophenyl)-4-nitromethylpyridinium ion (10).

Table 1. Composition of the reaction mixture from the reaction of *N*-(2,4-dinitrophenyl)pyridinium chloride with sodium sulfite in $^2\text{H}_2\text{O}$ – $[\text{DMSO}]$.

$[\text{DMSO}]$ – $^2\text{H}_2\text{O}$	6/5	7/5
0	0.66	0.77
0.05	2.21	0.46
0.10	9.17	0.76

Discussion

Two different pyridinium ion systems were studied in this investigation, the *N*-nitropyridinium ion (2) and the *N*-(2,4-dinitrophenyl)pyridinium ion (5). For both of these, the pyridinium ring is strongly electrophilic. For 5, the substituent on the pyridinium nitrogen atom is also electrophilic and for that compound nucleophilic attack took place on both the pyridinium and the 2,4-dinitrophenyl ring. We will first discuss the reactions of 5 and then compare these results with those from the reactions of the *N*-nitropyridinium ion.

The addition of nucleophiles to phenyl rings activated by nitro groups is a well studied reaction.⁷ However, for the *N*-(2,4-dinitrophenyl)pyridinium ion there have been only a limited number of reports and most of these have been concerned with its reactions with bases which resulted in opening of the pyridine ring.^{8,9} In the reaction of 5 with SO_3^{2-} we have a very reactive nucleophile¹⁰ which is not a strong base. It is also a soft nucleophile, compared with the hydroxide ion.¹¹ These points may explain the different course of reactions from the ring-opening reactions reported earlier.^{8,9}

We observed two intermediates from the reaction of 5 with sodium sulfite, one (6) from attack at the pyridinium ring, the other (7) from attack by two sulfite ions at the 2,4-dinitrophenyl ring (Scheme 2). As we could find no way that the end products, pyridine and 2,4-dinitrobenzenesulfonate, could have been formed directly from either of the two observed intermediates, it was necessary also to postulate a third one, 8. The reaction at the pyridinium ring took place in the 4-position as expected

for a soft nucleophile.¹² This is analogous to the results of reactions of pyridinium salts carrying activating substituents at the 3-position of the pyridinium ring.¹³⁻¹⁶

The reaction at the 2,4-dinitrophenyl ring resulted in a diadduct **7**. Sulfite diadducts are well known for the 2,4,6-trinitrophenyl system and in some cases they are the thermodynamically stable.¹⁷ To our knowledge they have not been reported for the 2,4-dinitrophenyl system and in our case the formation of the diadduct reflects the electron withdrawing power of the pyridinium ring.

The structure of the diadduct **7** was elucidated from the NMR spectra. The ratio **6/5** at the start of the reaction was dependent on the reaction medium, increasing with increased DMSO-water ratio (Table 1). The **7/5** ratio did not show the same type of variation. By increasing the mole fraction of DMSO, the polarity of the medium was decreased. This would decrease the stability of both the inorganic ions and the multi-charged ion **7**. On the other hand, the formation of the 1,4-dihydropyridine derivative **6** eliminated one positive and one negative charge and this may be the explanation for the observed change in the ratio **6/5** with the change in the solvent composition.

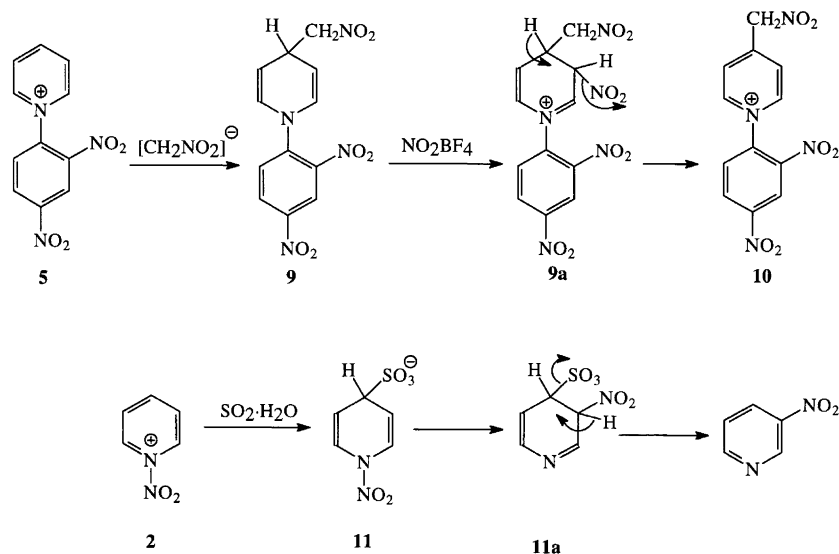
The mode of reaction of the nitromethanide anion on the *N*-(2,4-dinitrophenyl)pyridinium ion **5** was in accordance with the results from the reactions with Na₂SO₃. The reaction at the 4-position of the pyridinium ring reflects both the softness of the nucleophile and the low polarity of the reaction medium (nitromethane). In **9** we have the same enamine configuration of the 1,4-dihydropyridine ring as in *N*-nitro-1,4-dihydro-4-pyridine-sulfonate (**11**) and we expected the 2,3-double bond to be activated for electrophilic attack, giving **9a** as an intermediate by analogy with **11a** from the reaction of *N*-nitropyridinium nitrate with SO₂·xH₂O (Scheme 3). However, on reaction with nitronium tetrafluoroborate, the *N*-(2,4-dinitrophenyl)-4-nitromethylpyridinium ion

was the product. An explanation for the formation of this and not of the *N*-(1,4-dinitrophenyl)-3-nitropyridinium ion might be the better leaving-group ability of NO₂⁻ over that of [CH₂NO₂]⁻.

In conclusion at this point, the reaction of *N*-(1,4-dinitrophenyl)pyridinium chloride was very sensitive to the medium composition: in mixtures of water and DMSO, addition of sulfite ions to both ring systems was observed, the proportions of products depending on the solvent composition. Pyridine and 2,4-dinitrobenzenesulfonic acid were the end products. In acetonitrile, the dihydro complex **6** was the only and apparently stable product in equilibrium with **5**.

N-Nitropyridinium nitrate (**2**) reacted with the two investigated nucleophiles at different sites: with hydroxide ion in the 2-position and with the pyridine nitrogen atom in the 4-position. This is in accordance with the hardness/softness of these two nucleophiles, the hard hydroxide ion attacked in the 2-position and the soft nitrogen atom of the pyridine molecule reacted in the 4-position.¹² The attack in the 2-position gave the ring opened product **4**, a result in accordance with earlier reports.^{4,5} However, under the mild conditions used in the present work, glutamic aldehyde was not the end product. Instead, the *N*-nitro group was not hydrolysed and as a solid **4** was stable at room temperature. The ring opening of **2** was reversible as it was reformed from the open chain compound **4** on acidification. Furthermore, if the water solution contained SO₂-HSO₃⁻, 3-nitropyridine was formed in accordance with the reports on the chemistry of **2**.¹

With pyridine, the *N*-nitropyridinium ion formed the 1,4-dihydropyridine derivative **3** (Scheme 1). This has a structure analogous to the intermediate **11** formed in the nitration reaction. However, **3** did not react as did **11**, that is with a migration of the nitro group to the 3-position. There may be several reasons for this, but the



Scheme 3.

leaving-group ability of the group in the 4-position of the 1,4-dihydropyridine ring must be important. If this is too high, the lifetime of the 1,4-dihydropyridine derivative will be too short for the nitro group to migrate to the 3-position. If it is too low, NO_2^- will leave from the 3-position instead of the group in the 4-position as was the case for **9a** with CH_2NO_2 in the 4-position. NMR saturation transfer experiments showed the *N*-nitro-4-pyridinium-1,4-dihydropyridine complex **3** to be in rapid exchange with pyridine and *N*-nitropyridinium nitrate (**2**). The analogous experiment with *N*-nitro-1,4-dihydro-4-pyridinesulfonate (**11**) gave no transfer of saturation, showing **11** to have a longer lifetime than **3**.

Our results in this investigation show that the mode of reaction of nucleophiles with pyridinium salts is very dependent on both the nucleophile and on the reaction medium. The position of the attack may be explained by the hardness/softness of the nucleophile. The polarity of the medium is important for the site of reaction of the *N*-(2,4-dinitrophenyl)pyridinium ion. Attack on the pyridinium ring becomes more important with decreasing polarity of the reaction medium, presumably because this eliminates one positive and one negative charge.

The fate of the initial product from the reaction on the pyridinium ring depends on both the nucleophile and the site of attack. With reaction in the 2-position, only a reversible ring opening was observed. With reaction in the 4-position of the *N*-nitropyridinium ion **2**, reversible addition of pyridine was observed. On the other hand, reaction of the same ion with $\text{SO}_2\text{-HSO}_3^-$ gave the 1,4-dihydro compound **11** which reacted further to give 3-nitropyridine.

Experimental

General. The NMR spectra were recorded on Bruker Avance DPX 300 or 400 MHz instruments. In organic solvents, Me_4Si was used as an internal standard, with $^2\text{H}_2\text{O}$, sodium 3-trimethylsilylpropionate. The NOEMUL Bruker program was used for the saturation transfer experiments. The chemicals used were all commercially available except for DNP. This was made from N_2O_4 by ozone oxidation.¹⁸ The solvents and reagents were purified by standard methods.¹⁹

Reactions of *N*-nitropyridinium nitrate with pyridine. (a) *Introductory experiment.* Pyridine (50 μl , 0.62 mmol) and $^2\text{H}_3\text{CNO}_2$ (0.7 ml) were injected through a septum into an NMR tube filled with Ar and kept at 0 °C. To this were added two portions of a $^2\text{H}_3\text{CNO}_2$ solution of DNP (1.9 M, 0.35 ml each, 0.67 mmol each). The reaction was monitored by ^1H NMR spectroscopy. Integration of the pyridine spectrum before addition of the DNP solution showed a 1.5/1 ratio of each pyridine proton per $\text{H}^2\text{H}_2\text{CNO}_2$. After addition of 0.35 ml of the DNP solution, the spectrum showed broad signals at 8.8, 8.2 and 7.8 ppm. After addition of another 0.35 ml of the DNP solution, sharp signals were observed. ^1H NMR

(400 Mz): δ 9.95 (d, $J=6.5$ Hz, H^2 , H^6), 9.1 (t, $J=7.5$ Hz, H^4), 8.6 (t, $J=7.2$ Hz, H^3 , H^5). The area ratio pyridine proton per $\text{H}^2\text{H}_2\text{CNO}_2$ was now 0.3/1 and a precipitate had formed. Sulfur dioxide was then passed through the solution until the precipitate had dissolved. The NMR spectrum of this solution was identical with that taken before addition of SO_2 , except for the integration ratio referred to above. This had increased from 0.3/1 to 3.1/1, close to that observed before the addition of DNP taking the dilution of the solution (from 0.7 to 1.4 ml) into account.

(b) *Reaction in a flask.* The addition of the reagents to the NMR tube was difficult to perform in a reproducible way. The experiment was therefore run in a 10 ml flask and samples removed for ^1H NMR analysis. To an Ar-filled 10 ml flask containing $^2\text{H}_3\text{CNO}_2$ (2 ml) at -30 °C was added SO_2 (gas, 300 ml, 12.5 mmol) through a septum. Pyridine (0.25 ml, 3.1 mmol) was then added followed by DNP in $^2\text{H}_3\text{CNO}_2$ (2.2 M, 0.75 ml, 1.6 mmol). ^1H NMR (400 MHz): δ 5.67 (dd, 2 H, $J=8.5$, 4.2 Hz), 6.44 (t, 1 H, $J=4.0$ Hz), 7.93 (t, 2 H, $J=6.6$ Hz), 8.05 (d, 2 H, $J=8.5$ Hz), 8.17 (t, 2 H, $J=7.0$ Hz), 8.38 (t, 1 H, $J=7.6$ Hz), 8.52 (t, 2 H, $J=7.3$ Hz), 8.63 (t, 1 H, $J=7.6$ Hz), 8.7 (d, 2 H, $J=5.2$ Hz), 8.96 (d, 2 H, $J=5.9$ Hz), 9.13 (t, 1 H, $J=7.6$ Hz), 9.95 (d, 2 H, $J=6.7$ Hz). After a further addition of DNP- $^2\text{H}_3\text{CNO}_2$ (0.75 ml, 1.6 mmol) a new ^1H NMR spectrum was recorded (400 MHz): δ 8.52 (t, 2 H, $J=7.2$ Hz), 9.13 (t, 1 H, $J=7.5$ Hz), 9.95 (d, 2 H, $J=6.6$ Hz) ppm.

Reaction of *N*-nitropyridinium nitrate with sodium bicarbonate. Solid DNP (1.4 g, 13 mmol) was added to nitromethane (25 ml) at 0 °C. Pyridine (1.3 ml, 16 mmol) was added through a septum. After 5 min the solution was poured into water, and NaHCO_3 (s) was added until $\text{pH}=7$. The organic phase was removed and the water phase washed twice with dichloromethane (2×50 ml). The water was evaporated off and the solid was extracted with ethanol several times. Compound **4** was precipitated from the ethanol solution by the addition of ether. We were not able completely to remove inorganic salts by this procedure. ^1H NMR (400 MHz, $^2\text{H}_2\text{O}$): δ 9.37 (d, 1 H, $J=8.53$ Hz, H^1), 8.10 (d, 1 H, $J=13.40$ Hz, H^5), 7.58 (dd, 1 H, $J=11.77$, 14.79 Hz, H^3), 6.40 (dd, 1 H, $J=11.95$, 13.16 Hz, H^4), 6.24 (dd, 1 H, $J=8.41$, 14.85 Hz, H^2). ^{13}C NMR (300 MHz, $^2\text{H}_2\text{O}$) 198.0, 157.6, 148.3, 128.6, 117.3. IR: ν/cm^{-1} 3426 (w), 2922 (w), 2843 (w), 1667 (m), 1655 (m), 1609 (s), 1399 (m), 1385 (s), 1324 (s), 1284 (m), 1204 (w), 1153 (s), 1131 (s), 1023 (m), 987 (m), 754 (w), 731 (w), 587 (w). UV-VIS: λ_{max} 295, 250 nm (**4**). There were also signals in the ^1H NMR spectrum from a minor component (300 MHz, $^2\text{H}_2\text{O}$, 65 °C): δ 5.88 (dd, 1 H, $J=8.32$, 11.70 Hz, H^4), 6.36 (dd, 1 H, $J=8.30$, 15.08 Hz, H^2), 7.67 (2, 1 H, $J=8.40$ Hz, H^5), 7.94 (dd, 1 H, $J=11.77$, 15.17 Hz, H^3), 9.44 (d, 1 H, $J=8.34$ Hz, H^1) (**4a**). The ratio $[\text{4}]/[\text{4a}]$ was temperature dependent as shown in Table 2.

Table 2. Temperature dependence of the ratio [4]/[4a] (from ^1H NMR spectra in $^2\text{H}_2\text{O}$).

$T/^\circ\text{C}$	[4]/[4a]
30	7.2
50	6.4
70	5.7
90	5.0

Reaction of 4 under acidic conditions. Compound **4** (4.5 mg, 0.057 mmol) was dissolved in $^2\text{H}_2\text{O}$ (0.7 ml in an NMR tube). To this 6 M HCl was added to give $\text{pH} \approx 0$. ^1H NMR spectroscopy showed that the signals from **4** disappeared over the course of an hour and that signals from the *N*-nitropyridinium ion at δ 8.46 (t, 2 H, $J=7.43$, $\text{H}^{3,5}$), 9.08 (t, 1 H, $J=7.55$ Hz, H^4), 10.00 (d, 2 H, $J=6.29$ Hz, $\text{H}^{2,6}$) increased. When most of the ring opened compound (**4**) had reacted sodium bisulfite (15 mg, 0.144 mmol) was added to the solution. The *N*-nitropyridinium ion reacted to give the 1,4-dihydro intermediate **11** which reacted further to 3-nitropyridine and pyridine itself.¹

Reactions of *N*-(2,4-dinitrophenyl)pyridinium chloride (5). (a) **Preparation of *N*-(2,4-dinitrophenyl)pyridinium chloride.** To a solution of 2,4-dinitrochlorobenzene (20.26 g, 0.1 mol) in acetone (100 ml), pyridine (15.82 g, 0.2 mol) was added. The mixture was stirred for 3 h under reflux. After cooling and addition of pentane

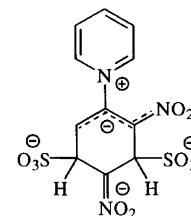
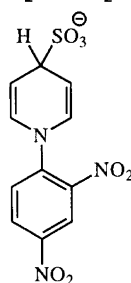
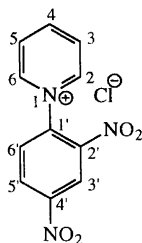
(200 ml), the precipitated product was isolated by filtration, washed with pentane and recrystallised from ethanol to give colourless crystals of *N*-(2,4-dinitrophenyl)pyridinium chloride. Yield 14.28 g (51%). ^1H NMR (400 MHz, $^2\text{H}_2\text{O}$): δ 8.28 (1 H, d, $J=8.68$ Hz, H^6), 8.40 (2 H, dd, $J=6.88$, 7.79 Hz, $\text{H}^{3,5}$), 8.96 (2 H, m, H^4 and H^5), 9.20 (2 H, dd, $J=1.15$, 6.66 Hz, $\text{H}^{2,6}$), 9.39 (1 H, d, $J=2.46$ Hz, H^3). ^{13}C NMR (400 MHz, $^2\text{H}_2\text{O}$): δ 125.5 ($\text{C}^{3'}$), 131.3 ($\text{C}^{3,5}$), 133.4 (C^5), 134.0 (C^6), 148.2 ($\text{C}^{2,6}$), 152.0 (C^4), 141.5, 145.7, 152.4 ($\text{C}^{1'}$, $\text{C}^{2'}$, C^4).

(b) **Reaction with Na_2SO_3 in $^2\text{H}_2\text{O}$.** *N*-(2,4-Dinitrophenyl)pyridinium chloride (**5**, 14.1 mg, 0.05 mmol) and Na_2SO_3 (6.3 mg, 0.05 mmol) were dissolved in (a) $^2\text{H}_2\text{O}$ 0.5 mL; (b) $^2\text{H}_2\text{O}$ -(C^2H_5) $_2\text{SO}$ (0.5 ml/0.1 ml) and (c) $^2\text{H}_2\text{O}$ -(C^2H_5) $_2\text{SO}$ (0.5 ml/0.2 ml). After 2 min, the ^1H NMR spectra were recorded. The compositions of the three solutions are given in Table 1. The NMR parameters from these experiments are given in Table 3. In all three cases the signals in Table 3 disappeared with time and after 3–4 h only signals from pyridine and 2,4-dinitrobenzenesulfonate were observed.

(c) **Reaction with nitromethanide ion (CH_2NO_2^-).** Cesium fluoride (2.279 g, 15.0 mmol) was added slowly to a dispersion of *N*-(2,4-dinitrophenyl)pyridinium chloride (**5**, 1.408 g, 5.0 mmol) in nitromethane (50 ml). The mixture was stirred at room temperature for 16 h under nitrogen. Benzene (100 ml) was added, and the mixture was stirred for 30 min and then filtered. The filtrate was

Table 3. NMR parameters for compounds **5**, **6** and **7** [300 MHz, D_2O or D_2O -(CD_3) $_2\text{SO}$].

	5	6	7
$\text{H}^{2,6}$	9.20 (2 H, dd, $J=1.15$, 6.66 Hz)	6.50 (2 H, d, $J=8.08$ Hz)	9.01 (2 H, d, $J=7.77$ Hz)
$\text{H}^{3,5}$	8.40 (2 H, dd, $J=6.88$, 7.79 Hz)	5.21 (2 H, dd, $J=4.13$, 8.13 Hz)	8.14 (2 H, m)
H^4	8.96 (1 H, m)	4.41 (1 H, t, $J=4.05$ Hz)	8.64 (1 H, t, $J=7.60$ Hz)
H^3 ($\text{C}^{3'}$)	9.39 (125.5) (1 H, d, $J=2.46$ Hz)	8.84 (1 H, d, $J=2.60$ Hz)	6.14 (63.0) (1 H, s)
H^5 ($\text{C}^{5'}$)	8.96 (133.4) (1 H, m)	8.49 (1 H, dd, $J=2.60$, 9.12 Hz)	5.41 (59.5) (1 H, d, $J=7.39$ Hz)
H^6	8.28 (1 H, d, $J=8.68$ Hz)	7.68 (1 H, d, $J=9.15$ Hz)	6.60 (1 H, d, $J=7.47$ Hz)



evaporated and the product dried *in vacuo* to give *N*-(2,4-dinitrophenyl)-4-nitromethyl-1,4-dihydropyridine (**9**) as red crystals. ^1H NMR (300 MHz, $^2\text{H}_3\text{CCN}$): δ 3.86 (1 H, m, H^4), 4.44 (2 H, d, $J=6.04$ Hz, CH_2NO_2), 5.00 (2 H, m, $\text{H}^{3,5}$), 6.32 (2 H, m, $\text{H}^{2,6}$), 7.54 (1 H, d, $J=9.12$ Hz, H^6), 8.39 (1 H, dd, $J=2.65, 9.06$ Hz, H^5), 8.70 (1 H, d, $J=2.66$ Hz, H^3). ^{13}C NMR (400 MHz, $^2\text{H}_3\text{CCN}$): δ 33.4 (C^4), 82.3 (CH_2NO_2), 105.3 (C^3), 123.7 ($\text{C}^{3,5}$), 125.6 (C^6), 129.4 (C^5), 129.8 ($\text{C}^{2,6}$), 141.6, 143.1, 143.6 ($\text{C}^1, \text{C}^2, \text{C}^4$). VIS: λ_{max} (CH_3CN): 417 nm ($\epsilon=11000$). M.p. 102–104 °C. Yield 1.150 g (75%).

(d) *Reaction with sodium nitrite.* Sodium nitrite (13.8 mg, 0.2 mmol) was placed in an NMR tube containing *N*-(2,4-dinitrophenyl)pyridinium chloride (28.2 mg, 0.1 mmol) in $[\text{H}_6]\text{DMSO}$ (0.6 ml). The only observable ^1H NMR signals were from the starting material and 2,4-dinitrophenol. No signals from 1,2,4-trinitrobenzene were observed.²⁰

(e) *Reactions with other nucleophiles.* *N*-(2,4-Dinitrophenyl)pyridinium chloride did not react with pyridine, sodium bisulfite or $\text{SO}_2 \cdot \text{H}_2\text{O}$.

Reaction of N-(2,4-dinitrophenyl)-4-nitromethyl-1,4-dihydropyridine (9) with nitronium tetrafluoroborate. Nitronium tetrafluoroborate (26.6 mg, 0.2 mmol) was added slowly to a well stirred solution of *N*-(2,4-dinitrophenyl)-4-nitromethyl-1,4-dihydropyridine (30.6 mg, 0.1 mmol) in $^2\text{H}_3\text{CCN}$ (1 ml) at -20 °C. ^1H NMR (**10**, 400 MHz, -20 °C, $^2\text{H}_3\text{CCN}$): δ 6.02 (2 H, s, CH_2NO_2), 8.18 (1 H, d, $J=8.68$ Hz, H^6), 8.38 (2 H, d, $J=6.74$ Hz, $\text{H}^{3,5}$), 8.86 (1 H, dd, $J=2.51, 8.78$, H^5), 8.98 (2 H, d, $J=6.69$ Hz, $\text{H}^{2,6}$), 9.18 (1 H, d, $J=2.49$ Hz, H^3).

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