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The Cyclisation of a Nitramine, Formation of 3-Nitropyridine from 5-Nitraminopenta-2,4-dienal.

Jan M. Bakke,* Eli Ranes and Jaroslav Riha

Organic Chemistry Laboratories, Norwegian University of Science and Technology, N-7034 Trondheim, Norway.

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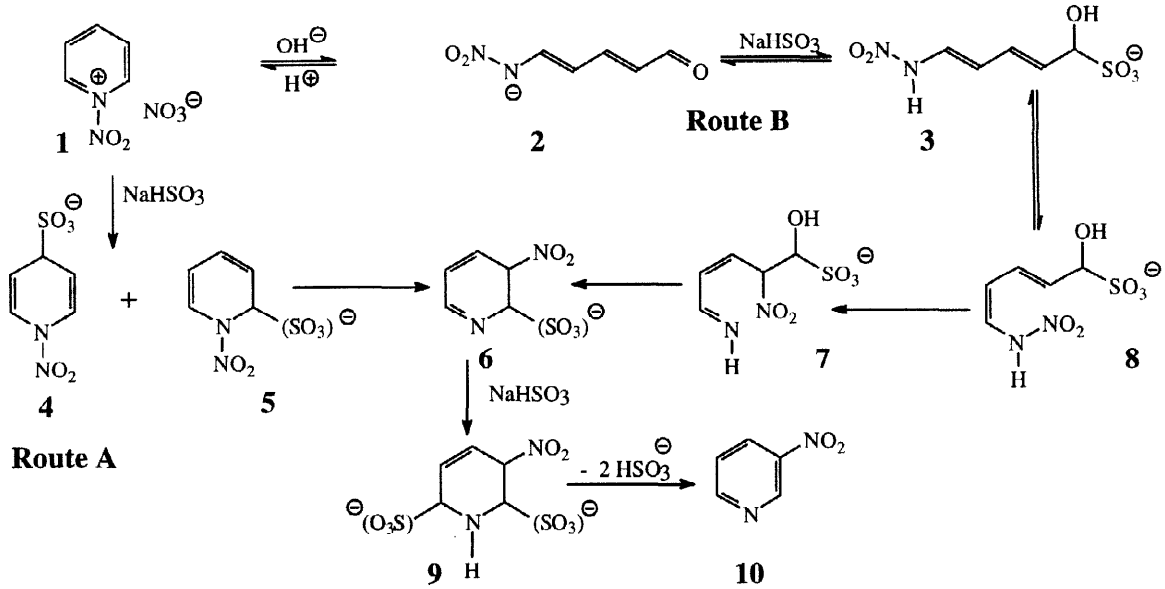
Abstract: On reaction of the sodium salt of 5-nitraminopenta-2,4-dienal (**2**) with sodium bisulfite at pH 4, 3-nitropyridine (**10**) was formed. Two reaction paths appeared possible for this reaction. From a ^{1}H NMR study of the reaction a route by the *N*-nitropyridinium ion **1** (Route A, Scheme 1) appeared likely. The results from the reaction of **1** under the same conditions supported this.

We have reported the successful nitration of pyridine and substituted pyridines to the corresponding β-nitro compounds.[1] We have also reported that *N*-nitropyridinium nitrate (**1**), an intermediate in the formation of 3-nitropyridine from pyridine, under mild alkaline conditions formed the stable sodium salt of 5-nitraminopenta-2,4-dienal (**2**). Furthermore, **2** cyclised to **1** under acidic conditions and reacted with sodium bisulfite to give 3-nitropyridine (**10**).[2]

We have studied the mechanism of the nitration reaction of pyridine in some detail.[3] As both compounds **1** and **2** gave 3-nitropyridine on reaction with sodium bisulfite, the reaction of **2** might have some bearing on the mechanism of the nitration reaction. We have therefore investigated the reaction of **2** further.



Scheme 1

For the nitration of pyridine we have presented evidence which indicated that *N*-nitropyridinium nitrate, formed from pyridine and dinitrogen pentoxide (N_2O_5) reacted with sodium bisulfite to give **5** (characterised by ^{1}H and ^{13}C NMR spectroscopy) which rearranged to give **6**. Upon reaction with one more bisulfite ion, **9** was formed which then gave 3-nitropyridine (**10**, Route A, Scheme 1) .[3]

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On reaction of the nitramine **2** with sodium bisulfite at pH 4, the hydroxysulfonates **3** and **8** were formed in a 5:1 ratio. These then reacted further to give 3-nitropyridine as the end product. In Scheme 1, two possible routes for the formation of 3-nitropyridine from **3/8** are depicted. One, Route A, is by a reversible formation of the *N*-nitropyridinium ion **1** from **3/8** and further reactions *via* **5**, **6** and **9** to 3-nitropyridine.[3] Route B is by a migration of the nitro group of **8** to give **7** and after ring closure of this, **6**.

We have now identified both compounds **3** and **8** in the product mixture from **2** and sodium bisulfite[4] and studied their reaction. This was followed by ^{1}H NMR. The ratio [**3**]/[**8**] was constant (5/1) during the reaction, indicating rapid equilibration. The concentrations of **3** and **8** decreased and that of 3-nitropyridine increased with time. For the tetrahydropyridine derivative **9** an increase in the concentration was first observed and then a decrease. Compounds **6** and **7** were not observed.

These results might be explained by both Route A and B in Scheme 1. However, one more intermediate was observed, *N*-nitro-1,4-dihydro-4-pyridinesulfonate (**4**). This was also formed in the nitration reaction of pyridine.[1,3] Its presence shows that the *N*-nitropyridinium ion **1** was formed from **3** and therefore indicate that Route A is possible for the reaction of **3**. Furthermore, when *N*-nitropyridinium nitrate was reacted with sodium bisulfite at pH 4, **4, 9** and **10** were formed in the same ratios as those from the reaction of the open chain nitramine **3**. These two points strongly suggest that compound **3** reacted *via* the *N*-nitropyridinium ion **1** as in Route A.

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References and notes:

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2. Andersen, E.; Bakke, J. M.; Ranes, E.; Riha, J. *Acta Chem. Scand.* ***Accepted***
3. Bakke, J. M. 72th Annual Meeting of the Chemical Society of Japan, Tokyo, March 1997.
   Bakke, J. M.; Ranes, E. *J. Chem. Soc. Perkin Trans 2,* 1997, 1919.
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4. NMR data for observed intermediates not reported before: For **3**: **^{1}H NMR** (400 MHz, ^2H_2O, pH 4): δ 5.00 (1H, d, *J* 7.37 Hz, H^1), 5.86 (1H, dd, *J* 7.29, 15.43 Hz, H^2), 6.22 (1H, dd, *J* 11.30, 13.75 Hz, H^4), 6.59 (1H, dd, *J* 11.09, 15.19 Hz, H^3), 7.46 (1H, d, *J* 13.85 Hz, H^5). **^{13}C NMR** (100 MHz, ^2H_2O, pH 3): δ 87.6 (C^1), 120.0 (C^4), 128.8 (C^2), 134.9 (C^5), 136.2 (C^3).
   For **8**: **^{1}H NMR** (400 MHz, ^2H_2O, pH 4): δ 5.03 (1H, d, *J* 7.07 Hz, H^1), 5.76 (1H, dd, *J* 8.64, 11.24 Hz, H^4), 5.86 (1H, dd, *J* 7.08, 15.33 Hz, H^2), 6.93 (1H, dd, *J* 11.46, 15.38 Hz, H^3), 7.10 (1H, d, *J* 8.62 Hz, H^5). **^{13}C NMR** (100 MHz, ^2H_2O, pH 3): δ 87.9 (C^1), 118.2 (C^4), 129.8 (C^2), 131.4 (C^5), 131.7 (C^3),.