Unusual Synthesis of Stable Pyridinium Dinitromethylides

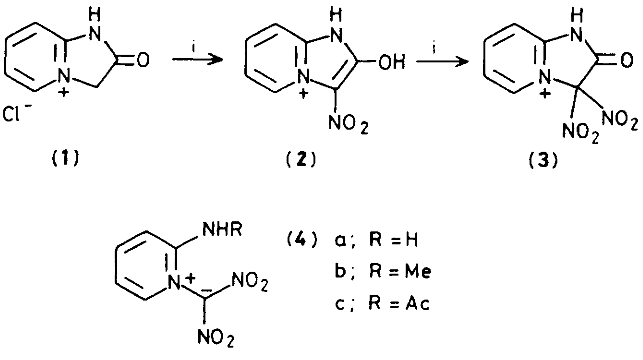
Eva Andréasson,[a] Christopher G. Newton,[b] W. David Ollis,[b] Charles W. Rees,[a] David I. Smith,[a] and Derek E. Wright[c]

[a] *Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY, U.K.*
[b] *Department of Chemistry, The University, Sheffield S3 7HF, U.K.*
[c] *The Research Laboratories, May and Baker Ltd., Dagenham, Essex RM10 7XS, U.K.*

Nitration of the imidazo[1,2-*a*]pyridines (**1**) or (**2**), (**5**) or (**6**), and (**9**) with nitric and sulphuric acids gives the pyridinium dinitromethylides (**4a**), (**8**), and (**10**), respectively, in which the pyridinium and dinitromethylide groups are orthogonal.

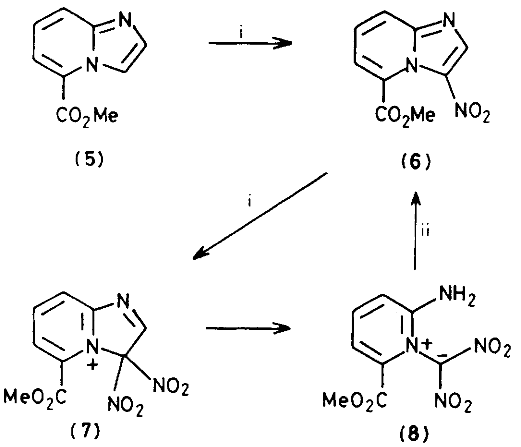
In contrast with many other pyridinium ylides[1] virtually nothing is known of pyridinium dinitromethylides; only pyridinium dinitromethylide itself has been prepared, by a hazardous, low-yielding route.[2] We now report a simple, if surprising, route to 2-aminopyridinium dinitromethylides involving ring cleavage of the readily available imidazo[1,2-*a*]pyridines[3] upon nitration with nitric and sulphuric acids. This reaction offers a new approach to the synthesis of azinium ylides.

When 2,3-dihydroimidazo[1,2-*a*]pyridin-2(3*H*)-one hydrochloride (**1**)[4] was treated with concentrated nitric and sulphuric acids at 2 °C and allowed to warm to room temperature, 2-aminopyridinium dinitromethylide (**4a**) (51%) was obtained as a stable crystalline solid, m.p. 246—248 °C (decomp.). A reasonable mechanism for this transformation (Scheme 1) involves mono- and *ipso* di-nitration of (**1**), *via* enolic forms, followed by opening of the five-membered ring in (**3**), and decarboxylation. As required by this mechanism, the mononitro compound, the mesoionic conjugate base of (**2**), m.p. 285 °C (decomp.), gave the ylide (**4a**) (60%) under the same nitrating conditions. The methylamino ylide (**4b**) (55%), m.p. 210—213 °C (decomp.), was similarly prepared by nitration of the *N*-methyl derivative of (**2**), m.p. >310 °C, and also by methylation (66%) of ylide (**4a**) with dimethyl sulphate and aqueous sodium hydroxide. Acetylation of (**4a**) with acetic anhydride and triethylamine gave the acetamido ylide (**4c**) (53%) as pale yellow crystals, m.p. 236—238 °C (decomp.).



Scheme 1. i, conc. HNO_3, conc. H_2SO_4, room temp.

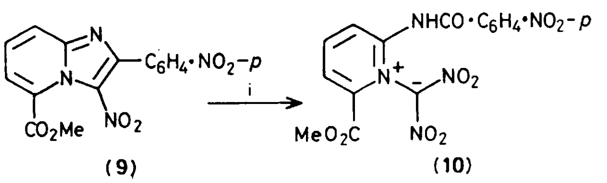
We have also found that the overall transformation can be more extensive than shown in Scheme 1; the fused imidazole ring need not bear an oxygen function since this can be introduced by the nitrating mixture. Thus when methyl imidazo[1,2-*a*]pyridine-5-carboxylate (**5**), m.p. 103—104 °C, was treated with fuming nitric acid in concentrated sulphuric acid at room temperature, the ylide (**8**) (61%) was formed as yellow crystals, m.p. 250 °C (decomp.), and carbon dioxide was evolved. This reaction is sensitive to concentration and if the volume of sulphuric acid was increased ten-fold the mononitro compound (**6**) (80%), m.p. 110—111 °C, was formed instead of the ylide (**8**). If (**6**) was then treated with



Scheme 2. i, fuming HNO_3, conc. H_2SO_4, room temp.; ii, dimethylformamide, 125 °C.

the more concentrated solution of fuming nitric acid in sulphuric acid it gave the ylide (**8**) in high yield (85%). A possible mechanism (Scheme 2) involves formation of the dinitro intermediate (**7**), acid-catalysed addition to its imine bond, and cleavage of the five-membered ring followed by oxidation and decarboxylation to give the observed products. Support for this mechanism is provided by the conversion of the 2-(*p*-nitrophenyl) derivative (**9**) into the amido-ylide (**10**) (74%), m.p. 163—165 °C (decomp.), under the same reaction conditions.

It is interesting to consider the extent of conjugation between the pyridinium ring and the dinitromethylide group in these ylides. *X*-Ray structure determination of (**4b**) monohydrate[5] and of (**8**)[6] shows that for both compounds, in the solid state, the planes of the two groups are almost exactly perpendicular, presumably to minimise intramolecular steric compressions. This stable orthogonal conformation probably extends to the molecules in solution since the two nitro groups were shown to be equivalent as follows. The ylide $[(^{15}NO_2)_2]$-(**4a**) was prepared using ^{15}N enriched nitric acid (95% ^{15}N), and its low temperature ^{15}N n.m.r. spectrum was recorded at 10 MHz for a heptadeuteriodimethylformamide–hexadeuterioacetone solution. The ^{15}N signal corresponding to the two nitro groups remained a sharp singlet with no line broadening down to −100 °C. Exchange of the nitro groups by rapid rotation around the ylide bond seems much less likely in view of the crystal structures and the result below.



i, fuming HNO_3, conc. H_2SO_4, room temp.

The orthogonality of these dinitromethylides should deprive them of the most characteristic reaction of pyridinium ylides, their ability to function as 1,3-dipoles. As yet we have been unable to observe any 1,3-dipolar cycloaddition reactions of the ylides, *e.g.* with dimethyl acetylenedicarboxylate or with carbon disulphide. The ylides are weak nucleophiles, presumably because of the extensive delocalisation of the negative charge, but ylide (**8**) did react slowly with hot dimethylformamide (125 °C), somewhat surprisingly to regenerate mononitroimidazopyridine (**6**).

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References

1 I. Zugrăvescu and M. Petrovanu, 'N-Ylid Chemistry,' McGraw-Hill International Book Company, New York, 1976, pp. 155—245.

2 V. V. Semenov, S. A. Shevelev, and A. A. Fainzil'berg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 2640 (*Chem. Abstr.*, 1977, **86**, 139517); V. V. Semenov and S. A. Shevelev, *ibid.*, 1978, 2355 (*Chem. Abstr.*, 1979, **90**, 86916).

3 H. L. Blewitt, in 'Special Topics in Heterocyclic Chemistry,' eds. A. Weissberger and E. C. Taylor, Interscience, New York, 1977, p. 117.

4 E. B. Knott, *J. Chem. Soc.*, 1951, 3033.

5 N. A. Bailey and C. G. Newton, *Cryst. Struct. Comm.*, 1980, **9**, 49.

6 Determined by Dr. D. J. Williams, Department of Chemistry, Imperial College of Science and Technology.