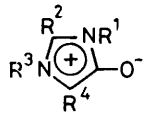
Cyclic Meso-ionic Compounds. Part 22.[1] Meso-ionic Derivatives of the Imidazo[1,2-*a*]pyridinium System and the Unexpected Synthesis of Stable Pyridinium Dinitromethylides

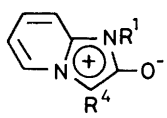
Christopher G. Newton and W. David Ollis *
Department of Chemistry, The University, Sheffield S3 7HF
Derek E. Wright
The Research Laboratories, May and Baker Ltd., Dagenham, Essex RM10 7XS

The chemistry of 1,3-diazolium-4-olates (1) has been extended by the synthesis of representatives of a new type (2) of bicyclic meso-ionic system. *N*-Methylation of the imidazo[1,2-*a*]pyridine (3) gave the salt (11) which reacted smoothly with appropriate nucleophilic reagents yielding the meso-ionic heterocycles (9) and (12)—(15). Nitration of the lactam (10) did not give the expected nitro-derivative (8), but instead a novel pyridinium dinitromethylide (16) was produced. The planar and orthogonal conformations of pyridinium ylides in the solid state are discussed.

The synthesis of meso-ionic structural analogues of useful pharmaceutical compounds containing nitro-substituents has been achieved.[1] However, the successful attainment of this objective was of limited value because the nitro-derivatives of the selected monocyclic meso-ionic heterocycles were found to be insufficiently stable to permit biological testing. Thus, although 1,2,3-trimethyl-5-nitro-1,3-diazolium-4-olate (1; $R^1 = R^2 = R^3 = Me$; $R^4 = NO_2$) was obtained as a pale yellow, crystalline compound, m.p. 173—174 °C (decomp.), it was unstable and decomposed at room temperature. In these circumstances it was decided to incorporate the monocyclic 1,3-diazolium-4-olate meso-ionic system (1) into the bicyclic structure (2). This decision was based upon the fact that a number of polycyclic meso-ionic 1,3-diazolium-4-olates is known [2,3] and these are much more stable than their monocyclic counterparts.



(1)



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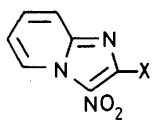
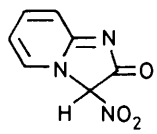


(3) X = Cl
(4) X = OMe
(5) X = OEt
(6) X = OH



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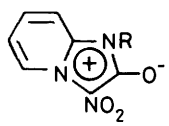
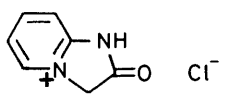


(8) R = H
(9) R = Me

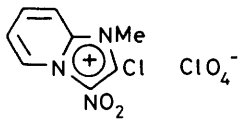


(10)

Our first approach to bicyclic meso-ionic heterocycles of the type (2; R^1 = alkyl; $R^4 = NO_2$) was based upon the earlier studies by Paolini and Robins [4] of the electrophilic substitution reactions of imidazo[1,2-*a*]pyridine derivatives. We have found that 2-chloro-3-nitroimidazo[1,2-*a*]pyridine (3) [4] undergoes smooth substitution reactions with nucleophilic reagents. Thus, the 2-chloro compound (3) in boiling methanol with sodium carbonate yielded the corresponding 2-methoxy compound (4). The 2-ethoxy compound (5) was similarly prepared using boiling ethanol. The attempted *N*-methylation of 2-methoxy-3-nitroimidazo[1,2-*a*]pyridine (4) using a variety of reagents including methyl iodide, dimethyl sulphate, methyl fluorosulphonate, and trimethyloxonium tetrafluoroborate, was unsuccessful. The synthetic approach was therefore modified in order to obtain a compound which was expected to be more reactive towards *N*-methylating reagents. Mild alkaline hydrolysis of 2-chloro-3-nitroimidazo[1,2-*a*]pyridine (3) yielded a product, $C_7H_5N_3O_3$, which could, in principle, be represented by three possible tautomeric structures (6), (7), or (8). The u.v. and i.r. spectra of the hydrolysis product clearly favoured its formulation as the meso-ionic tautomer (8). The *N*-methyl derivative (9) was easily prepared from the hydrolysis product (8) by treatment with dimethyl sulphate in aqueous potassium carbonate at room temperature. The nitration of 2,3-dihydroimidazo[1,2-*a*]pyridin-2(3*H*)-one hydrochloride (10) was examined as a possible route to the meso-ionic compound (8). The product was in fact the pyridinium dinitromethylide (16). This result, although it was not expected, is not without intrinsic interest: its significance is discussed later.

A more direct route to meso-ionic derivatives containing the imidazo[1,2-*a*]pyridinium system was examined which was based upon the opinion that the salt (11) could be a versatile intermediate. Fortunately the reaction between 2-chloro-3-nitroimidazo[1,2-*a*]pyridine (3) and dimethyl sulphate yielded the corresponding *N*-methyl methosulphate which was transformed into the perchlorate salt (11).

The cation of the salt (11) was expected to be much more reactive towards nucleophilic reagents than its precursor (3). This belief was shown to be well-based because the perchlorate salt (11) does, in fact, react with nucleophilic reagents giving a number of new types of meso-ionic heterocycles. The perchlorate salt (11) and aqueous potassium carbonate yielded 1-methyl-3-nitroimidazo[1,2-*a*]pyridinium-2-olate (9) identical with the *N*-methylation product described above.



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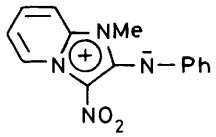

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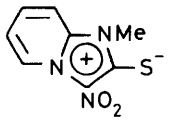

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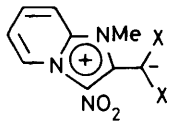
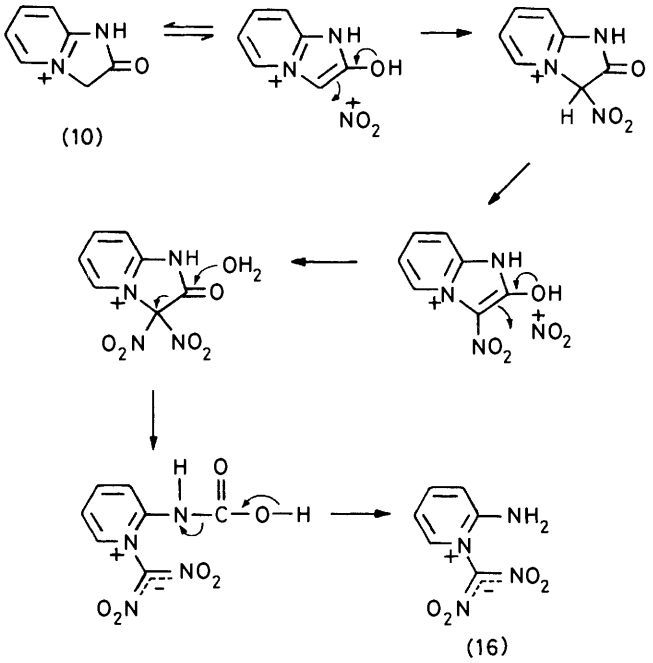


(14) X = CN
(15) X = CO_2Et



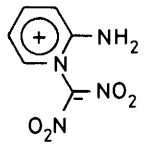
(10)

Scheme. Mechanism for the formation of 2-aminopyridinium nitromethylide (16)

Reaction with aniline in aqueous triethylamine yielded 1-methyl-3-nitroimidazo[1,2-*a*]pyridinium-2-anilide (12) and the corresponding reaction with sodium hydrogen sulphide gave the meso-ionic 2-thiolate (13). The orange 2-dicyanomethylide (14) and the red 2-diethoxycarbonylmethylide (15) were similarly prepared by triethylamine catalysed condensation of the perchlorate salt (11) with malononitrile and diethyl malonate respectively. The compounds (12)—(15) represent novel additions to the type A class of meso-ionic heterocycles.[2,3]

Formation of Pyridinium Dinitromethylides.—The unexpected formation of 2-aminopyridinium dinitromethylide (16) by nitration of 2,3-dihydroimidazo[1,2-*a*]pyridin-2(3*H*)-one hydrochloride (10) has already been mentioned. The ylide (16) was obtained as colourless rhombs, m.p. 246—248 °C, and a mechanism for the transformation (10) ⟶ (16) is given in the Scheme.

In the mechanism suggested (Scheme) for the formation of 2-aminopyridinium dinitromethylide (16) by the nitration of



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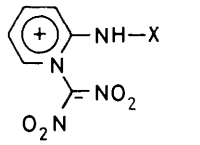
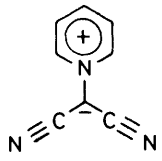


(17) X = Me
(18) X = Me—CO



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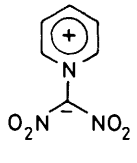

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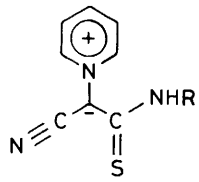

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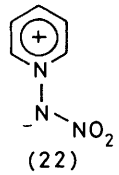

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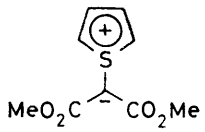

(23)

2,3-dihydroimidazo[1,2-*a*]pyridin-2(3*H*)-one hydrochloride it is inferred that the mononitro-cation corresponding with (8) is an intermediate. It was established that the conversion (8) ⟶ (16) could be achieved under the same conditions as those used for the conversion (10) ⟶ (16).

Two further examples of pyridinium dinitromethylides have been prepared in the present study. The *N*-methyl derivative (17) was obtained by two routes: (i) base-catalysed methylation of the aminopyridinium methylide (16) and (ii) nitration of the *N*-methyl derivative (9). Acetylation of 2-aminopyridinium dinitromethylide gave the *N*-acetyl derivative (18). The existence of these pyridinium dinitromethylides (16), (17), and (18) raised the interesting question of the nature and the extent of conjugative interaction between the pyridinium ring and the exocyclic dinitromethylide grouping. Two particular conformations could be considered. One conformation in which the pyridinium ring and the dinitromethylide grouping are coplanar and the other conformation in which these two groupings are orthogonal. In the coplanar conformation, the two nitro groups would be geometrically non-equivalent. Hence, in order to examine these possibilities, the compound [($^{15}NO_2$)$_2$]-(16) was synthesised using ^{15}N-enriched nitric acid (95% ^{15}N). The ^{15}N n.m.r. spectrum of this compound showed one singlet for the two nitro groups and there was no sign of line broadening on lowering the temperature to −100 °C in dimethylformamide–hexadeuterioacetone solution. This result was compatible either with an orthogonal disposition of the dinitromethylide group with respect to the pyridinium ring or with rapid site exchange due to rapid rate of rotation of the dinitromethylide group about its bond to the pyridinium ring. A decision between these two possibilities emerged from a crystal structure determination on 2-methylaminopyridinium dinitromethylide monohydrate (17).[5] In this compound the torsion angle about the ylide bond between the planes of the pyridinium ring and the dinitromethylide group is reported as 91.7°.

The orthogonality exhibited by the pyridinium dinitromethylide (17) contrasts with the virtual planarity adopted by pyridinium dicyanomethylide (19).[6] It is possible that this

difference between the adoption of either planar or orthogonal conformations in the solid state could well be due to a reduction of intramolecular steric interaction which is possible in the orthogonal conformation. Recently the syntheses of the pyridinium dinitromethylide (20)[7] and the pyridinium cyanothiocarbamidomethylide (21)[8] have been described, but their solid state conformations have not yet been determined. Finally, mention should be made of an interesting investigation of the crystal structure of pyridine 1-nitro-imide (22).[9,10] In this case the planar $\overset{+}{N}-\overset{-}{N}-NO_2$ system adopts a torsion angle of 71.7° to the planar pyridinium ring.

It is interesting to compare the solid state conformations of the pyridinium ylides (17), (19), and (22) with the result of the *X*-ray analysis of thiophenium bismethoxycarbonylmethylide (23).[11] The sulphur atom is pyramidal and the bismethoxycarbonylmethylide group is approximately orthogonal to the thiophene ring. At this stage is it not possible to discuss with confidence the factors which cause the ylides (17), (19), (22), and (23) to adopt a variety of conformations in the solid state.

Pyridinium *N*-methylides containing the groupings $\overset{+}{\geq}\overset{-}{N}-C(CO_2Et)_2$, $\overset{+}{\geq}\overset{-}{N}-C(CO_2Et)CN$, $\overset{+}{\geq}\overset{-}{N}-C(CO_2Et)R$, and $\overset{+}{\geq}\overset{-}{N}-C(CN)_2$ show an interesting range of cycloaddition reactions with 1,3-dipolarophiles.[12] No cycloaddition reactions of the pyridinium dinitromethylides (16), (17), or (18) have been achieved.

Since the completion of our investigation we have been informed that additional examples of pyridinium dinitromethylides have been encountered by Andréasson, Rees, and Smith. This work and our work have been reported in a joint preliminary publication.[13]

Experimental

General experimental directions are given in Part 21.[1]

2-*Methoxy*-3-*nitroimidazo*[1,2-a]*pyridine* (4).—A mixture of 2-chloro-3-nitroimidazo[1,2-*a*]pyridine (3)[4] (8.31 g), sodium carbonate (38 g), and methanol (450 ml) was heated under reflux (2.5 h), evaporated to low volume, and added to water (500 ml). The product which separated was extracted into chloroform. Evaporation of the chloroform extract and crystallisation of the residue from ethyl acetate gave 2-methoxy-3-nitroimidazo[1,2-*a*]pyridine (4) as colourless crystals (6 g, 74%), m.p. 207—209 °C (lit.,[14] m.p. 208 °C) (Found: C, 49.6; H, 3.4; N, 21.7%; $M^{+\cdot}$, 193. Calc. for $C_8H_7N_3O_3$: C, 49.7; H, 3.7; N, 21.8%; *M*, 193); $\lambda_{max.}$ (MeCN) 258, 266, 274, 320sh, and 358 nm (ε 11 580, 11 400, 10 850, 6 760, and 16 900); δ 4.30 (3 H, s, OCH_3), 7.26 (1 H, t, *J* 7 Hz, 6-H), 7.60—7.75 (2 H, m, 7-H and 8-H) and 9.47 (1 H, d, *J* 7 Hz, 5-H); δ_C [$(CD_3)_2SO$] 56.9 (OCH_3), 116.2 (C-6 or C-8), 116.4 (C-8 or C-6), 128.3 (C-7), 132.8 (C-5), and 141.7 (C-8a or C-2 or C-3).

2-*Ethoxy*-3-*nitroimidazo*[1,2-a]*pyridine* (5).—This *compound* was prepared from 2-chloro-3-nitroimidazo[1,2-*a*]pyridine, sodium carbonate, and ethanol by the method described for the corresponding 2-methoxy analogue (4). It was obtained (47%) as colourless crystals (from ethyl acetate), m.p. 148—149 °C (Found: C, 52.5; H, 4.2; N, 20.4%; $M^{+\cdot}$, 207. $C_9H_9N_3O_3$ requires C, 52.2; H, 4.4; N, 20.3%; *M*, 207); δ 1.54 (3 H, t, *J* 7 Hz, CH_2CH_3), 4.71 (2 H, q, *J* 7 Hz, CH_2CH_3), 7.20 (1 H, t, *J* 7.5 Hz, 6-H), 7.5—7.7 (2 H, m, 7-H and 8-H), and 9.44 (1 H, d, *J* 7.5 Hz, 5-H).

3-*Nitro*-1H-*imidazo*[1,2-a]*pyridinium*-2-*olate* (8).—A solution containing 2-chloro-3-nitroimidazo[1,2-*a*]pyridine (530 mg) and sodium hydroxide (300 mg) in a mixture of water (2 ml) and ethanol (20 ml) was heated under reflux (30 min) and kept at 0 °C (30 min). The solid which separated was filtered off, washed with ethanol, and shaken with a mixture of chloroform and water. The aqueous phase was washed with chloroform, acidified with concentrated hydrochloric acid and kept at 0 °C (1 h) when 3-*nitro*-1H-*imidazo*[1,2-a]*pyridinium*-2-*olate* was obtained as colourless crystals (378 mg, 79%), m.p. 285 °C (decomp.) (Found: C, 47.1; H, 2.9; N, 23.7%; $M^{+\cdot}$, 179. $C_7H_5N_3O_3$ requires C, 46.9; H, 2.8; N, 23.5%; *M*, 179); $\lambda_{max.}$ (MeCN) 270sh, 274, 330, and 368 nm (ε 13 000, 15 000, 4 480, and 13 400); $\nu_{max.}$ (KBr) 3 070 and 1 710 cm^{-1}; δ (CF_3CO_2H) 7.66 (1 H, t, *J* 9 Hz, 6-H), 7.92 (1 H, d, *J* 9 Hz, 8-H), 8.18 (1 H, br t, 7-H), and 9.72 (1 H, br d, 5-H).

Evaporation of the combined chloroform extracts gave 2-ethoxy-3-nitroimidazo[1,2-*a*]pyridine as a colourless solid (17 mg, 3%), identical with that described above.

1-*Methyl*-3-*nitroimidazo*[1,2-a]*pyridinium*-2-*olate* (9).—A solution of 3-nitro-1*H*-imidazo[1,2-*a*]pyridinium-2-olate (367 mg) in aqueous potassium carbonate solution (5 ml, 25% w/v) was treated with dimethyl sulphate (0.3 ml) and stirred (10 min) at room temperature. The product which separated was filtered off and successively washed with aqueous potassium carbonate, water, and ethanol, when 1-*methyl*-3-*nitroimidazo*[1,2-a]*pyridinium*-2-*olate* was obtained as a colourless solid (153 mg, 39%), m.p. >310 °C (unchanged after recrystallisation from acetonitrile) (Found: C, 50.0; H, 3.5; N, 21.7%; $M^{+\cdot}$, 193.0492. $C_8H_7N_3O_3$ requires C, 49.8; H, 3.7; N, 21.8%; *M*, 193.0487); $\lambda_{max.}$ (MeCN) 274sh, 278, 335sh, and 370 nm (ε 13 160, 16 050, 7 720, and 17 000); $\nu_{max.}$ (KBr) 1 705 cm^{-1}; δ (100 MHz) [$(CD_3)_2SO$] 3.42 (3 H, s, NCH_3), 7.46 (1 H, t, *J* 7.5 Hz, 6-H), 7.72 (1 H, d, *J* 7.5 Hz, 8-H), 8.01 (1 H, t, *J* 7.5 Hz, 7-H), and 9.62 (1 H, d, *J* 7.5 Hz, 5-H); δ (CF_3CO_2H) 3.70 (3 H, s, NCH_3), 7.6—7.75 (2 H, m, 6-H and 8-H), 8.25 (1 H, br t, 7-H), and 9.70 (1 H, br d, 5-H).

2-*Chloro*-1-*methyl*-3-*nitroimidazo*[1,2-a]*pyridinium Perchlorate* (11).—A mixture of 2-chloro-3-nitroimidazo[1,2-*a*]pyridine (840 mg) and dimethyl sulphate (5 ml) was heated (5 min) at 100 °C, cooled, and triturated with ether. The insoluble solid was recrystallised from a mixture of acetonitrile and ether when the *methosulphate* was obtained as colourless crystals (810 mg, 59%), m.p. 138—140 °C (decomp.). Dissolution of this methosulphate (101 mg) in acetic acid (2 ml) and aqueous perchloric acid (2 ml; 60% w/v) followed by the addition of ether (100 ml) yielded the *perchlorate* as colourless crystals (93 mg, 96%), m.p. 239—241 °C (decomp.) (Found: C, 30.9; H, 2.4; Cl, 22.8; N, 13.8. $C_8H_7Cl_2N_3O_6$ requires C, 30.8; H, 2.3; Cl, 22.7; N, 13.5%); $\nu_{max.}$ (KBr) 1 090 cm^{-1} ($\overset{+}{N}$, ClO_4^-); δ (CF_3CO_2H) 4.21 (3 H, s, $\overset{+}{N}CH_3$), 7.90 (1 H, t, *J* 7.5 Hz, 6-H), 8.20 (1 H, d, *J* 7.5 Hz, 8-H), 8.39 (1 H, t, *J* 7.5 Hz, 7-H), and 9.73 (1 H, d, *J* 7.5 Hz, 5-H).

A mixture of the perchlorate (106 mg), water (6 ml), and aqueous potassium carbonate solution (2 ml; 5% w/v) was stirred (18 h) at room temperature when 1-methyl-3-nitroimidazo[1,2-*a*]pyridinium-2-olate (9) was obtained as a colourless solid (44 mg, 68%), m.p. >310 °C, identical in all respects with a sample obtained by the method described above.

1-*Methyl*-3-*nitroimidazo*[1,2-a]*pyridinium*-2-*anilide* (12).—A mixture of 2-chloro-1-methyl-3-nitroimidazo[1,2-*a*]pyridinium perchlorate (220 mg), water (10 ml), and aniline (100 mg) was treated with triethylamine (0.5 ml) and stirred (2 h) at room temperature. The solid was filtered off and crystallised from aqueous ethanol (95%) when the *anilide* was obtained as orange needles (108 mg, 57%), m.p. 257—258 °C (decomp.)

(Found: $M^{+\cdot}$, 268.0959. $C_{14}H_{12}N_4O_2$ requires M, 268.0960); $\lambda_{max.}$ 224, 249, 281, 310, 340sh, 360sh, and 432 nm (ε 18 340, 17 640, 17 090, 16 500, 10 330, 8 790, and 6 110); $\nu_{max.}$ (KBr) 1 630 cm^{-1}; δ [$(CD_3)_2SO$] 3.56 (3 H, s, NCH_3), 6.68 (2 H, d, J 7 Hz, 2,6-phenyl-H), 6.84 (1 H, t, J 7 Hz, 4-phenyl-H), 7.13 (2 H, t, J 7 Hz, 3,5-phenyl-H), 7.36 (1 H, t, J 7.5 Hz, 6-H), 7.7 (1 H, d, J 7.5 Hz, 8-H), 8.00 (1 H, t, J 7.5 Hz, 7-H), and 9.70 (1 H, d, J 7.5 Hz, 5-H).

1-*Methyl*-3-*nitroimidazo*[1,2-a]*pyridinium*-2-*thiolate* (13).—This *thiolate* was prepared from 2-chloro-1-methyl-3-nitroimidazo[1,2-*a*]pyridinium perchlorate, sodium hydrogen sulphide hydrate, and triethylamine by the method described above for the corresponding anilide (12), and was obtained (95%) as yellow crystals (from acetonitrile), m.p. 275—277 °C (Found: C, 45.9; H, 3.3; N, 19.9; S, 15.3%; $M^{+\cdot}$, 209. $C_8H_7N_3O_2S$ requires C, 45.9; H, 3.4; N, 20.1; S, 15.3%; M, 209); $\lambda_{max.}$ 206, 280sh, 307, 361, and 409 nm (ε 18 720, 12 070, 30 570, 8 330, and 8 960); $\nu_{max.}$ (KBr) 1 490—1 460 cm^{-1}; δ (100 MHz) [$(CD_3)_2SO$] 3.77 (3 H, s, NCH_3), 7.54 (1 H, dt, J 7 and 2 Hz, 6-H), 7.98—8.10 (2 H, m, 7-H and 8-H), and 9.64 (1 H, d, J 7 Hz, 5-H).

1-*Methyl*-3-*nitroimidazo*[1,2-a]*pyridinium*-2-*dicyanomethylide* (14).—This *dicyanomethylide* was prepared from 2-chloro-1-methyl-3-nitroimidazo[1,2-*a*]pyridinium perchlorate, malononitrile, and triethylamine by the method described above for the corresponding anilide (12) and was obtained (88%) as orange crystals (from acetonitrile), m.p. 282—283 °C (decomp.) (Found: C, 55.0; H, 3.2; N, 28.9%; $M^{+\cdot}$, 241. $C_{11}H_7N_5O_2$ requires C, 54.8; H, 3.0; N, 29.0%; M, 241); $\lambda_{max.}$ 206, 241sh, 283sh, 307, 369, and 428 nm (ε 25 180, 11 850, 12 180, 27 010, 8 960, and 9 990); $\nu_{max.}$ (KBr) 2 200, and 2 180 cm^{-1}; δ (100 MHz) [$(CD_3)_2SO$] 3.90 (3 H, s, NCH_3), 7.6—7.75 (1 H, m, 6-H), 8.15—8.25 (2 H, m, 7-H and 8-H), and 9.67 (1 H, dm, J 7 Hz, 5-H).

1-*Methyl*-3-*nitroimidazo*[1,2-a]*pyridinium*-2-*diethoxycarbonylmethylide* (15).—This *diethoxycarbonylmethylide* was prepared from 2-chloro-1-methyl-3-nitroimidazo[1,2-*a*]pyridinium perchlorate, diethyl malonate, and triethylamine by the method described above for the corresponding anilide (12), and was obtained (33%) as red crystals after purification by column chromatography (silica gel, acetone), m.p. 215—218 °C (decomp.) (Found: $M^{+\cdot}$, 335.1118. $C_{15}H_{17}N_3O_6$ requires M, 335.1117); $\lambda_{max.}$ 244, 278sh, 318, 374, and 454 nm (ε 23 750, 9 270, 16 060, 5 000, and 5 350); $\nu_{max.}$ (KBr) 1 705 cm^{-1}; δ [$(CD_3)_2SO$] 1.12 (6 H, t, J 6 Hz, 2 × CH_2CH_3), 3.59 (3 H, s, NCH_3), 4.03 (4 H, q, J 6 Hz, 2 × CH_2CH_3), 7.65—7.75 (1 H, m, 6-H), 8.15—8.3 (2 H, m, 7-H and 8-H), and 9.72 (1 H, d, J 7 Hz, 5-H).

Imidazo[1,2-a]*pyridin*-2(3H)-*one Hydrochloride* (10).—This compound was prepared (84%) by the method of Knott [15] as colourless crystals (from isopropyl alcohol), m.p. 232—233 °C (decomp.) (Found: C, 49.1; H, 4.4; Cl, 21.1; N, 16.7. Calc. for $C_7H_7ClN_2O$: C, 49.3; H, 4.2; Cl, 20.8; N, 16.4%); $\nu_{max.}$ (KBr) 3 000—2 500 and 1 765 cm^{-1}; δ (CF_3CO_2H) 5.53 (2 H, s, CH_2), 7.68 (1 H, t, J 7 Hz, 6-H), 7.81 (1 H, d, J 7 Hz, 8-H), 8.46 (1 H, t, J 7 Hz, 7-H), and 8.62 (1 H, d, J 7 Hz, 5-H).

2-*Aminopyridinium Dinitromethylide* (16).—*Method A*. A solution of imidazo[1,2-*a*]pyridin-2(3*H*)-one hydrochloride (3 g) in concentrated sulphuric acid (12 ml) was treated at 2 °C with a mixture of concentrated nitric acid (3 ml) and concentrated sulphuric acid (3 ml). The mixture was kept at room temperature (1 h) and added to ice. The solid which precipitated on addition of sodium carbonate to the mixture was dissolved in aqueous sodium hydroxide. Filtration and addition of an excess of dilute aqueous hydrochloric acid to the alkaline filtrate gave the *dinitromethylide* as a colourless solid (1.78 g, 51%), m.p. 246—248 °C (decomp.) (Found: C, 36.2; H, 3.2; N, 28.5%; $M^{+\cdot}$, 198. $C_6H_6N_4O_4$ requires C, 36.4; H, 3.1; N, 28.3%; M, 198); $\lambda_{max.}$ (MeCN) 335 nm (ε 19 080); δ [$(CD_3)_2SO$] 6.87 (1 H, t, J 9 Hz, 5-H), 7.08 (1 H, d, J 9 Hz, 3-H), 7.91 (1 H, t, J 9 Hz, 4-H), 8.07 (1 H, d, J 9 Hz, 6-H), and 8.86 (2 H, br s, NH_2); δ_C [$(CD_3)_2SO$] 112.7 (d, C-3 or C-5), 114.4 (d, C-5 or C-3), 131.4 [s, C-$(NO_2)_2$], 141.8 (d, C-4 or C-6), 144.0 (d, C-6 or C-4), and 155.1 (s, C-2); the ^{15}N n.m.r. spectrum of the dinitromethylide was recorded at 10 MHz in [$^2H_6$]dimethyl sulphoxide solution containing $Cr(acac)_3$ with an external reference of the NO_3^- signal of aqueous ammonium nitrate: δ_N −26.2 (2 × NO_2), −218.4 (N-1), and −282.5 (NH_2).

Method B. Nitration of 3-nitro-1*H*-imidazo[1,2-*a*]pyridinium-2-olate (8) by the method described above for the nitration of 2,3-dihydroimidazo[1,2-*a*]pyridin-2(3*H*)-one hydrochloride gave (60%) the dinitromethylide (16) as a colourless solid, identical in all respects with that obtained in method A above.

2-*Aminopyridinium* [$^{15}N_2$]*Dinitromethylide* [$(^{15}NO_2)_2$]-(16).—Nitration of imidazo[1,2-*a*]pyridin-2(3*H*)-one hydrochloride with [^{15}N]nitric acid (9M) of 95% isotopic purity by method A described above gave (44%) 2-*aminopyridinium* [$^{15}N_2$]*dinitromethylide* as a colourless solid, m.p. 235—236 °C (decomp.) (Found: $M^{+\cdot}$, 200. $C_6H_6{}^{14}N_2{}^{15}N_2O_4$ requires M, 200); the low temperature ^{15}N n.m.r. spectra of the nitro-groups in [$(^{15}NO_2)_2$]-(16) were recorded at 10 MHz for a heptadeuteriodimethylformamide–hexadeuterioacetone solution containing no external reference. The signal corresponding to the two ^{15}N-nitro atoms remained a sharp singlet at −100 °C.

2-*Methylaminopyridinium Dinitromethylide* (17).—*Method A*. Dimethyl sulphate (1 ml) was added to a solution of 2-aminopyridinium dinitromethylide (500 mg) in aqueous sodium hydroxide solution (10 ml; 1M), and the mixture was stirred (18 h) at room temperature. The solid which separated was recrystallised from water, when the *dinitromethylide* was obtained as colourless prisms (351 mg, 66%), m.p. 208—210 °C (decomp.) (Found: C, 39.8; H, 3.7; N, 26.6%; $M^{+\cdot}$, 212. $C_7H_8N_4O_4$ requires C, 39.6; H, 3.8; N, 26.4%; M, 212); δ [$(CD_3)_2SO$] 2.91 (3 H, d, J 6 Hz, $NHCH_3$), 6.95 (1 H, t, J 9 Hz, 5-H), 7.24 (1 H, d, J 9 Hz, 3-H), 8.08 (1 H, t, J 9 Hz, 4-H), 8.20 (1 H, d, J 9 Hz, 6-H), and 8.95 (1 H, br q, $NHCH_3$); δ_C [$(CD_3)_2SO$] 29.1 (NCH_3), 111.1 (C-3 or C-5), 112.2 (C-5 or C-3), 130.9 [C-$(NO_2)_2$], 142.9 (C-6 or C-4), 144.8 (C-4 or C-6), and 153.3 (C-2).

Method B. Nitration of 1-methyl-3-nitroimidazo[1,2-*a*]pyridinium-2-olate (9) by the method A described for the preparation of 2-aminopyridinium dinitromethylide (16) gave (55%) the dinitromethylide (17), m.p. 210—213 °C (decomp.), identical in all respects with that obtained above.

2-*Acetamidopyridinium Dinitromethylide* (18).—A mixture of 2-aminopyridinium dinitromethylide (610 mg), acetic anhydride (15 ml), and triethylamine (2 ml) was stirred (19 h) at room temperature. Evaporation and trituration of the residue with chloroform yielded an insoluble solid which on crystallisation from a mixture of acetonitrile and ether gave the *dinitromethylide* as pale yellow crystals (395 mg, 53%), m.p. 236—238 °C (decomp.) (Found: C, 40.3; H, 3.5; N, 23.4%; $M^{+\cdot}$, 240. $C_8H_8N_4O_5$ requires C, 40.0; H, 3.4; N, 23.3%; M, 240); $\nu_{max.}$ (Nujol) 1 730 cm^{-1}; δ [$(CD_3)_2SO$] 2.28

(3 H, s, $COCH_3$), 7.72 (1 H, t, *J* 6 Hz, 5-H), 8.55—8.65 (2 H, m, 3-H and 4-H), and 8.94 (1 H, d, *J* 6 Hz, 6-H).

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References

1 Part 21, C. G. Newton, W. D. Ollis, M. L. Podmore, and D. E. Wright, preceding paper.
2 W. D. Ollis and C. A. Ramsden, *Adv. Heterocycl. Chem.*, 1976, **19**, 1.
3 C. A. Ramsden, 'Comprehensive Organic Chemistry,' eds. D. H. R. Barton and W. D. Ollis, Pergamon Press, Oxford, 1979, vol. 4, p. 1171.
4 J. P. Paolini and R. K. Robins, *J. Org. Chem.*, 1965, **30**, 4085.
5 N. A. Bailey and C. G. Newton, *Cryst. Struct. Commun.*, 1980, **9**, 49.
6 C. Bugg and R. L. Sass, *Acta Crystallogr.*, 1965, **18**, 591; L. Devos, F. Baert, R. Fouret, and M. Thomas, *Acta Crystallogr., Ser. B*, 1980, **36**, 1807.
7 V. V. Semenov, S. A. Shevelev, and A. A. Fainzil'berg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 2640 (*Chem. Abstr.*, 1977, **86**, 139517t); V. V. Semenov and S. A. Shevelev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 2355 (*Chem. Abstr.*, 1979, **90**, 86916w).
8 E. Fischer, G. Rembarz, and K.-M. Wollin, *Z. Chem.*, 1978, **18**, 137; *J. Prakt. Chem.*, 1979, **321**, 429; 1980, **322**, 375.
9 J. Arriau, J. Deschamps, J. R. C. Duke, J. Epsztajn, A. R. Katritzky, E. Lunt, J. W. Mitchell, S. Q. Abbas Rizvi, and G. Roch, *Tetrahedron Lett.*, 1974, 3865.
10 J. Arriau, A. Dargelos, J. Epsztajn, A. R. Katritzky, E. Lunt, J. W. Mitchell, S. Q. Abbas Rizvi, and G. Roch, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1245.
11 R. J. Gillespie, J. Murray-Rust, P. Murray-Rust, and A. E. A. Porter, *J. Chem. Soc., Chem. Commun.*, 1978, 83.
12 I. Zugrăvescu and M. Petrovanu, 'N-Ylid Chemistry,' Editura Academiei Republicii Socialiste Romania, McGraw-Hill International Book Company, 1976, pp. 155—246; W. Sliwa, *Heterocycles*, 1980, **14**, 1793.
13 E. Andréasson, C. G. Newton, W. D. Ollis, C. W. Rees, D. I. Smith, and D. E. Wright, *J. Chem. Soc., Chem. Commun.*, 1983, 816.
14 E. Winkelmann, W. Raether, H. Hartung, and W.-H. Wagner, *Arzneim.-Forsch.*, 1977, **27**, 82.
15 E. B. Knott, *J. Chem. Soc.*, 1951, 3033.

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