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SYNTHESIS OF β-NITROPYRROLES FROM AMINO SUGARS AND NITROACETONE*†‡

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ABSTRACT

Reactions of 2-amino-2-deoxy-D-glucose and 1-amino-1-deoxy-D-fructose with nitroacetone produced 2-methyl-3-nitro-5-(D-*arabino*-tetritol-1-yl)pyrrole (**7**) and 2-methyl-3-nitro-4-(D-*arabino*-tetritol-1-yl)pyrrole (**11**), respectively, in good yields. The reactions take place through the intermediacy of the unstable 2-nitrovinylamino sugars **5** and **13**, the former compound having been isolated as its 1,3,4,6-tetra-*O*-acetyl derivative **9**. Acetylation of **7** and **11** afforded the corresponding tetra-acetates **8** and **12**. Periodate oxidation of **7** and **11** gave 5-methyl-4-nitro-2-pyrrolecarbaldehyde and 5-methyl-4-nitro-3-pyrrolecarbaldehyde, respectively, in good yields.

INTRODUCTION

Aldoses and 2-amino-2-deoxyaldoses react with 1,3-dicarbonyl compounds, yielding[2] 3-acyl-furans or -pyrroles (**1**). These reactions are considered to take place *via* aldol products **2**, which then undergo cyclization and dehydration. The reaction with aminodeoxy sugars has an additional pathway[3] in which the *N*-(2-acylvinyl)aminodeoxy sugars **3** (or the tautomeric imino form) are the key intermediates: the intramolecular aldehyde–enamine (or aldol) reaction of these compounds produces the 3-acylpyrroles **1b**. In these reactions, one of the carbonyl groups of the 1,3-dicarbonyl compound remains unchanged, acting only by activating the contiguous methylene group. Therefore, it might be anticipated that ketones R–CO–CH_2–Y, where Y is an electron-withdrawing group, would react with the sugars in a similar way, giving furans and pyrroles bearing the Y-sub-

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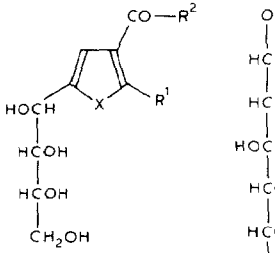
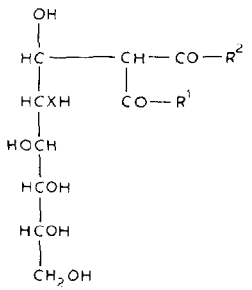
stituent at position 3. In order to test this hypothesis, the reactions of several aldoses and aminodeoxy sugars with nitroacetone have been investigated in the expectation of obtaining 3-nitro-furans and -pyrroles. Nitroalkanes readily undergo aldol-type (Henry) reactions with aldoses, yielding higher-carbon nitroalditols[4], and, on the other hand, 1-ethoxy-2-nitroethene (a synthetic equivalent for nitroacetaldehyde) reacts with aminodeoxy sugars to yield *N*-(2-nitrovinyl)aminodeoxy sugars (*e.g.*, **4**) which cyclize readily, affording[5] 2-(alditol-1-yl)-4-nitropyrroles (*e.g.*, **6**).



1a X = O
1b X = NH



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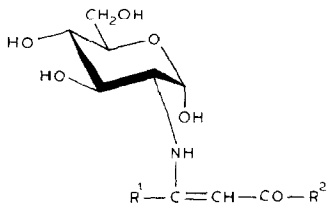

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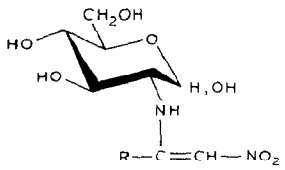
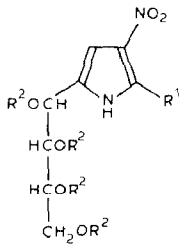
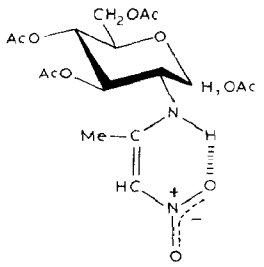


4 R = H
5 R = Me



6 R^1 = R^2 = H
7 R^1 = Me, R^2 = H
8 R^1 = Me, R^2 = Ac



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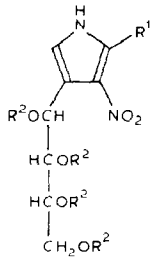
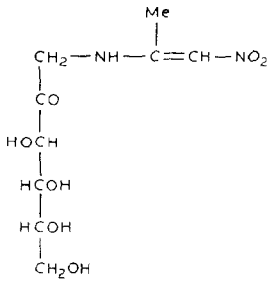


10 R^1 = R^2 = H
11 R^1 = Me, R^2 = H
12 R^1 = Me, R^2 = Ac



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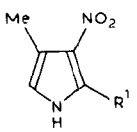
RESULTS AND DISCUSSION

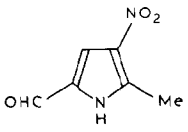
2-Amino-2-deoxy-D-glucose reacted with nitroacetone in boiling methanol to give crystalline 2-methyl-3-nitro-5-(D-*arabino*-tetritol-1-yl)pyrrole (**7**, >52%), which gave the tetra-acetate **8**. The reaction proceeded through the nitroenamine **5** which cyclized readily at neutral or weakly basic pH. When the reaction between the aminodeoxy sugar and nitroacetone was performed in the presence of acetic acid, the cyclization was inhibited, and an almost quantitative yield of the syrupy nitroenamine **5** was obtained. Purification of **5** was precluded by its conversion into **7**. Acetylation (acetic anhydride–pyridine) of freshly prepared **5** afforded (>70%) crystalline 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-[(1-methyl-2-nitrovinyl)amino]-α,β-D-glucopyranose (**9**).

Similarly, the reaction of 1-amino-1-deoxy-D-fructose with nitroacetone afforded 2-methyl-3-nitro-4-(D-*arabino*-tetritol-1-yl)pyrrole (**11**) in admixture with a second product having a similar chromatographic mobility, presumably the *N*-(1-methyl-2-nitrovinyl) derivative **13** of the aminodeoxyketose. This intermediate was more stable than **5** and its cyclization to the nitropyrrole **11** took longer and was accompanied by side reactions. Pure **11** (~40%) crystallized from the reaction mixture, and gave the tetra-acetate **12**.

Aminoacetone reacted with nitroacetone and with 1-ethoxy-2-nitroethylene, giving rise to 2,4-dimethyl-3-nitropyrrole (**14**, 14%) and 3-methyl-4-nitropyrrole (**15**, 21%), respectively. An unstable intermediate was also detected in these reactions, which could not be isolated because of its easy transformation into the final pyrrole. The lower efficiency of these reactions is probably due to self-condensation of the aminoketone. In the aminodeoxy sugars, this reaction is prevented by the cyclic hemiacetal structure.



14 R^1 = Me
15 R^1 = H



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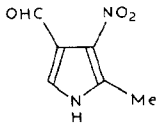

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Evidence for the structure of **9** was provided by analytical and spectral data (see Experimental). The spectra showed the presence of the nitroenamine system, and the geometric configuration was assigned by comparison with the spectra of the *Z* and *E* forms of 2-(alkylamino)-1-nitropropenes[6,7]. Both in the solid state and in chloroform solution, **9** exhibited the i.r. bands at 3230 (N–H) and 1605 cm^{-1} (C=C + N–H) characteristic of the intramolecularly bonded *Z* configuration. The ^{1}H-n.m.r. spectrum ($CDCl_3$) showed the presence of the α and β anomers, both with the *Z* configuration, in the ratio ~9:1. The anomers exhibited well separated signals for AcO-1, H-1,3,4, and NH, and the presence of the chelated structure,

and hence the *Z* configuration, was deduced from the high δ value of the signals for the amino proton. The i.r. and n.m.r. spectra (see Experimental) of the 4- and 5-(alditol-1-yl)-2-methyl-3-nitropyrroles **7, 8, 11**, and **12** were consistent with the proposed structures and were assigned by taking into consideration the data[5] for the analogous compounds **6** (and its tetra-acetate) and **10** (and its tetra-acetate), together with those for the simple 3-nitropyrroles **14** and **15**. Periodate oxidation of **7** and **11** afforded the anticipated pyrrolecarbaldehydes **16** and **17**, respectively, in good yields.

Attempts to react D-glucose and 4,6-*O*-ethylidene-D-glucose with nitroacetone in the presence of a base (MeONa, Et_3N), or with the potassium salt of nitroacetone, in various solvents at room temperature were unsuccessful. Likewise, no reaction was observed between D-glucose and the nitroketone in the presence of zinc chloride (*i.e.*, the conditions under which monosaccharides react[2] with 1,3-dicarbonyl compounds to yield the furans **1a**).

The above results indicate that the aldol reaction of monosaccharides with nitroacetone does not take place unless, as happens with aminodeoxy sugars (and aminoketones), it is an intramolecular process following the formation of a nitroenamine (or the tautomeric nitroimine). Substituted 3-nitropyrroles are then the final products which can often be obtained in good yields. These reactions of aminodeoxy sugars with nitroacetone (and eventually with other α-nitroketones), and those previously reported[5] with 1-ethoxy-2-nitroethene, provide an easy route to the 3-nitropyrroles which are otherwise accessible with difficulty.

EXPERIMENTAL

General methods. — Melting points were determined in open glass capillaries in a Büchi apparatus and are uncorrected. Optical rotations were recorded with a Perkin–Elmer 241Mc polarimeter. I.r. spectra were recorded with a Perkin–Elmer 299 spectrophotometer. ^{1}H-N.m.r. and ^{13}C-n.m.r. spectra (internal Me_4Si) were determined at 200 and 50.3 MHz, respectively, with a Varian XL-200 spectrometer. T.l.c. was performed on Silica Gel 60 HF_{254} (Merck) with detection with u.v. light (254 nm) and/or by charring with sulphuric acid. Elemental analyses were conducted at the Instituto de Química Orgánica (C.S.I.C., Madrid). Acetates were prepared by treating a cooled solution of the polyol (1 part) in pyridine (10 parts) with acetic anhydride (5 parts); after 24 h at 0°, the mixture was poured onto ice, and the crystalline precipitate was collected and recrystallized from the solvent indicated. Solutions were concentrated under diminished pressure at <50°.

*2-Methyl-3-nitro-5-(*D-arabino-*tetritol-1-yl)pyrrole* (**7**) *and its tetra-acetate* (**8**). — Finely powdered 2-amino-2-deoxy-D-glucose hydrochloride (1.0 g, 4.64 mmol) and $NaHCO_3$ (0.39 g, 4.64 mmol) were stirred in MeOH (25 mL) for 30 min. The mixture was filtered, nitroacetone (0.48 g, 4.64 mmol) was added to the filtrate, and the solution was heated under reflux. Monitoring of the reaction (t.l.c.; BuOH–AcOH–H_2O, 4:1:1) indicated the formation of the nitroenamine **5** (R_F 0.83) and

the nitropyrrole **7** (R_F 0.77), the concentration of which increased at the expense of **5**; after 6–7 h, only **7** was detected. Evaporation of the solvent and recrystallization of the residue from H_2O afforded **7** (0.60 g, 52%), m.p. 148–150°, $[\alpha]_D$ −55° (*c* 0.8, pyridine); ν_{max}^{KBr} 3390w (NH), 1475m and 1354m cm^{-1} (NO_2). N.m.r. data [$(CD_3)_2SO$]: ^1H, δ 2.50 (s, 3 H, Me-2), 4.40–4.60 (m, 3 H, exchangeable with D_2O, HO-2′,3′,4′), 5.10 (d, 1 H, $J_{1',OH}$ 6.5 Hz, exchangeable with D_2O, HO-1′), 3.30–3.70 (m, 4 H, H-2′,3′,4′,4′), 4.70 (ddd, 1 H, $J_{1',2'}$ 2.2, $J_{4,1'}$ 1.0 Hz, H-1′), 6.40 (dd, 1 H, $J_{NH,4}$ 2.7 Hz, H-4), 11.66 (s, 1 H, exchangeable with D_2O, NH); ^{13}C, δ 13.1 (q, Me-2), 63.2 (t, C-4′), 71.1 (d, C-3′), 73.6 (d, C-2′), 65.7 (d, C-1′), 101.4 (d, C-4), 132.0 (s, C-5), 132.9 (s, C-3), 132.1 (s, C-2).

Anal. Calc. for $C_9H_{14}N_2O_6$: C, 43.9; H, 5.7; N, 11.4. Found: C, 43.7; H, 5.7; N, 11.5.

The tetra-acetate (**8**) of **7** had m.p. 164–165° (from EtOH), $[\alpha]_D^{33}$ −62° (*c* 1, chloroform); ν_{max}^{KBr} 3270s (NH), 1765s, 1755vs, 1740vs and 1714vs (AcO), 1480m and 1355s cm^{-1} (NO_2). N.m.r. data ($CDCl_3$): ^1H, δ 2.07, 2.08, 2.09, and 2.12 (4 s, 12 H, 4 AcO), 2.60 (s, 3 H, Me-2), 4.13 (dd, 1 H, $J_{3',4'a}$ 6.2, $J_{4'a,4'b}$ 12.6 Hz, H-4′a), 4.26 (dd, 1 H, $J_{3',4'b}$ 3.1 Hz, H-4′b), 5.15 (dt, 1 H, $J_{2',3'}$ 6.1 Hz, H-3′), 5.59 (t, 1 H, $J_{1,2'}$ 6.1 Hz, H-2′), 5.95 (dd, 1 H, $J_{4,1'}$ 3.0 Hz, H-1′), 6.77 (d, 1 H, H-4), 9.57 (s, 1 H, NH); ^{13}C, δ 20.5 (q, Me-2), 20.6 and 20.7 (2 q, 2 CH_3CO), 61.6 (t, C-4′), 65.5 (d, C-1′), 69.4 (d, C-3′), 70.4 (d, C-2′), 105.9 (d, C-4), 123.6 (s, C-2), 133.1 (s, C-5), 133.5 (s, C-3), 170.0, 170.1, 170.5, and 170.7 (4 s, 4 CH_3CO).

Anal. Calc. for $C_{17}H_{22}N_2O_{10}$: C, 49.2; H, 5.3; N, 6.7. Found: C, 49.2; H, 5.2; N, 7.1.

*1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-[(1-methyl-2-nitrovinyl)amino]-α,β-*D*-glucopyranose* (**9**). — To a suspension of 2-amino-2-deoxy-β-D-glucopyranose (0.36 g, 2 mmol) in MeOH (25 mL) were added nitroacetone (0.41 g, 4 mmol) and acetic acid (0.5 mL), and the mixture was stirred for 2 h at room temperature. T.l.c. then indicated the presence of **5** and the absence of **7**. Concentration of the solution left a syrup, which was treated with C_6H_6 to remove the excess of nitroacetone. The product, containing (t.l.c.) **5** (main component) and minor amounts of 2-amino-2-deoxy-D-glucose, was unstable and was readily transformed into **7**. Acetylation of freshly prepared **5** yielded (71%) almost pure (t.l.c.) **9**, which, after recrystallization from EtOH, afforded the analytical sample (45%), m.p. 175–177°, $[\alpha]_D$ +160° (*c* 1, chloroform), αβ-ratio 9:1; ν_{max}^{KBr} 3230w (NH), 1750s (AcO), 1605s (C=C + N–H), 1490m and 1242m cm^{-1} (NO_2). N.m.r. data: ^1H ($CDCl_3$), δ (α anomer) 2.27 (s, 3 H, AcO-1), 4.38 (dd, 1 H, $J_{5,6a}$ 4.1, $J_{6a,6b}$ 12.7 Hz, H-6a), 5.16 (t, 1 H, $J_{3,4} \simeq J_{4,5}$ 10.3 Hz, H-4), 5.40 (t, 1 H, $J_{2,3} \simeq J_{3,4}$ 10.0 Hz, H-3), 6.23 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 9.90 (d, 1 H, $J_{2,NH}$ 10.0 Hz, NH); (β anomer) 2.13 (s, 3 H, AcO-1), 5.14 (t, 1 H, $J_{3,4} \simeq J_{4,5}$ 10.0 Hz, H-4), 5.31 (t, 1 H, $J_{2,3} \simeq J_{3,4}$ 10.3 Hz, H-3), 5.75 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1), 9.80 (d, 1 H, $J_{2,NH}$ 11.0 Hz, NH); other signals, 2.03, 2.05, and 2.10 (3 s, 12 H, 3 AcO and Me-1′), 3.80–4.20 (m, 4 H, H-2,5,6b), 6.49 (s, 1 H, H-2′); ^{13}C [$(CD_3)_2SO$], δ 16.9 (q, Me-1′), 20.2, 20.3, 20.4, and 20.5 (4 q, 4 CH_3CO), 53.7 (d, C-2), 61.1 (d, C-6), 66.9 (d, C-4), 69.3 (d, C-3), 71.1 (d, C-5), 90.1 (d, C-1), 111.1 (d, C-2′), 159.35 (d, C-1′), 168.9, 169.2, 169.8, and 170.0 (4 s, 4 CH_3CO).

Anal. Calc. for $C_{17}H_{24}N_2O_{11}$: C, 47.2; H, 5.6; N, 6.5. Found: C, 46.9; H, 5.5; N, 6.2.

*2-Methyl-3-nitro-4-(*D-arabino-*tetritol-1-yl)pyrrole* (**11**) *and its tetra-acetate* (**12**). — To a solution of 1-amino-1-deoxy-D-fructose acetate (0.478 g, 2 mmol) in H_2O (25 mL) was added nitroacetone (0.206 g, 2 mmol) and the amount of acetone required to obtain a homogeneous solution. The mixture was heated under reflux for 4 h, during which time **11** began to crystallize. The mixture was refrigerated, and the solid was collected and recrystallized from H_2O to yield **11** (50%), m.p. 160–161°, $[\alpha]_D^{33}$ −0.5° (*c* 1, pyridine); ν_{max}^{KBr} 3285w (NH), 1468m and 1350s cm^{-1} (NO_2). N.m.r. data [$(CD_3)_2SO$]: ^1H, δ 2.5 (s, 3 H, Me-2), 4.16–4.65 (m, 4 H, exchangeable with D_2O, HO-1′,2′,3′,4′), 3.3–3.7 (m, 4 H, H-2′,3′,4′,4′), 5.3 (ddd, 1 H, $J_{5,1'}$ 1.0, $J_{1',2'}$ 1.2, $J_{1',OH}$ 6.6 Hz, H-1′), 6.6 (d, 1 H, H-5), 11.6 (s, 1 H, exchangeable with D_2O, NH); ^{13}C, δ 14.0 (q, Me-2), 63.8 (t, C-4′), 65.3 (d, C-1′), 71.9 (d, C-3′), 73.1 (d, C-2′), 116.2 (d, C-5), 123.2 (s, C-4), 130.2 (s, C-2), 133.3 (s, C-3).

Anal. Cac. for $C_9H_{14}N_2O_6$: C, 43.9; H, 5.7; N, 11.4. Found: C, 43.8; H, 5.9; N, 11.6.

The tetra-acetate (**12**) of **11** had m.p. 154–155° (from EtOH), $[\alpha]_D^{33}$ +8.6° (*c* 1, chloroform); ν_{max}^{KBr} 3275br,s (NH), 1742vs and 1725vs (AcO), 1475m and 1349s (NO_2). N.m.r. data ($CDCl_3$): ^1H, δ 1.9, 2.0, and 2.1 (3 s, 12 H, 4 AcO), 2.5 (s, 3 H, Me-2), 4.2 (dd, 1 H, $J_{4'a,4'b}$ 12.4, $J_{3',4'a}$ 5.2 Hz, H-4′a), 4.3 (dd, 1 H, $J_{3',4'b}$ 2.7 Hz, H-4′b), 5.3 (ddd, 1 H, $J_{2',3'}$ 8.5 Hz, H-3′), 5.6 (dd, 1 H, $J_{1',2'}$ 2.7 Hz, H-2′), 6.6 (dd, 1 H, $J_{5,1'}$ 0.8 Hz, H-1′), 6.5 (dd, 1 H, $J_{NH,5}$ 2.6 Hz, H-5), 9.2 (s, 1 H, exchangeable with D_2O, NH); ^{13}C, δ 14.1 (q, Me-2), 20.4, 20.6, and 20.8 (3 q, 3 CH_3CO), 62.3 (t, C-4′), 67.1 (d, C-1′), 68.1 (d, C-3′), 69.9 (d, C-2′), 114.9 (d, C-5), 117.1 (s, C-4), 130.9 (s, C-2), 134.0 (s, C-3), 169.3, 169.8, 170.2, and 170.8 (4 s, 4 CH_3CO).

Anal. Calc. for $C_{17}H_{22}N_2O_{10}$: C, 49.2; H, 5.3; N, 6.7. Found: C, 49.2; H, 5.5; N, 6.9.

2,4-Dimethyl-3-nitropyrrole (**14**). — To a stirred solution of aminoacetone hydrochloride (0.50 g, 4.5 mmol) and Et_3N (0.62 mL, ~4.5 mmol) in MeOH (20 mL) was rapidly added nitroacetone (0.46 g, 4.5 mmol), and the mixture was heated under reflux for 14 h. Monitoring of the reaction (t.l.c.; ether–hexane, 2:1) indicated the formation of **14** and minor amounts of a second product. Evaporation of the solvent and recrystallization of the residue from H_2O afforded **14** (0.08 g, 14%), m.p. 142–143°; ν_{max}^{KBr} 3290 (NH), 1468 and 1335s cm^{-1} (NO_2). N.m.r. data ($CDCl_3$): ^1H, δ 2.31 (d, 3 H, $J_{5,Me}$ 1.1 Hz, Me-4), 2.61 (s, 3 H, Me-2), 6.36 (dq, 1 H, $J_{5,NH}$ 2.5 Hz, H-5), 8.40 (d, 1 H, NH); ^{13}C, δ 12.2 and 14.6 (2 q, Me-2 and Me-4), 114.6 (d, C-5), 117.0 (s, C-4), 132.5 (s, C-2), 134.1 (s, C-3).

Anal. Calc. for $C_6H_8N_2O_2$: C, 51.4; H, 5.8; N, 20.0. Found: C, 51.6; H, 5.4; N, 20.0.

3-Methyl-4-nitropyrrole (**15**). — A suspension of aminoacetone hydrochloride (0.48 g, 4.40 mmol) and $NaHCO_3$ (0.37 g, 4.40 mmol) in MeOH (20 mL) was stirred until neutralization. 1-Ethoxy-2-nitroethene (1.99 g, 4.40 mmol) was quickly added, and the mixture was heated under reflux for 16 h. Monitoring of the reaction

(t.l.c.; ether–hexane, 2:1) indicated the formation of **15** and minor amounts of a second product. The residue after concentration of the reaction mixture was subjected to column chromatography (ether–hexane) to yield **15** (0.04 g, 21%), m.p. 108–109°; ν_{max}^{KBr} 3260w (NH), 1473m and 1355s cm^{-1} (NO_2). N.m.r. data ($CDCl_3$): ^1H, δ 2.34 (d, 3 H, $J_{5,Me}$ 1.1 Hz, Me-4), 6.54 (ddq, 1 H, $J_{2,5}$ 2.34, $J_{NH,5}$ 1.26 Hz, H-5), 7.65 (dd, 1 H, $J_{NH,2}$ 1.26 Hz, H-2), 8.57 (dd, 1 H, NH); ^{13}C, δ 11.4 (q, Me-4), 116.6 (d, C-5), 117.5 (s, C-4), 120.8 (d, C-2), 136.0 (s, C-3).

Anal. Calc. for $C_5H_6N_2O_2$: C, 47.6; H, 4.8; N, 22.2. Found: C, 47.6; H, 4.6; N, 21.9.

5-Methyl-4-nitro-2-pyrrolecarbaldehyde (**16**). — A solution of **2** (0.04 g, 0.16 mmol) and $NaIO_4$ (0.10 g, 0.48 mmol) in H_2O (8 mL) was stirred for 4 h at room temperature. The product that crystallized was chromatographically pure **6**. After recrystallization from H_2O, **16** (50%) had m.p. 148–150°; ν_{max}^{KBr} 3230 (NH), 1655s (C=O), 1485m and 1320m cm^{-1} (NO_2). N.m.r. data [$(CD_3)_2SO$]: ^1H, δ 2.58 (s, 3 H, Me-5), 3.37 (s, 1 H, NH), 7.61 (s, 1 H, H-3), 9.52 (s, 1 H, CHO); ^{13}C, δ 13.31 (q, Me-5), 116.28 (d, C-3), 129.04 and 134.03 (2 s, C-2,5), 139.02 (s, C-4), 180.45 (s, CHO).

Anal. Calc. for $C_6H_6N_2O_3$: C, 46.8; H, 3.9; N, 18.2. Found: C, 46.7; H, 4.0; N, 18.0.

5-Methyl-4-nitro-3-pyrrolecarbaldehyde (**7**). — Treatment of **5** (0.09 g, 0.37 mmol) with $NaIO_4$, as described for **2**, gave **17**. After recrystallization from H_2O, **17** (72%) had m.p. 185–187°; ν_{max}^{KBr} 3250w, 1660s (C=O), 1480m and 1340m cm^{-1} (NO_2). N.m.r. data [$(CD_3)_2SO$]: ^1H, δ 2.53 (s, 3 H, Me-5), 3.42 (s, 1 H, NH), 7.54 (s, 1 H, H-2), 10.18 (s, 1 H, CHO); ^{13}C, δ 13.16 (q, Me-5), 119.71 (d, C-2), 122.88 and 131.21 (2 s, C-3 and C-5), 135.59 (s, C-4), 185.75 (s, CHO).

Anal. Calc. for $C_6H_6N_2O_3$: C, 46.8; H, 3.9; N, 18.2. Found: C, 46.6; H, 3.9; N, 18.0.

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