v-Triazolines. Part 36.[1] New synthesis of ethyl 1-alkyl-1,4,5,6-tetrahydro-6-oxopyridine-3-carboxylates and 1-alkyl-1,4,5,6-tetrahydro-6-oxopyridine-3-carbonitriles through reduction of *N*-2-nitroarylamidines

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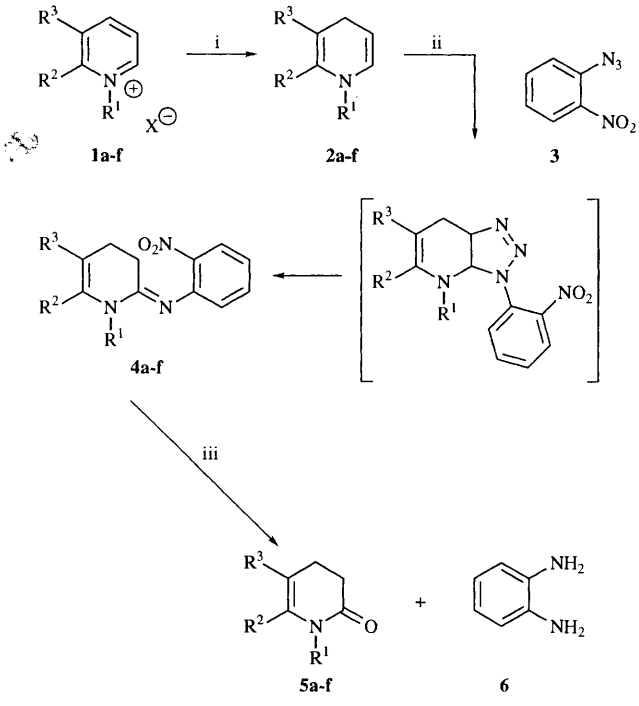
Ethyl 1-alkyl-1,4-dihydropyridine-3-carboxylates 2a–d and 1-alkyl-1,4-dihydropyridine-3-carbonitriles 2e,f were allowed to react with 2-nitrophenyl azide 3 to give tertiary amidines 4 by spontaneous rearrangement of the triazoline cycloadducts. Ready catalytic hydrogenation with Pd–C of 4 gave the corresponding ethyl 1-alkyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carboxylates 5a–d and 1-alkyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitriles 5e,f.

6-Oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile and 6-oxo-1,4,5,6-tetrahydropyridine-3-carboxylic acid and its esters together with their derivatives have received attention in the literature both as synthetic intermediates and as biologically significant compounds. They are involved in metabolic pathways[2,3] and are active in some instances as drugs.[4] Several synthetic methods for their preparation have been reported. The most general route is by reaction of β-alkoxycarbonyl- or β-cyanoenamines with α,β-unsaturated nitriles or acids and their derivatives[5–14] or by reaction of γ-oxopentanoic acid derivatives with ammonia or amines.[15–18] Less general methods include photochemical routes,[19] diene syntheses[20] and cyclocondensations.[21]

This paper, which is a part of our continuing studies devoted to exploitation of the synthetic potential of 5-amino-*v*-triazolines,[22–24] describes a new and useful entry to the above compounds. Starting materials are the readily available nicotinonitrile and alkyl nicotinates.

Cycloaddition of enamines and azides results in the formation of 5-amino-*v*-triazolines whose thermal rearrangement to tertiary amidines is a well established reaction. It is made easier by electron-withdrawing groups on N-1.[25] Cyclic enamines as 1-alkyl-1,2,3,4-tetrahydropyridines have been already reported to react with arylsulfonyl azides affording 1-alkyl-2-arylsulfonyliminopiperidines through spontaneous cleavage and rearrangement of triazoline cycloadducts.[26]

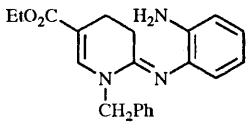
1-Alkyl-1,4-dihydropyridine-3-carboxylic acid esters **2a–d** and -3-carbonitriles **2e,f** were allowed to react with 2-nitrophenyl azide **3**; compounds **2e,f** are known. The new compounds **2a–d** were obtained according to described procedures by reduction of the corresponding pyridinium salts **1a–d** with sodium dithionite and base[27] (Scheme 1). The cycloaddition occurred smoothly at room temperature and in benzene solution. As expected, only the less hindered double bond was reactive under the adopted conditions and the labile triazoline adduct underwent direct rearrangement through N_2 elimination and a hydrogen shift to give ethyl 6-(2-nitrophenylimino)-1,4,5,6-tetrahydropyridine-3-carboxylates **4a–d** and -3-carbonitriles **4e,f**. Their structures were readily confirmed on the basis of IR and ^1H NMR results—typically a singlet at δ 7.6–7.2 (2-H) and a multiplet in the δ 2.6–2.2 region (CH_2CH_2). Attempts to bring about direct hydrolysis of compounds **4** gave poor results. The resistance of tertiary amidines to hydrolysis is high and in the present case severe conditions were impracticable owing to the presence of carboxylate and nitrile groups. Compounds **4** underwent ready



	R^1	R^2	R^3
1, 2, 4, 5 a	Me	H	CO_2Et
b	Me	Me	CO_2Et
c	Et	H	CO_2Et
d	CH_2Ph	H	CO_2Et
e	Me	H	CN
f	Et	H	CN

Scheme 1 *Reagents and conditions:* i, $Na_2S_2O_4$; ii, PhH, room temp.; iii, EtOH, 10% Pd–C, H_2, room temp., 1 bar

hydrogenation with 10% Pd–C to give the corresponding ethyl 1-alkyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carboxylates **5a–d** and -3-carbonitriles **5e,f**. The nitro compounds **4** were reduced in ethanol solution and at room temperature and pressure with consumption of 3 equiv. of H_2. Chromatographic separation of the reaction mixtures afforded pure products **5a–f** and, as a by-product, an equivalent amount of phenylene-1,2-diamine; product **5b** is known.[5] Structural assignments were made on the basis of analytical and



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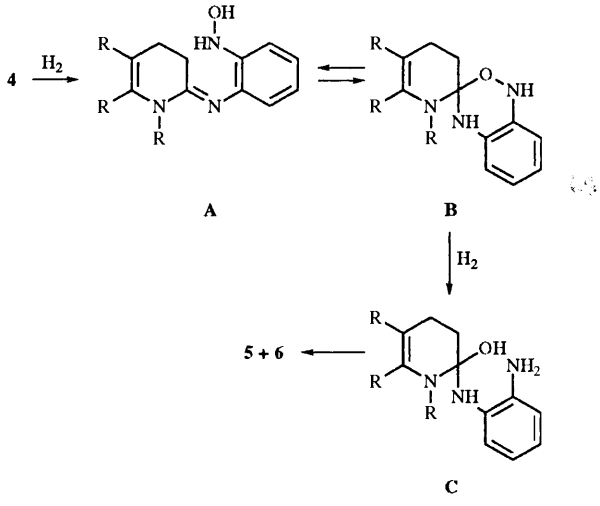
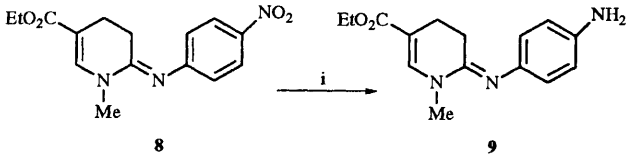
spectroscopic results. Typical features in the ^{1}H NMR spectra are a singlet at δ 7.6–7.2 which is associated with 2-H and a multiplet at δ 2.7–2.5 corresponding to 4-H and 5-H, respectively. Product **5d** was accompanied by the reduced amidine **7** which could be isolated as the picrate.

The formation of compounds **5** upon hydrogenation of the amidines **4** deserves some comment. Formally, compounds **5** are hydrolysis products of **4**. However, the reduction step is essential for the final outcome. Indeed, the nitro amidines **4** are completely unaffected by moist ethanol both in presence and in absence of the catalyst when molecular hydrogen is absent. Moreover, the amino amidine **7** resisted hydrolysis under the same conditions. The rationale of the reaction is suggested in Scheme 2. During reduction, the spiro dihydrobenzoxadiazine



Scheme 2

intermediates **B** are formed by intramolecular cyclization of the hydroxylamines **A**. The intermediacy of hydroxylamines in the reduction of nitro compounds is well substantiated [28] and some examples of intramolecular ring closure of hydroxylamines have been reported.[29] Further reduction of the N–O bond in **B** results in the formation of the hydroxy aminals **C** which decompose into the amides **5** and phenylenediamine **6**. This reaction is precedented by the easy reduction of pyrimido[5,4-*c*]-1,2,5-oxadiazines to diaminouracyls and ketones.[30] Expectedly, the *para*-isomer of **4a**, *i.e.* compound **8**, was smoothly reduced to the corresponding amine **9** without formation of other products (Scheme 3).



8 **9**

Scheme 3 *Reagents and conditions:* i, EtOH, 10% Pd–C, H_2, room temp., 1 bar

In conclusion, the catalytic reduction of *o*-nitro amidines of the general formula **4** offers an alternative entry to tetrahydro-6-pyridones. This method seems to be most useful in the case of unsubstituted products at C-2 which are relatively inaccessible by known procedures.

Experimental

Mps were determined using a Büchi 510 (capillary) apparatus. IR spectra were measured using a JASCO IR Report 100 instrument. NMR spectra were obtained with Bruker AC 200 and EM-390 Varian at 200 MHz. *J* Values are given in Hz (solvent was $CDCl_3$ if not indicated). Column chromatography was performed on silica gel [Kieselgel 60–70 230 ASTM (Merck)]. Mass spectra were obtained with V G Analytical 7070 EQ. The quaternary salts **1e,f** are known compounds [27] and the dihydropyridines **2e,f** have been already described.[27]

1-Methyl-3-ethoxycarbonylpyridinium iodide 1a
A solution of ethyl nicotinate (10.0 g, 66 mmol) in nitromethane (80 cm^3) with methyl iodide (28.0 g, 197 mmol) was stirred at room temperature for 12 h after which it was evaporated and the resulting residue crystallized from diethyl ether; the product (91%) had mp 88 °C; δ_H(DMSO) 1.42 (3 H, t, CH_3, *J* 7.10), 4.33 (3 H, s, CH_3N), 4.40 (2 H, q, CH_2, *J* 7.10), 8.27 (1 H, dd, 5-H, $J_{4,5}$ 8.12, $J_{5,6}$ 6.12), 8.94 (1 H, d, 4-H, $J_{4,5}$ 8.12), 9.19 (1 H, d, 6-H, $J_{5,6}$ 6.12) and 9.59 (1 H, s, 2-H).

1,2-Dimethyl-3-ethoxycarbonylpyridinium iodide 1b
A solution of ethyl 2-methylnicotinate (5 g, 30 mmol) in ethyl acetate (20 cm^3) was treated with methyl iodide (8.6 g, 60 mmol) and the mixture heated at 40 °C for 24 h. It was then cooled in ice and diluted with diethyl ether to induce precipitation of a yellow salt (74%); mp 115 °C; δ_H(DMSO) 1.37 (3 H, t, CH_3, *J* 7.08), 2.92 (3 H, s, 2-CH_3), 4.31 (3 H, s, CH_3N), 4.43 (2 H, q, CH_2, *J* 7.08), 8.08 (1 H, dd, 5-H, $J_{5,6}$ 4.97, $J_{4,5}$ 8.06), 8.83 (1 H, dd, 4-H, $J_{4,5}$ 8.06, $J_{4,6}$ 1.3) and 9.16 (1 H, dd, 6-H, $J_{5,6}$ 4.97, $J_{6,4}$ 1.3).

1-Ethyl-3-ethoxycarbonylpyridinium iodide 1c
Ethyl nicotinate (5.0 g, 33 mmol) and ethyl iodide (9.9 g, 66 mmol) were heated at reflux in ethyl acetate for 36 h. Evaporation of the mixture gave an uncrystallizable oil which was employed directly for the following reaction; δ_H 1.42 (3 H, t, CH_3, *J* 7.16), 1.73 (3 H, t, CH_3, *J* 7.38), 4.45 (2 H, q, CH_2O, *J* 7.16), 5.10 (2 H, q, CH_2N, *J* 7.38), 8.36 (1 H, dd, 5-H, $J_{4,5}$ 8.22, $J_{5,6}$ 6.14), 8.95 (1 H, d, 4-H, $J_{4,5}$ 8.22), 9.56 (1 H, s, 2-H) and 9.80 (1 H, d, 6-H, $J_{5,6}$ 6.14).

1-Benzyl-3-ethoxycarbonylpyridinium chloride 1d
A solution of ethyl nicotinate (4.0 g, 26 mmol) in benzyl chloride (4.4 cm^3, 4.86 g, 38 mmol) was heated at 110 °C for 3 h. Addition of diethyl ether to the mixture gave a hygroscopic salt which was filtered off (58%); δ_H(DMSO) 1.39 (3 H, t, CH_3, *J* 7.10), 4.46 (2 H, q, CH_2, *J* 7.10), 6.05 (2 H, s, CH_2Ph), 7.39–7.63 (5 H, m, Ph), 8.32 (1 H, dd, 5-H, $J_{5,4}$ 8.2, $J_{5,6}$ 6.14), 9.02 (1 H, dt, 4-H, $J_{4,5}$ 8.2, $J_{4,6}$ 1.3, $J_{2,4}$ 1.0), 9.48 (1 H, dd, 6-H, $J_{6,5}$ 6.14, $J_{6,4}$ 1.3) and 9.82 (1 H, d, 2-H, $J_{2,4}$ 1.3).

General procedure for the preparation of dihydropyridines 2a–d
A solution of the appropriate quaternary salt **1** (30 mmol) in a mixture of water (100 cm^3) and ethyl acetate (80 cm^3) under nitrogen at 0–5 °C were heated simultaneously with sodium dithionite (12 mmol) and sodium hydrogen carbonate (135 mmol). After 1 h the organic phase was separated and the aqueous phase extracted with ethyl acetate (× 3). The combined organic phase and extracts were washed with cold water, dried and evaporated to give a crude oil which was used directly in the following reaction.

Ethyl 1-methyl-1,4-dihydropyridine-3-carboxylate 2a. Yellow oil (80%); δ_H 1.22 (3 H, t, CH_3, *J* 7.1), 2.98 (3 H, s, CH_3N), 3.02–3.03 (2 H, m, 4-CH_2), 4.11 (2 H, q, CH_2, *J* 7.1), 4.72 (1 H, m, 5-H), 5.60 (1 H, m, 6-H) and 6.94 (1 H, d, 2-H, *J* 1.32).

Ethyl 1,2-dimethyl-1,4-dihydropyridine-3-carboxylate 2b. Red oil (73%); δ_H 1.24 (3 H, t, CH_3, *J* 7.11), 2.33 (3 H, s, 2-CH_3), 2.96 (3 H, s, CH_3N), 3.10–3.12 (2 H, m, 4-CH_2), 4.10 (2 H, q, CH_2, *J* 7.11), 4.67–4.76 (1 H, m, 5-H) and 5.63–5.69 (1 H, m, 6-H).

Ethyl 1-ethyl-1,4-dihydropyridine-3-carboxylate 2c. Yellow oil (55%); δ_H 1.13–1.27 (6 H, m, 2-CH_3), 3.08–3.19 (4 H, m, 4-CH_2 and CH_2N), 4.14 (2 H, q, CH_2O, *J* 7.10), 4.22–4.81 (1 H, m, 5-H), 5.64–5.70 (1 H, m, 6-H) and 7.01 (1 H, d, 2-H, *J* 1.5).

Ethyl 1-benzyl-1,4-dihydropyridine-3-carboxylate 2d. The reaction was performed at 40 °C; red oil (80%); δ_H 2.25 (3 H, t, CH_3, *J* 7.12), 3.12–3.14 (2 H, m, 4-CH_2), 4.14 (2 H, q, CH_2, *J* 7.12), 4.29 (2 H, s, CH_2Ph), 4.74–4.81 (1 H, m, 5-H), 5.65–5.70 (1 H, m, 6-H), 7.12 (1 H, d, 2-H, *J* 1.5) and 7.13–7.41 (5 H, m, Ph).

Preparation of ethyl 6-(2-nitrophenylimino)-1,4,5,6-tetrahydropyridine-3-carboxylates and 6-(2-nitrophenylimino)-1,4,5,6-tetrahydropyridine-3-carbonitriles 4a–f

General procedure. The crude dihydropyridine **2** (10 mmol) was added to a solution of 2-nitrophenylazide **3** (10 mmol) in benzene (30 cm^3) and the reaction mixture stirred at room temperature for 12 h until disappearance of the reagents. The brown solution, after evaporation, was purified by column chromatography with cyclohexane–ethyl acetate (3 : 7) as eluent.

Ethyl 1-methyl-6-(2-nitrophenylimino)-1,4,5,6-tetrahydropyridine-3-carboxylate 4a. Solid (45%), mp 87–88 °C (from ethanol) (Found: C, 59.45; H, 5.8; N, 13.2. $C_{15}H_{17}N_3O_4$ requires C, 59.4; H, 5.6; N, 13.15%); ν_{max}(Nujol)/cm^{-1} 1695 (C=O); δ_H 1.28 (3 H, t, CH_3, *J* 7.01), 2.36–2.54 (4 H, m, CH_2CH_2), 4.19 (2 H, q, CH_2, *J* 7.01), 3.28 (3 H, s, CH_3N), 7.35 (1 H, s, 2-H), 6.83 (1 H, dd, 6′-H, $J_{5',6'}$ 8.10, $J_{4',6'}$ 1.30), 7.10 (1 H, dt, 4′-H, $J_{4',5'}$ 8.10, $J_{3',4'}$ 8.10, $J_{6',4'}$ 1.30), 7.48 (1 H, dt, 5′-H, $J_{4',5'}$ 8.10, $J_{5',6'}$ 8.10, $J_{3',5'}$ 1.30) and 7.93 (1 H, dd, 3′-H, $J_{3',4'}$ 8.10, $J_{3',5'}$ 1.30).

Ethyl 1,2-dimethyl-6-(2-nitrophenylimino)-1,4,5,6-tetrahydropyridine-3-carboxylate 4b. Yellow oil (30%); ν_{max}(Nujol)/cm^{-1} 1695 (C=O); δ_H 1.28 (3 H, t, CH_3, *J* 7.01), 2.29–2.59 (4 H, m, CH_2CH_2), 2.54 (3 H, s, 2-CH_3), 3.54 (3 H, s, CH_3N), 4.17 (2 H, q, CH_2, *J* 7.01), 6.82 (1 H, dd, 6′-H, $J_{5',6'}$ 8.22, $J_{4',6'}$ 1.51), 7.09 (1 H, dt, 4′-H, $J_{4',5'}$ 8.22, $J_{4',3'}$ 8.22, $J_{4',6'}$ 1.51), 7.48 (1 H, dt, 5′-H, $J_{4',5'}$ 8.22, $J_{5',6'}$ 8.22, $J_{5',3'}$ 1.51) and 7.93 (1 H, dd, 3′-H, $J_{3',4'}$, 8.22, $J_{3',5'}$ 1.51); *m*/*z* 317(M^+, 100%), 272 (38), 196 (25), 182 (18), 168 (40), 161 (20), 150 (21), 138 (21) and 110 (23).

Ethyl 1-ethyl-6-(2-nitrophenylimino)-1,4,5,6-tetrahydropyridine-3-carboxylate 4c. Yellow oil (70%); ν_{max}(Nujol)/cm^{-1} 1695 (C=O); δ_H 1.25–1.33 (6 H, m, 2-CH_3), 2.41–2.51 (4 H, m, CH_2CH_2), 3.76 (2 H, q, CH_2N, *J* 7.12), 4.20 (2 H, q, CH_2O, *J* 7.09), 6.82 (1 H, dd, 6′-H, $J_{6',5'}$ 8.01, $J_{6',4'}$ 1.12), 7.15 (1 H, dt, 4′-H, $J_{4',5'}$ 8.01, $J_{4',3'}$ 8.01, $J_{4',6'}$ 1.12), 5.37 (1 H, s, 2-H), 7.48 (1 H, dt, 5′-H, $J_{5',4'}$ 8.01, $J_{5',6'}$ 8.01, $J_{5',3'}$ 1.12), 7.94 (1 H, dd, 3′-H, $J_{3',4'}$ 8.01, $J_{3',5'}$, 1.12).

Ethyl 1-benzyl-6-(2-nitrophenylimino)-1,4,5,6-tetrahydropyridine-3-carboxylate 4d. Yellow oil (40%); ν_{max}(Nujol)/cm^{-1} 1698 (C=O); δ_H 1.26 (3 H, t, CH_3, *J* 7.04), 2.45–2.54 (4 H, m, CH_2CH_2), 4.17 (2 H, q, CH_2, *J* 7.04), 4.96 (2 H, s, CH_2Ph), 6.77 (1 H, dd, 6′-H, $J_{4',6'}$ 1.22, $J_{5',6'}$ 8.06), 7.10 (1 H, dt, 4′-H, $J_{4',6'}$ 1.22, $J_{4',5'}$ 8.06, $J_{3',4'}$ 8.06), 7.25–7.38 (5 H, m, Ph), 7.33 (1 H, s, 2-H), 7.46 (1 H, dt, 5′-H, $J_{4',5'}$ 8.06, $J_{5',6'}$ 8.06, $J_{3',5'}$ 1.22) and 7.94 (1 H, dd, 3′-H, $J_{3',4'}$ 8.06, $J_{3',5'}$ 1.22); *m*/*z* 379 (M^+, 1%), 333 (8), 259 (21), 230 (12), 214 (7), 138 (21), 91 (100) and 65 (25).

1-Methyl-6-(2-nitrophenylimino)-1,4,5,6-tetrahydropyridine-3-carbonitrile 4e. Solid (66%); mp 110 °C (from diisopropyl ether) (Found: C, 60.75; H, 4.55; N, 22.7. $C_{13}H_{12}N_4O_2$ requires C, 60.9; H, 4.7; N, 22.85 %); ν_{max}(Nujol)/cm^{-1} 2190 (CN); δ_H 2.42–2.49 (4 H, m, CH_2CH_2), 3.28 (3 H, s, CH_3N), 6.82 (1 H, dd, 6′-H, $J_{5',6'}$ 8.02, $J_{4',6'}$ 1.31), 6.94 (1 H, s, 2-H), 7.14 (1 H, dt, 4′-H, $J_{4',5'}$ 8.02, $J_{3',4'}$ 8.02, $J_{4',6'}$ 1.31), 7.51 (1 H, dt, 5′-H, $J_{5',4'}$ 8.02, $J_{5',6'}$ 8.02, $J_{3',5'}$ 1.31) and 7.95 (1 H, dd, 3′-H, $J_{3',4'}$ 8.02, $J_{3',5'}$ 1.31).

1-Ethyl-6-(2-nitrophenylimino)-1,4,5,6-tetrahydropyridine-3-carbonitrile 4f. Yellow oil (42%); ν_{max}(Nujol)/cm^{-1} 2195 (CN); δ_H 1.28 (3 H, t, CH_3, *J* 7.10), 2.45–2.49 (4 H, m, CH_2CH_2), 3.74 (2 H, q, CH_2, *J* 7.10), 6.80 (1 H, dd, 6′-H, $J_{6',5'}$ 8.01, $J_{6',4'}$ 1.01), 6.95 (1 H, s, 2-H), 7.15 (1 H, dt, 4′-H, $J_{4',5'}$ 8.01, $J_{4',3'}$ 8.01, $J_{4',6'}$ 1.01), 7.50 (1 H, dt, 5′-H, $J_{5',6'}$ 8.01, $J_{5',4'}$ 8.01, $J_{5',3'}$ 1.01) and 7.96 (1 H, dd, 3′-H, $J_{3',4'}$ 8.01, $J_{3',5'}$ 1.01).

Ethyl 1-methyl-6-(4-nitrophenylimino)-1,4,5,6-tetrahydropyridine-3-carboxylate 8. This compound was prepared as described for **4a** starting from **2a** (1.7 g, 10 mmol) and 4-nitrophenyl azide (1.6 g, 10 mmol); solid (40%); mp 134 °C (from ethanol) (Found: C, 59.3; H, 5.75; N, 13.05. $C_{15}H_{17}N_3O_4$ requires C, 59.4; H, 5.6; N, 13.15%); ν_{max}(Nujol)/cm^{-1} 1695 (C=O); δ_H 1.29 (3 H, t, CH_3, *J* 7.10), 2.46 (4 H, s, CH_2CH_2), 3.30 (3 H, s, CH_3N), 4.20 (2 H, q, CH_2, *J* 7.10), 6.83 (2 H, d, 2′-H and 6′-H, *J* 8.9), 7.34 (1 H, s, 2-H), 8.18 (2 H, d, 3′-H and 5′-H, *J* 8.9).

Reduction of ethyl 1-alkyl-6-(2-nitrophenylimino)-1,4,5,6-tetrahydropyridine-3-carboxylates and 1-alkyl-6-(2-nitrophenylimino)-1,4,5,6-tetrahydropyridine-3-carbonitriles

General procedure. 10% Pd–C (0.2 g) was added to a solution of compound **4** (5 mmol) in ethanol (50 cm^3) and the mixture was hydrogenated at room temperature and pressure. After this, the crude reaction mixture was filtered through a bed of Celite and evaporated to dryness and the residue was chromatographed on a silica gel column to afford the corresponding compound **5** and *o*-phenylenediamine **6** as main products.

Ethyl 1-methyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carboxylate 5a. Solid (50%); mp 37 °C (from diisopropyl ether) (Found: C, 58.7; H, 7.2; N, 7.9. $C_9H_{13}NO_3$ requires C, 59.0; H, 7.1; H, 7.65%); ν_{max}(Nujol)/cm^{-1} 1680 (CO_2Et) and 1630 (C=O); δ_H 1.26 (3 H, t, CH_3, *J* 7.08), 2.51–2.62 (4 H, m, CH_2CH_2), 3.12 (3 H, s, 1-CH_3), 4.17 (2 H, q, CH_2, *J* 7.08) and 7.22 (1 H, s, 2-CH).

Ethyl 1,2-dimethyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carboxylate 5b. Uncrystallizable oil (30%); ν_{max}(Nujol)/cm^{-1} 1685 (CO_2Et) and 1640 (C=O); δ_H 1.29 (3 H, t, CH_3, *J* 7.10), 2.43 (3 H, s, 2-CH_3), 2.43–2.61 (4 H, m, CH_2CH_2), 3.17 (3 H, s, 1-CH_3) and 4.18 (2 H, q, CH_2, *J* 7.10).

Ethyl 1-ethyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carboxylate 5c. Solid (40%); mp 42–43 °C (from diisopropyl ether) (Found: C, 64.9; H, 6.9; N, 6.25. $C_{10}H_{15}NO_3$ requires C, 65.15; H, 6.8; N, 6.7%); ν_{max}(Nujol)/cm^{-1} 1695 (CO_2Et) and 1638 (C=O); δ_H 1.20 (3 H, t, CH_3, *J* 7.20), 1.30 (3 H, t, CH_3, *J* 7.12), 2.49–2.64 (4 H, m, CH_2CH_2), 3.59 (2 H, q, CH_2N, *J* 7.20), 4.20 (2 H, q, CH_2O, *J* 7.12) and 7.27 (1 H, s, 2-CH).

Ethyl 1-benzyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carboxylate 5d. Uncrystallizable oil (19%); ν_{max}(Nujol)/cm^{-1} 1690 (CO_2Et) and 1645 (C=O); δ_H 1.26 (3 H, t, CH_3, *J* 7.12), 2.64–2.70 (4 H, m, CH_2CH_2), 4.17 (2 H, q, CH_2, *J* 7.12), 4.74 (2 H, s, CH_2Ph) and 7.15–7.45 (6 H, m, 2-CH and Ph); *m*/*z* 259 (M^+, 95%), 230 (42), 214 (31), 186 (13), 145 (14), 132 (16), 91 (100) and 65 (20).

1-Methyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile 5e. Solid (30%); mp 94 °C (from diisopropyl ether) (Found: C, 61.45; H, 5.9; N, 20.25. $C_7H_8N_2O$ requires C, 61.75; H, 5.9; N, 20.6%); ν_{max}(Nujol)/cm^{-1} 2198 (CN) and 1645 (C=O); δ_H 2.57–2.67 (4 H, m, CH_2CH_2), 3.14 (3 H, s, 1-CH_3) and 6.86 (1 H, s, 2-CH).

1-Ethyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile 5f. Solid (52%); mp 68–69 °C (from CH_2Cl_2–diisopropyl ether) (Found: C, 65.5; H, 7.0; N, 16.2. $C_8H_{10}N_2O$ requires C, 65.75; H, 6.85; N, 16.4%); ν_{max}(Nujol)/cm^{-1} 2200 (CN), 1640 (C=O); δ_H 1.19 (3 H, t, CH_3, *J* 7.20), 2.53–2.68 (4 H, m, CH_2–CH_2), 3.59 (2 H, q, CH_2, *J* 7.20) and 6.89 (1 H, s, 2-CH).

Ethyl 6-(2-aminophenylimino)-1-benzyl-1,4,5,6-tetrahydropyridine-3-carboxylate 7. Uncrystallizable oil (19%); ν_{max}(Nujol)/cm^{-1} 3450–3350 (NH_2) and 1690 (C=O); δ_H 1.27 (3 H, t, CH_3, *J* 7.15), 2.45–2.66 (4 H, m, CH_2CH_2), 3.25 (2 H, br s, NH_2), 4.17 (2 H, q, CH_2, *J* 7.15), 4.98 (2 H, s, CH_2Ph), 6.48–6.92 (4 H, m, ArH), 7.20–7.38 (5 H, m, Ph), 7.53 (1 H, s, 2-CH); picrate of **7**, mp 147 °C (from ethanol) (Found: C, 55.8; H, 4.6;

N, 14.45. $C_{27}H_{26}N_6O_9$ requires C, 56.05; H, 4.5; N, 14.5%); δ_H 1.29 (3 H, t, CH_3, *J* 7.04), 2.97 (2 H, t, 5-CH_2, *J* 6.91), 3.64 (2 H, t, 4-CH_2, *J* 6.91), 4.17 (2 H, q, CH_2O, *J* 7.04), 4.41–4.44 (2 H, m, CH_2Ph), 5.70–5.81 (3 H, br s, NH_3^+), 7.15–7.89 (9 H, m, ArH) and 8.92 (1 H, s, 2-CH).

Ethyl 6-(4-aminophenylimino)-1-methyl-1,4,5,6-tetrahydropyridine-3-carboxylate 9. Uncrystallizable oil (70%); ν_{max}(Nujol)/cm $^{-1}$ 3460–3360 (NH_2) and 1690 (C=O); δ_H 1.29 (3 H, t, CH_3, *J* 7.10), 2.41–2.55 (4 H, m, CH_2CH_2), 3.30 (3 H, s, CH_3N), 3.51 (2 H, s br, NH_2), 4.19 (2 H, q, CH_2, *J* 7.1), 6.55–7.38 (4 H, m, ArH) and 7.38 (1 H, s, 2-H).

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