REACTIONS OF 3,5-DIMETHYL-4-NITROISOXAZOLE WITH CYCLIC ENAMINES AND 1-DIETHYLAMINOPROPYNE

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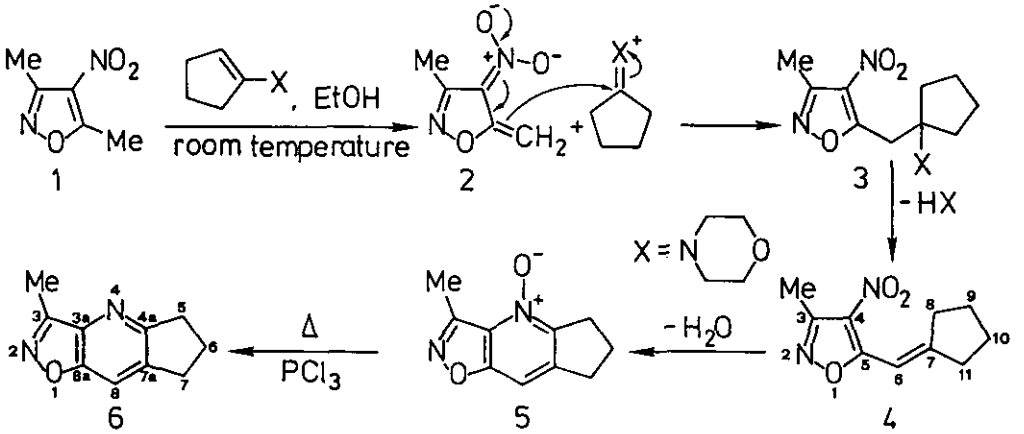
Abstract - 3,5-Dimethyl-4-nitroisoxazole **(1)** was found to undergo tandem condensation-cyclization processes with 4-(1-cyclopenten-1-yl)- and 4-(1-cyclohexen-1-yl)morpholine in ethanol solution to give, through the intermediates **(4)** and **(7)**, the N-oxides **(5)** and **(9)**, respectively. The reactivity of **1** towards 1-diethylaminopropyne in different solvents was also investigated; the structure of the unexpected acyloxime **(13)**, coming from the above reagents in acetonitrile, was determined by an X-ray analysis. Plausible mechanistic pathways for these new reactions are suggested.

Despite the interest shown over the past fifty years in the reactivity of the title compound with a variety of reagents,[1] its behaviour towards enamines and ynamines has been completely disregarded. On this basis, we wish now to report some findings on this topic.

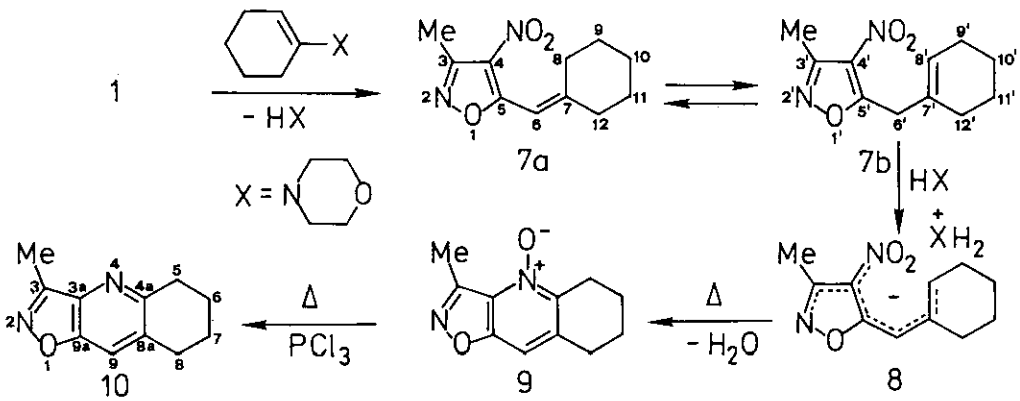


Scheme 1

When the nitro derivative **(1)** was allowed to react with an excess (molar ratio 1:2) of 4-(1-cyclopenten-1-yl)morpholine in anhydrous ethanol at room temperature for 5 days, the tricyclic N-oxide **(5)** was isolated in 80% yield; treatment of the latter with PCl_3 in refluxing chloroform afforded the cyclopentisoxazolopyridine **(6)** in good yield.

Due to the remarkable acidity of the 5-methyl group of the starting material,[2] the formation of **5** can be accounted for by assuming that the corresponding carbanion **(2)** gives rise to the condensation product **(4)** through the adduct **(3)**; the subsequent base-catalyzed cyclization of **4** into **5**, involving the attack of the C-8 carbon on the electrophilic nitrogen of the NO_2 group, closely resembles other ring closures previously described for suitably ortho-substituted nitrobenzene derivatives [3] (Scheme 1).

Tlc monitoring of the reaction course clearly showed the presence of a key intermediate that slowly evolved into the final product; thus, when the reaction was carried out with 1 equiv. of the same reagent for 12 h, we succeeded in isolating compound **(4)** by flash chromatography.



Scheme 2

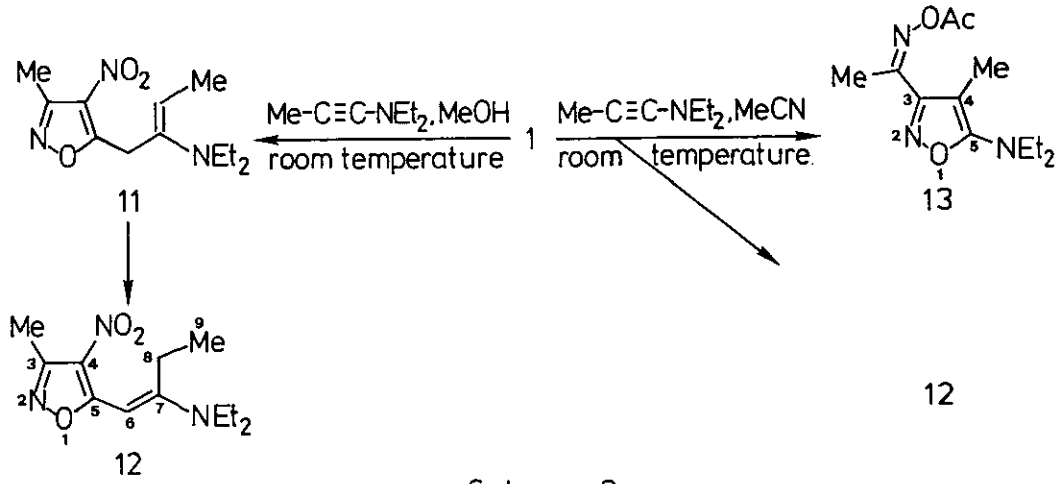
Replacement of the above enamine with the corresponding cyclohexene derivative afforded, under the original conditions, only a small amount of the N-oxide **(9)**; the reaction mixture now contained predominantly the salt **(8)**, that separated as a pure product by treatment with ether. Likewise for **4**, the precursor **(7)** was obtained with 1 equiv. of the same reagent and shorter reaction times; on the contrary, when the reaction was carried out under forcing conditions, we isolated in 39% yield the desired compound **(9)** which was easily converted into the tetrahydroisoxazoloquinoline **(10)** (Scheme 2). Comparable results were obtained by treatment of **1** with the same reagents in dry acetonitrile.

The dramatic difference observed for the terminal ring closure of the nitro derivatives **(4)** and **(7)** can be explained on the basis of the Brown's generalization for the reactivity trend of five- and six-membered rings containing an exocyclic double bond.[4]

On the same ground, whereas the former compound exists exclusively as **4** in chloroform solution,

the latter gives rise to a tautomeric equilibrium between **7a** and **7b** (ca. 2:1) in the same solvent.

The structures of the isoxazoles **(4)**, **(7)**, and **(8)**, as well as those of the novel ring systems **(5)**, **(6)**, **(9)**, and **(10)** were determined by analytical and spectral evidence (Experimental). In particular, the ir bands of **4** and **7** (1570 and 1360 cm^{-1}) were replaced by a strong N^{+}–O^{-} absorption at 1342 and 1322 cm^{-1} in the spectra of compounds **(5)** and **(9)**, respectively. Moreover, whereas the ^{1}H nmr spectrum of **4** showed a quintet at δ 7.11 for the vinyl proton, the coupled ^{13}C nmr pattern was characterized by a doublet and a singlet at δ 105.85 and 169.87, attributable to the C-6 and C-7 carbons of the exocyclic double bond; similar resonances also appeared in the corresponding spectra of **7** for the same moiety of the form **(7a)**, but the concomitant presence of **7b** was easily ascertained on the basis of a signal at δ 3.81 (6'-CH_2) in the former, and a singlet and a doublet at δ 130.70 and 126.66 in the latter, for the endocyclic C(7')-C(8') double bond. Finally, both the ^{1}H and ^{13}C nmr resonances of the CH group exhibited diagnostic downfield shifts on going from compounds **(5)** and **(9)** to the corresponding deoxygenation products **(6)** and **(10)** (δ 7.205, 7.17 and δ 105.15, 108.24 vs. δ 7.57, 7.77 and δ 113.69, 120.95, respectively).

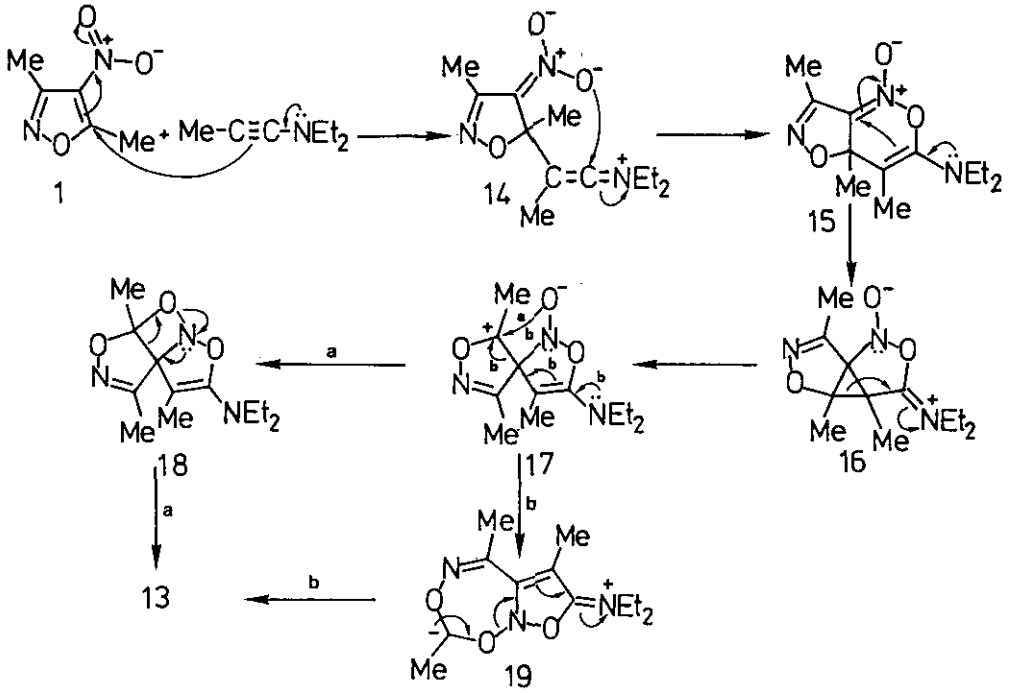


Scheme 3

Treatment of **1** with 1 equiv. of 1-diethylaminopropyne in methanol[5] at room temperature gave almost quantitatively compound **(12)**, whose stereochemistry followed from a NOESY experiment; although **12,** coming from a prototropic isomerization of the enamine intermediate **(11)**, formally resembled the nitro derivatives **(4)** and **(7)**, no cyclization was observed for this product even under more drastic conditions (molar ratio 1:2, prolonged reflux), probably due to the reduced electrophilic properties of the NO_2 nitrogen at δ position of a dienamine system (Scheme 3).

On the other hand, when methanol was replaced with acetonitrile, surprisingly we isolated from the complex reaction mixture only a small amount of **12** together with the more abundant isoxazole derivative **(13)**, whose structure was determined by a single crystal X-ray analysis.

This not straightforward alternative reaction of **1** was tentatively explained as shown in the Scheme 4.



Scheme 4

According to the well known behaviour of 4-nitroisoxazoles with nucleophiles,[6] it probably starts with a Michael addition leading to the nitronate **(14)** that, in turn, evolves into the derivative **(15)**, through a formal [4 + 2] cycloaddition; ring contraction of the oxazine moiety of **15** gives rise to the spiran **(17)** via the unstable cyclopropane derivative **(16)**. The final product can then arise from **17** through the tricyclic compound **(18)** (route a), or by conversion of the same intermediate into the seven-membered bicyclic system **(19)**, followed by N-O ring opening of the latter (route b).

This mechanistic rationale appears to be confirmed by the firmly established Z configuration of the acyloxime **(13)** (see Figure).

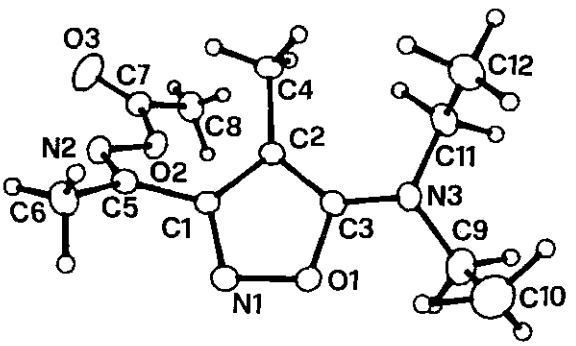


Figure: A computer-generated drawing of **13** derived from the X-ray coordinates with hydrogens omitted for clarity.

EXPERIMENTAL

Melting points were taken on a Büchi 510 apparatus and are uncorrected. Except where otherwise stated, infrared spectra were measured for dispersions in KBr with a Perkin-Elmer 283 spectrophotometer, while ^{1}H and ^{13}C nmr spectra were recorded in $CDCl_3$ solutions on a Varian Gemini-200 instrument operating at 200 MHz and 50 MHz, respectively; the relative assignment of the ^{13}C resonances was achieved on the basis of the coupled spectra and long-range heteronuclear correlation experiments. Elemental analyses were obtained by a Perkin-Elmer 240C Analyzer. Silica gel plates (Merck F_{254}) and silica gel 60 (Merck; 230-400 mesh) were used for analytical and flash chromatographies, respectively. Petroleum ether refers to the fraction bp 40-70°C.

Reactions of the Nitroisoxazole (1) with 4-(1-Cylopenten-1-yl)morpholine. Preparation of Compounds (4) and (5).

A - Compound **(1)** (0.142 g, 1 mmol) was allowed to react with the title enamine (0.153 g, 0.16 ml, 1 mmol) in anhydrous ethanol (1 ml) at room temperature for 12 h; removal of the solvent left a semi-solid orange residue, which was subjected to flash chromatography with petroleum ether-ethyl acetate (12:1 v/v) as eluent. The first fraction ($R_f = 0.57$) afforded 5-cyclopentylidenemethyl-3-methyl-4-nitroisoxazole **(4)** as a pale yellow solid [0.030 g, 33% yield based on the starting material recovered from the second band ($R_f = 0.38$; 0.080 g)], mp 62-62.5°C (from pentane); ir ν_{max}: 3075 (CH), 1570, and 1360 cm^{-1} (NO_2); ^{1}H nmr δ: 1.70-1.90 (m, 4H, 9-CH_2 and 10-CH_2), 2.55 (s, 3H, 3-CH_3), 2.60-2.70 (m, 2H, 8-CH_2/11-CH_2), 2.80-2.90 (m, 2H, 11-CH_2/8-CH_2), 7.11 (quintet, J = 2.2 Hz, 1H, H-6); ^{13}C nmr δ: 11.88 (q, 3-CH_3), 25.79 (t, 9-CH_2/10-CH_2), 26.71 (t, 10-CH_2/9-CH_2), 34.12 (t, 8-CH_2/11-CH_2), 37.50 (t, 11-CH_2/8- CH_2), 105.85 (d, C- 6), 126.60 (br s, C-4), 155.49 (s, C-3), 168.05 (s, C-5), 169.87 (s, C-7). Anal. Calcd for $C_{10}H_{12}N_2O_3$: C, 57.69; H, 5.81; N, 13.45. Found: C, 57.46; H, 5.79; N, 13.23.

B - Treatment of **1** (0.142 g, 1 mmol) with an excess of the above reagent (0.306 g, 0.32 ml, 2 mmol) under the same conditions for 5 days gave 3-methylcyclopent[b]isoxazolo[5,4-e]pyridine-4-oxide **(5)**, that was separated by filtration as an ivory-coloured solid (0.082 g, 43%); a second crop of the same product was recovered from the residue left by evaporation to dryness of the filtrate, by flash chromatography with ethyl acetate-acetone (5:1 v/v) as eluent ($R_f = 0.33$, 0.070 g, 80% overall yield): silk needles mp 183-184°C (from ethyl acetate); ir ν_{max}: 3080, 3060 (CH), and 1342 cm^{-1} ($N^+–O^-$); ^{1}H nmr δ: 2.14-2.29 (m, 2H, 6-CH_2), 2.75 (s, 3H, 3-CH_3), 3.02-3.14 (m, 4H, 5-CH_2 and 7-CH_2), 7.21 (m, 1H, H-8); ^{13}C nmr δ: 11.02 (q, 3-CH_3), 22.79 (t, 6-CH_2), 27.90 (t, 5-CH_2), 31.53 (t, 7-CH_2), 105.15 (d, C-8), 129.85 (s, C-3a), 143.98 (s, C-7a), 150.24 (s, C-4a), 152.52 (s, C-3), 160.73 (s, C-8a). Anal. Calcd for $C_{10}H_{10}N_2O_2$: C, 63.15; H, 5.30; N, 14.73. Found: C, 63.04; H, 5.29; N, 14.45.

Reactions of 1 with 4-(1-Cyclohexen-1-yl)morpholine. Synthesis of Compounds (7), (8), and (9).

A - A mixture of **1** (0.142 g, 1 mmol) and the title enamine (0.167 g, 0.17 ml, 1 mmol) in anhydrous ethanol (1 ml) was stirred at room temperature for 12 h and evaporated to dryness; the residue was

resolved into two components by flash chromatography with petroleum ether-ethyl acetate (16:1 v/v) as eluent. The first fractions ($R_f = 0.46$) gave 5-cyclohexylidenemethyl-3-methyl-4-nitroisoxazole **(7)** [0.030 g, 60% yield based on **1** recovered from the following band ($R_f = 0.31$, 0.11 g)] as a pale yellow oil; an analytical sample was obtained as a colourless liquid by dissolution in pentane, treatment with charcoal, filtration, evaporation to dryness, and prolonged evacuation under reduced pressure (10^{-2} mmHg); ir ν_{max} (neat): 3040 (CH), 1570, and 1360 cm^{-1} (NO_2); ^1H nmr δ: 1.50-1.80 [m, 6H, (9-CH_2, 10-CH_2, and 11-CH_2) and 4H, (10'-CH_2 and 11'-CH_2)], 1.93-2.06 (m, 4H, 9'-CH_2 and 12'-CH_2), 2.38-2.45 (m, 2H, 8-CH_2/12-CH_2), 2.56 [s, 3H, (3-CH_3) and 3H, (3'-CH_3)], 2.74-2.81 (m, 2H, 12-CH_2/8-CH_2), 3.81 (br s, 2H, 6'-CH_2), 5.58 (m, 1H, H-8'), 6.78 (quintet, J = 1.1 Hz, 1H, H-6); ^{13}C nmr δ: 11.73 (q, 3'-CH_3), 11.83 (q, 3-CH_3), 21.75 (t, 10'-CH_2/11'-CH_2), 22.58 (t, 11'-CH_2/10'-CH_2), 25.25 (t, 9'-CH_2/12'-CH_2), 25.92 (t, 9-CH_2/10-CH_2/11-CH_2), 28.04 (t, 10-CH_2/11-CH_2/9-CH_2), 28.58 (t, 12'-CH_2/9'-CH_2), 28.82 (t, 11-CH_2/9-CH_2/10-CH_2), 32.13 (t, 8-CH_2/12-CH_2), 35.49 (t, 6'-CH_2), 38.97 (t, 12-CH_2/8-CH_2), 106.85 (d, C- 6), 126.66 (d, C-8'), 128.20 (br s, C-4), 129.50 (br s, C- 4'), 130.70 (s, C-7'), 155.52 (s, C-3), 155.65 (s, C-3'), 163.94 (s, C-7), 168.14 (s, C-5), 173.36 (s, C-5'). Anal. Calcd for $C_{11}H_{14}N_2O_3$: C, 59.45; H, 6.35; N, 12.60. Found: C, 59.68; H, 6.56; N, 12.27.

B - When **1** (0.142 g, 1 mmol) was treated with 2 equiv. of the above reagent (0.334 g, 0.34 ml) under the same conditions for 5 days, a small amount of compound **(9)** (0.015 g) was separated by filtration; evaporation to dryness of the filtrate gave a red-brown semisolid residue (0.285 g) containing (tlc, ^1H and ^{13}C nmr) morpholinium 5-[(1-cyclohexen-1-yl)methylene]-3-methyl-4,5-dihydroisoxazole-4-nitronate **(8)** as the largely predominant product (ca. 90%). An analytical sample, obtained as a pale yellow solid by repeated treatments with ether, gradually wrinkled above 85°C and melted at 102-103°C; ir ν_{max}: 3300-2300 and 2200-1700 cm^{-1} ($\overset{+}{N}H_2$); ^1H nmr δ: 1.05-1.53 (m, 3H, methylene protons), 1.67-1.86 (m, 2H, CH_2), 1.91-2.20 (m, 2H, CH_2), 1.98 (s, 3H, 3-CH_3), 2.52-2.68 (m, 1H, methylene proton), 2.80-2.87 (m, 4H, 2 $H_2\overset{+}{N}CH_2$), 3.61-3.67 (m, 4H, 2 OCH_2), 4.56-4.68 (m, 1H, H-8), 5.25 (t, J = 2.0 Hz, 1H, H-6), 7.30 (br s, 2 H, exchangeable $\overset{+}{N}H_2$); ^{13}C nmr δ: 9.68 (q, 3-CH_3), 22.57 (t, 10-CH_2/11-CH_2), 25.91 (t, 11-CH_2/10-CH_2), 27.01 (t, 9-CH_2/12-CH_2), 32.39 (t, 12-CH_2/9-CH_2), 45.37 (t, 2 $H_2\overset{+}{N}CH_2$), 66.88 (t, 2 OCH_2), 84.34 (d, C-8), 111.39 (s, C-4), 112.52 (d, C- 6), 149.11 (s, C-7), 153.06 (s, C-3), 154.22 (s, C-5). Anal. Calcd for $C_{15}H_{23}N_3O_4$: C, 58.24; H, 7.49; N, 13.58. Found: C, 58.45; H, 7.25; N, 13.42.

C - Heating of **1** (0.142 g, 1 mmol) with the enamine (0.334 g, 0.34 ml, 2 mmol) in the same solvent (1 ml) under reflux for 24 h yielded 3-methyl-5,6,7,8-tetrahydroisoxazolo[4,5-b]quinoline-4-oxide **(9)**, that was isolated by filtration (0.040 g); chromatographic workup [toluene-methanol (5:1 v/v) as eluent] of the residue recovered from the filtrate, afforded a further amount of the same compound ($R_f = 0.51$, 0.040 g, 39% overall yield): white crystals mp 206-207°C (from ethyl acetate); ir ν_{max}: 3070, 3040 (CH), and 1322 cm^{-1} (N^+-O^-); ^1H nmr δ: 1.70-1.98 (m, 4H, 6-CH_2 and 7-CH_2), 2.80 (s, 3H, 3-CH_3), 2.85-2.98 (m, 4H, 5-CH_2 and 8-CH_2), 7.17 (br s, 1H, H-9); ^{13}C nmr δ: 11.42 (q, 3-CH_3), 21.51 (t, 6-CH_2 and 7-CH_2), 24.12 (t, 5-CH_2/8-CH_2), 29.80 (t, 8-CH_2/5-CH_2), 108.24 (d, C-9), 129.10 (s, C-

3a), 137.45 (s, C-8a), 145.31 (s, C-4a), 152.46 (s, C-3), 157.96 (s, C-9a). Anal. Calcd for $C_{11}H_{12}N_2O_2$: C, 64.69; H, 5.92; N, 13.72. Found: C, 64.78; H, 5.90; N, 13.71.

Deoxygenation of the N-oxides (5) and (9) into 6 and 10.

A - A solution of PCl_3 (0.412 g, 0.262 ml, 3 mmol) in chloroform (5 ml) was added dropwise to **5** (0.19 g, 1 mmol) in the same solvent (5 ml); the mixture was stirred at room temperature for 3 h and then refluxed for 1 h. The resulting solution was cooled, treated with ice water (15 ml), and made basic (pH 10) with 20% aqueous NaOH. After removal of the organic phase, the aqueous solution was extracted with $CHCl_3$ (3x10 ml); evaporation to dryness of the combined extracts left a solid residue which was sublimed at 50°C (10^{-2} mmHg) to give 3-methylcyclopent[b]isoxazolo[5,4-e]pyridine **(6)** as a white solid (0.16 g, 92%), mp 101.5-102°C (from ether); ir ν_{max}: 3045 cm^{-1} (CH); ^{1}H nmr δ: 2.18 (quintet, J=7.5 Hz, 2H, 6-CH_2), 2.56 (s, 3H, 3-CH_3), 2.99 (dt, J=7.5 and 1.2 Hz, 2H, 7-CH_2), 3.05 (t, J=7.5 Hz, 2H, 5-CH_2), 7.57 (t, J=1.2 Hz, 1H, H-8); ^{13}C nmr δ: 9.11 (q, 3-CH_3), 24.16 (t, 6-CH_2), 30.60 (t, 7-CH_2), 33.00 (t, 5-CH_2), 113.69 (d, C-8), 138.52 (s, C-3a), 139.82 (s, C-7a), 155.08 (s, C-3), 155.98 (s, C-8a), 164.37 (s, C-4a). Anal. Calcd for $C_{10}H_{10}N_2O$: C, 68.95; H, 5.79; N, 16.08. Found: C, 69.21; H, 5.90; N, 15.87.

B - Operating as above, compound **(9)** (0.204 g, 1 mmol) afforded 3-methyl-5,6,7,8-tetrahydroisoxazolo[4,5-b]quinoline **(10)** as a white solid (0.162 g, 86 %), mp 88-88.5°C after sublimation at 50°C (10^{-2} mmHg); ir ν_{max}: 3040 cm^{-1} (CH); ^{1}H nmr δ: 2.68-2.88 (m, 4H, 6-CH_2 and 7-CH_2), 2.62 (s, 3H, 3-CH_3), 2.85-2.96 (m, 2H, 5-CH_2/8-CH_2), 3.10-3.19 (m, 2H, 8-CH_2/5-CH_2), 7.77 (br s, 1H, H-9); ^{13}C nmr δ: 9.83 (q, 3-CH_3), 21.38 (t, 6-CH_2/7-CH_2), 21.49 (t, 7-CH_2/6-CH_2), 29.15 (t, 8-CH_2), 30.08 (t, 5-CH_2), 120.95 (d, C-9), 134.00 (s, C-3a), 135.63 (s, C-8a), 153.36 (s, C-3), 154.60 (s, C-4a), 155.51 (s, C-9a). Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.19; H, 6.43; N, 14.88. Found: C, 70.09; H, 6.54; N, 14.64.

Reactions of Compound (1) with 1-Diethylaminopropyne. Synthesis of the Isoxazole Derivatives (12) and (13).

A - A solution of **1** (0.142 g, 1 mmol) and ynamine[7] (0.111 g, 0.137 ml, 1 mmol) in methanol (5 ml) was stirred at room temperature for 24 h; removal of the solvent left a residue which was resolved into two components by flash chromatography with petroleum ether-ethyl acetate (3:1 v/v) as eluent. After the unreacted starting material was isolated from the first band (R_f=0.64, 0.060 g), the second one afforded 5-[(E)2-diethylamino-1-buten-1-yl]-3-methyl-4-nitroisoxazole **(12)** as a yellow solid (R_f=0.30; 0.14 g, 96% yield based on the recovered **1**), mp 64-65°C (from pentane); ir ν_{max}: 1571 cm^{-1} (NO_2); ^{1}H nmr δ: 1.21 (t, J=7.5 Hz, 3H, 9-CH_3), 1.26 (t, J=7.2 Hz, 6H, 2 NCH_2CH_3), 2.46 (s, 3H, 3-CH_3), 2.82 (br q, J=7.5 Hz, 2H, 8-CH_2), 3.43 (q, J=7.2 Hz, 4H, 2 NCH_2CH_3), 6.23 (br s, 1H, H- 6); ^{13}C nmr δ: 12.40 (q, 9-CH_3), 12.70 (br q, two slowly interchangeable NCH_2CH_3), 12.95 (q, 9-CH_3), 23.84 (t, 8-CH_2), 45.15 (br t, two slowly interchangeable NCH_2CH_3), 81.75 (d, C- 6), 121.86 (br s, C-4), 155.47 (s, C-3), 166.13 (s, C-7), 168.65 (s, C-5). Anal. Calcd for $C_{12}H_{19}N_3O_3$: C, 56.90; H, 7.56; N, 16.59. Found: C, 57.21; H, 7.75; N, 16.30.

B - The reaction was carried out in dry acetonitrile (5 ml) under the same conditions for 48 h; the raw

product was resolved into three components by chromatographic workup with toluene-ethyl acetate (5:1 v/v) as eluent. Whereas the fastest running fractions gave the unreacted nitro derivative (0.070 g), the second band afforded compound **(12)** (R_f = 0.58, 0.015 g, 12% yield based on the recovered **1**) identical (ir, ^{1}H and ^{13}C nmr) with the material obtained as above; finally, the following band gave 3-[(Z)1-acethoxyimino-1-ethyl]-5-diethylamino-4-methylisoxazole **(13)** (R_f = 0.42, 0.030 g, 23% yield based on the recovered **1**) that was crystallized from pentane as colourless needles, mp 67-68°C; ir ν_{max} 1780 cm^{-1} (CO); ^{1}H nmr δ: 1.19 (t, J = 7.1 Hz, 6H, 2 $NCH_2\underline{CH_3}$), 1.83 (s, 3H, 4-CH_3), 2.08 (s, 3H, CH_3CO), 2.33 (s, 3H, $CH_3C{=}N$), 3.38 (q, J = 7.1 Hz, 4H, 2 $N\underline{CH_2}CH_3$); ^{13}C nmr δ: 8.27 (q, 4-CH_3), 13.78 (q, 2 $NCH_2\underline{CH_3}$), 19.25 (q, $\underline{CH_3}CO$), 21.01 (q, $\underline{CH_3}C{=}N$), 43.61 (t, 2 $N\underline{CH_2}CH_3$), 85.63 (s, C-4), 156.13 (s, $CH_3\underline{C}{=}N$), 160.07 (s, C-3), 167.15 (s, C-5), 168.20 (s, CO). Anal. Calcd for $C_{12}H_{19}N_3O_3$: C, 56.90; H, 7.56; N, 16.59. Found: C, 57.01; H, 7.76; N, 16.40.

***X-ray Crystal Structure Determination for* 13.**

A single crystal of the product $C_{12}H_{19}N_3O_3$, grown from pentane, was mounted on an Enraf-Nonius CAD4 diffractometer. No loss of intensity of three standard reflections was observed. Computer programs were those of SHELX76.[8] An absorption correction was applied once the structure was solved.[9] Crystal data: monoclinic; space group $P2_1/n$; M = 253.3; a = 6.749(6) Å, b = 21.574(5) Å, c = 9.799(3) Å, β = 105.77(5)°; cell vol = 1373(1) Å^3; Z = 4; d = 1.22 g cm^{-3}; abs coeff μ = 6.99 cm^{-1}; Cu-Kα radiation (λ = 1.5418 Å), graphite monochromator. Intensity data were collected in the range $5 \leq 2\theta \leq 120°$ by using the $\theta/2\theta$ scan. A total of 2230 reflections were collected of which 1795 having $I \geq 3\sigma(I)$ were used in the structure solution and refinement. The stucture was solved by using direct methods and successive Fourier syntheses; then it was refined with the full-matrix least-squares technique. Anisotropic temperature factors were assigned to all the atoms except the hydrogen ones which were refined isotropically. The final difference map showed no significant features. A weighting scheme of $w = 1/\sigma^2(F)$ was used. Final agreement factors were R = 0.063 and R_w = 0.063 (239 parameters).

Crystallographic data were deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England, and are available from there.

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REFERENCES AND NOTES

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