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Effective Synthesis of Functionalized Furazano[4,5-*b*]pyridines by Condensation of 3-Amino-4-cyanofurazan with β-Dicarbonyl Compounds

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Derivatives of furazano[4,5-*b*]pyridine have been synthesized by condensation of 3-amino-4-cyanofurazan with β-dicarbonyl compounds.

Only two methods of constructing the [1,2,5]oxadiazolo[4,5-*b*]pyridine system, *i.e.*, thermolysis of *o*-azidonitropyridines[1,2] and oxidative condensation of *o*-aminonitropyridines,[3] are known. These methods starting from a pyridine precursor produce the bicyclic 1-oxide, furoxano[4,5-*b*]pyridine. An attempt at *N*-oxide reduction to afford the corresponding furazan was not successful.[2]

We report herein a facile and effective method of constructing the furazano[4,5-*b*]pyridine system starting from a furazan such as 3-amino-4-cyanofurazan **1**.[4]

We have found that reaction of **1** with β-dicarbonyl compounds in the presence of catalytic amounts of nickel acetylacetonate[5] gives labile compound **2a,b**, which was treated with acetic acid to give *via* cyclization the bicycles **3a,b** in a 80–95% total yield.

The transformation of **1** to **3** proceeds according to route A, *i.e.* by initial addition of the activated methylene fragment of the β-dicarbonyl compound to the nitrile group of **1**, and **not** in

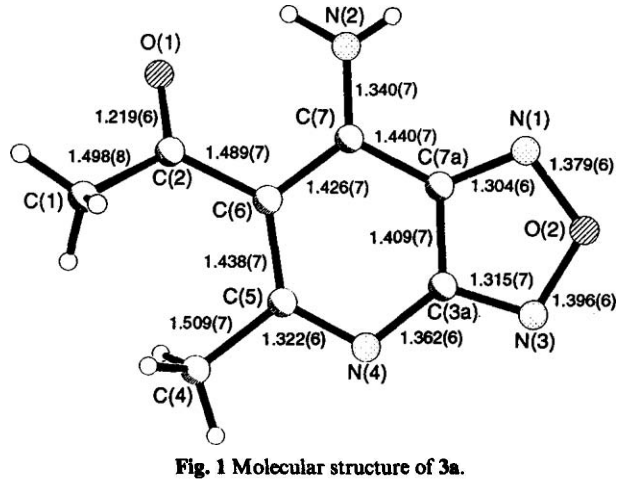

Fig. 1 Molecular structure of **3a**.

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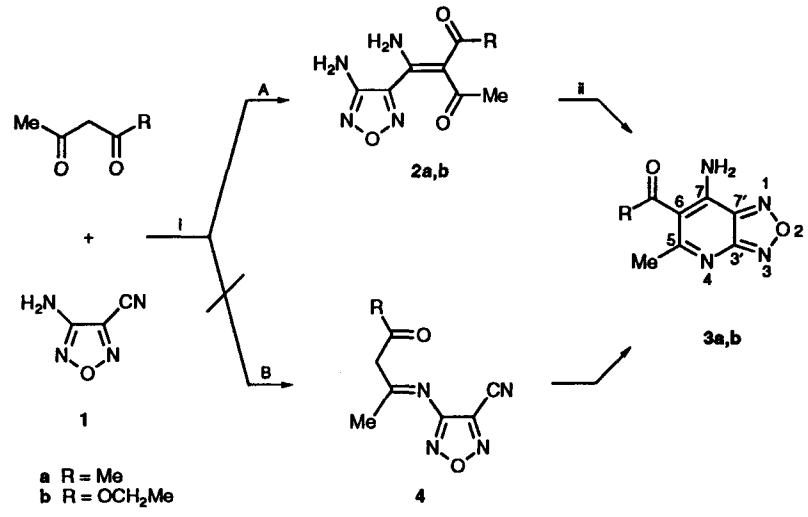

Scheme 1 *Reagents and conditions:* i, 1% nickel acetylacetonate, CH_2Cl_2, ii, AcOH, reflux.

accordance with the alternative route B via the product of condensation at the amino group **4** and subsequent Thorpe-type cyclization.

The considerable electron-withdrawing effect of the furazan ring, the activating nitrile group[6] and the deactivating amino group[7] all contribute to the formation of **2** and not **4**.

The structure of all the compounds obtained was confirmed by elemental analysis, MS, IR and ^1H and ^{13}C NMR spectroscopy.† The molecular structure of **3a** has been unambiguously established by means of a single crystal X-ray diffraction study (Fig. 1).‡ The bicyclic moiety of **3a** is essentially planar and the atomic displacements from its mean plane do not exceed 0.059 Å [for the C(6) atom]. The N(2) and C(4) atoms are displaced from this plane by 0.148 and 0.112 Å to one side and the C(2) atom is situated in the plane, though the acetyl group forms a dihedral angle of 31.5° with the plane of the bicyclic system. Molecules **3a** in the crystal are linked *via* H-bonds [N(2)H···N(4) ($-0.5+x$, $0.5+y$, z): N···N 2.945(6) Å, N···H 2.20(4) Å, NH···N 148(3)°] into infinite chains along the [110] crystallographic direction.

† Selected spectroscopic data for **2a**: m.p. 152–153 °C (decomp.); MS *m/z*: 210 (M^+), ^1H NMR ([$^2H_6$]DMSO) δ 2.12(6H, 2Ac), 6.30(2H, NH_2), 8.74(1H, NH), 10.42(1H, NH); IR (KBr) ν/cm^{-1} 3395, 3295, 3200, 1650, 1615, 1595, 1550, 1475, 1445, 1415, 1395, 1360, 1305, 1255, 1190, 1135, 1030, 1000, 945, 895, 870, 815. For **3a**: m.p. 197–198 °C, MS *m/z*: 192 (M^+), ^1H NMR ([$^2H_6$]DMSO) δ 2.51 (3H, Me), 2.58 (3H, Ac), 8.23 (2H, NH_2); **3b**: m.p. 179–180 °C, ^1H NMR ($CDCl_3$) δ 1.42 (3H, CH_3CH_2), 2.74 (3H, Me), 4.44 (2H, OCH_2), 8.31(2H, NH_2).

‡ Crystal data for **3a**: $C_8H_8N_4O_2$, $M = 192.2$, orthorhombic, space group *Pccn*, $a = 8.952(2)$, $b = 9.914(3)$, $c = 19.067(6)$ Å, $V = 1692.3(8)$ Å^3, $Z = 8$, $D_c = 1.509$ g cm^{-3}. Cell parameters and intensities of 770 reflections with $I \geqslant 3\sigma(I)$ were measured at 153 K with a Siemens P3/PC difractometer λ(Mokα) = 0.71073 Å, graphite monochromator, $\theta < 30°$, $\theta/2\theta$ scan).

The structure was solved by direct methods and refined in full-matrix anisotropic approximation for non-hydrogen atoms. The hydrogen atoms were located in the difference Fourier map. In the final least-squares cycles the H atoms were refined isotropically with fixed $U_{iso} = 0.05$ Å^2. The final discrepancy factors are $R = 0.054$ and $R_w = 0.057$. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, *Mendeleev Commun*, 1994, issue 1.

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