Chemistry of Heterocyclic Compounds, Vol. 36, No. 11, 2000

SYNTHESIS OF ENAMINO NITRILE OF A NEW TYPE, 2-HETARYL-2-(2-PYRROLIDINYLIDENE)ACETONITRILES, AND THEIR TAUTOMERISM

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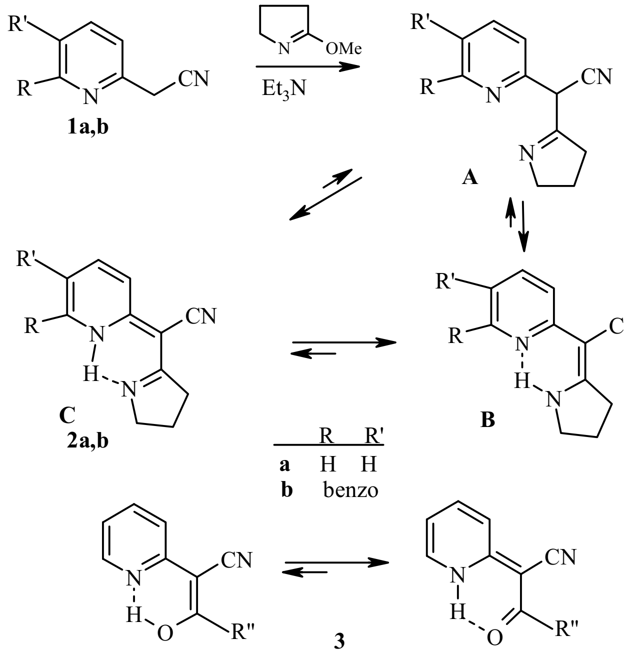
Keywords: 2-hetaryl-2-(2-pyrrolidinylidene)acetonitrile, enamino nitriles, tautomerism.

β-Enamino nitriles are widely used in the synthesis of polyfunctional monocyclic and annelated azines and azoles [1]. We have obtained enamino nitriles of a new type with heterocyclic substituents in the α-position to the cyano group: the reaction of 2-pyridyl- and 2-quinolylacetonitriles **1a,b** with O-methylbutyrolactim, catalyzed by triethylamine, gave 2-hetaryl-2-(2-pyrrolidinyliden)acetonitriles, **2a,b**.

Nitriles **2a,b** can exist in three tautomeric forms **A**-**C**. The KBr disk IR spectra of compounds **2a,b** contain strong stretching frequencies attributable to conjugated nitrile groups in the 2175-2180 cm^{-1} region and stretching vibrations of average intensity attributable to the NH bond in the 3175-3180 cm^{-1} region. This excludes the existence of tautomer **A** in the solid phase, but allows no conclusion about the ratio of tautomers **B** and **C** under these conditions. ^{1}H NMR spectroscopic data also rule out the presence of tautomer **A** in DMSO-d_6 solution. The ^{1}H NMR spectra of compounds **2a,b** contain no signals attributable to the methine proton of tautomer **A**, but they do contain broad one hydrogen signal in the 11.0-10.3 ppm region (which disappears on the addition of D_2O), assigned to the chelated proton of tautomer **B** or **C**.



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A comparison of the ^{1}H NMR spectra of the pyridyl derivative **2** with those of the previously described C-acyl derivatives of pyridylacetonitrile **3** [2] led to the conclusion that tautomer **B** predominated in DMSO-d_6 solutions of nitriles **2**. For example in compounds **3**, for which the predominance of the NH-tautomeric form in solution has been established [2], there is spin-spin coupling between the protons in positions 1 and 6 of the pyridine unit. As a result the proton in position 6 is observed in the ^{1}H NMR spectra of the acyl derivatives **3** as a distorted triplet which is converted into a doublet on addition of D_2O. Similarly in the ^{1}H NMR spectrum of the enamino nitrile **2a** the signal of the proton at position 6 of the pyridine ring appears as a doublet of doublets ($^3J = 5.5$, $^4J = 2.0$ Hz) at 8.42 ppm which is unchanged on addition of D_2O. Consequently, in compound **2a** the described spin-spin interaction, which should appear for tautomer **C**, is not observed, which indicates that enamino nitrile tautomer **B** predominates in DMSO-d_6 solutions.

2-(2-Pyridyl)-2-(2-pyrrolidinylidene)acetonitrile (2a). O-Methylbutyrolactim (1.1 ml, 0.011 mol) was added to a solution of pyridylacetonitrile **1a** (1 ml, 0.01 mol) and triethylamine (0.01 ml, 0.0007 mol) in toluene (3 ml). The mixture was boiled for 15 h. After cooling, the reaction mixture was chromatographed on a silica gel column (100-250 mesh) with toluene as eluent. The eluate was evaporated in vacuum to give colorless crystals of **2a** (1 g, 57%); mp 97°C. Found, %: N 22.73. $C_{11}H_{11}N_3$. Calculated, %: 22.69.

2-(2-Pyrrolidinylidene)-2-(2-quinolyl)acetonitrile (2b). O-Methylbutyrolactim (0.55 ml, 0.0055 mol) was added to a solution of quinolylacetonitrile **1b** (0.8 g, 0.005 mol) and triethylamine (0.01 ml, 0.0007 mol) in toluene (5 ml). The mixture was boiled for 10 h. After cooling, the precipitate was filtered off and washed with toluene to give enamino nitrile **2b** (0.8 g, 73%); mp 207°C (toluene). Found, %: N 17.75. $C_{15}H_{13}N_3$. Calculated, %: N 17.86.

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