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Solvent-free synthesis of Pyridine-2-aminium-6-methyl Pyridine-2,6-dicarboxylate under ball-milling conditions

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Abstract: A novel proton transfer compound, pyridine-2-aminium-6-methyl pyridine-2,6-dicarboxylate, has been synthesized by the reaction between 2,6-pyridinedicarboxylic acid, [pydc,H₂], and 2-amino-6-methyl- pyridine, [pya], in 1:1 molar ratio under ball milling conditions. The title compound has been characterized by spectral methods (¹H-, ¹³CNMR, IR).

Keywords: Solvent free; Pyridine-2,6-dicarboxylic acid; Proton transfer; Ball milling; Ion pairs.

Introduction

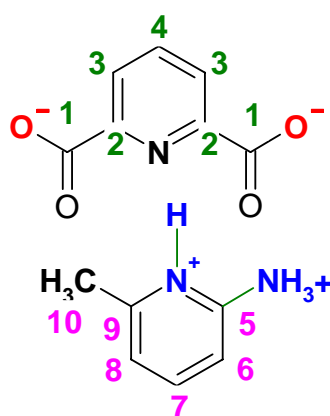
Solvent-free organic syntheses are gathering increasing interest from the viewpoints of green chemistry [1-6]. In any solvent-free reactions, interaction between dissimilar species becomes sensitive since solvation and associated shielding by solvent molecules are absent. Specific interactions between dissimilar solid organic species, among other hydrogen bonding and/or π interaction may, therefore, play a more significant role than those in a solution state, provided that the distance between the solid particles is shorter than the critical distance, through which electrons or protons can move across [7].

Here, we report solvent-free synthesis of Pyridine-2-aminium-6-methyl Pyridine-2, 6-dicarboxylate under ball-milling conditions.

Results and Discussion

The relatively weak band in the region of 3059-3433 cm^{-1} is due to the ν (CH) vibrations of pyridine ring. The absorption bands at 1367 cm^{-1} are attributed to ν (CH) vibrations of CH₃ group in pyridine. The carboxylate groups exhibit strong bands in the region of 1687–1559 cm^{-1} [8]. The presence of carboxylate COO⁻ group is reflected by IR spectrum in absorption bands of the asymmetric (ν_{as}) and symmetric (ν_s) stretching vibrations at 1637 and 1429 cm^{-1} , respectively. The absorption band at 1599 cm^{-1} is due to ν (C=C) + ν (C=N) + ν_{as} (COO) vibrations of dipic ligand. The lack of peak of OH group in carboxylic acid, indicate that H transferred to amine group and made proton- transfer compound.

In ^1H NMR spectrum of title compound, there are two resonances at 8.33 and 8.52 *ppm* and a singlet peak at 2.37 *ppm* (methyl group) for $(\text{pyaH}_2)^{2+}$ fragment. Also, one well defined doublet (corresponding to H^3 on the anion ring at $\delta = 6.65$ *ppm*) and one singlet (corresponding to H^4 on the anion ring at $\delta = 7.69$ *ppm*) can be observed in ^1H NMR spectrum. There are ten signals in ^{13}C NMR spectrum. The peak at $\delta = 19.81$ *ppm* could be assigned to the methyl group of pyridine. Sharp signal at $\delta = 166.33$ *ppm* is related to carboxylate groups. The signals of C^5 , C^6 , C^7 , C^8 and C^9 appear at $\delta = 155.52$, 114.18, 111.65, 48.36, 147.72 *ppm*, respectively. The peak at $\delta = 148.49$ *ppm* is related to C^2 in anionic group. Based on the presented ^1H NMR, ^{13}C NMR and IR spectroscopy for this compound, structure can be proposed as shown in scheme 1.



Scheme 1. The structure of Pyridine-2-aminium-6-methyl Pyridine-2,6-dicarboxylate

Experimental Section

A mixture of pyridin-2, 6-dicarboxylic acid powders (1mmol, 0.167 g), $[\text{pydc}, \text{H}_2]$, and 2-amino-6-methyl- pyridine (1mmol, 0.1081 g), $[\text{pya}]$, in 1:1 molar ratio, and a zirconium oxide ball was placed into a stainless-steel jar. The reactants were milled vigorously at a rate of 1200-1500 rpm (20-25 Hz) at room temperature for 9 h. After this time, the result white powder was produced (scheme 1). mp. 173-175 °C.

IR (KBr, cm^{-1}): 3525(w), 3433(m), 3269(w), 3059(w), 2977(w), 2677(m), 2491(m), 1687(vs), 1637(m), 1599(m), 1559(m), 1429(s), 1367(vs), 1165(s), 1073(s), 940(m), 701(vs), 646(m).

^1H NMR (D_2O , *ppm*) δH : 2.37 (s, 3H, H of methyl $(\text{pyaH}_2)^+$), 6.65 (d, 2H, H^3 $(\text{pydc})^{2-}$), 7.69 (s, 1H, H^4 $(\text{pydc})^{2-}$), 8.33 (s, 2H, $\text{H}^{6,8}$ $(\text{pyaH}_2)^+$), 8.53 (s, 1H, H^7 $(\text{pyaH}_2)^+$).

^{13}C NMR (D_2O , *ppm*) δC : 19.813 (C^{10}), 111.654 (C^8), 114.181 (C^7), 128.866 (C^6), 146.354 (C^4), 147.827 (C^3), 148.490 (C^9), 146.251 (C^2), 155.527 (C^5), 166.332 (C^1).

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