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Synthesis of 3,5-di-(4-pyridyl)-1*H*-1,2,4-triazole

Li-Li Liu and Guang Yang *

Department of Chemistry, Zhengzhou University, Zhengzhou, 450001, China.

* Author to whom correspondence should be addressed. E-mail: yang@zzu.edu.cn; Tel.: +86 371 63912869

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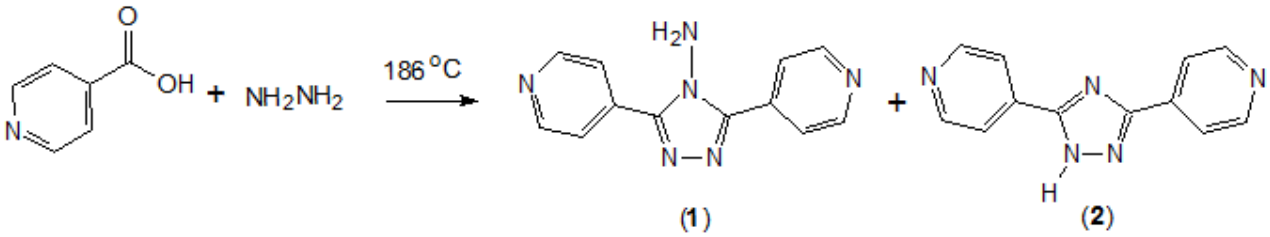
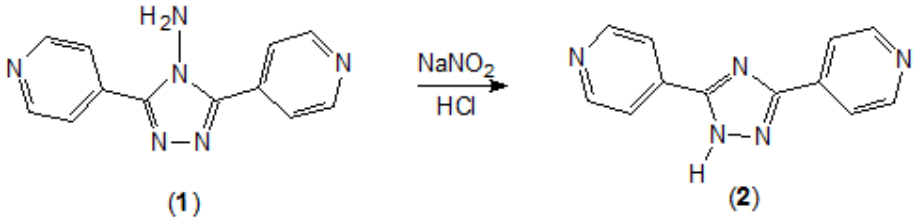
Introduction

4-Amino-3,5-di-(4-pyridyl)-4*H*-1,2,4-triazole (**1**) and 3,5-di-(4-pyridyl)-1*H*-1,2,4-triazole (**2**) are potential multi-topic bridging ligands in preparation of coordination compounds of 1 – 3D structures.[1] In an early literature, a method to prepare compound **1** has been reported [2], which involves the reaction of isonicotinonitrile with excess amount of hydrazine in ethylene glycol at 130°C. Polymeric copper complexes of **2** have been prepared by Chen *et al.*; **2** was generated by an *in situ* cycloaddition of 4-pyridylnitrile and ammonia in presence of Cu^{2+} under hydrothermal condition.[3] However, no synthetic procedures about the compound **2** – the deaminated product of **1** has appeared in the literature to the best of our knowledge. In this paper, we describe a facile method to prepare compound **2** starting from isonicotinic acid and hydrazine.

Synthesis

Isonicotinic acid (2.46g,0.02mol) and 2ml of 80% hydrazine were mixed in a 15 ml Teflon-lined reactor and heated for 48 h at 186°C [4]. The resulting liquid was diluted by water, and then the pH was adjusted from 9 to 6 by addition of HCl solution. White precipitate was obtained, and recrystallised from ethanol. The product is actually a mixture of 4-amino-3,5-di-(4-pyridyl)-4*H*-1,2,4-triazole (**1**) and 3,5-di-(4-pyridyl)-1*H*-1,2,4-triazole (**2**) in *ca* 1:7 molar ratio, estimated from the HNMR spectrum.
Pure sample of **2** was prepared by a successive deamination process [5]. The mixture of **1** and **2** (2.38 g, *ca* 10 mmol) was dissolved in aqueous HCl (6M, 3 mL). To it was added slowly an aqueous solution of $NaNO_2$ (0.76 g, 11 mmol); a lot of bubbles were generated quickly. The mixture was stirred for 5~6 h, then the pH was adjusted from 4 to 6.5 by 10% NaOH solution. White precipitate appeared and it was filtered and dried in air. Recrystallisation of the crude product from ethanol afforded colorless needles of **2**. The overall yield of this method is 9%.





Melting point: sublimated at 242°C

IR (KBr pellet, cm^{-1}): 1607 s, 1448 m, 1144 w, 983 m, 838 w, 724 m, 513 w.

^{1}H-NMR (400 MHz, DMSO-d_6): δ = 8.78 (4H, d, py-H), 8.02 (4H, d, py-H).

Elemental Analysis: Calculated for $C_{12}H_9N_5 \cdot 0.5H_2O$: C 57.59, H 4.83, N 27.98%; Found: C 57.28, H 4.70, N 27.90%.

MS (m/z): 225.2 (15%), 224.2 (100%, M+H), 218.3 (5%).

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