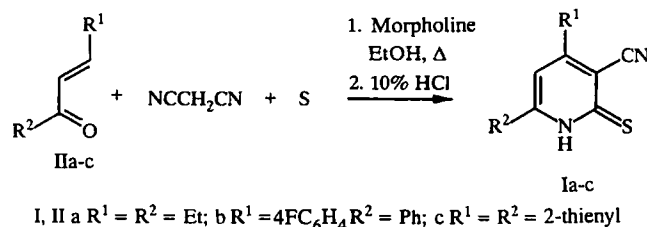


ONE STAGE SYNTHESIS OF 4,6-DIARYL-3-CYANOPYRIDINE-2(1H)-THIONES

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4,6-diaryl-3-cyanopyridine-2(1H)-thiones (I) have been used in the synthesis of practically important compounds including pesticides, antioxidants, and dyes [1]. The simplest method for synthesizing these compounds includes a preliminary preparation of 2-aryl-3-aryl-1,1-dicyanopropanes from α,β -unsaturated ketones and malononitrile and their subsequent thiolation by elemental sulfur [1, 2]. However, it is not always possible to separate the 1,1-dicyanopropanes thus limiting the possibilities of this method.

We have developed a one stage synthesis of pyridine-2(1H)-thiones I. These compounds are prepared from the corresponding α,β -unsaturated ketones II, malononitrile, and elemental sulfur by refluxing for 2 h in ethanol in the presence of morpholine.



In contrast to method [2], there is now no need to first prepare and separate the 2-aryl-3-aryl-1,1-dicyanopropanes.

4,6-Diphenyl-3-cyanopyridine-2(1H)-thione (Ia). A mixture of IIa (0.01 mole), malononitrile (0.01 mole), sulfur (0.012 mole), and morpholine (1 ml) in ethanol (25 ml) was refluxed with stirring for 2 h. The product was cooled to 20°C, acidified with hydrochloric acid (10%, 5 ml), and the precipitate separated and recrystallized from acetic acid. Yield 92%, mp 228-229°C, according to [2] mp 228-229°C. The remaining compounds were prepared similarly.

6-Phenyl-4-(4-fluorophenyl)-3-cyanopyridine-2(1H)-thione (Ib). Yield 87%, mp 218-220°C, according to [2] mp 218-220°C.

4,6-Di-(2-thienyl)-3-cyanopyridine-2(1H)-thione (Ic). Yield 83%, mp 242-244°C (decomp.). IR spectrum (KBr): 2228 (C≡N), 1623 (NH). PMR spectrum (DMSO- D_6): 7.10 (1H, q, 4- $H_{\text{thienyl}}(4)$, $^3J_{4-H,5-H} = 4.2$ Hz, $^3J_{3-H,4-H} = 2.7$ Hz); 7.30 (1H, q, 4- $H_{\text{thienyl}}(6)$, $^3J_{4-H,5-H} = 4.2$ Hz, $^3J_{3-H,4-H} = 2.4$ Hz); 7.75 (1H, d, 3- $H_{\text{thienyl}}(4)$); 7.80 (1H, s, $\text{CH}_{\text{pyridine}}$); 7.86 (1H, d, 3- $H_{\text{thienyl}}(6)$); 7.92 (1H, d, 5- $H_{\text{thienyl}}(4)$); 8.05 (1H, d, 5- $H_{\text{thienyl}}(6)$); 12.5 ppm (1H, br. s, NH). Found %: C 55.48; H 2.47; N 9.08; S 31.83. $\text{C}_{14}\text{H}_8\text{N}_2\text{S}_3$. Calculated %: C 55.97; H 2.68; N 9.32; S 32.02.

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