SYNTHESIS OF 2-AMINO-4(5H)-KETOTHIOPHENES

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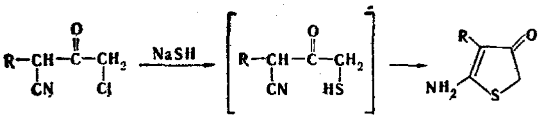
We have established that 3-keto-4-chlorobutyronitriles (Ia, b) react with sodium hydrosulfide in alcohol solution on brief heating to give the previously unknown 2-amino-4(5H)-ketothiophenes II [R = 1-methyl-2-benzimidazolyl, mp 256-257°C (from o-xylene), 67% yield] and IIb [R = 2-pyridyl, mp 182-183°C (from toluene), 73% yield].



I a,b

II a,b

The reaction proceeds through a step involving exchange of the chlorine atom by a sulfhydryl group and subsequent addition of this group to the triple bond of the nitrile group. The IR spectra of IIa, b do not contain the absorption band of a nitrile group. The PMR spectrum of IIa in d_6-DMSO contains singlets of protons of the α-methylene group of thiophene (3.78 ppm) and the N-methyl group of benzimidazole (3.66 ppm), signals of aromatic protons of the benzimidazole ring (7.0-7.6 ppm), and a two-proton singlet of an amino group at 8.75 ppm, which gradually vanishes when the sample is treated with heavy water.

The thiophene derivatives obtained in this research exist in the keto form rather than in the tautomeric enol form. Evidence for this is provided by the presence of a signal of a methylene group in the α-position of the thiophene ring at 3.8 ppm and of an absorption band of a keto group in the IR spectra (KBr pellets) at 1620 cm^{-1}. At the same time, the presence of the signal of an amino group excludes the hydroxyimine form. The results of elementary analysis for nitrogen and sulfur confirm the empirical formulas of the new compounds.

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