NEW METHOD FOR OBTAINING 3-CYANO-1,4-DIHYDROPYRIDINE-2(3H)-THIONES

A. A. Krauze and G. Ya. Dubur

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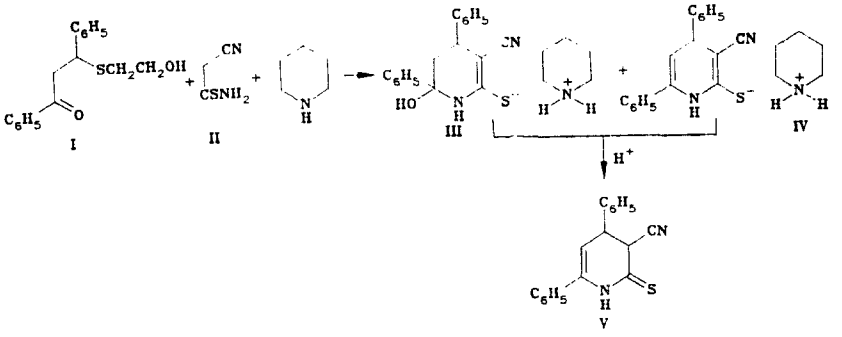
3-Cyano-1,4-dihydropyridine-2(3H)-thiones are unstable in solutions and can be oxidized by air oxygen or by the starting compounds in their synthesis – α,β-unsaturated ketones; this hinders the preparative isolation of the dihydropyridinethiones or makes it impossible [1, 2].



We have observed that the condensation of 1-(2'-hydroxyethylthio)-1-phenyl-2-benzoylethane (I) with cyanothioacetamide (II) in the presence of a small excess amount of piperidine in ethanol at room temperature gives a mixture of piperidinium 6-hydroxy-1,4,5,6-tetrahydropyridine-2-thiolate III and piperidinium 1,4-dihydropyridine-2-thiolate IV; acidification of the mixture with an equimolar amount of HCl in ethanol (0.5 M) leads to the known 1,4-dihydropyridine-2(3H)-thione V in 44% yield [2].

Compound I was obtained in 87% yield by brief heating of chalcone with 2-mercaptoethanol in the presence of catalytic amounts of KOH in ethanol.

The advantages of the method are that it excludes the oxidizing agent – the α,β-unsaturated ketone – and that 2-mercaptoethanol, which is a specific reducing agent for the disulfide bond [3] and possible bis(1,4-dihydro-2-pyridyl) disulfides, is liberated during the reaction.

Compound I. This compound had mp 65-67°C (from ethanol). IR spectrum: 1686 (C=O), 3170-3350 cm^{-1} (OH). PMR spectrum ($CDCl_3$): 7.2-8.0 (10H, m, two C_6H_5), 4.58 (1H, t, one CH), 3.64 (2H, q, OCH_2), 3.50 (2H, m, two CH_2), 2.57 (2H, t, SCH_2), 2.50 ppm (1H, t, OH). UV spectrum (ethanol), λ_{max}: 246, 276 nm.

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Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006.
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