METHOD FOR THE PRODUCTION OF 2-ALKYLTHIO-3-CYANO-1,4-DIHYDROPYRIDINES

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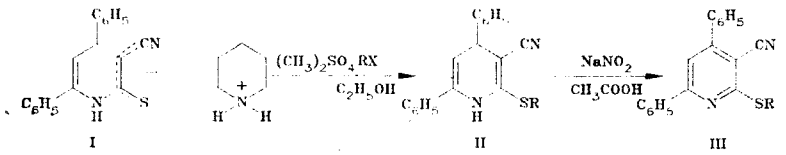
UDC 547.825

We were the first to carry out the conversion from 3,4-dihydropyridine-2-thiones to 2-alkylthio-1,4-dihydropyridines by alkylation of piperidinium salts of 3,4-dihydropyridine-2-thiones (I) [1] with an excess of alkyl halide or dimethyl sulfate.



II,IIIa R=CH_3; b R=C_2H_5

2-Methylthio-3-cyano-4,6-diphenyl-1,4-dihydropyridine (IIa) was produced by mixing the piperidinium salt of 3,4-dihydropyridine-2-thione I and dimethyl sulfate in absolute ethanol for 30 min at room temperature, followed by cooling to 0°C. Yield 72%, mp 147-149°C (from ethanol). IR spectrum: 3290, 2188, 1655 cm^{-1}. PMR spectrum, δ: 8.93 (n.s, NH), 7.49-7.18 (m, 2-C_6H_5), 5,06 (d, J = 5.0 Hz, 5-H), 4.33 (d, J = 5.0 Hz, 4-H), 2.50 ppm (s, S—CH_3).

2-Ethylthio-3-cyano-4,6-diphenyl-1,4-dihydropyridine (IIb) was produced analogously from the salt I and ethyl iodide. Yield 61%, mp 95-97°C (from ethanol). IR spectrum 3286, 2202, 1650 cm^{-1}. PMR spectrum, δ: 9.00 (n.s, NH), 7.31-7.18 (m, 2-C_6H_5), 5.02 (d, J = 5.0 Hz, 5-H), 4.36 (d, J = 5.0 Hz, 4-H), 2.91 (m, CH_2), 1.20 ppm (t, CH_3).

In the oxidation of dihydropyridines II with sodium nitrite, 2-(alkylthio)pyridines III, previously produced by alkylation of 3-cyanopyridine-2-thiones [2] are formed. The data of elementary analysis of the substances obtained correspond to the calculated values.

LITERATURE CITED

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1140-1141, August, 1984.
Original article submitted February 6, 1984.

0009-3122/84/2008-0935$08.50