4-METHYL-3-CYANOPYRIDIN-2(1H)-THIONE

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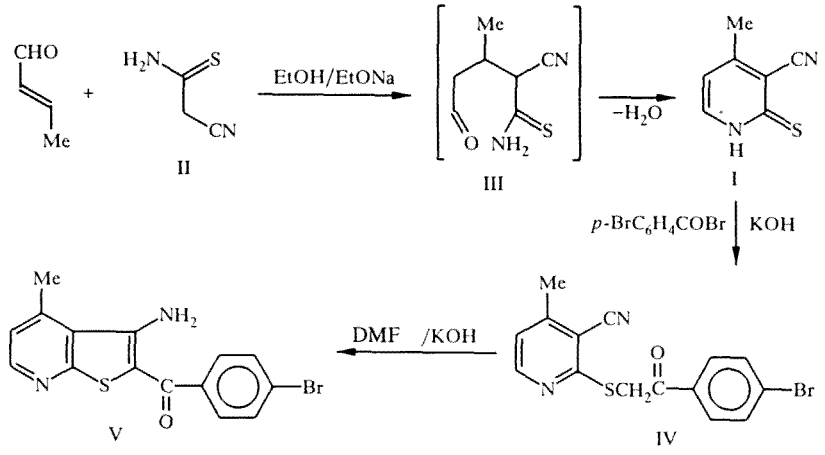
3-Cyanopyridin-2(1H)-thione [1-3] and its close homologs, 6-methyl- [4] and 5-methyl-3-cyano-pyridin-2-(1H)-thiones [5], have been prepared previously by the interaction of cyanothioacetamide with formylacetone and β-ethoxy-methylenepropanal respectively. The isomeric 4-methyl-3-cyanopyridin-2(1H)-thione (I) has not been described in the literature (see the reviews [2, 6]). We have shown for the first time that the pyridinthione (I) is formed by the reaction of crotonaldehyde (2-butenal) with cyanothioacetamide in boiling ethanol in the presence of sodium ethoxide.



The formation of product I shows that the first step in the reaction is the addition of the thioamide (II) to the C=C double bond of the aldehyde to give intermediate III.

The structure of thione I was confirmed by alkylation with *p*-bromophenacyl bromide to 2-(*p*-bromophenacylthio)-4-methyl-3-cyanopyridine (IV) which was converted to 3-amino-2-(*p*-bromobenzoyl)-4-methylthieno[2,3-*b*]pyridine (V) under Thorpe–Ziegler conditions.

Compound I ($C_7H_6N_2S$). Yield 48%. M.p. 248-250°C. IR spectrum (in Nujol): 3090, 3140 (NH), 2222 cm^{-1} (CN). ^1H NMR spectrum (DMSO-D_6): 13.9 (1 H, br.s, N–H), 7.80 (1 H, t, 6-H), 6.82 (1 H, d, 5-H, ^3J = 6.5 Hz), 2.40 ppm (3 H, s, CH_3).

Compound IV ($C_{15}H_{11}BrN_2OS$). Yield 89%. M.p. 138-140°C. IR spectrum: 2223 (CN), 1696 cm^{-1} (CO). ^1H NMR spectrum (DMSO-D_6): 8.36 (1 H, d, 6-H), 7.19 (1 H, d, 5-H, ^3J = 5.2 Hz), 7.99 (2 H, d, 3-H and 5-H), 7.77 (2 H, d, 2-H and 6-H), 4.91 (2 H, s, CH_2), 2.46 ppm (3 H, s, CH_3).

Compound V ($C_{15}H_{11}BrN_2OS$). Yield 90%. M.p. 225-228°C. IR spectrum: 3270, 3460 (NH_2), 1640 cm^{-1} (CO). ^1H NMR spectrum (DMSO-D_6): 7.24 (1 H, d, 5-H, ^3J = 5.3 Hz), 8.53 (1 H, d, 6-H), 8.09 (2 H, br.s, NH_2), 7.73 (4 H, s, C_6H_4), 2.82 ppm (3 H, s, CH_3).

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