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SHORT COMMUNICATIONS

Unusual Reaction of Ethyl 2-Cyano-3,3-bis(methylsulfanyl)-acrylate with Cyanothioacetamide

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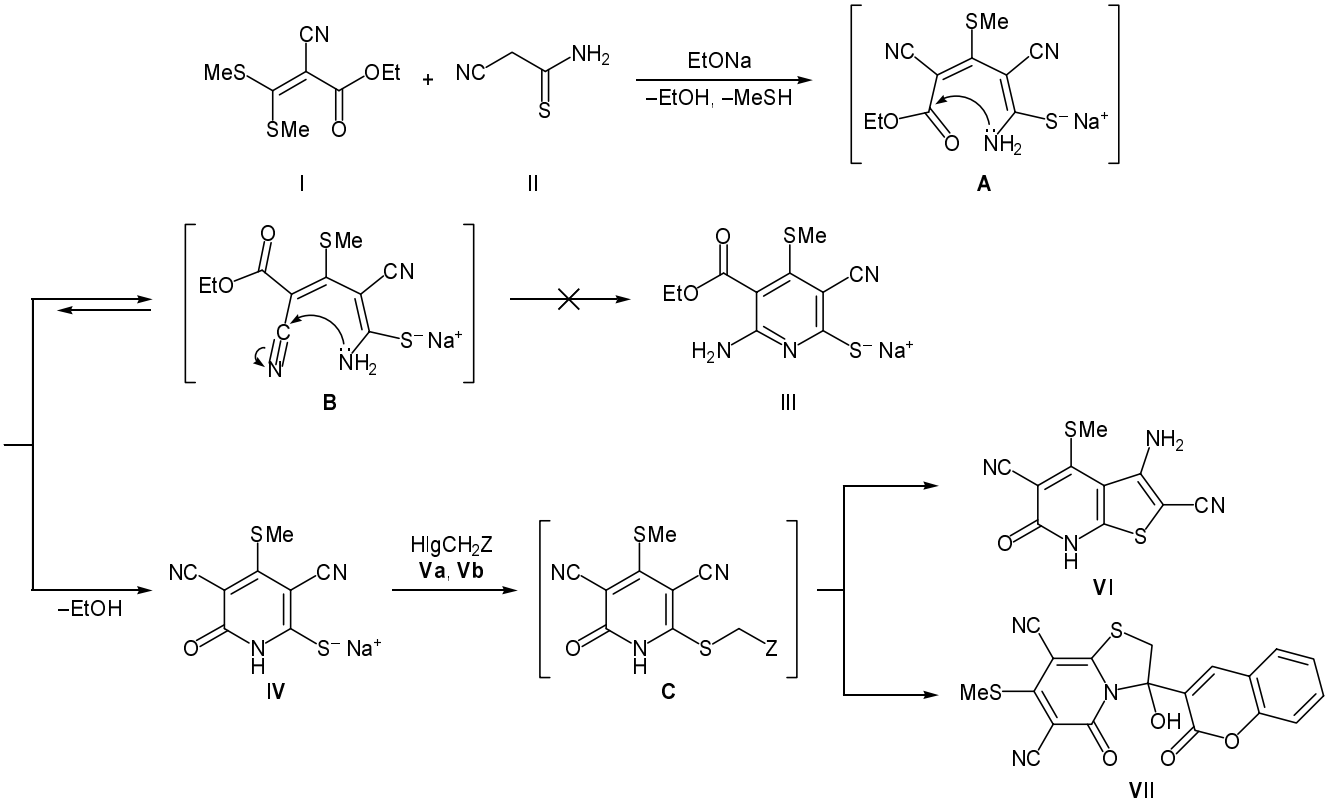
Acrylonitrile derivatives having a nucleofugal group in the β-position react with cyanothioacetamide according to the vinyl nucleophilic substitution pattern (S_NVin) [1] with formation of substituted 6-aminopyridine-2-thiols [2]. Intermediate butadienes like **A** and **B** were isolated and characterized [2].

Alkene **I** possessing two nucleofugal methylsulfanyl groups was found to react with cyanothioacetamide (**II**) in the presence of an equimolar amount of sodium ethoxide in anhydrous ethanol at 20°C according to a different pattern. In this case, no substituted sodium 6-aminopyridine-2-thiolate (**III**) was formed, but the product was sodium 6-oxo-1,6-dihydropyridine-2-thiolate (**IV**). These data indicate that the cyclization involves the ester rather than cyano group. The structure of salt **IV** was confirmed by its alkylation with chloroacetonitrile (**Va**) and 3-bromoacetyl-2*H*-chromen-2-one (**Vb**). However, intermediate sulfides **C** could not be isolated, for they undergo fast intramolecular ring closure to heterocyclic systems **VI**



V, Hlg = Cl, Z = CN (**a**); Hlg = Br, Z = 2-oxo-2*H*-chromen-3-ylcarbonyl (**b**).

and **VII**, respectively. Analogous cyclizations are well known for structurally related compounds [3].

Sodium 3,5-dicyano-4-methylsulfanyl-6-oxo-1,6-dihydropyridine-2-thiolate (IV). A solution of sodium ethoxide prepared from 0.23 g (10 mmol) of metallic sodium and 15 ml of anhydrous ethanol was added under stirring at 20°C to a suspension of 1.0 g (10 mmol) of cyanothioacetamide (**II**) in 15 ml of anhydrous ethanol, the mixture was stirred for 2 min until it became homogeneous, and 2.17 g (10 mmol) of ethyl 2-cyano-3,3-bis(methylsulfanyl)acrylate (**I**) was added. The mixture was stirred until complete dissolution of compound **I** (4 min), filtered through a folded filter paper, and left to stand for 24 h. The precipitate was filtered off and washed with anhydrous ethanol and hexane. Yield 1.69 g (69%), white powder, mp 350°C (decomp.). IR spectrum, ν, cm^{-1}: 2222 sh (C≡N), 1674 (CONH). ^{1}H NMR spectrum, δ, ppm: 2.56 s (3H, Me), 11.53 br.s (1H, NH). Found, %: C 38.95; H 1.49; N 16.88. *M* 245. $C_8H_4N_3NaOS_2$. Calculated, %: C 39.18; H 1.64; N 17.13. *M* 245.27.

3-Amino-4-methylsulfanyl-6-oxo-6,7-dihydrothieno[2,3-*b*]pyridine-2,5-dicarbonitrile (VI). 2-Chloroacetonitrile (**Va**), 0.63 ml (10 mmol), was added under stirring to a suspension of 2.45 g (10 mmol) of salt **IV** in 15 ml of DMF. The mixture was stirred for 4 h and diluted with an equal volume of water, and the precipitate was filtered off and washed in succession with water, ethanol, and hexane. Yield 2.12 g (81%), yellow powder, mp 360°C (decomp.). IR spectrum, ν, cm^{-1}: 3214, 3335, 3410 (NH_2); 2205, 2224 (C≡N); 1672 (CONH); 1648 (δNH_2). ^{1}H NMR spectrum, δ, ppm: 2.58 s (3H, Me), 6.68 br.s (2H, NH_2), 10.99 br.s (1H, NH). Found, %: C 45.60; H 2.08; N 21.14. *M* 262. $C_{10}H_6N_4OS_2$. Calculated, %: C 45.79; H 2.31; N 21.36. *M* 262.32.

3-Hydroxy-7-methylsulfanyl-5-oxo-3-(2-oxo-2*H*-chromen-3-yl)-2,3,4,5-tetrahydrothiazolo[3,2-*a*]-pyridine-6,8-dicarbonitrile (VII) was synthesized as described above for compound **VI** using 2.67 g (10 mmol) of 3-bromoacetyl-2*H*-chromen-2-one (**Vb**) instead of compound **Va**. Yield 3.09 g (76%), yellow powder, mp 230°C (decomp.). IR spectrum, ν, cm^{-1}: 2224 sh (C≡N), 1722 (C=O, lactone), 1672 (C^5=O). ^{1}H NMR spectrum, δ, ppm: 2.90 s (3H, Me), 3.61 d and 4.05 d (1H each, SCH_2, ^2J = 16.92 Hz), 7.40 t (1H, 7'-H, ^3J = 8.02 Hz), 7.49 d (1H, 5'-H, ^3J = 8.02 Hz), 7.67 t (1H, 6'-H, ^3J = 8.08 Hz), 7.95 d (1H, 8'-H, ^3J = 8.00 Hz), 8.34 br.s (1H, OH), 8.81 s (1H, 4'-H). Mass spectrum, *m*/*z* (I_{rel}, %): 410 (32) $[M + 1]^+$, 409 (8) $[M]^+$, 385 (14), 337 (9), 295 (11), 267 (5), 179 (25), 138 (100), 124 (28), 111 (93), 99 (87), 97 (12). Found, %: C 55.52; H 2.63; N 10.06. *M* 409. $C_{19}H_{11}N_3O_4S_2$. Calculated, %: C 55.74; H 2.71; N 10.26. *M* 409.45.

Initial ethyl 2-cyano-3,3-bis(methylsulfanyl)acrylate (**I**) was synthesized as described in [4].

The IR spectra were recorded on an IKS-40 spectrometer from samples dispersed in mineral oil. The ^{1}H NMR spectra were measured on Varian Gemini-200 (199.975 MHz, compound **IV**), Bruker AM-300 (300.13 MHz, **VI**), and Varian Mercury-400 spectrometers (400.397 MHz, **VII**) using DMSO-d_6 as solvent and tetramethylsilane as internal reference. The mass spectrum (70 eV) of compound **VII** was obtained on a Hewlett–Packard Chrommas GC/MS system (HP 5890/HP 5972) using HP-5MS column; sample was injected as a solution in methylene chloride.

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