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LETTERS TO THE EDITOR

Amine Interchange of Cyanothioacetamide with Morpholine and Synthesis of 3-Amino-2-(4-acetylphenylcarbamoyl)-5-morpholinothiophene

V. D. Dyachenko

Shevchenko Lugansk State Pedagogical University, Lugansk, Ukraine

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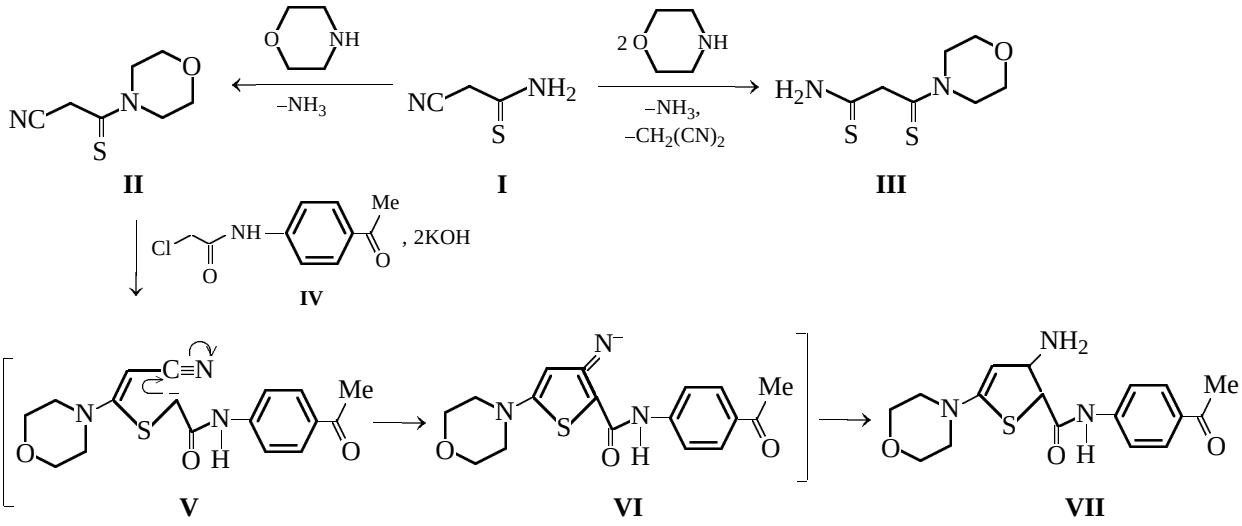
There is only one published example of amine interchange of thioacetamide with piperidine [1], as follows from reviews [2–5]. We found that cyanothioacetamide **I** undergoes amine interchange in the reaction with morpholine in ethanol at 20°C. Compound **II** is formed at equimolar ratio of the reactants, and compound **III**, at the 1 : 2 ratio. Alkylation of **II** with α-chloro-(4-acetyl)acetanilide in DMF in the presence of a twofold excess of KOH yields previously unknown 3-amino-2-(4-acetylphenylcarbamoyl)-5-morpholinothiophene **VII** via intermediates **V** and **VI**. The mechanisms of the reactions discovered and the synthetic potential of new CH acids **II** and **III** and of thiophene derivative **VII** as nucleophilic agent were studied.



3-Morpholino-3-thioxopropanonitrile II. Yield 76%, mp 89°C (from EtOH). IR spectrum, ν, cm^{-1}: 2264 (C≡N). ^1H NMR spectrum, δ, ppm: 3.70 m (6H, CH_2NCH_2 and CH_2CN), 4.16 m (4H, CH_2OCH_2). Found, %: C 49.20; H 6.07; N 16.28. $C_7H_{10}N_2OS$. Calculated, %: C 49.39; H 5.92; N 16.46.

1-Amino-3-morpholino-1,3-propanedithione III. Yield 39%, mp 143–150°C (dec.). IR spectrum, ν, cm^{-1}: 3190, 3278, 3356 (NH_2). ^1H NMR spectrum, δ, ppm: 3.70 m (4H, CH_2NCH_2), 3.91 s (2H, CH_2), 4.42 m (4H, CH_2OCH_2), 8.87 br.s and 9.43 br.s (1H each, NH_2). Mass spectrum, *m/z* (I_{rel}, %): 206 (6) $[M + 2]^+$, 205 (7) $[M + 1]^+$, 204 (55) $[M]^+$, 171 (8), 144 (9), 119 (22), 110 (20), 101 (8), 86 (100), 60 (39), 54 (18), 42 (23). Found, %: C 40.93; H 6.07; N 13.58. $C_7H_{12}N_2OS_2$. Calculated, %: C 41.15; H 5.92; N 13.71.

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3-Amino-2-(4-acetylphenylcarbamoyl)-5-morpholinothiophene VII. Yield 71%, mp 199–200°C (from BuOH). IR spectrum, ν, cm^{-1}: 3242, 3297, 3425 (NH_2), 1680 (C=O), 1657 [CONH, δ(NH_2)]. ^1H NMR spectrum, δ, ppm: 2.50 s (3H, Me), 3.17 m (4H, CH_2NCH_2), 3.75 m (4H, CH_2OCH_2), 5.67 s (1H, C_4H), 6.68 br.s (2H, NH_2), 7.80 br.s (4H, C_6H_4), 8.87 br.s (1H, CONH). Found, %: C 58.87; H 5.32; N 12.30. $C_{17}H_{19}N_3O_3S$. Calculated, %: C 59.11; H 5.54; N 12.16.

The IR spectra were recorded on an IKS-40 spectrophotometer (mulls in mineral oil). The ^1H NMR spectra were measured on Gemini-200 (199.975 MHz, compounds **II**, **VII**) and Bruker DR-500 (500.13 MHz, compound **III**) spectrometers in DMSO-d_6 (reference TMS). The mass spectrum of **III** was taken on a Kratos MS-890 mass spectrometer (70 eV). The structures of **II** and **III** were studied by single crystal X-ray diffraction; the results will be reported later.

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