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DIMER OF 5-METHYL-3-ISOXAZOLYL ISOTHIOCYANATE

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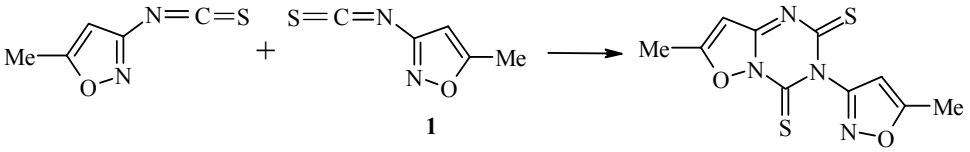
In a search for physiologically active compounds among 1,2,4-thiadiazole derivatives, we prepared 5-methyl-3-isoxazolyl isothiocyanate (**1**) by the reaction of 3-amino-5-methylisoxazole with thiophosgene. The structure of the product was supported by the preparation of products of its reactions with amines and established using the ^{1}H and ^{13}C NMR spectral data.

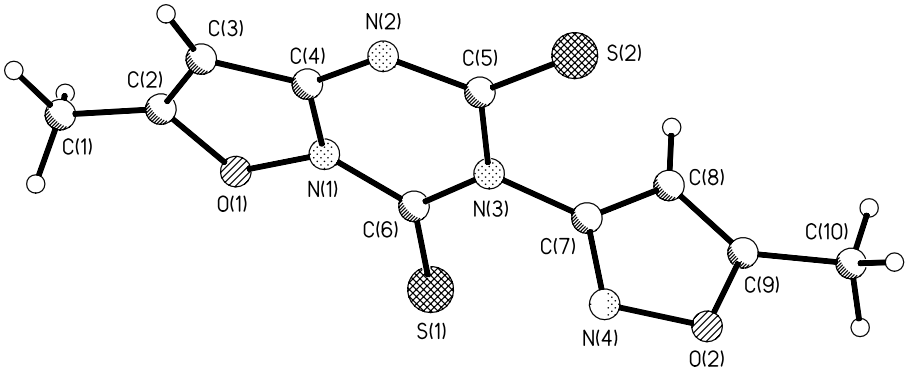
At room temperature, isothiocyanate **1** gradually crystallizes to give **2**, which is the product of a [4+2] cycloaddition:



1 **2**

An NMR and X-ray diffraction structure investigation supported the structure assigned for the dimer of 5-methyl-3-isoxazolyl isothiocyanate **2**.

Dimer **2** monomerizes in $CDCl_3$ solution. Spectra of both the monomer and dimer were found in the ^{1}H NMR spectra. Eventually, we obtained the hydrolysis products.



Molecular structure of **2**

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The ^{1}H and ^{13}C NMR spectra were taken on a Bruker DPX-200 spectrometer at 200 and 50 MHz, respectively, in $CDCl_3$ with TMS as the internal standard.

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5-Methylisoxazolyl 3-isothiocyanate (1). A solution of 3-amino-5-methylisoxazole (49.05 g, 0.5 mol) in methylene chloride (300 ml) was added dropwise to a rapidly stirred solution of a mixture thiophosgene (42.2 ml, 0.55 mol) and sodium bicarbonate (92.4 g, 1.1 mol) in water (200 ml) cooled to 0°C over 1 h. The reaction mixture was stirred for an additional 30 min. The organic phase was removed, washed with two 100-ml portions of saturated aqueous sodium chloride, dried over sodium sulfate, and evaporated. The oil obtained was distilled, taking the fraction at 39-41°C (1 mm Hg) to give 36.8 g (53%). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.00 (1H, q, $J = 0.8$, H-4); 2.50 (3H, d, $J = 0.8$, CH_3). ^{13}C NMR spectrum, δ, ppm: 172.9 (C-5); 153.1 (C-3); 145.4 (NCS); 100.1 (C-4); 13.2 (CH_3). The signals were assigned relative to proton-coupled ^{13}C NMR spectra. Found, %: C 42.61; H 2.53; N 20.21. $C_5H_4N_2OS$. Calculated, %: C 42.85; H 2.88; N 19.99.

Dimer of 5-methylisoxazolyl 3-isothiocyanate (2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.25 (1H, q, $J = 0.8$, CH); 6.15 (1H, q, $J = 0.8$, CH); 2.70 (3H, d, $J = 0.8$, CH_3); 2.60 (3H, d, $J = 0.8$, CH_3). Found, %: C 42.44; H 2.49; N 20.13. $C_{10}H_8N_4O_2S_2$. Calculated, %r: 42.85; H 2.88; N 19.99.

The synthesis of 5-(disubstituted amino)-3-(2-oxopropyl)[1,2,4]thiadiazoles starting from our new product, 5-methyl-3-isoxazolyl isothiocyanate will be the subject of a separate communication.

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