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REACTION OF THIOAMIDES OF HETARENECARBOXYLIC ACIDS WITH DIMETHYL ACETYLENEDICARBOXYLATE

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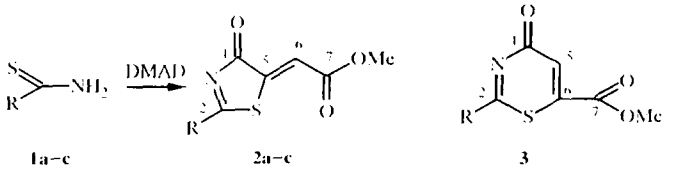
Reactions of thioamides of hetarenecarboxylic acids with the dimethyl ester of acetylenedicarboxylic acid (DMAD) have not been described in the literature. In principle, both thiazolines and thiazines and also mixtures of them might be expected to be formed from the reaction [1].

We discovered that on interacting 5-methyl-3-phenylisoxazole-4-carbothioamide (**1a**), and 5-ethylthio- and 5-benzylthioimidazole-4-carbothioamides (**1b,c**) and DMAD in ethanol at room temperature the individual compounds **2a-c** containing a thiazoline ring were formed.



1a–c **2a–c** **3**

a R = 5-methyl-3-phenylisoxazol-4-yl, **b** 5-(ethylthio)imidazol-4-yl, **c** 5-(benzylthio)imidazol-4-yl

The structure of the cyclization products **2a-c** were confirmed as thiazolin-4-ones by data of ^{1}H and ^{13}C NMR spectra. The values of the long-range H–^{13}C constants in the spectrum of compound **2a** were 1.0 Hz for $C_{(7)}$–$H_{(6)}$ and 4.0 Hz for $C_{(4)}$–$H_{(6)}$, which is in agreement with a thiazoline structure for **2** but is in conflict with structure **3** with a thiazine ring [1]. The value of the chemical shift of $C_{(4)}$ of compounds **2a,b** at about 180 ppm is also characteristic of a thiazoline ring. The corresponding signal for a thiazine ring is displayed at higher field at 158-162 ppm [2].

4-(5-Methoxycarbonylmethylene-4-oxothiazolin-2-yl)-5-methyl-3-phenylisoxazole (2a). DMAD (0.01 mol) was added to a solution of thioamide **1** (0.01 mol) in ethanol. The mixture was stirred at about 20°C for 2 h and the yellow solid product **2a** filtered off. Yield 36%; mp 228-231°C (acetone). ^{1}H NMR spectrum ($CDCl_3$): 2.97 (3H, s, CH_3); 3.80 (3H, s, CH_3); 7.04 (1H, s, =CH); 7.50-7.60 ppm (5H, m, Ph). ^{13}C NMR spectrum ($CDCl_3$): 183.2 ($C_{(2)}$); 180.8 ($C_{(4)}$, d, ^3J = 4.0 Hz); 142.2 ($C_{(5)}$, d, ^2J = 1.0 Hz); 122.6 ($C_{(6)}$, J = 173.0 Hz); 165.7 ppm ($C_{(7)}$, ^2J = 1.0 Hz). Found, %: C 59.03; H 3.87; N 8.76; S 10.20. $C_{16}H_{12}N_2O_4S$. Calculated, %: C 58.60; H 3.70; N 8.54; S 9.76.

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2-(5-Ethylthioimidazol-4-yl)-5-methoxycarbonylmethylenethiazolin-4-one (2b) was obtained analogously to compound **2a** from 5-ethylthioimidazole-4-carbothioamide. Yield 50%; mp 250-252°C (ethanol). ^{1}H NMR spectrum (DMSO-d_6): 1.32 (3H, t, CH_3); 3.25 (2H, q, CH_2); 3.80 (3H, s, OCH_3); 6.85 (1H, s, =CH); 8.15 ppm (1H, s, =CH). Found, %: C 44.89; H 3.92; N 14.32; S 22.0. $C_{11}H_{11}N_3O_3S_2$. Calculated, %: C 44.42; H 3.73; N 14.13; S 21.56.

2-(5-Benzylthioimidazol-4-yl)-5-methoxycarbonylmethylenethiazolin-4-one (2c) was obtained analogously to **2a** from 5-benzylthioimidazole-4-carbothioamide. Yield 71%; mp 232°C (decomp., from ethanol). ^{1}H NMR spectrum (DMSO-d_6): 3.80 (3H, s, OCH_3); 4.53 (2H, q, CH_2); 6.87 (1H, s, =CH); 7.2-7.5 (5H, m, Ph); 8.20 ppm (1H, s, =CH). ^{13}C NMR spectrum (DMSO-d_6): 182.2 (C_{12}, s); 180.7 (C_{14}); 144.6 (C_{15}); 119.3 (C_{16}); 165.8 (C_{17}). Found, %: C 53.32; H 4.11; N 11.46; S 18.10. $C_{16}H_{14}N_3O_3S_2$. Calculated, %: C 53.5; H 3.93; N 11.67; S 17.78.

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