SYNTHESIS OF 6-ACYLMETHYLHEXAHYDRO-1,2,4,5-TETRAZINE-3-THIONES

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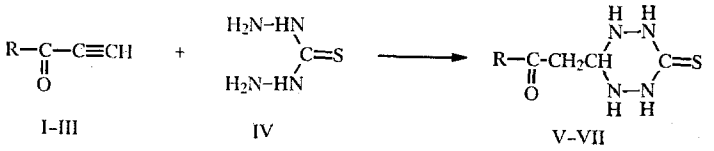
Methods for obtaining substituted 1,2,4,5-tetrazine-3-thiones based on the reaction of thiocarbohydrazide and dimethylthiocarbohydrazide with aldehydes and ketones in aqueous ethanol solutions with prolonged heating are known [1-3].

We have found that new 1,2,4,5--tetrazine-3-thione derivatives, viz., 6-acylmethylhexahydro-1,2,4,5-tetrazine-3-thiones V-VII in the form of light-yellow crystals that are soluble in DMSO, DMF, and ethanol (with heating), are formed in good yields in the reaction of terminal α-acetylenic ketones I and II and methyl propiolate (III) with thiocarbohydrazide (IV) in an aqueous ethanol solution (1:1) by heating (60-65°C) for 1 h.



I-III IV V-VII

I, V R=Ph; II, VI R=2-thienyl; III, VII R=OMe

Compound V ($C_{10}H_{12}N_4OS$). This compound had mp 140-141°C. IR spectrum (KBr): 1200 (C=S), 1675 (C=O), 3175 cm^{-1} (NH). PMR spectrum (80 MHz, d_6-DMSO), ppm: 3.16 (2H, d, CH_2), 4.09 (1H, m, CH), 5.01 (2H, 1-NH, 5-NH), 7.56-7.93 (5H, m, C_6H_5), 9.28 (2H, s, 2-NH, 4-NH). ^{13}C NMR spectrum (22.49 MHz, d_6-DMSO), ppm: 41.14 (CH_2), 63.48 (CH), 172.45 (C=S), 196.21 (C=O), 128.09-136.60 (C_6H_5). The yield was 79%.

Compound VI ($C_8H_{11}N_4OS$). This compound had mp 141-143°C. IR spectrum (KBr): 720 (C—S), 1210 (C=S), 1645 (C=O), 3160 cm^{-1} (NH). PMR spectrum (80 MHz, d_6-DMSO), ppm: 3.06 (2H, d, CH_2), 4.05 (1H, m, CH), 5.02 (2H, 1-NH, 5-NH), 7.25-8.03 (3H, m, C_4H_3S), 9.28 (2H, s, 2-NH, 4-NH). The yield was 75%.

Compound VII ($C_5H_{10}N_4O_2S$). This compound had mp 141-143°C. IR spectrum (KBr): 1210 (C=S), 1720 (C=O), 3165 cm^{-1} (NH). PMR spectrum (80 MHz, d_6-DMSO), ppm: 2.47 (2H, d, CH_2), 3.59 (3H, s, CH_3O), 3.91 (1H, m, CH), 4.97 (2H, 1-NH, 5-NH), 9.23 (2H, s, 2-NH, 4-NH). The yield was 66%.

The results of elementary analysis of the synthesized compounds were in agreement with the calculated values.

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