DERIVATIVES OF PYRAZOLE AND 1,2,4-TRIAZINE FROM THIOCARBAZIDES AND 1,2- AND 1,3-DIOXOCOMPOUNDS

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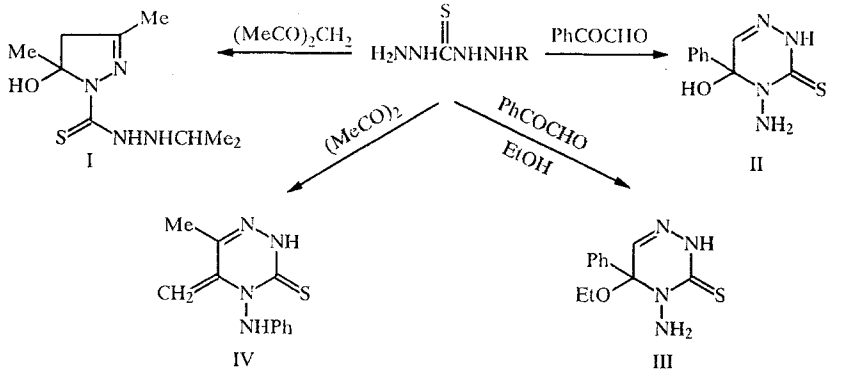
Thiocarbazide is readily accessible and is used in synthesis, particularly in the synthesis of heterocycles [1]. In this connection, the reactions of 1,2- and 1,3-dioxocompounds with thiocarbazide and its derivatives are of interest. The only reactions of this type reported are the formation of derivatives of 1,2,4,5-tetrazepine and 1,3,4-oxadiazine from thiocarbazide [2] and 1-phenylthiocarbazide [3] and certain 1,2-dioxo-compounds; the structure of the products has not been proved. 3,5-Dimethylpyrazole is formed from acetylacetone and thiocarbazide [1]. Our own experiments confirm these reactions; however, with 1-substituted thiocarbazides the reaction products (room temperature, $CHCl_3$) are 5-hydroxy-2-pyrazolines of the type of I.



With α-dicarbonyl compounds derivatives of 1,2,4-triazine are formed; their structure depends to a great extent on the structure of the initial 1,2-dioxocompounds and the nature of the solvent. Thus, with phenylglyoxal thiocarbazide gives, in benzene, compound II, and in ethanol the derivative III. From 1-phenylthiocarbazide and diacetyl one obtains a derivative of 5-methylene-1,2,4-triazin-3-thione IV.

1-(2-Isopropylhydrazinoylthiocarbonyl)-3,5-dimethyl-5-hydroxy-2-pyrazoline (I, $C_8H_{18}N_4OS$). mp 102-103°C (from hexane). PMR spectrum ($CDCl_3$, δ, ppm): 1.02 (6H, d, CH_3), 1.98 (3H, s, CH_3), 2.03 (3H, s, CH_3), 2.76 and 3.04 (2H, AB system, J_{AB} 18.0 Hz, CH_2), 3.0-3.3 (1H, m, CH), 5.90 (2H, s, OH + NH), 8.20 (1H, s, NH). Yield 50%.

4-Amino-5-hydroxy-5-phenyl-1,2,4-triazin-3-thione (II, $C_9H_{10}N_4OS$). mp 189-190 (from benzene). PMR spectrum (DMSO-D_6, δ, ppm): 5.10 (2H, s, NH_2), 6.75 (1H, s, CH), 7.2-8.0 (H_{arom}), 7.70 (1H, s, OH), 11.65 (1H, s, NH). ^{13}C NMR spectrum (DMSO-D_6, ppm): 80.4 ($C_{(5)}$), 128.5-130.8, 140.8 (C_{arom}), 140.4 ($C_{(6)}$), 170.8 ($C_{(3)}$). Yield 70%.

4-Amino-5-phenyl-5-ethoxy-1,2,4-triazin-3-thione (III, $C_{11}H_{14}N_4OS$). PMR spectrum ($CDCl_3$, δ, ppm): 1.39 (3H, t, CH_3), 4.37 (2H, q, CH_2), 7.3-8.2 (5H, m, C_6H_5), 7.35 (1H, s, CH), 11.65 (1H, s, NH). Oil. Yield 15%.

6-Methyl-5-methylene-4-phenylamino-1,2,4-triazine (IV, $C_{11}H_{12}N_4S$). mp 130-131°C (from 1:1 benzene–hexane). PMR spectrum ($CDCl_3$, δ ppm): 2.02 (3H, s, CH_3), 4.40 and 4.85 (2H, d, J = 0.5 Hz, CH_2), 6.7-7.3 (5H, m, C_6H_5), 7.40 (1H, s, NH), 9.60 (1H, s, NH). Yield 80%.

The results of elemental analyses for C, H, and N corresponded to those calculated.

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