NEW SYNTHESIS OF 2-ACYLMETHYL-5-IMINO-3-PHENYL-4H-1,3,4-THIADIAZOLES

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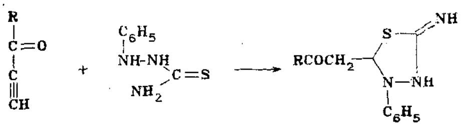
It was shown in [1] that mixtures of cis,cis- and cis,trans-dimethyl-β-thiodiacrylic esters in a ratio of 1:1 are formed in the reaction of 1-substituted thiosemicarbazides with methyl propiolate in methanol, i.e., 1-substituted thiosemicarbazides are thiylating agents.

We have found that the corresponding 2-acylmethyl-5-imino-3-phenyl-4H-1,3,4-thiadiazoles (IIa,b) are formed in equimolar amounts in the reaction of terminal α-acetylenic ketones Ia,b with 1-phenylthiosemicarbazide in a protic solvent (methanol) at 20°C:



Ia,b IIa,b

a $R=C_6H_5$, b R= 2-thienyl

Compound IIa, with mp 181-182°C (from methanol), was obtained in 78% yield. IR spectrum (KBr): 708 (C—S); 1650 (V=0); 3170, 3320 cm^{-1} (NH). Mass spectrum:* M^+ 297, 255 $[M - CH_2N_2]$, 233 $[M - \overset{S}{\underset{NH}{|}}\!\!>C{=}NH]$, 221 $[M - CH_4N_2S]$, 220 $[M - C_6H_5]$, 178 $[M - C_6H_5COCH_2]$, 105 $[C_6H_5CO]$, 91 $[C_6H_5N]$, 77 $[C_6H_5]$. Compound IIb, with mp 186-187°C (from methanol), was obtained in 72% yield. IR spectrum (KBr): 685 (C—S), 1640 (C=O), 3150, 3300 cm^{-1} (NH). Mass spectrum: M^+ 303, 261 $[M - CH_2N_2]$, 229 $[M - \overset{S}{\underset{HN}{|}}\!\!>C{=}NH]$, 227 $[M - CH_4N_2S]$, 226 $[M - C_6H_5]$, 178 $[M - C_4H_3S - COCH_2]$, 111 $[C_4H_3S - CO]$, 91 $[C_6H_5N]$, 83 $[C_4H_3S]$. The results of elementary analysis were in agreement with the calculated values.

It was established that cleavage of the C—S bond in IIa,b occurs in a strongly aprotic medium (DMSO) and that they are converted to 1-acylvinyl-1-phenylthiosemicarbazides. The structures of the latter were confirmed by PMR spectroscopic data.

LITERATURE CITED

1. J. W. Lown and J. C. N. Ma, Can. J. Chem., 45, 953 (1967).

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*Here and subsequently, the m/z values are given for the ion peaks.

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