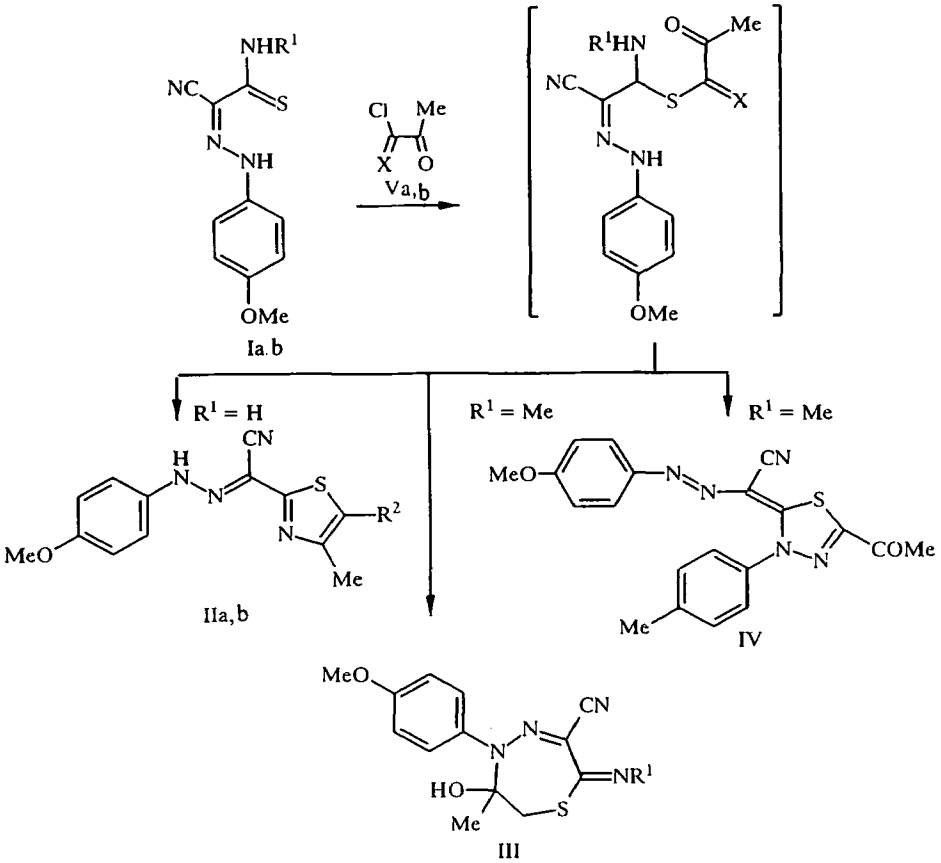
Chemistry of Heterocyclic Compounds, Vol. 34, No. 12, 1998

2-(4-METHOXYPHENYL)HYDRAZONO-2-THIOCARBAMOYLACETAMIDES IN THE SYNTHESIS OF SULFUR-CONTAINING HETEROCYCLES

N. P. Bel'skaya, I. V. Paramonov, M. V. Mukhacheva, and V. A. Bakulev

We have shown for the first time that the direction of the reaction of 2-(4-methoxyphenyl)hydrazono-2-thiocarbamoylacetamide Ia and its N-methyl derivative Ib with chloroacetone Va and hydrazonoyl chloride Vb and consequently the structure of the reaction products is completely determined by the nature of the substituent R^1 in the thioamide fragment of the initial hydrazone I and also by the nature of the haloketone used, Va or Vb. The hydrazone Ia, which contains an unsubstituted thioamide group, gave the thiazoles IIa and b when heated with compounds Va



I a R^1 = H, b R^1 = Me; II a R^2 = H, b R^2 = N=NC$_6$H$_4$Me-4;
V a X = H, b X = NNHC$_6$H$_4$Me-4

Ural State Technical University, Ekaterinburg 620002, Russia. E-mail: belska@htf.ustu.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1700-1701, December, 1998, Original article submitted October 1, 1998.

0009-3122/98/3412-1447$20.00

and Vb in DMF in the presence of triethylamine. Under the same conditions the N-methylthioacetamide Ib gave the thiadiazepin III and the thiadiazole IV respectively.

2-(4-Methoxyphenyl)hydrazono-2-(4-methylthiazol-2-yl)acetonitrile (IIa). 2-(4-Methoxyphenyl)hydrazono-2-thiocyanoacetamide Ia (0.1 g, 0.09 mmol) was dissolved in DMF (10 ml), triethylamine (0.1 ml, 0.09 mmol) was added and then chloroacetone (0.07 ml 0.09 mmol) was added dropwise. The mixture was heated to 40°C and maintained at that temperature for 1 h with stirring, then cooled in ice, the precipitate filtered off and washed with water. Yield 91%. M.p. 139°C. Mass spectrum, *m/z*: 272 [M^+]. ^{1}H NMR spectrum (DMSO-D_6): 13.96 (1H, s, NH), 1170 (1H, s, NH), 7.56 (1H, s, CH), 7.23 (1H, s, CH), 7.36 and 6.96 (4H, AB_{system}, J = 9.1 Hz, CH_{arom}), 7.51 and 6.99 (4H, AB_{system}, J = 9.3 Hz, CH_{arom}), 3.77 (3H, s, OCH_3), 3.75 (3H, s, OCH_3), 2.54 (3H, s, CH_3), 2.49 ppm (3H, s, CH_3).

2-(4-Methoxyphenylhydrazono)-2-[5-(4-tolylazo)-4-methylthiazol-2-yl]acetonitrile (IIb) was obtained by the method described above for II a. Yield 93%. M.p. 235-237°C. Mass spectrum , *m/z*: 390 [M^+]. ^{1}H NMR spectrum (DMSO-D_6): 12.09 (1H, s, NH), 7.73 and 7.35 (4H, AB_{system}, J = 7.9 Hz, CH_{arom}), 7.45 and 6.99 (4H, AB_{system}, J = 9.2 Hz, CH_{arom}), 3.77 (3H, s, OCH_3), 2.75 (3H, s, CH_3), 2.39 ppm (3H, s, CH_3).

6-Hydroxy-2(7H)-methylimino-6-methyl-5-(4-methoxyphenyl)-5,6-dihydro-1,4,5-thiadiazepin-3-carbonitrile (III) was obtained by the method described above for IIa. Yield 93%. M.p. 147-149°C. Mass spectrum, *m/z*: 304 [M^+]. ^{1}H NMR spectrum (DMSO-D_6): 7.48 and 6.99 (4H, AB_{system}, J = 9.1 Hz, CH_{arom}), 7.08 (1H, s, CH), 3.79 (3H, s, OCH_3), 3.28 and 3.20 (2H, AB_{system}, J = 11.5 Hz,CH_2), 3.34 (3H, s, NCH_3), 1.56 ppm (3H, s, CCH_3).

2-[2-Acetyl-4-(4-tolyl)1,3,4-thiadiazol-ylidene]-2-(4-methyoxyphenylazo)acetonitrile (IV) was obtained by the method described above for IIa. Yield 90%. M.p. 204-205°C. Mass spectrum, *m/z*: 391 [M^+]. ^{1}H NMR spectrum (DMSO-D_6): 7.63 and 7.43 (4H, AB_{system}, J = 8.1 Hz, CH_{arom}), 7.62 and 7.03 (4H, AB_{system}, J = 9.1 Hz, CH_{arom}), 3.82 (3H, s, OCH_3), 2.58 (3H, s, $COCH_3$), 2.44 ppm (3H, s, CCH_3).

This work was carried out with a financial subvention from the Russian Fund for Fundamental Research (grant 98-03-33044-a).