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# TWO DIRECTIONS FOR THE HETEROCYCLIZATION OF 2-ARYLHYDRAZONOTHIOACETAMIDES ON REACTION WITH CHLOROACETONE

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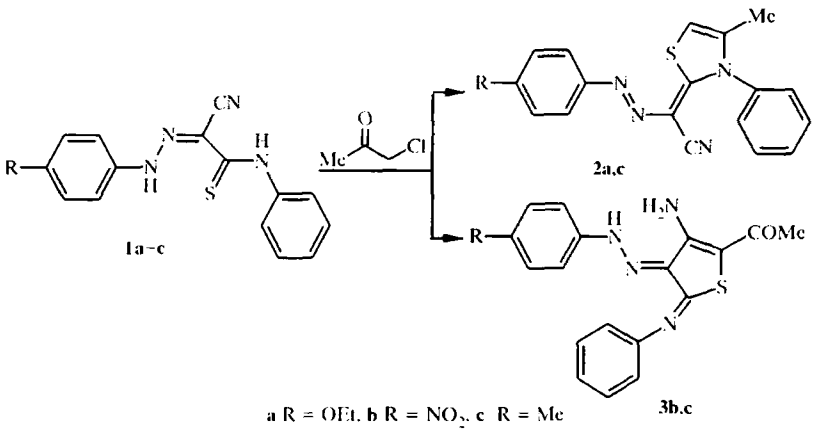
We have found that the reaction of 2-arylhydrazonothioacetamides **1** with chloroacetone proceeds in two directions and leads to the formation of thiazoles **2** or thiophenes **3**, depending on the properties of the substituent R. The presence of an electron-donating ethoxy group in the aromatic ring of the arylhydrazone residue enables the formation of thiazole **2a**, but hydrazone **1b**, containing an electron-withdrawing nitro group, is subject to intramolecular cyclization into thiophene **3b**. A limiting structure, for which both reaction directions are realized, is 2-cyano-N-phenyl-2-(p-tolylhydrazono)thioacetamide **1c**. In this case the formation of both thiazole **2b** and thiophene **3c** is observed (1:1).




The rule discovered for the heterocyclization of 2-hydrazonothioacetamides coupled with the known ability of the hydrazone group to be converted into an amino or hydroxy function [1-3] by the action of reducing or oxidizing agents respectively, may be a theoretical basis for synthesis of 2-methylenethiazole and 2,3-diiminothiophene derivatives.

## EXPERIMENTAL

**(4-Methyl-3-phenyl-3H-2-thiazolylidene)-(4-ethoxyphenylazo)acetonitrile (2a).** Triethylamine (0.086 ml, 0.062 mmol) and chloroacetone (0.052 ml, 0.062 mmol) (dropwise) were added to a solution of 2-cyano-2-[(4-ethoxyphenyl)hydrazono]-N-phenylthioacetamide **1** in DMF (7 ml). The mixture obtained was heated to 80°C

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and stirred for 1 h, then cooled with ice, the solid filtered off, and washed with water. Yield 95%; mp 158-160°C. Mass spectrum, *m/z* 362 [$M^+$]. $^1$H NMR spectrum (DMSO-$d_6$): 7.60-7.58 (3H, m, $CH_{arom}$); 7.48-7.47 (4H, m, $CH_{arom}$); 6.81-6.87 (3H, m, $CH_{arom}$ + $CH_{thiaz}$); 4.02 (2H, q, $J$ = 6.71 Hz, $\underline{CH_2}CH_3$); 1.92 (3H, s, $CH_3$); 1.36 (3H, t, $J$ = 6.71 Hz, $CH_2\underline{CH_3}$). Found, %: C 66.54; H 5.31; N 15.62; S 8.80. $C_{20}H_{18}N_4OS$. Calculated, %: C 66.30; H 4.97; N 15.47; S 8.84.

**2-Acetyl-3-amino-4-(4-nitrophenylhydrazono)-5-phenylimino-4,5-dihydrothiophene (3b)** was obtained by the procedure described for compound **2a**. Yield 97%; mp 255-257°C. Mass spectrum, *m/z* 381 [$M^+$]. $^1$H NMR spectrum (DMSO-$d_6$): 13.93 (1H, br. s, NH); 8.26 (2H, d, $J$ = 9.16 Hz, $CH_{arom}$); 7.97 (2H, d, $J$ = 9.16 Hz, $CH_{arom}$); 7.82 (2H, br. s, $NH_2$); 7.55-7.49 (2H, m, $CH_{arom}$); 7.38-7.41 (2H, m, $CH_{arom}$); 7.34-7.28 (2H, m, $CH_{arom}$); 2.12 (3H, s, $COCH_3$). Found, %: C 56.33; H 4.02; N 18.73; S 8.91. $C_{18}H_{15}N_5O_3S$. Calculated, %: C 56.69; H 3.94; N 18.37; S 8.40.

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