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LETTERS TO THE EDITOR

Specific Features of the Reaction of *m*-Phenoxybenzyl Chloride with Sodium Thiobarbiturate

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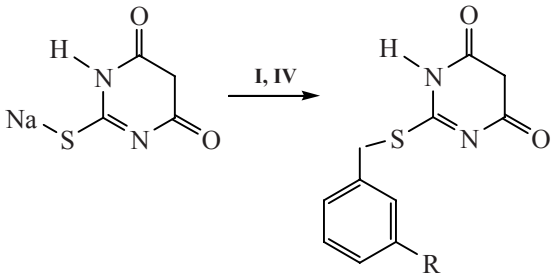
Recently [1, 2] by kinetic experiments was established that introduction of phenoxy substituent to *meta* position of benzyl chloride decreases its reactivity with sodium salt of 6-methyl-2-thiouracyl 5.8 times.

In the report presented it is shown that the reaction of *m*-phenoxybenzyl chloride **I** with sodium thiobarbiturate **II** proceeds with the lower (50%) conversion (as compared to benzyl chloride **IV**) of the reagent **II** to form 2-[(3-phenoxybenzyl)thio] pyrimidin-4,6(1*H*,5*H*)-dione **III**.



R = H (**V**), R = OC_6H_5 (**III**).

The yield of S-benzylation product is 70% for compound **V** and 54% for compound **III**.

Quantum chemical analysis (AM1 method [3, 4]) of ions generated from thiobarbituric acid under the action of sodium hydroxide shows a high stability of the carbanion (E = –1351.4 kcal mol^{-1}) and the thiolate anion (E = –1345.5 kcal mol^{-1}). Direction of the reaction with the participation of the thiolate anion is determined evidently by steric availability of the reaction center. It is also proved by the decrease in reactivity of halide after introduction of the phenoxy substituent to *meta* position of benzyl chloride.

2-[(3-Phenoxybenzyl)thio]pyrimidin-4,6-(1*H*,5*H*)-dione (III). To a suspension of 4.4 g of thiobarbituric acid in 60 ml of water–dioxane mixture (45 ml of dioxane and 15 ml of water) a solution of 1.3 g of sodium hydroxide in 30 ml of water was added dropwise with stirring. The mixture obtained was kept for 1 h until the complete homogenization. After that a solution of 7.3 g of compound **I** in 5 ml of dioxane was added dropwise. Resulting mixture was stirred for 1 h and left overnight. On the next day the solvent was evaporated in a vacuum, and the precipitate formed was filtered off and crystallized from absolute ethanol. Yield 5.3 g (54%), mp 192°C (with decomposition). ^{1}H NMR spectrum, δ, ppm: 4.72 s (2H, CH_2–C=O), 5.18 s (2H, CH_2–C_6H_4), 6.67–7.41 m (9H, H_{arom}), 11.8 s (1H, NH). Found, %: N 7.54. $C_{17}H_{14}N_2O_3S$. Calculated, %: N 8.58.

2-(Benzylthio)pyrimidin-4,6(1*H*,5*H*)-dione (V) was obtained analogously. Yield 70%, mp 230°C (with decomposition). ^{1}H NMR spectrum, δ, ppm: 4.78 s (2H, CH_2–C=O), 5.15 s (2H, CH_2–C_6H_5), 6.93–7.11 m (5H, H_{arom}), 11.8 s (1H, NH). Found, %: N 11.63. $C_{11}H_{10}N_2O_2S$. Calculated, %: N 11.96.

^{1}H NMR spectra were registered on a Varian Mercury 300 (300 MHz) spectrometer in DMSO-d_6 against internal HMDS. Melting points were measured according to [5].

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