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LETTERS TO THE EDITOR

About Reactivity of Thiolate and Carbonium Anions Generated from Thiobarbituric Acid Derivatives

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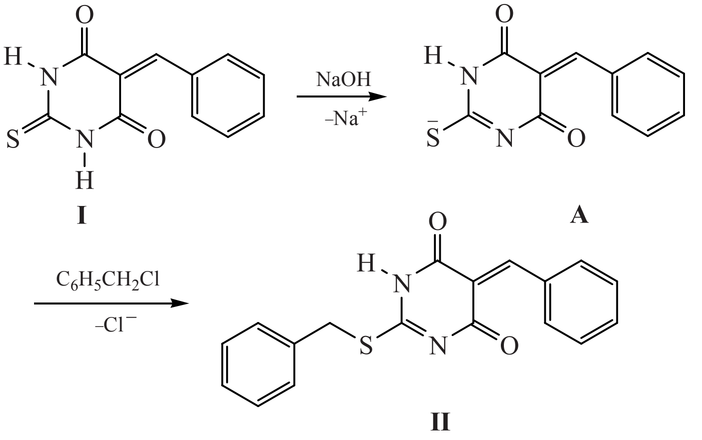
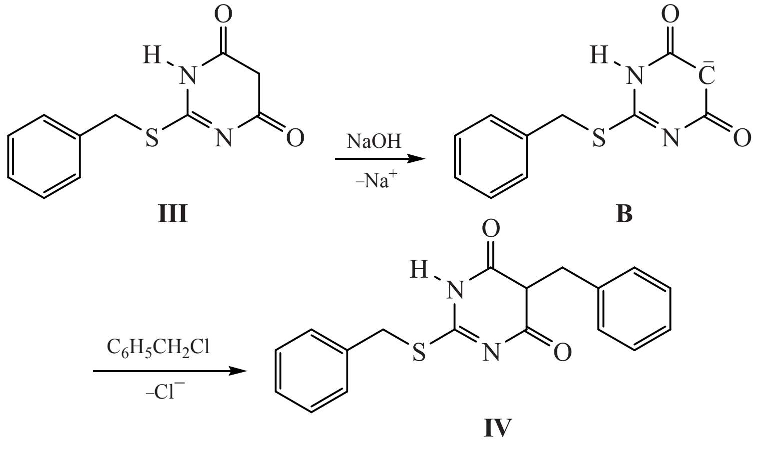
Thiolate, oxy- and carbonium ions generated from thiobarbituric acid were shown earlier [1] to be be essentially different by their nature. In this work we examined thiolate anion **A** generated from 5-benzylidene-2-thioxodihydropyrimi-dine-4,6(1*H*,5*H*)-dione **I** [scheme (1)] and carbonium anion **B** generated from 2-(benzylthio)pyrimidine-4,6(*1H,5H*)-dione **III** [scheme (2)]:



(1)

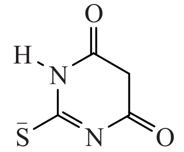


(2)

Yields of the S- and C-benzylation products (on the reacted **I**) are 40% (**II**) and 10% (**IV**), respectively.

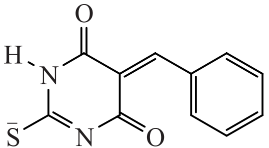
The quantum-chemical analysis by AM1 method [2, 3] of S- and C-anions generated from **I** and **III** respectively indicates a distinction in charges and energy on the reaction centre of anions in comparison with the corresponding anions from thiobarbituric acid.

Benzylidene group incorporation into the position 5 (anion **A**) leads to decrease in the electron density of the thiolate anion in comparison with anion **C** and to decrease in its reactivity. Benzylthiolate group incorporation increases electron density on the carbon atom in carbanion **B** in comparison with anion **D** and makes possible C-benzylation.



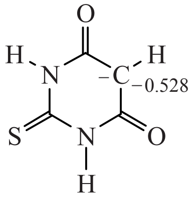
C

$E = -1345.5$ kcal mol^{-1}



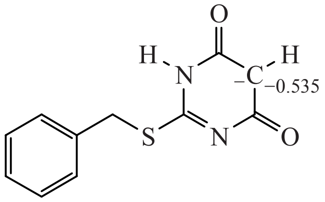
A

$E = -2693.8$ kcal mol^{-1}



D

$E = -1351.3$ kcal mol^{-1}



B

$E = -2816.7$ kcal mol^{-1}

(5*Z*)-5-Benzylidene-2-(benzylthio)pyrimidine-4,6-(1*H*,5*H*)-dione (II). To a suspension of 5 g (21.5 mmol) of **I** in 60 ml of water–dioxane mixture (50 ml of dioxane and 10 ml of water) was added dropwise a solution of 0.9 g (22.6 mmol) of sodium hydroxide in 40 ml of water. This mixture was stirred for 2 h to the reaction mixture solidification. To the suspension obtained was dropwise added a solution of benzyl chloride (2.7 ml, 23.6 mmol) in 5 ml of dioxane. This mixture was stirred for 3 h and left kept overnight. At the next day the reaction mixture was filtered. The filtrate was concentrated, and precipitate was filtered off and recrystallized from absolute ethanol. Yield 1.1 g (40% on the reacted **I**), mp 182–183°C (decomp.). ^{1}H NMR spectrum, δ, ppm: 4.26 m (2H, CH_2–C_6H_5), 5.96 s (1H, C=CH–), 6.92–7.45 m (10H, H_{Ar}), 11.7 s (1H, NH). Found, %: N 8.78. $C_{18}H_{14}N_2O_2S$. Calculated, %: N 8.69.

5-Benzyl-2-(benzylthio)pyrimidine-4,6(1*H*,5*H*)-dione (IV). To a suspension of 2 g (8.5 mmol) of **III** in 30 ml of water–dioxane mixture (20 ml of dioxane and 10 ml of water) was dropwise added a solution of 0.4 g (8.9 mmol) of sodium hydroxide in 10 ml of water. The solid residue was fileterd off and to the filtrate obtained was dropwise added a solution of benzyl chloride (1.1 ml, 9.4 mmol) in 5 ml of dioxane. This mixture was stirred for 2 h and then it was kept overnight. At the next day the reaction mixture was filtered. The filtrate was concentrated, and precipitate was filtered off and recrystallized from absolute ethanol. Yield 0.28 g (10%), mp 185°C (decomp.). ^{1}H NMR spectrum, δ, ppm: 3.22 s (1H, O=C–CH–), 3.51 s (1H, C–C*H*–C_6H_5), 4.33 s (2H, S–CH_2), 7.06–7.40 m (10H, H_{Ar}), 11.7 s (1H, NH). Found, %: N 8.81. $C_{18}H_{16}N_2O_2S$. Calculated, %: N 8.63.

The ^{1}H NMR spectra were registered on a Varian Mercury device (300 MHz) in DMSO-d_6 relative to internal HMDS. Melting points were determined in accordance with procedure [4].

REFERENCES

1. Rakhimov, A.I., Avdeev, S.A., and Le Thi Doan Chang, *Zh. Obshch. Khim.*, 2009, vol. 79, no. 2, p. 348.
2. Schmidt, M.W., Baldridge, K.K., and Boatz, J.A., *J. Comput. Chem.*, 1993, vol. 14, p. 1347.
3. Voets, R., *J. Comput. Chem.*, 1990, vol. 11, p. 269.
4. Stepin, B.D., *Tekhnika laboratornogo eksperimenta v khimii* (Technique of Laboratory Experiment in Chemistry), Moscow: Khimiya, 1999, p. 600.