ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 8, pp. 1760–1761. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © A.I. Rakhimov, S.A. Avdeev, 2009, published in Zhurnal Obshchei Khimii, 2009, Vol. 79, No. 8, pp. 1402–1403.

LETTERS
TO THE EDITOR

S-Benzylation of 5-Benzylidene-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione Under Conditions of Phase-Transfer Catalysis

A. I. Rakhimov[a] **and S. A. Avdeev**[b]

[a] *Volgograd State Technical University,*
pr. Lenina, 28, Volgograd, 400131 Russia
e-mail: organic@vstu.ru

[b] *Institute of Chemical Problems of Ecology, Russian Academy of Natural Sciences, Volgograd, 400066 Russia*
e-mail: rakhimov@sprint-v.com.ru

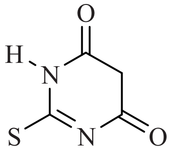
Received February 9, 2009

DOI: 10.1134/S1070363209080337

It has been shown earlier [1] that S-benzylation of thiobarbituric acid in the water-dioxane medium gives rise to 2-(benzylthio)pyrimidine-4,6(1*H,*5*H*)dione and is determined by stability of generated thiolate anion **A**.

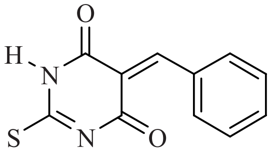
In this report we consider the influence of benzylidene group incorporation into position 5 of 2-thioxodihydropyrimidine-4,6(1*H,*5*H*)dione on the electronic structure of the generated thiolate anion **B** and the use of the latter for the synthesis of (5*Z*)-5-benzylidene-2-(benzylthio)pyrimidine-4,6(1*H,*5*H*)-dione.

The quantum-chemical analysis by AM1 method [2, 3] of anion **B** generated from the 5-benzylidene derivative indicates that its stability increases ($E_\mathbf{B}$ = –2693.8 kcal mol^{-1} as compared with $E_\mathbf{A}$ = –2693.8 kcal mol^{-1}) accompanied with decrease of electronic density on the sulfur atom (S_A = –0.450 in comparison with S_B = –0.458). This leads to anion **B** reactivity decrease in comparison with anion **A**:



A

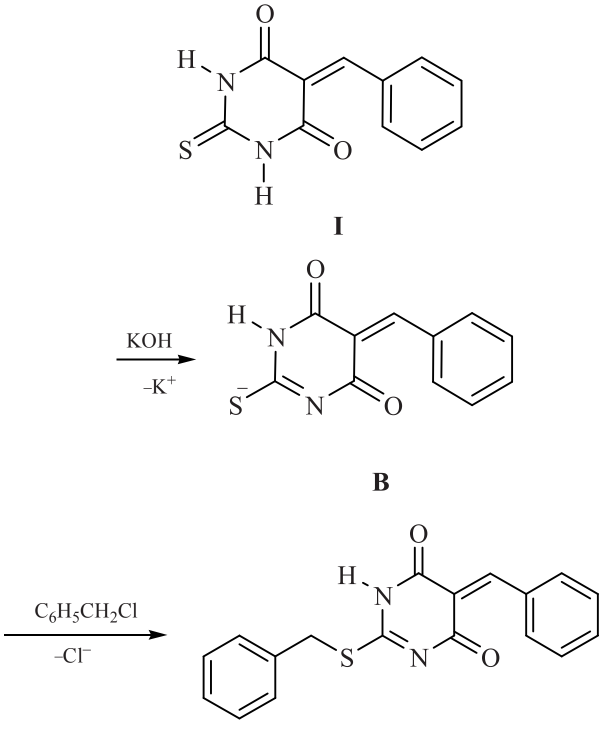
$E_\mathbf{A}$ –1345.5 kcal mol^{-1}



B

$E_\mathbf{B}$ –2693.8 kcal mol^{-1}

This fact underlies the low reactivity of 5-benzylidene substituted thiolate anion in the nucleophilic substitution reactions, in particular, at the chlorine substitution in benzyl chloride. In this connection we used phase-transfer catalysis in the reaction of benzyl chloride with 5-benzylidene-2-thioxodihydropyrimidine-4,6-(1*H,*5*H*)-dione **I**:



II

It was established that use of dibenzo-18-crown-6 as a phase-transfer catalyst permitted to increase the yield of (5*Z*)-5-benzylidene-2-(benzylthio)pyrimidine-4,6-(1*H*,5*H*)-dione **II** from 16 to 35%. Reaction was carried out with toluene as organic phase and potassium hydroxide water solution as water phase.

The published data analysis [4] shows that dibenzo-18-crown-6 gives rise to the most stable complex with potassium cation. This fact confirms the need to use just potassium hydroxide as a base.

(5*Z*)-5-Benzylidene-2-(benzylthio)pyrimidine-4,6-(1*H*,5*H*)-dione (II). To a suspension of 1.5 g (6.5 mmol) of **I** in 15 ml of water was dropwise added a solution of 0.4 g (6.5 mmol) of potassium hydroxide in 25 ml of water. This mixture was stirred for 45 min. To the suspension obtained were added 120 ml of toluene, 0.8 ml (7.2 mmol) of benzyl chloride and 0.1 g of dibenzo-18-crown-6. The mixture was stirred for 7 h. Then a solid phase was filtered off, washed with water and recrystalled from anhydrous ethanol. Yield 0.7 g (35%), mp 182–183^{0}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 9.58. $C_{18}H_{14}N_2O_2S$. Calculated, %: N 8.69.

The ^{1}H NMR spectrum was registered on a Varian Mercury device (300 MHz) in DMSO-d_6 relative to internal HMDS. Melting points were determined in accordance with procedure [5].

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. Khiraoka, M., *Kraun-soyedineniya. Svojstva i primeneniye* (Crown Compounds. Properties and Application), Moscow: Mir, 1986, p. 363.
5. Stepin, B.D., *Tekhnika laboratornogo eksperimenta v khimii* (Laboratory Experimental Technique in The Chemistry), Moscow: Khimiya, 1999, p. 600.