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LETTERS TO THE EDITOR

S-Benzylation of Arylidene Thiobarbituric Acids under Phase-Transfer Catalysis

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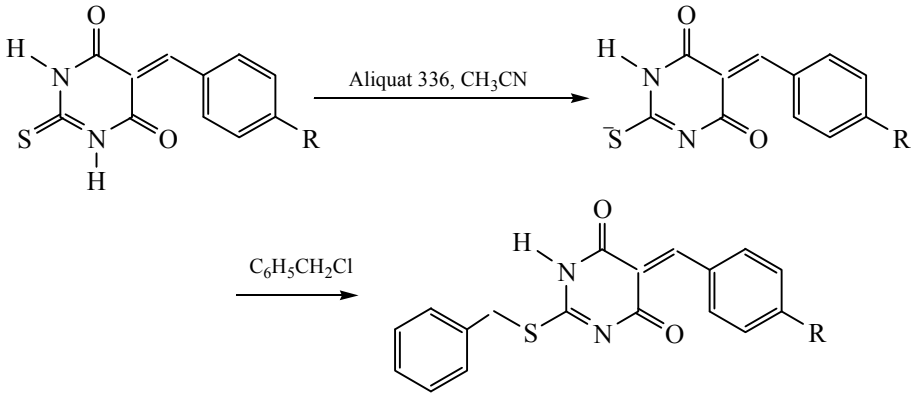
It has been established earlier that the use of dibenzo-18-crown-6 as a phase-transfer catalyst for S-benzylation of 5-benzylidene-2-thioxodihydropyrimidine-4,6-(1*H*,5*H*)-dione allows to obtain the end product with the yield of 35% using toluene and potassium hydroxide aqueous solution as organic and water phases respectively.

In this report we show that use of methyltrioctylammonium chloride (aliquat 336) as phase-transfer catalyst makes it possible to increase yields of the S-benzylation products of thiobarbituric acid arylidene derivatives to 60–75%. Acetonitrile was used as the organic phase.



R = H (**I**), CH_3 (**II**), OCH_3 (**III**), F (**IV**), NO_2 (**V**).

Reactivity of the S-anion generated from thiobarbituric acid arylidene derivatives by the action of polar acetonitrile was established by the quantum-chemical analysis using AM1 method [1] to depend on substituent on *para*-position of benzene ring. The sulfur atom electron density (*S*) and S-anion full energy (*E*) dependence on substituent R is as follows: (1) R = H: S = –0.450, E = –2693.8 kcal mol^{-1}; (2) R = CH_3: S = –0.449, E = –2977.2 kcal mol^{-1}; (3) R = OCH_3: S = –0.451, E = –3070.0 kcal mol^{-1}; (4) R = F: S = –0.443, E = –2710.5 kcal mol^{-1}; (5) R = NO_2: S = –0.421, E = –2878.4 kcal mol^{-1}.

Hence electron-donating substituent (CH_3, OCH_3) incorporated in the *para*-position of benzene ring causes the full energy of anion **A** to increase, the sulfur atom charge to change slightly and therefore reactivity to decrease negligibly. The presence in the *para*-position of the benzene ring of an electron-withdrawing substituent leads to a decrease in the

sulfur atom charge, in the increase of the anion full energy and hence in high decrease in S-anion reactivity.

(5*Z*)-5-Benzylidene-2-(benzylthio)pyrimidine-4,6-(1*H*, 5*H*)-dione. To a suspension of 0.4 g (1.7 mmol) of **I** in 15 ml of acetonitrile was added 0.1 ml of aliquat 336. This mixture was stirred at 50°C for 10 min. Then 0.2 ml (1.9 mmol) of benzyl chloride was added and the mixture was stirred for 2 h at 50°C. The solid phase was filtered off, washed with water and alcohol, and recrystalled from anhydrous ethanol. Yield 0.4 g (75%), mp 182–183°C (decomp.). ^{1}H NMR spectrum, δ, ppm: 4.26 m (2H, CH_2–C_6H_5), 5.92 s (1H, C=CH–), 6.92–7.45 m (10H, H_{Ar}), 11.6 s (1H, NH). Found, %: N 9.45. $C_{18}H_{14}N_2O_2S$. Calculated, %: N 8.69.

(5*Z*)-2-(Benzylthio)-5-(4-methylbenzylidene)pyrimidine-4,6(1*H*,5*H*)-dione was prepared similarly from 0.4 g (1.6 mmol) of **II**, 15 ml of acetonitrile, 0.1 ml of aliquat 336, and 0.2 ml (1.8 mmol) of benzyl chloride. Yield 0.4 g (74%), mp 190–192°C (decomp.). ^{1}H NMR spectrum, δ, ppm: 2.8 s (3H, CH_3), 4.28 m (2H, CH_2–C_6H_5), 5.87 s (1H, C=CH–), 6.80–7.45 m (9H, H_{Ar}), 11.5 s (1H, NH). Found, %: N 9.21. $C_{19}H_{16}N_2O_2S$. Calculated, %: N 8.33.

(5*Z*)-2-(Benzylthio)-5-(4-methoxybenzylidene)pyrimidine-4,6(1*H*,5*H*)-dione was prepared similarly from 0.4 g (1.5 mmol) of **III**, 20 ml of acetonitrile, 0.1 ml of aliquat 336 and 0.2 ml (1.7 mmol) of benzyl chloride. Yield 0.35 g (70%), mp 172–174°C (decomp.). ^{1}H NMR spectrum, δ, ppm: 3.8 s (3H, CH_3), 4.30 m (2H, CH_2–C_6H_5), 5.84 s (1H, C=CH–), 6.64–6.98 m (9H, H_{Ar}), 11.4 s (1H, NH). Found, %: N 8.87. $C_{19}H_{16}N_2O_3S$. Calculated, %: N 7.95.

(5*Z*)-2-(Benzylthio)-5-(4-fluorobenzylidene)pyrimidine-4,6(1*H*,5*H*)-dione was prepared similarly from 0.5 g (2.0 mmol) of **IV**, 12 ml of acetonotrile, 0.1 ml of aliquat 336 and 0.25 ml (2.2 mmol) of benzyl chloride. Yield 0.45 g (65%), mp 189–190°C (decomp.). ^{1}H NMR spectrum, δ, ppm: 4.25 m (2H, CH_2–C_6H_5), 5.90 s (1H, C=CH–), 6.92–7.44 m (9H, H_{Ar}), 11.6 s (1H, NH). Found, %: N 9.11. $C_{18}H_{13}FN_2O_2S$. Calculated, %: N 8.23.

(5*Z*)-2-(Benzylthio)-5-(4-nitrobenzylidene)pyrimidine-4,6(1*H*,5*H*)-dione was prepared similarly from 0.5 g (1.8 mmol) of **V**, 12 ml of acetonitrile, 0.1 ml of aliquat 336 and 0.2 ml (2.0 mmol) of benzyl chloride. Yield 0.4 g (60%), mp 200–202°C (decomp.). ^{1}H NMR spectrum, δ, ppm: 4.22 m (2H, CH_2–C_6H_5), 6.01 s (1H, C=CH–), 6.84–7.44 m (7H, H_{Ar}), 8.02–8.12 m (2H, –CH_{Ar}–NO_2–CH_{Ar}–), 11.7 s (1H, NH). Found, %: N 12.05. $C_{18}H_{13}N_3O_4S$. Calculated, %: N 11.44.

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