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LETTERS TO THE EDITOR

Recyclization of 5-[Methyl(phenyl)amino]-2-(4-nitrobenzyl)-3-*p*-tolyl-1,2,4-thiadiazolium Perchlorate into 9-Methyl-3a-(4-nitrophenyl)-2-*p*-tolyl-3a,9-dihydrobenzo[*b*]-imidazo[4,5-*e*][1,4]thiazine

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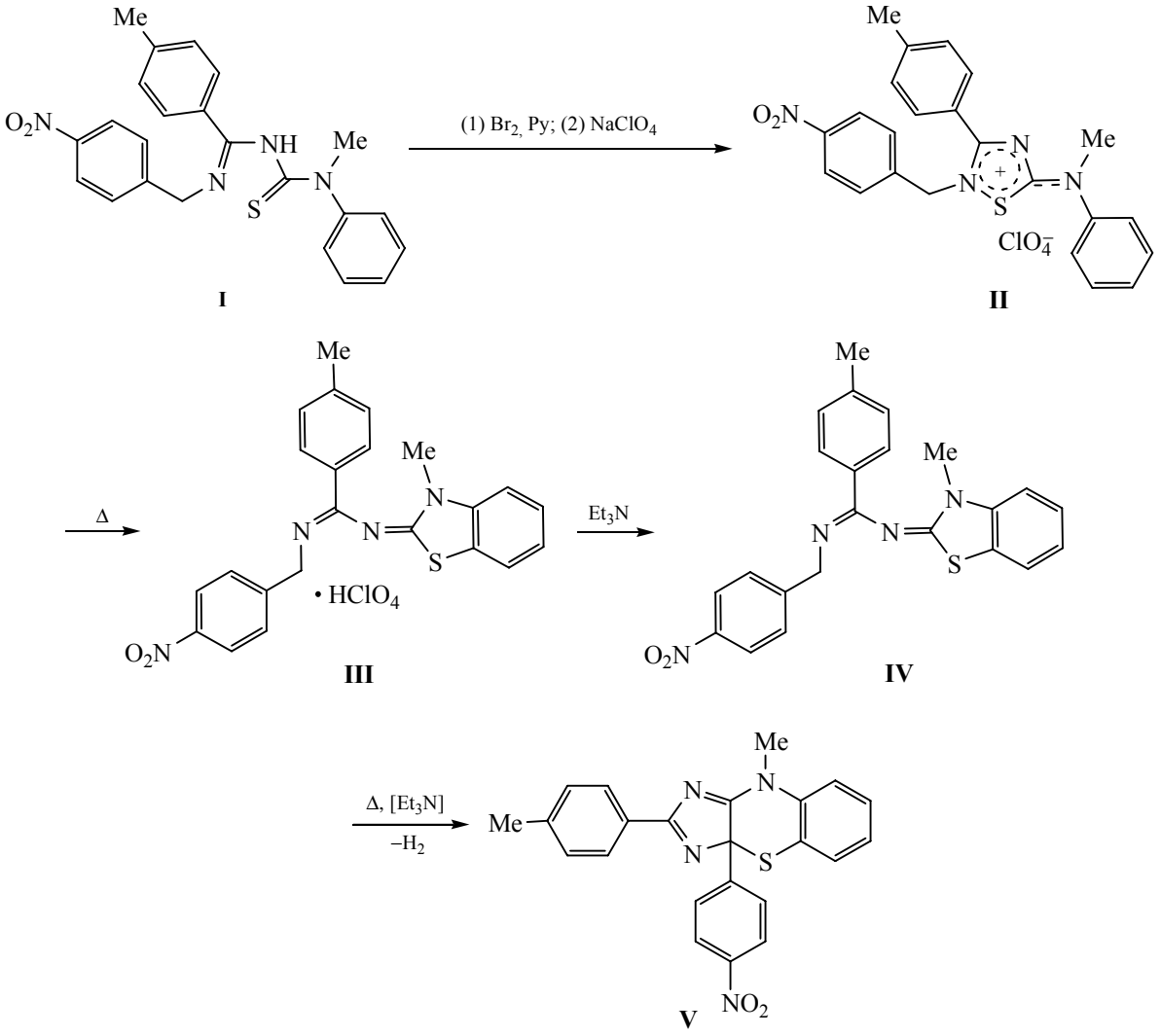
Previously was shown that 5-[methyl(phenyl)amino]-3-*p*-tolyl-2-phenyl-1,2,4-thiadiazolium perchlorates isomerize under heating into the benzothiazole derivatives [1]. Using the well-known approaches [2, 3], we synthesized an analog of 1,2,4-tiadiazolium salt containing *p*-nitrobenzyl substituent in position 2 (transformation **I** → **II**) and obtained the corresponding benzothiazole derivatives: salt **III** and base **IV** (see the scheme bellow).

In DMSO-d_6 solution, the compound **IV** exists as a mixture of stereoisomers in 1:1.3 ratio, as seen from the signals doubling in the ^{1}H NMR spectrum. This is due obviously to the hindered *syn-anti*-isomerization at the nitrogen and (or) the hindered rotation around the C–N bond in 1,3-diazadiene fragment. This isomers ratio does not change at raising temperature to 90ºC or at replacing the solvent by $CDCl_3$. However, adding trifluoroacetic acid simplifies spectrum: in the region of 2.9 ppm it becomes identical to the spectrum of the salt **III**.

We found that at heating and due to the catalytic effect of triethylamine the compound **IV** undergo an unexpected rearrangement into benzo[*b*]imidazo[4,5-*e*]-1,4-thiazine derivative **V**, structure of which was determined by the X-ray diffraction study. In such transformation occurring with the hydrogen molecule eliminating the *p*-nitrophenyl substituent plays important role. It activates the methylene group and promotes the intermediate cyclization.

5-[Methyl(phenyl)amino]-2-(4-nitrobenzyl)-3-*p*-tolyl-1,2,4-thiadiazolium perchlorate (II). To a solution of 68 mmol imidoylthiocarbamide **I** [4] and 68 mmol of pyridine in 140 ml of dichloromethane was added a solution of 68 mmol of bromine in 40 ml of dichloromethane for 1 h. The mixture was stirred for 4 h, then was added 100 ml of water. The organic layer was separated and concentrated in a vacuum. The oily residue was dissolved in 80 ml of ethanol and added to 40 ml of 3 M. aqueous solution of sodium perchlorate, the resulting precipitate was filtered off. Yield 88%, mp 195–198ºC (EtOH). ^{1}H NMR spectrum ($CDCl_3$, 200 MHz), δ, ppm: 2.44 s (CH_3), 3.78 s (CH_3), 5.49 s (CH_2), 7.36 d (2H aromatic, J_{HH} 7.6 Hz), 7.49–7.54 m (7H aromatic), 7.77 d (2H aromatic, J_{HH} 8.0 Hz), 8.18 d (2H aromatic, J_{HH} 8.8 Hz). Found, %: N 11.10, S 6.32. $C_{23}H_{21}ClN_4O_6S$. Calculated, %: N 10.84, S 6.20.

4-Methyl-N^1-(3-methylbenzyl[*d*]thiazol-2(3*H*)-ylidene)-N^2-(4-nitrobenzyl)benzamidine hydroperchlorate (III). 0.135 mmol of compound **II** was slowly heated to 190ºC and maintained at this temperature for 40 min. The melt was cooled to 20ºC and recrystalled from 5 ml of ethanol. The precipitate was filtered off. Yield 86%, mp 111–114ºC (EtOH). ^{1}H NMR spectrum (DMSO-d_6, 400 MHz), δ, ppm: 2.41 s (CH_3), 3.86 s (CH_3), 5.01 s (CH_2), 7.40-7.46 m (3H aromatic), 7.61 t (1H aromatic, J_{HH} 7.8 Hz), 7.66 d (2H aromatic, J_{HH} 8.0 Hz), 7.76 d (2H aromatic, J_{HH} 8.4 Hz), 7.82 d (1H aromatic, J_{HH} 8.4 Hz), 7.88 d (1H aromatic, J_{HH} 7.6 Hz), 8.29 d (2H aromatic, J_{HH}



8.4 Hz), 11.02 s (NH). ^{13}C NMR spectrum ($CDCl_3$, 75 MHz), δ_C, ppm: 21.84, 32.94, 46.39, 113.41, 122.69, 123.80, 123.84, 124.07, 126.08, 128.34, 129.26, 130.06, 130.58, 137.82, 144.15, 145.54, 147.33, 168.58, 169.39. Found, %: C 53.44, H 3.80, Cl 6.94, S 6.32. $C_{23}H_{20}N_4O_2S{\cdot}HClO_4$. Calculated, %: C 53.44, H 4.09, Cl 6.85, S 6.20.

Attention! The use of large charges of compound ***II*** *in this reaction is hazardous.*

4-Methyl-*N*^{1}-(3-methylbenzyl[*d*]thiazol-2(3*H*)-ylidene)-*N*^{2}-(4-nitrobenzyl)enzamidine (IV). To a suspension of 1.5 mmol of compound **III** in 5 ml of THF was added 1.5 mmol of triethylamine, the mixture was stirred for 4 h. The formed precipitate of triethylamine salts was filtered off. The filtrate was concentrated. To the oily residue was added 5 ml of ethanol crystallize, the precipitate **IV** was filtered off. Yield 88%, mp 125–127ºC (MeOH:$CHCl_3$ = 3:1). ^{1}H NMR spectrum (DMSO-d_6, 400 MHz), δ, ppm: 2.32 s, 2.35 s (1.3/1.0, CH_3), 3.61 s, 3.73 s (1.4/1.0, CH_3), 4.69 s, 4.87 s (1.3/1.0, CH_2), 7.06-8.22 м (12H aromatic). Found, %: C 65.93, H 4.88, N 13.30, S 7.61. $C_{23}H_{20}N_4O_2S$. Calculated, %: C 66.33, H 4.84, N 13.45, S 7.70.

9-Methyl-3a-(4-nitrophenyl)-2-*p*-tolyl-3a,9-dihydrobenzo[*b*]imidazo[4,5-*e*]-1,4-thiazine (V). A solution of 3 mmol of compound **IV** and 3 mmol of triethylamine in 10 ml of dioxane was refluxed for 8 h. The volatiles were removed in a vacuum, the residue was washed with ethanol and chromatographed on a silica gel column, eluent–chloroform. Yield 53%, mp 249–251ºC ($MeNO_2$). ^{1}H NMR spectrum ($CDCl_3$, 400 MHz), δ_H, ppm: 2.42 s (CH_3), 3.90 s (CH_3), 7.00 t

(1H aromatic, J_{HH} 8.0 Hz, 6.0 Hz), 7.13 d (1H aromatic, J_{HH} 8.0 Hz), 7.19-7.27 m (3H aromatic), 7.34 d (1H aromatic, J_{HH} 7.6 Hz), 7.64 d (2H aromatic, J_{HH} 6.8 Hz), 8.03 d (2H aromatic, J_{HH} 8.8 Hz), 8.17 d (2H aromatic, J_{HH} 6.4 Hz). ^{13}C NMR spectrum ($CDCl_3$, 75 MHz), δ_C, ppm: 21.66, 36.55, 117.87, 123.63, 125.14, 127.51, 128.00, 128.97, 129.05, 129.15, 129.23, 140.29, 142.36, 143.18, 147.67, 176.57, 179.71. Found, %: C 66.82, H 4.34, N 13.68, S 7.62. $C_{23}H_{18}N_4O_2S$. Calculated, %: C 66.65, H 4.38, N 13.52, S 7.74.

REFERENCES

1. Renskii, M.A. and Zyabrev, V.S., *Zh. Obshch. Khim.,* 2003, vol. 73, no. 8, p. 1400.
2. Goerdeler, J. and Löbach, W., *Chem. Ber.,* 1979, vol. 112, no. 2, p. 517.
3. Zyabrev, V.S., Harchenko, A.V., Pirozhenko, V.V., and Drach, B.S., *Zh. Org. Khim.,* 1988, vol. 24, no. 8, p. 1754.
4. Zyabrev, V.S., Chernega, A.N., and Drach, B.S., *Zh. Org. Khim.,* 1997, vol. 33, no. 11, p. 1728.