LETTERS TO THE EDITOR

1H-THIAZOLO[3,2-b]-sym-TRIAZOLIUM SALTS

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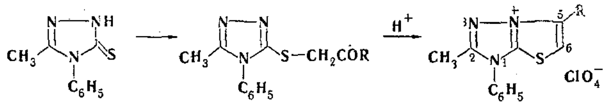
Derivatives of the 1H-thiazolo[3,2-b]-sym-triazolium ion – a new heteroaromatic cation – were obtained in good yields by cyclization of β-keto sulfides I in acidic sulfides I in acidic media (more readily in the case of Ib), as was done in the synthesis of a pyrido[2,1-b]thiazolium salt [1, 2].



Ia, b IIa, b

I, II a R=CH$_3$; b R=C$_6$H$_5$

Sulfides Ia, b were obtained by alkylation of 3-methyl-4-phenyl-4H-sym-triazole-5-thione with α-halo ketones. Methylation of the sym-triazolethiones gives S-methyl derivatives [3]. The UV spectrum of Ia coincides with the spectrum of the corresponding S-methyl derivative. On the basis of this, structure I is assumed for the products of reaction of sym-triazolethione with α-halo ketones.

EXPERIMENTAL

5-Acetonylthio-3-methyl-4-phenyl-4H-sym-triazole (Ia). A 1.91-g (0.01 mole) sample of 3-methyl-4-phenyl-4H-sym-triazole-5-thione was dissolved in sodium methoxide solution [from 0.23 g (0.01-g-atom) of sodium and 100 ml of methanol], and a solution of 0.83 ml (0.01 mole) of bromoacetone in methanol was added dropwise with stirring. The mixture was then allowed to stand for 12 h, after which the alcohol was removed in vacuo, and the residue was treated with water. The resulting oil was extracted from the neutral medium with chloroform (three 25-ml portions). The chloroform was removed in vacuo, and the solid residue was crystallized from CCl_4 to give 2.24 g (90%) of a product with mp 101° (from CCl_4). PMR spectrum (in $CDCl_3$, here and subsequently on the δ scale, ppm, with respect to tetramethylsilane): singlets at 2.32 and 2.35 ppm (each with an intensity of 3 proton units), which correspond to 3-CH_3 and $COCH_3$ groups; 4.17 (S=CH_2); m* 7.45 (N=C_6H_5). Found: N 16.8; S 13.1%. $C_{12}H_{13}N_3OS$. Calculated: N 16.9; S 12.9%.

5-Phenacylthio-3-methyl-4-phenyl-4H-sym-triazole (Ib). This compound was similarly obtained from phenacyl bromide and 3-methyl-4-phenyl-4H-sym-triazole-5-thione. Extraction with chloroform was not necessary here, inasmuch as treatment with water precipitated solid Ib. Workup gave a product with mp 105° (from CCl_4) in 96% yield. PMR spectrum (in $CDCl_3$): 2.36 (3-CH_3), m 7.85 (COC_6H_5), 4.92 (S−CH_2), and 7.42 (N−C_6H_5). Found: N 13.5; S 10.4%. $C_{17}H_{15}N_3OS$. Calculated: N 13.5; S 10.3%.

2,5-Dimethyl-1-phenyl-1H-thiazolo[3,2-b]-sym-triazolium Perchlorate (IIa). A 2.47-g (0.01 mole) sample of Ia was refluxed in 30 ml of 48% HBr for 30 h, after which the acid was removed in vacuo, and 25 ml of water was added to the residue. The solution was purified with activated charcoal, and a saturated aqueous $NaClO_4$ solution was added. The precipitate that formed after brief standing was separated and washed with water to give 2.2 g (66%) of a product with mp 151° (dec., from CH_3OH). PMR spectrum (in CF_3COOH): 2.78 (2-CH_3 and 5-CH_3), 7.26 (6-H), and m 7.68 (N−C_6H_5). Found: Cl 10.8; N 12.6; S 9.9%. $C_{12}H_{12}ClN_3O_4S$. Calculated: Cl 10.7; N 12.7; S 9.7%.

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*Here and subsequently, m is multiplet.

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2-Methyl-1,5-diphenyl-1H-thiazolo[3,2-b]-sym-triazolium Perchlorate (IIb). A 3.1-g (0.01 mole) sample of sulfide Ib was dissolved in 40 ml of concentrated H_2SO_4, and the solution was stirred at room temperature for 5 days. The dark solution was poured over ice, and the mixture was treated with excess 42% $HClO_4$. The precipitate that formed on brief standing was removed by filtration and washed with water to give 3.4 g (87%) of a product with mp 291° (dec., from CH_3COOH). PMR spectrum (in CF_3COOH): 2.74 (2-CH_3) and m 7.41-8.01 (two phenyl groups). Found: Cl 9.04; N 10.6; S 8.13%. $C_{17}H_{14}ClN_3O_4S$. Calculated: Cl 9.05; N 10.7; S 8.18%.

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3. J.-L.Barascut, J. Daunis, and R. Jacquier, Bull. Soc. Chim. France, 323 (1973).