

UNSYMMETRICALLY SUBSTITUTED BENZOTHAZOLYL- HYDRAZINES

M. Z. Peretyazhko and P. S. Pel'kis

UDC 547.789.6

New unsymmetrically substituted hydrazines containing benzothiazole residues with substituents in the 6-position were obtained by the oxidative cyclization of substituted 1,4-diphenylthiosemicarbazides with potassium ferricyanide in alkaline aqueous alcoholic media. The reaction of these new hydrazines with trichloromethyl mercaptan gave N-(6-R'-2-benzothiazolyl)-N-[p-(trichloromethylthioamidosulfonyl)phenyl]hydrazines.

Substituted hydrazines have different physiologically active properties, and some of them also have antitumorigenic activity. Compounds which contain trichloromethylthio groups have fungicidal and anti-tumorigenic action [1].

It was of interest to obtain unsymmetrically substituted benzothiazolylhydrazines containing trichloromethylthio groups and to study their properties. We obtained N-aryl-N'-(2-benzothiazolyl)hydrazines (A) containing various substituents in the 6-position of the benzothiazole ring by the oxidative cyclization of substituted 1,4-diphenylthiosemicarbazides with potassium ferricyanide in alcoholic alkaline media [2,3]. Compounds B were obtained by subsequent treatment of A ($R = SO_2NH_2$) with trichloromethyl mercaptan in aqueous alkaline media [4].

Compounds A and B are brown, crystalline substances that are soluble in dimethylformamide.

TABLE 1

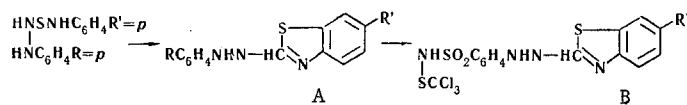
$$RC_6H_4NHNHC \begin{array}{c} S \\ \diagup \quad \diagdown \\ \text{Benzothiazole ring} \end{array} R$$

R	R'	Mp	Empirical formula	S, %		Yield, %
				found	calc.	
H ₂ NSO ₂	p-Cl	196	C ₁₃ H ₁₁ ClN ₄ O ₂ S ₂	17,3	18,0	60
H ₂ NSO ₂	OC ₂ H ₅	140	C ₁₅ H ₁₆ N ₄ O ₃ S ₂	17,3	17,6	54
H ₂ NSO ₂	COOC ₂ H ₅	146	C ₁₆ H ₁₆ N ₄ O ₄ S ₂	16,1	16,3	60
H ₂ NSO ₂	COOH	186	C ₁₄ H ₁₂ N ₄ O ₄ S ₂	17,0	17,6	64
		(dec.)				
SO ₃ Na	H ₂ NSO ₂	172	C ₁₃ H ₁₁ NaN ₄ O ₅ S ₃ *			53
CH ₃	COOH	147	C ₁₅ H ₁₃ N ₃ O ₂ S	11,2	10,7	51
CH ₃	OC ₂ H ₅	142	C ₁₆ H ₁₇ N ₃ OS	10,6	10,7	41
CH ₃	COOC ₂ H ₅	104	C ₁₇ H ₁₇ N ₃ O ₂ S	9,7	9,8	61
CH ₃	H ₂ NSO ₂	127	C ₁₄ H ₁₄ N ₄ O ₂ S ₂	19,7	19,2	42
C ₆ H ₅ SO ₂	COOH	>305	C ₁₄ H ₁₁ N ₃ O ₄ S ₂	18,2	18,3	50
O ₂ SNHSCCl ₃	COOC ₂ H ₅	180	C ₁₇ H ₁₅ Cl ₃ N ₄ O ₄ S ₃	10,0	10,3	52
O ₂ SNHSCCl ₃	Cl	138	C ₁₄ H ₁₀ Cl ₄ N ₄ O ₂ S ₃	18,9	19,0	40
O ₂ SNHSCCl ₃	OC ₂ H ₅	132	C ₁₆ H ₁₅ Cl ₃ N ₄ O ₃ S ₃	18,2	18,7	52
O ₂ SNHSCCl ₃	COOH	204	C ₁₅ H ₁₁ Cl ₃ N ₄ O ₄ S ₃	18,7	18,6	47

* Found %: N 13.3. Calculated %: N 13.3.

Kiev Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 6, pp. 765-766, June, 1971. Original article submitted January 5, 1970.

© 1973 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00.



EXPERIMENTAL

N-(p-Sulfamoylphenyl)-N'-(6-ethoxy-2-benzothiazolyl)hydrazine. A mixture of 1.1 g (3 mmole) of 1-(p-sulfamoylphenyl)-4-(p-ethoxyphenyl)thiosemicarbazide and 0.24 g (6 mmole) of NaOH in 10 ml of 50% alcohol was added with stirring to an aqueous solution of 2.7 g (9 mmole) of potassium ferricyanide, and the mixture was stirred at room temperature for 8 h. The resulting precipitate was filtered, washed with water, and reprecipitated by alcohol from dimethylformamide to give 0.59 g of product.

N-(6-Ethoxy-2-benzothiazolyl)-N'-[p-(trichloromethylthioamidossulfonyl)phenyl]hydrazine. A total of 1 g (2.7 mmole) of N-(p-sulfamoylphenyl)-N'-(6-ethoxy-2-benzothiazolyl)hydrazine was dissolved in 4 ml of 1 N KOH (4 mmole), and 0.5 g (3 mmole) of trichloromethyl mercaptan was added gradually with vigorous stirring. The resulting brown precipitate was filtered, washed with water, and purified by reprecipitation from dimethylformamide by the addition of ethanol.

The remaining compounds, presented in Table 1, were similarly obtained.

LITERATURE CITED

1. M. Z. Peretyazhko and P. S. Pel'kis, Zh. Organ. Khim., 3, 2183 (1967); A. Seuning, Chem. Rev., 65, 385 (1965).
2. P. Jacobson, Ber., 19, 1067 (1886); 26, 2363 (1893).
3. P. C. Gaha and S. Roy-Choudhury, J. Indian Chem. Soc., 5, 163 (1928).
4. A. R. Kittelsson, Science, 115, 84 (1952); Chem. Abstr., 46, 10,134d (1952).