

SYNTHESIS AND INVESTIGATION OF THIOCARBOHYDRAZIDE DERIVATIVES

VI.* SYNTHESIS AND CYCLIZATION OF SUBSTITUTED 1-(3-METHYL-2-BENZOTHAZOLINIDENYL)-5-(PHENYLAMINOTHIOCARBO)- THIOCARBOHYDRAZIDES

R. G. Dubenko, I. M. Bazavova,
and P. S. Pel'kis

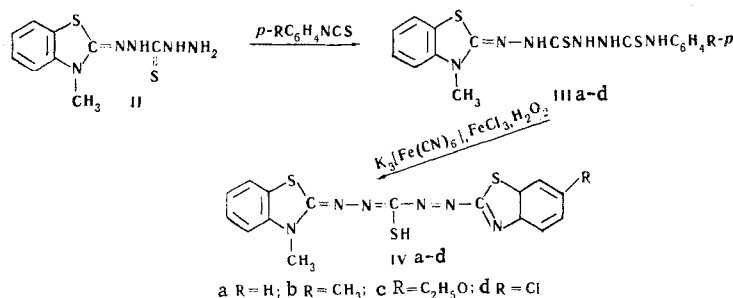
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Substituted 1-(3-methyl-2-benzothiazolinidenyl)-5-(phenylaminothiocarbo)thiocarbohydrazides are cyclized under the influence of potassium ferricyanide, hydrogen peroxide, or ferric chloride to substituted 1-(3-methyl-2-benzothiazolinidenyl)-5-(2-benzothiazolyl)-1,2,4,5-tetraza-3-mercaptopentamethinylcyanine bases; unsymmetrical 1-(3-methyl-2-benzothiazolinidenyl)-5-(3-aryl-4-phenyl-2-thiazolyl)-1,2,4,5-tetraza-3-mercaptopentamethinylcyanine bromides are formed by the action of ω -bromoacetophenone.

We have previously established [2] that the same reaction products, viz., 2-(p-tolylazo)-5-arylamino-1,3,4-thiadiazoles, are formed by the oxidative cyclization of 1-(p-tolyl)-5-(arylaminothiocarbo)thiocarbohydrazides under the influence of an alkaline potassium ferricyanide solution, hydrogen peroxide, or ferric chloride. Substituted 1,5-bis(2-benzothiazolyl)-1,2,4,5-tetraza-3-mercaptopentamethinylcyanine bases are obtained by the cyclization of substituted 1,5-bis(phenylaminothiocarbo)thiocarbohydrazides under the same conditions.

The condensation of thiocarbohydrazide with 2-methylthio-3-methylbenzothiazolium methylmethosulfate (I) in water yielded 1-(3-methyl-2-benzothiazolinidenyl)thiocarbohydrazide (II) [3]. By reaction of the latter with aryl isothiocyanates in alcohol, we obtained substituted 1-(3-methyl-2-benzothiazolinidenyl)-5-(phenylaminothiocarbo)thiocarbohydrazides (III).

The oxidative cyclization of III under the influence of alkaline potassium ferricyanide solution, hydrogen peroxide, or ferric chloride yields substituted 1-(3-methyl-2-benzothiazolinidenyl)-5-(2-benzothiazolyl)-1,2,4,5-tetraza-3-mercaptopentamethinylcyanine bases (IV), the absorption maxima of which in chloroform lie at 542-558 nm.

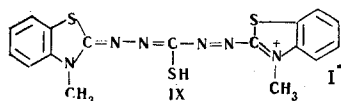


* See [1] for communication V.

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TABLE 1. Characteristics of the Compounds Obtained



Compound	μ , a	λ_{max} (lg e) ^b	Empirical formula	N, %		Yield, %
				found	calc.	
IIIa	184—185	320 (4,24)	$C_{16}H_{16}N_6S_3$	21,51	21,63	82
IIIb	196—197	317 (4,22)	$C_{17}H_{18}N_6S_3$ ^c			60
IIIc	197—198		$C_{18}H_{20}N_6OS_3$ ^d			66
IIId	200—201		$C_{16}H_{15}ClN_6S_3$ ^e			84
IVa	217—218	542 (4,54)	$C_{16}H_{12}N_6S_3$	21,98	21,86	86
IVb	221—222	544 (4,43)	$C_{17}H_{14}N_6S_3$	20,69	21,09	95
IVc	235—236	558 (4,56)	$C_{18}H_{16}N_6OS_3$	20,12	19,61	92
IVd	236—237	548 (4,51)	$C_{16}H_{11}ClN_6S_3$ ^f			95
Va	224—225	542 (4,51)	$C_{17}H_{14}N_6S_3$	21,10	21,09	77
Vb	240—241	544 (4,36)	$C_{18}H_{16}N_6S_3$	21,15	20,37	85
VIa	113—114	544 (4,15)	$C_{24}H_{19}BrN_6S_3$	14,79	14,81	54
VIb	119—120	544 (4,00)	$C_{25}H_{21}BrN_6S_3$	13,89	14,45	48
VIc	106—107	545 —	$C_{26}H_{23}BrN_6OS_3$	13,32	13,72	46
VIId	118—119	545 —	$C_{24}H_{18}BrClN_6S_3$	13,43	13,94	39
VIIa	83—84	565 —	$C_{31}H_{20}BrN_6S_3$ ^g	12,97	12,82	47
VIIb	111—112	580 (4,06)	$C_{33}H_{27}BrN_6S_3$	11,89	12,25	52
VIIc	79—80	580 —	$C_{35}H_{31}BrN_6O_2S_3$ ^h			38
VIIId	107—108	570 (3,98)	$C_{31}H_{20}BrCl_2N_6S_3$ ⁱ			41
IX	211—212	332 (4,44) 620 (4,38)	$C_{17}H_{15}N_6S_3J$	16,09	15,95	25

^aThe crystallization solvents were alcohol for IIIa-Vb, chloroform-benzene for VIa-VIII d, and chloroform for IX.

^b The solvents were benzene for IIIa-IIIId and chloroform for IVa-IX.

^cFound %: S 23.99. Calculated %: S 23.89.

^dFound %: S 22.64. Calculated %: S 22.24.

^eFound %: Cl 7.91. Calculated %: Cl 8.38.

f Found %: Cl 8.30. Calculated %: Cl 8.46.

Found %: Br 12.08. Calculated %: Br 12.18.

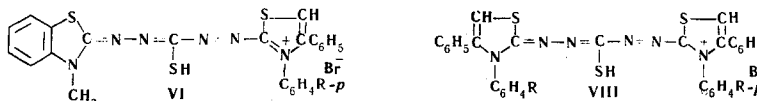
^hFound %: Br 10.51. Calculated %: Br 10.74.

ⁱ Found %: Br + 2Cl 19.95. Calculated %: Br + 2Cl 20.8.

S-Methyl derivatives V were isolated by methylation of IV with methyl iodide in alcoholic alkali. The reaction at the thiomethyl group [4] confirms the formation of V.

Compounds III react with ω -bromoacetophenone in alcohol to form unsymmetrical dyes, viz., 1-(3-methyl-2-benzothiazolinidenyl)-5-(3-aryl-4-phenyl-2-thiazolyl)-1,2,4,5-tetraza-3-mercaptopentamethinyl-cyanine bromides (VI).

The condensation of 1,5-bis(arylaminothiocarbo)thiocarbohydrazides (VII) with ω -bromoacetophenone in alcohol leads to 1-(3-aryl-4-phenyl-2-thiazolinidenyl)-5-(3-aryl-4-phenyl-2-thiazolium)-1,2,4,5-tetraza-3-mercaptopentamethinylcyanine bromides (VIII).



The absorption maxima of VIII in chloroform lie at 560–580 nm.

To compare the colors of symmetrical and unsymmetrical dyes, we obtained 1-(3-methyl-2-benzothiazolinidenyl)-5-(3-methyl-2-benzothiazolium)-1,2,4,5-tetraza-3-mercaptopentamethinylcyanine iodide (IX) (absorption maximum in chloroform 620 nm) by the reaction of I and II (Table 1).

As seen from Table 1, on comparing the absorption maxima of the two symmetrical dyes, VIIIb and IX, with the absorption maximum of unsymmetrical dye VIIb, the deviation for the latter is 56 nm, which is

in agreement with the data in [5, 6]. Dyes similar to IVa and IX, which contain a hydrogen atom instead of an SH group in the meso position, were previously [7, 8] prepared by another route - oxidative coupling of the appropriate substituted hydrazines with 2-benzothiazolone formalazine in the presence of ferric chloride.

EXPERIMENTAL

1-(3-Methyl-2-benzothiazolinidenyl)-5-(phenylaminothiocarbo)thiocarbohydrazide (IIIa). Compound II [1] [1 g (4 mmole)] was dissolved in alcohol, an alcohol solution of 0.54 g (4 mmole) of phenyl isothiocyanate was added to the resulting solution, and the mixture was heated for 15 min. It was then cooled, and the precipitate was filtered and washed with alcohol and ether to give 1.27 g (52%) of a product with mp 184-185° (from alcohol).

Compounds IIIb-d were obtained under similar conditions.

1-(3-Methyl-2-benzothiazolinidenyl)-5-(2-benzothiazolyl)-1,2,4,5-tetraza-3-mercaptopentamethinylcyanine Base (IVa). A. A total of 20 ml of aqueous alcohol (1:1) and 0.2 g (5 mmole) of sodium hydroxide were added to 0.77 g (2 mmole) of IIIa. The solution was filtered and added with stirring to an aqueous solution of 1.96 g (5 mmole) of potassium ferricyanide. The mixture was stirred at room temperature for 1 h. The resulting precipitate was filtered, washed with water, alcohol, and ether, and vacuum dried to give 0.66 g (86%) of dark-violet crystals with a metallic luster and mp 217-218°.

B. An aqueous solution of ferric chloride was added to a suspension of 0.4 g (1 mmole) of IIIa in water, the mixture was refluxed for 30 min and cooled, and the precipitate was filtered and washed with water, alcohol, and ether. It was then dissolved in chloroform, and the solution was filtered. The solvent was removed, and the residue was vacuum dried to give 0.34 g (88%) of IVa with mp 217-218°.

C. A total of 20 ml of a 2% alcohol solution of KOH and 5 ml of 30% hydrogen peroxide were added to 0.4 g (1 mmole) of IIIa. The mixture was stirred for 30 min, neutralized with hydrochloric acid, and the resulting precipitate was washed with water, alcohol, and ether, and vacuum dried to give 0.2 g (53%) of a product with mp 217-218°.

The products obtained via methods B and C did not depress the melting point of the compound obtained via method A.

1-(3-Methyl-2-benzothiazolinidenyl)-5-(2-benzothiazolyl)-1,2,4,5-tetraza-3-methylthiopentamethinylcyanine Base (Va). A total of 0.6 ml of a 10% alcohol solution of KOH and 0.2 ml of methyl iodide were added to 0.38 g (11 mmole) of IVa, and the mixture was allowed to stand for 6 h. It was then treated with water, and the precipitate was filtered, washed with water, alcohol, and ether and vacuum dried to give 0.3 g (77%) of a product with mp 224-225°. Compound Vb was obtained under similar conditions.

1-(3-Methyl-2-benzothiazolinidenyl)-5-(3,4-diphenyl-2-thiazolyl)-1,2,4,5-tetraza-3-mercaptopentamethinylcyanine Bromide (VIa). A total of 1.94 g (5 mmole) of IIIa and 1 g (5 mmole) of ω -bromoacetophenone were mixed, 5 ml of ethanol was added, and the mixture was heated for 1 h. The alcohol was removed by distillation, and the residue was dissolved in chloroform and passed through a column filled with aluminum oxide with chloroform-benzene (1:3) as the eluent. Evaporation of the solvent and vacuum drying of the residue gave 1.52 g (47%) of a product with mp 113-114°.

Compounds VIb-d were obtained under similar conditions.

1-(3,4-Diphenyl-2-thiazolinidenyl)-5-(3,4-diphenyl-2-thiazolyl)-1,2,4,5-tetraza-3-mercaptopentamethinylcyanine Bromide (VIIa). A mixture of 1.88 g (5 mmole) of VIIa and 2 g (10 mmole) of ω -bromoacetophenone in 5 ml of alcohol was heated for 1 h. The alcohol was removed, and the residue was dissolved in chloroform and chromatographed on aluminum oxide as described above to give 1.54 g (47%) of a product with mp 83-84°.

Compounds VIIb-d were obtained under similar conditions.

1-(4-Methyl-2-benzothiazolinidenyl)-5-(3-methyl-2-benzothiazolyl)-1,2,4,5-tetraza-3-mercaptopentamethinylcyanine Iodide (IX). An aqueous solution of 0.61 g (2 mmole) of I was mixed with an alcohol solution of 0.5 g (2 mmole) of II, and the mixture was heated at 90° for 1 h. It was then cooled with ice, and the colorless precipitate of 1,5-bis(3-methyl-2-benzothiazolyl)thiocarbohydrazide methyl methosulfate, which gradually turned blue in air, was filtered. The latter was oxidized with alcoholic alkali and acidified with hydro-

chloric acid. The filtered blue-green crystals were washed with alcohol and ether, dissolved in alcohol, and a saturated aqueous potassium iodide solution was added. The precipitated iodide was filtered, washed with alcohol and ether, and vacuum dried to give 0.26 g (25%) of a product with mp 210-211° (from chloroform).

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