RESEARCH IN THE BENZAZOLE AND NAPHTHAZOLE SERIES

XXXIII.* UNSYMMETRICAL FORMAZANS CONTAINING SUBSTITUTED BENZOTHIAZOLE RINGS

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A series of 1-benzothiazolyl-3,5-diphenylformazans with substituents in the 6-position of the benzothiazole ring were synthesized. The introduction of halogens and methyl and alkoxy groups into this position induces deepening of the color of the corresponding formazans as compared with the unsubstituted benzothiazolyldiphenylformazan. Benzothiazolylazo- and 6-methylbenzothiazolylazophenylhydrazones of benzaldehyde were isolated along with formazans in the coupling of benzothiazolinediazonium and 6-methylbenzothiazolinediazonium sulfates with benzaldehyde phenylhydrazone.

Substituents in the 5 position of the benzimidazole ring of symmetrical formazans of the benzimidazole series have a considerable effect on the properties of complexes with metal salts [2]. In the present research, we have studied the effect of substituents of formazans of the benzothiazole series on their coloration and complexing ability.

The 6-substituted benzaldehyde benzothiazolylhydrazones (I) were obtained by the cyclization of p-substituted 4-arylthiosemicarbazones [3]. Formazans II-IV with electron-donor substituents in the benzothiazole ring were obtained by coupling benzenediazonium chloride with I (method A). However, the cyclization of benzaldehyde 4-(p-bromophenyl)thiosemicarbazone did not give the expected 6-bromobenzothiazolylhydrazone, and it was necessary to develop a new method for the synthesis of benzothiazolylformazan. For this, we made an attempt to synthesize the formazans by coupling of diazonium salts (VIII) obtained from 2-aminobenzothiazoles with benzaldehyde phenylhydrazone (IX). Up until now, the coupling of heterocyclic diazonium salts with an arylhydrazone has been described only for thiazole and quinoline derivatives [4].

A strongly acidic medium is required for the successful diazotization of aminobenzothiazole [5], and the initial step in the coupling therefore proceeds at low pH values. Formazans II-VII were obtained as a result of the coupling reaction (method B, Table 1). All of the formazans were purified by chromatography on aluminum oxide and subsequent crystallization. The formazans absorbed at 470-530 nm, and both electron-donor and electron-acceptor substituents induced a bathochromic shift. Color deepening, associated with the formation of an anion, occurs when alkali is added to an alcohol solution of the formazan. (See scheme on following page).

The direction of coupling depends to a considerable degree on the pH of the medium and, in addition to the synthesis of formazans, can lead to tetrazenes or arylazohydrazones [6]. In addition to II-VII, the presence of another product, which was isolated chromatographically, is always detected in the reaction mass obtained as a result of coupling. The compound is quite soluble in organic solvents to give a crimson-colored solution that changes reversibly to blue when a strong acid is added.

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*See [1] for communication XXXII.

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TABLE 1. 1-Benzothiazolyl-3,5-diphenylformazans

Compound	Mp, °C	Empirical formula	Found, %			Calc., %			Yield, %		Absorption spectra in the visible region, λ_{max}, nm		
			C	H	N	C	H	N	method A	method B	in chloroform	in alcoholic alkali	complexes with Cu
II	183—184*	$C_{20}H_{15}N_5S$	—	—	—	—	—	—	50	24	474 (4,02) †	552	646
III	175—176	$C_{21}H_{17}N_5S \cdot C_2H_5OH$	66,6	5,2	16,4	66,2	5,5	16,8	55	30	490 (4,02)	493	666
IV	130—132	$C_{21}H_{17}N_5OS \cdot H_2O$	62,8	5,1	16,9	62,2	4,77	17,3	5	22	530 (3,87)	566	674
V	78—81	$C_{22}H_{19}N_5OS \cdot H_2O$	63,0	4,6	16,3	63,0	5,1	16,7	—	28	510 (3,72)	540	690
VI	106—108	$C_{20}H_{14}ClN_5S$	61,7	4,1	17,2	61,3	3,6	17,9	—	10	496 (3,36)	520	664
VII	88—90	$C_{20}H_{14}BrN_5S$	55,6	3,6	15,6	55,0	3,2	16,1	—	8	482 (3,81)	517	656

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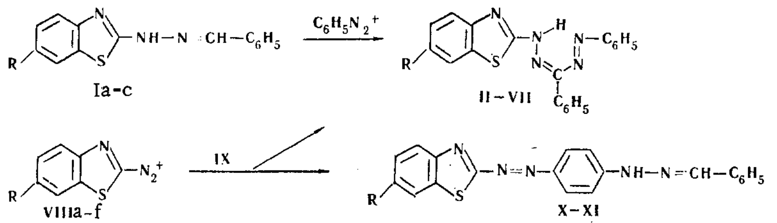
* Mp 183-185° [7].

† The log ε values are given in parentheses.



Ia, II, VIIIa, X R=H; Ib, III, VIIIb, XI R=CH_3; Ic, IV, VIIIc R=OCH_3; V, VIIId R=OC_2H_5; VI, VIIIe R=Cl; VII, VIIIf R=Br

It might have been assumed that benzaldehyde benzothiazolylazophenylhydrazone (X), which is converted to the quinoid form in acid, is formed along with formazan under the given conditions. For proof of this, VIIIa was coupled with acetophenone phenylhydrazone (XII); i.e., the possibility of the formation of a formazan was deliberately excluded. Acetophenone benzothiazolylazophenylhydrazone (XIII), which is also capable of reversibly changing its color in acidic media, was isolated from the reaction mixture.

Compounds II-VII form deeply colored complexes with metal salts (Cu, Zn, Ni, and Co) in the cold. The structures of the complexes are under investigation.

EXPERIMENTAL

1-(6-Methyl-2-benzothiazolyl)-3,5-diphenylformazan (III). A) A diazonium solution (obtained from 0.002 mole of aniline, 2 ml of concentrated HCl, and 0.14 g of $NaNO_2$ in 3 ml of water) was added to a cooled (to 0°) solution of 0.55 g (0.002 mole) of Ib in 30 ml of ethanol. The mixture was neutralized to pH 6 with 2 N NaOH and allowed to stand in the cold to isolate the formazan. After the mixture had stood for 24 h, it was diluted with water, and the shiny crystals with a green luster were removed by filtration. Compounds II and IV were similarly obtained.

B) A solution of VIIIb [obtained from 0.33 g (0.002 mole) of 6-methyl-2-aminobenzothiazole, 5 ml of 60% sulfuric acid, and 0.14 g of $NaNO_2$ in 3 ml of water] was added to a cooled (to 0°) solution of 0.39 g (0.002 mole) of IX in 30 ml of ethanol. The mixture was made alkaline to pH 4-5 with 2 N NaOH and allowed to stand in the cold for 24 h. The reaction mass was diluted with water, and the resulting precipitate was removed by filtration and washed with water. The presence of III (R_f 0.9) and benzaldehyde 6-methylbenzothiazolylazophenylhydrazone (XI) (R_f 0.55) was detected by chromatography of a sample on a loose thin layer of aluminum oxide with elution by chloroform–diethyl ether (1 : 1). The substances were separated with a column filled with aluminum oxide to give 0.23 g (30%) of III. The column was washed out with ether to give 0.31 g (42%) of XI with mp 235-236° (needles from ethanol). Found: C 65.80; H 5.30; N 16.30%. $C_{21}H_{17}N_5S \cdot C_2H_5OH$. Calculated: C 66.20; H 5.50; N 16.80%. Compounds II-VII (Table 1) were similarly obtained from VIIIa-f.

Compound X [0.36 g (50%)] was similarly obtained from VIIIa and had λ_{max} 524 nm (in ethanol), λ_{max} 652 nm (in acidic media), and mp 208-209° (needles from ethanol). Found: C 64.80; H 4.20; N 17.30%. $C_{20}H_{15}N_5S \cdot C_2H_5OH$. Calculated: C 65.20; H 5.20; N 17.40%.

Acetophenone Benzothiazolylazophenylhydrazone (XIII). A solution of VIIIa [obtained from 0.6 g (0.004 mole) of aminobenzothiazole, 10 ml of 60% sulfuric acid, and 0.28 g of $NaNO_2$ in 6 ml of water] was added to a cooled (to 0°) solution of 0.84 g (0.004 mole) of XII in 30 ml of ethanol. The solution was made alkaline to pH 4-5 and held in the cold for 24 h. The reaction mass was diluted with water, and the precipitate was removed by filtration to give 0.32 g (22%) of red plates (from aqueous ethanol) with mp 73-75° and R_f 0.58 [chloroform–diethyl ether (1 : 1)]. A blue coloration appeared when a mineral acid was added to an alcohol solution of this compound. Found: C 61.60; H 4.60; N 17.60%. $C_{21}H_{17}N_5S \cdot 2H_2O$. Calculated: C 61.90; H 5.20; N 17.20%.

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