BENZAZOLES AND NAPHTHAZOLES

XXXIV.* SYNTHESIS OF MONO-, DI-, AND TRIHETERYLFORMAZANS BY AUTOOXIDATION OF 2-HYDRAZINOBENZAZOLES

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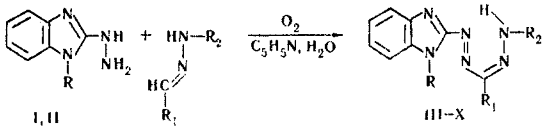
Mono-, di-, and triheterylformazans were obtained by the autooxidative coupling (in pyridine solution) of 1-alkyl-2-hydrazinobenzimidazoles with the aryl(azolyl)hydrazones of aliphatic or heterocyclic aldehydes.

A method for the preparation of symmetrical 1,5-dibenzazolylformazans was developed on the basis of the spontaneous oxidation of 1-alkyl-2-hydrazinobenzimidazoles in solutions of primary alcohols [2]. The method consists in the joint autooxidation of 2-hydrazinobenzazoles and their hydrazones. Formazans containing different benzazoles in the 1 and 5 positions have been unknown until now.

In the present paper, we propose a variant of the method that makes it possible to extend the possibility of autooxidative coupling. By using pyridine [which excludes side reactions (resinification and disproportionation)] as the reaction medium and the catalyst, the autooxidative coupling of 2-hydrazinobenzazoles can be carried out with any hydrazines, and various mono-, di-, or triheterylformazans can be obtained (see the scheme below and Table 1).



I $R=CH_3$; II $R=CH_2C_6H_5$

A mixture of 1-alkyl-2-hydrazinobenzimidazole with an equimolecular amount of the arylhydrazone or azolylhydrazone of acetaldehyde, benzaldehyde, or formylquinoxaline was dissolved in pyridine with the addition of water, and the mixture was allowed to oxidize spontaneously in the air for several days.

The 1-(1-alkyl-2-benzimidazolyl)-3-methyl-5-arylformazans (III–V) were identical to the compounds previously obtained [3] by the known method of azo coupling of the arenediazonium salts with benzimidazolylhydrazones. Formazans VI and X were also obtained by alternative synthesis by the autooxidative coupling of 2-hydrazinobenzothiazole with 1-methyl-2-benzimidazolylhydrazones. In this case, since 2-hydrazinobenzothiazole displays a lesser tendency for autooxidation than 1-alkyl-2-hydrazinobenzimidazoles, pyridine with added aqueous sodium acetate solution, which accelerates the autooxidative coupling, was used as the reaction medium.

EXPERIMENTAL

1-(1-Methyl-2-benzimidazolyl)-3-methyl-5-phenylformazan (III). A 4.65-g (0.0287 mole) sample of I [4] and 3.85 g (0.0287 mole) of acetaldehyde phenylhydrazone were dissolved in 15 ml of pyridine and 10 ml of

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*See [1] for communication XXXIII.

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TABLE 1. 1-(1-Alkyl-2-benzimidazolyl)-3-R-5-heteryl(aryl)formazans

Compound	R	R_1	R_2	Mp, °C
III	CH_3	CH_3	C_6H_5	207—210
IV	CH_3	CH_3	p-$C_6H_4CH_3$	192—194*
V	CH_3	CH_3	p-$C_6H_4NO_2$	242—245†
VI	CH_3	CH_3	2-Benzothiazolyl	230—233
VII	$CH_2C_6H_5$	CH_3	The same	207—208
VIII	$CH_2C_6H_5$	CH_3	2-Benzoxazolyl	264—265
IX	CH_3	C_6H_5	1-Phenyl-5-tetrazolyl	198—201
X	CH_3	2-Quinoxalyl	The same	151—154

TABLE 1. (Continued)

Compound	Empirical formula	Found, %			Calc., %			Yield, %
		C	H	N(S)	C	H	N(S)	
III	$C_{16}H_{16}N_6$	65,38	5,65	28,65	65,73	5,51	28,75	15
IV	$C_{17}H_{18}N_6 \cdot H_2O$	63,35	6,26	26,11	62,94	6,29	25,90	11
V	$C_{16}H_{15}N_7O_2$	57,21	4,69	28,86	56,96	4,48	29,06	40
VI	$C_{17}H_{15}N_7S \cdot C_3H_7NO$	57,16	4,97	26,72 (7,54)	56,85	5,24	26,52 (7,58)	40
VII	$C_{23}H_{19}N_7S$	64,44	5,20	21,79 (7,10)	64,89	4,50	23,04 (7,53)	71
VIII	$C_{23}H_{19}N_7O \cdot 2C_5H_5N$	69,82	5,15	22,21	69,96	5,25	21,81	40
IX	$C_{22}H_{18}N_{10} \cdot H_2O$	59,87	4,69	32,41	59,98	4,57	31,80	50
X	$C_{24}H_{17}N_9S \cdot 2H_2O$	60,03	4,58	25,70 (6,52)	59,86	4,39	26,18 (6,65)	52

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*Mp 193-194° [3].

†Mp 225-228° [3].

water, and the mixture was allowed to stand in an open flask at room temperature for 5 h. Compound III gradually crystallized from the red solution to give red plates (from alcohol).

1-(1-Methyl-2-benzimidazolyl)-3-methyl-5-(p-tolyl)formazan (IV). This compound was similarly obtained from 3.2 g (0.02 mole) of I and 2.8 g (0.02 mole) of acetaldehyde p-tolylhydrazone in 10 ml of pyridine and 5 ml of water. The product was obtained as long, orange needles (from 50% alcohol).

1-(1-Methyl-2-benzimidazolyl)-3-methyl-5-(p-nitrophenyl)formazan (V). This was similarly obtained as dark-red needles [from dimethylformamide—water (3 : 1)] from 3.2 g (0.02 mole) of I and 3.5 g (0.02 mole) of acetaldehyde p-nitrophenylhydrazone in 20 ml of pyridine and 5 ml of water.

1-(1-Methyl-2-benzimidazolyl)-3-methyl-5-(2-benzothiazolyl)formazan (VI). A) A 1.9-g (0.01 mole) sample of acetaldehyde 2-benzothiazolylhydrazone and 1.7 g (0.01 mole) of I were dissolved in 20 ml of pyridine with slight heating, and the mixture was allowed to stand in air. After 5 days, the dark-violet solution was diluted with 100 ml of water, and 2 N HCl was added to pH 6-7 to give dark-violet crystals [from dimethylformamide—water (3 : 1)] that were quite soluble in pyridine and dimethylformamide and less soluble in alcohol, acetone, and chloroform. λ_{max} 570 nm, $\varepsilon \cdot 10^{-4}$ 11.03.

B) A 1.9-g (0.01 mole) sample of acetaldehyde 1-methylbenzimidazolylhydrazone and 1.8 g (0.01 mole) of 2-hydrazinobenzothiazole were dissolved in 40 ml of pyridine with slight heating, and the mixture was introduced into a solution of 1 g of sodium acetate in 10 ml of water. Compound VI was isolated as in method A. The product did not depress the melting point of the product from method A. A comparison of the IR spectra at 730-1600 cm^{-1} demonstrated that the compounds were identical.

1-(1-Benzyl-2-benzimidazolyl)-3-methyl-5-(2-benzothiazolyl)formazan (VII). A 2.38-g (0.01 mole) sample of II and 1.9 g (0.01 mole) of acetaldehyde benzothiazolylhydrazone were dissolved in 50 ml of distilled pyridine with slight heating, and the solution was filtered and allowed to stand for 5-6 days. The solution rapidly became intensely violet, and VII gradually crystallized from it. A certain additional amount of VII was obtained from the mother liquor after half of the solvent was removed from it by distillation. The product was obtained as large, beautiful, violet prisms with a green luster on the faces (from alcohol).

1-(1-Benzyl-2-benzimidazolyl)-3-methyl-5-(2-benzoxazolyl)formazan (VIII). This compound was similarly obtained from II and acetaldehyde benzoxazolylhydrazone.

1-(1-Methyl-2-benzimidazolyl)-3-phenyl-5-(1-phenyl-5-tetrazolyl)formazan (IX). This compound was similarly obtained as red needles (from butanol) from 1.6 g (0.01 mole) of I and 2.6 g (0.01 mole) of benzaldehyde 1-phenyl-5-tetrazolylhydrazone [5] in 20 ml of pyridine.

1-(1-Methyl-2-benzimidazolyl)-3-(2-quinoxalyl)-5-(2-benzothiazolyl)formazan (X). A) A 1.5-g (0.005 mole) sample of formylquinoxaline 2-benzothiazolylhydrazone [6] and 0.9 g (0.005 mole) of I were dissolved by heating in 160 ml of pyridine, and the solution was allowed to stand in air for 8 days. The reaction mass was diluted with 1 liter of water, and the mixture was neutralized to pH 6-7 with 2 N HCl to give green plates with a metallic luster [from dimethylformamide–water (2:1)]. λ_{max} 568 nm.

B) A 1.5-g (0.005 mole) sample of formylquinoxaline 1-methyl-2-benzimidazolylhydrazone and 0.9 g (0.005 mole) of 2-hydrazinobenzothiazole were dissolved in 110 ml of pyridine, and the solution was added to a solution of 1 g of sodium acetate in 10 ml of water. Compound X was isolated as in method A.

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