

STUDIES IN THE BENZ- AND NAPHTHAZOLE SERIES. XII. SYNTHESIS AND REDUCTION OF 1,5-DI(1'-BENZYL-BENZIMIDAZOLYL-2')-3-METHYLFORMAZANE*

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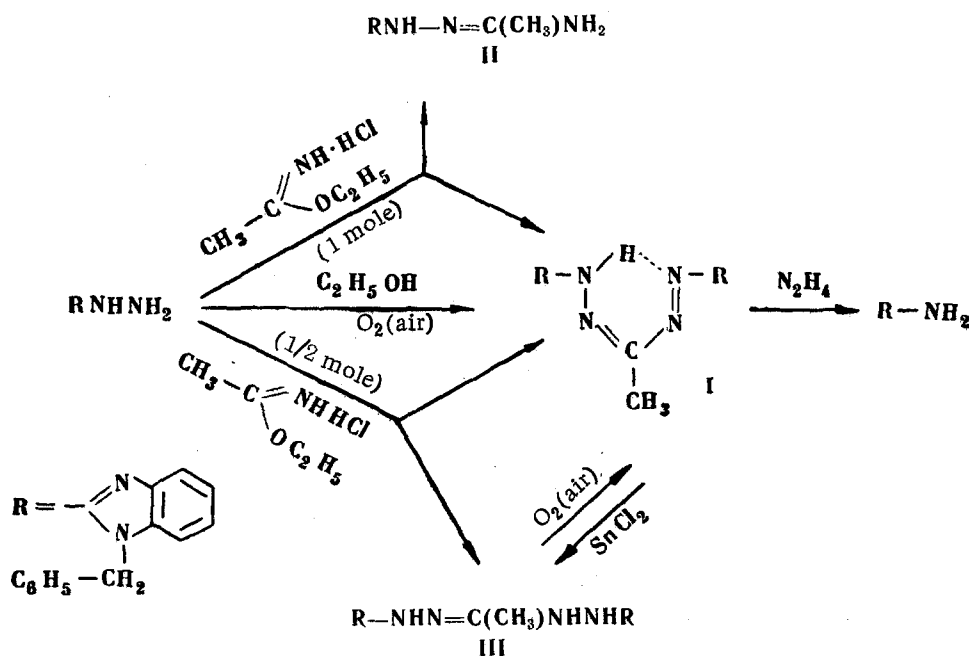
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The structure of 1,5-di(1'-benzylbenzimidazolyl-2)-3-methylformazan, previously obtained as a result of the autoxidation of 1-benzyl-2-hydrazinobenzimidazole in ethanol, is confirmed by synthesis from 1-benzyl-2-hydrazinobenzimidazole and ethyl acetimidate. N-benzylbenzimidazolylacetamidrazone and ethenyl-di(N-benzylbenzimidazolyl)hydrazidine are formed as the by-product and intermediate product of the synthesis. The hydrazine obtained oxidizes spontaneously in alcohol to give formazan, which, in its turn, is easily reduced to hydrazidine.

The formation of 1,5-di(1'-alkylbenzimidazolyl-2)-3-alkylformazans as a result of spontaneous oxidation of 1-alkyl-2-hydrazinobenzimidazoles in solutions of primary alcohols has already been described [2]. It was therefore of some interest to study the synthesis of these formazans and to compare their properties with those of arylformazans.

This paper gives an account of the synthesis of 1,5-di(1'-benzylbenzimidazolyl-2)-3-methylformazan (I). This formazan was obtained on heating 1-benzyl-2-hydrazinobenzimidazole and ethyl acetimidate hydrochloride in a benzene medium, when, in addition to the deep-colored formazan I, colorless products were formed. When the starting reagents were taken in molar ratio (1:1), the chief product was N-benzylbenzimidazolylacetamidrazone (II) together with formazan I. At a ratio of 2 moles 1-benzyl-2-hydrazinobenzimidazole to 1 mole imido ester we obtained formazan I and ethenyl-di(N-benzylbenzimidazolyl)hydrazidine (III).

The hydrazidine III is the leuco base of dye I. It is stable in the form of the hydrochloride, but if it is dissolved in alcohol and the solution alkalinized it is quickly oxidized by atmospheric oxygen and converted to formazan I. Conversely, formazan I, when reduced under mild conditions (sodium bisulfite, Raney nickel, etc.), becomes decolorized and goes over into hydrazidine III. When formazan I is briefly boiled with stannous chloride in conc. hydrochloric acid, the chief reduction product is hydrazidine III. When formazan I is subjected to prolonged boiling with hydrazine hydrate, the end product of the reducing degradation is 1-benzyl-2-aminobenzimidazole.



Thus, 1,5-di(1'-benzylbenzimidazolyl-2)-3-methylformazan bears a resemblance to the 1,5-diaryl-3-alkylformazans [3], manifested in the ease with which it participates in the redox reactions: formazan \rightleftharpoons hydrazidine. When formazan I is synthesized from acetimido ester and 1-benzyl-2-hydrazinobenzimidazole, the same products (formazan, hydrazidine, amidrazone) may be formed as in the synthesis of arylformazans from imido esters and arylhydrazines [3, 4].

*For part XI see [1].

The synthesis of compound I by the method described here does not have any advantages over the synthesis of the same formazan by autoxidation of 1-benzyl-2-hydrazinobenzimidazole in ethanol.

EXPERIMENTAL

Interaction of 1-benzyl-2-hydrazinobenzimidazole and acetimido ester

a) 0.005 mole 1-benzyl-2-hydrazinobenzimidazole is dissolved in 50 ml benzene and a finely ground powder of 0.005 mole ethyl acetimidate hydrochloride (freshly prepared by the method of [5]) is added to the solution. The mixture is boiled for 1 hr 30 min. The loose colorless precipitate is filtered off from the dark-violet benzene solution and washed with benzene. The benzene solution is evaporated to dryness and the remaining dark-violet resin is thinned with ethanol (or methanol). Immediately a crystalline precipitate (needles) of 1,5-di(1'-benzylbenzimidazolyl-2')-3-methylformazan (I) is formed. Yield 20%. Mp 143-145°, mixed mp with dye obtained by autoxidation of 1-benzyl-2-hydrazinobenzimidazole in ethanol undepressed.

The colorless precipitate, amidrazone II with an admixture of hydrazidine III, is dissolved with heating in 20 ml water, acidified with 2 ml conc. HCl, and the solution decolorized with charcoal. When the solution cools, fine colorless fibrous needles of N-benzylbenzimidazolylacetamidrazone hydrochloride (II) separate. Yield 25%. Mp 248-249°. Amidrazone hydrochloride II is soluble in water and alcohol, but insoluble in acetone and benzene. With copper salts in water-alcohol solution it gives an intensely violet coloration that disappears after a short period of standing. The base of amidrazone II can be obtained by alkalizing an aqueous solution of the hydrochloride; it is insoluble in water, but soluble in alcohol, acetone and benzene. The solutions do not turn blue on standing. Found: C 52.07, 52.38; H 5.38, 5.39; N 18.82; Cl 19.23; H₂O 5.07%. Calculated for C₁₆H₁₇N₅ · 2HCl · H₂O: C 51.89; H 5.71; N 18.91; Cl 19.14; H₂O 4.86%. The water content was determined by drying a weighed portion of the substance at 200-220°.

b) 0.005 mole 1-benzyl-2-hydrazinobenzimidazole, 0.0025 mole ethyl acetimidate hydrochloride and 50 ml benzene are boiled for 1 hr 30 min. The violet benzene solution is separated from the fine colorless powder. When the benzene is evaporated off and the violet resin thinned with alcohol, needles of formazan I separate out. Yield 12%. The colorless precipitate is dissolved in 10 ml water acidified with hydrochloric acid. After purification with charcoal, star-like clusters of hydrazidine III platelets are precipitated as the solution cools. Yield 10%. Mp 76-77°, mixed mp with the substance obtained by reducing formazan I with stannous chloride undepressed.

Reduction of formazan I

a) 0.53 g formazan I and 2 g SnCl₂ · 2H₂O in 10 ml conc. HCl are boiled for about 30 min until the dye is decolorized and a yellow oil is formed. The heavy oil is washed with water and then alkali, and dissolved in 15 ml 6N HCl, whereupon the solution is decolorized with charcoal. If the solution is left to stand, crystals of ethenyl-di(N-benzylbenzimidazolyl)hydrazidine (III) separate out in nodules. Yield 60%. Mp 76-77°. Hydrazidine hydrochloride III is soluble in water and alcohol, but insoluble in acetone and benzene. An alcohol solution does not give coloration with copper salts. Upon alkalization of the alcohol solution rapid autoxidation of hydrazidine III into formazan I is observed: 0.25 g substance III is dissolved in 10 ml alcohol and alkalized to pH 8. The solution quickly turns violet. In 24 hr crystals of formazan I separate out, yield about 50%. Found: C 57.51, 57.50; H 6.03, 5.65; N 18.83; Cl 11.60%. Calculated for C₃₀H₂₈N₈ · 2HCl · 3H₂O: C 57.41; H 5.74; N 17.91; Cl 11.32%

b) 2.6 g formazan I are boiled with 30 ml hydrazine hydrate for 5 hr. On cooling the solution crystallizes into a solid mass of crystal flakes. After multiple recrystallization from alcohol the yield is about 1 g (45%). Mp 192-193°, mixed mp with 1-benzyl-2-aminobenzimidazole, obtained by the method of [5] or [6], undepressed.

Found: N 18.85%. Calculated for C₁₄H₁₃N₃: N 18.82%.

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