BENZAZOLES AND NAPHTHAZOLES

XXXV.* AUTOOXIDATIVE COUPLING OF 1-BENZYL-2-HYDRAZINOBENZIMIDAZOLE WITH NITROFORMALDEHYDE ARYLHYDRAZONES

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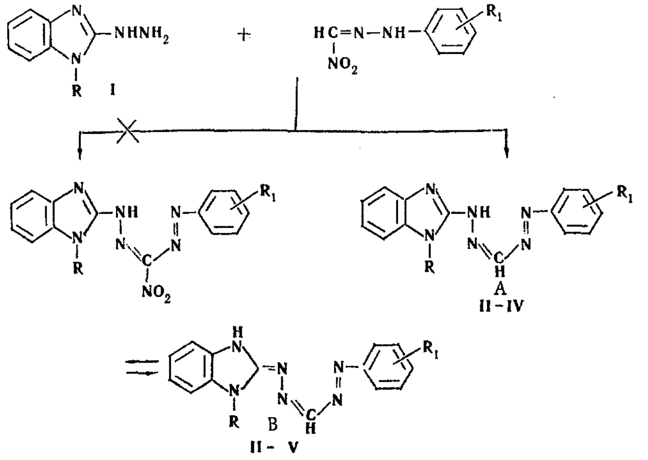
1-Benzyl-2-hydrazinobenzimidazole undergoes autooxidative coupling with nitroformaldehyde arylhydrazones to give meso-carbon-unsubstituted 1-(1-benzyl-2-benzimidazolyl)-5-arylformazans (instead of the expected formazans with a nitro group in the meso position). Data on the structures and complexing abilities of the new unsymmetrical formazans of the benzimidazole series are presented.

As demonstrated in [1], 1-alkyl-2-hydrazinobenzimidazoles undergo spontaneous oxidation and coupling with heterocyclic hydrazones or arylhydrazones to form symmetrical or unsymmetrical formazans of benzimidazole. The reaction has a certain similarity to Hünig oxidative azo coupling, which has been studied in the benzothiazole series [3].

In order to obtain new complexing formazans, we investigated the autooxidative coupling of 1-benzyl-2-hydrozinobenzimidazole (I) with nitroformaldehyde arylhydrazones. One might have expected the formation of formazans that contain a nitro group attached to the meso carbon, but 3-unsubstituted formazans were actually obtained.



I—V $R=CH_2C_6H_5$; II $R_1=H$; III $R_1=o\text{-}CH_3$; IV $R_1=p\text{-}CH_3$; V $R_1=p\text{-}NO_2$

The reaction proceeds when a solution of equimolecular amounts of I and the nitroformaldehyde arylhydrazone in pyridine is allowed to stand in air. The resulting formazans (II-V) gradually crystallize from

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*See [1] for communication XXXIV.

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TABLE 1. Spectral Characteristics of 1-(1-Benzyl-2-benzimidazolyl)-5-arylformazans and Their Complexes

Compound	IR spectra, ν_{NH}, cm^{-1} (CCl_4)	UV spectra, short-wave region (alcohol)	λ_{max}, nm (lg ε) visible region		λ_{max}, nm (log ε) of complexes in alcohol		
			alcohol	alcoholic NaOH	Ni^{2+}	Cu^{2+}	Zn^{2+}
II	3449	250 (3,96); 295 (4,01)	468 (4,55)	544 (4,71)	604 (4,23)	518 (4,25)	502 (4,47)
III	3450	250 (4,05); 295 (4,12)	460 (4,68)	536 (4,92)	580 (3,98)	550 (4,42)	496 (4,43)
IV	3450	255 (4,22); 295 (4,28)	466 (4,52)	534 (4,48)	606 (4,32)	622 (4,31)	512 (4,70)
V	3440	265 (3,87); 295 (3,99)	520 (4,67)	622 (4,23)	654 (4,47)	620 (4,43)	562 (4,60)

the solution. Compounds II-IV precipitate in several hours, while V precipitates in an hour. The increased rate of autooxidation in the case of V can be explained by the electron-acceptor effect of the nitro group of the aromatic ring, which increases the electron deficit on the hydrazone carbon atom and thereby promotes nucleophilic attack on the part of I. The mechanism of the removal of the nitro group in the meso position has not been ascertained.

The conclusion that II-V have the meso-unsubstituted 1-(1-benzyl-2-benzimidazolyl)-5-arylformazan structure was drawn on the basis of a comparison of the IR and UV spectra of II-V with the spectra of the previously studied [4] 1-(1-benzylbenzimidazolyl)-3-methyl-5-arylformazans and also on the basis of the results of elementary analysis.

It is apparent from the data in Table 1 that a ν_{NH} band is present at 3450 cm^{-1} in the IR spectra of all of the formazans. There is a similar narrow, intense band (assignable to the imino form of the formazan grouping, according to [5]) in the spectra of chloroform solutions of 1-benzimidazolyl-3-methyl-5-arylformazans [5, 6]. It can be concluded that the tautomeric equilibrium in solutions of II-V is also shifted to favor imino form B.

The electronic spectra of II-V in the UV and visible regions are almost indistinguishable from the spectra of the corresponding formazans [4] that have a methyl group in the meso position. The bathochromic effects of salt formation and complexing are also very close. Compounds II-V display positive solvatochromism. The bathochromic shift of the absorption maximum on passing from a nonpolar solvent (benzene) to a polar solvent (nitrobenzene) is 20 nm for II, III, and V and 12 nm for IV. Like other 1-benzimidazolyl-5-arylformazans, II-V have photochromic properties. Under the influence of sunlight, the color of solutions of II-V in carbon tetrachloride changes from yellow through green to blue-green in several days. The bathochromic effect of the photoreaction is ~ 200 nm.

The nitroformaldehyde hydrazones were synthesized via the methods in [8-10] by coupling arenediazonium salts with nitromethane in acidic media. 1,5-Diarylformazans were obtained as side products in this case.

EXPERIMENTAL

Nitroformaldehyde Phenylhydrazone. A solution of 6.4 g of sodium nitrite in 25 ml of water at 0-3° was added dropwise to a cooled (to 0°) solution of 11.42 g (0.1 mole) of aniline hydrochloride in a mixture of 75 ml of water and 20 ml of concentrated hydrochloric acid. The diazonium salt solution was added gradually with stirring to a freshly prepared solution of 6 ml (0.1 mole) of nitromethane in 12 ml of 2 N NaOH cooled to 0°. (The pH of the solution formed after mixing should be acidic.) A resin precipitated from the solution and was transferred with a spatula to a beaker containing alcohol. The alcohol solution was heated and filtered, and the filtrate was cooled to precipitate beautiful bright-red crystals of 1,5-diphenyl-3-nitroformazan with mp 163° (mp 162-163° [7]). Yellow crystals of nitroformaldehyde phenylhydrazone with mp 83° (mp 84-85° [7], 87-89° [9]) precipitated from the filtrate.

Nitroformaldehyde p-Tolylhydrazone. This compound was similarly obtained and had mp 84-86°. Found: C 53.97; H 5.19%. $C_8H_9N_3O_2$. Calculated: C 53.60; H 5.07%.

Nitroformaldehyde p-Nitrophenylhydrazone. A solution of the diazonium salt was added carefully dropwise with cooling to a solution of 6 ml (0.1 mole) of nitromethane in 12 ml of 2 N NaOH. A 13.8-g (0.1 mole) sample of p-nitroaniline was dissolved in 200 ml of water containing 30 ml of concentrated hydrochloric acid. A solution of 7 g (0.1 mole) of sodium nitrite in 20 ml of water was then added at 0°. A light-yellow precipitate of the hydrazone formed immediately (the pH of the solution should be no more than 5). Under the given conditions, the hydrazone is the only reaction product and has mp 152° (mp 159° [10]). Found: C 40.44; H 3.05; N 26.72%. $C_7H_6N_4O_4$. Calculated: C 40.20; H 2.88; N 26.80%.

1-(1-Benzyl-2-benzimidazolyl)-5-phenylformazan (II). A 0.5-g (0.03 mole) sample of nitroformaldehyde phenylhydrazone and 0.72 g (0.03 mole) of I were dissolved in 10 ml of freshly distilled pyridine, and the solution was heated to 70-80° (without reaching the boiling point) and filtered. Crystals of II precipitated from the solution after standing for 3 days. Recrystallization from aqueous alcohol or aqueous pyridine gave beautiful, yellow-orange needles of II with mp 185°. The product was dried in a vacuum-drying pistol heated by m-xylene vapors. Found: C 71.34; H 5.50%. $C_{21}H_{18}N_6$. Calculated: C 71.30; H 5.11%.

1-(1-Benzyl-2-benzimidazolyl)-5-[o(p)-tolyl]formazans (III, IV). These compounds were similarly obtained. Compound III was obtained as brown-red plates with mp 146° (aqueous pyridine). Found: C 72.13; H 5.30%. $C_{22}H_{20}N_6$. Calculated: C 71.80; H 5.47%. Compound IV was obtained as orange needles with mp 170° (aqueous alcohol). Found: C 71.82; H 5.77%. $C_{22}H_{20}N_6$. Calculated: C 71.80; H 5.47%.

1-(1-Benzyl-2-benzimidazolyl)-5-(p-nitrophenyl)formazan (V). A 0.63-g (0.03 mole) sample of nitroformaldehyde p-nitrophenylhydrazone and 0.07 g (0.03 mole) of I were dissolved in 10-12 ml of freshly distilled pyridine, and the solution was heated and filtered. Dark-green crystals of V precipitated from the solution in 1-2 h and were recrystallized from alcohol and dried in a vacuum-drying pistol (heating with xylene vapors) for 20 h to give a product with mp 231°. Found: C 63.69; H 4.52%. $C_{21}H_{17}N_7O_2$. Calculated: C 63.16; H 4.30%.

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