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Original Scientific Paper

Thioamides. XIV.^a The Oxidative Cyclisation of some Substituted Bisthioamides^b

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Disubstituted benzobisthiazoles (Figure 1.) and bis(benzothiazolyl)benzenes (Figure 2.) were prepared by the oxidative cyclization of *N,N'*-bis(thioaroyl)phenylenediamines and benzenebis(carbothioanilides), respectively. It has been found that in the oxidation of *N,N'*-bis(thioaroyl)phenylenediamines with alkaline ferricyanide the isomers of an angular structure (B) were obtained.

Most of the methods reported for preparation of benzothiazoles are based upon various intra- or intermolecular cyclisations of appropriate benzene derivatives¹. Since Jacobson² many authors have started from *N*-aryltioamides using oxidative cyclisation with potassium ferricyanide. Nevertheless, some other oxidations could be useful as well and the recently reported electrochemical intramolecular oxidative cyclisation of thiobenzanilide to 2-phenylbenzothiazole³ is also worth mentioning.

In this paper we wish to report the preparation of some disubstituted benzobisthiazoles and bisbenzothiazolilbenzenes. Few such thiazole derivatives have been reported so far, although they may be of some chemotherapeutic or technical usefulness like some simpler benzothiazole derivatives.

In the preceeding paper of this series⁴ we reported the preparation of several *N,N'*-bis(thioaroyl)phenylene-diamines and benzenebis(carbothioanilides). By oxidative cyclisation such compounds should give disubstituted benzobisthiazoles and bisbenzothiazolilbenzenes. In the case of bisthioamides derived from *m*- and *p*-phenylenediamine a question appeared whether a linear (A) or an angular (B) structure could be attributed to the product. (Figure 1).

^a Part XIII.: D. Petrova and K. Jakopčić, *Croat. Chem. Acta* 48 (1976) 49.

^b Taken in part from Ph. D. Thesis of D. Petrova, University of Zagreb, 1973.

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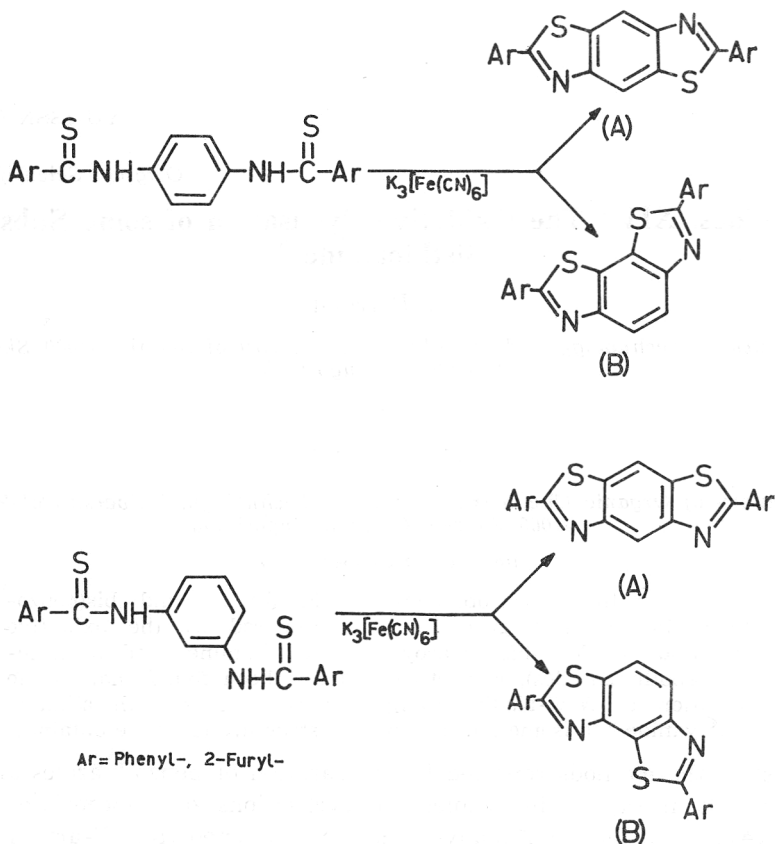


Fig. 1.

Green and Perkin⁵ reported the preparation of dimethyl- and diphenyl-benzobisthiazole from *p*-phenylenediamine dithiosulphonic acid and acetic anhydride or benzaldehyde respectively. Some other authors⁶ supposed a linear structure for the compounds. Later Kiprianov and Mihailenko⁷ claimed the incorrectness of such a structure and showed that dimethyl-benzobisthiazole obtained by Green and Perkin was in fact an angular isomer, *i. e.* 2,7-dimethylbenzo[1,2-*d*:4,3-*d'*]bisthiazole. Similarly, Finzi and Grandolini^{8,9} found that the linear structure of dimethylbenzobisthiazole proposed by Edge¹⁰ for the compound obtained by the oxidative cyclisation of *N,N'*-dithioacetyl-*m*-phenylenediamine was incorrect. They found that the oxidative cyclisation of 5-thioacetyl-amino-2-methyl-benzothiazole gave angular 2,7-dimethylbenzo[1,2-*d*:3,4-*d'*]bisthiazole identical with the Edge's product.

In our experiments the oxidation of bistioamides⁴ was performed by alkaline ferricyanide. The oxidation of *N,N'*-dithiobenzoyl- and *N,N'*-dithiofuroyl-*m*-phenylenediamine gave the corresponding disubstituted benzobisthiazoles of angular structure. The 2,7-diphenylbenzo[1,2-*d*:3,4-*d'*]bisthiazole obtained has proved to be identical with the authentic sample prepared according

to Finzi and Grandolini⁸. Moreover, the angular structure was confirmed by the ir band at 810 cm^{-1} (out of plane deformation) which could be present only if two vicinal CH groups in the aromatic nucleus are present^{7,11}. Similarly, the angular structure of 2,7-di(2-furyl)-benzo[1,2-d:3,4-d']bisthiazole was confirmed by the strong ir band at 800 cm^{-1} (γ_{CH}).

The oxidation of thioamides derived from *p*-phenylenediamine was not so unequivocal. In the case of *N,N'*-dithiobenzoyl-*p*-phenylenediamine the oxidation product was a mixture of disubstituted benzobisthiazole and *N,N'*-dibenzoyl-*p*-phenylenediamine as a result of partial desulphuration of the starting thioamide. The structure of the benzobisthiazole obtained was proved to be angular one, since the strong ir band at 815 cm^{-1} (γ_{CH}) was present*. This conclusion was confirmed by an independent synthesis through 6-benzalmino-2-phenylbenzothiazole. Several attempts were made to achieve oxidative cyclisation of *N,N'*-di-(2-thiofuroyl)-*p*-phenylenediamine under various reaction conditions without any success. The products were the mixtures of thioamide and of the partially or completely desulphurized starting material, but the corresponding benzothiazole was not detected.

The other part of this work was devoted to the preparation of bisbenzothiazolilbenzenes by ferricyanide oxidation of *m*- and *p*-benzenebis(carbothioanilides). (Figure 2). The oxidative cyclisation of isophthaloyl- and terephthaloyl-

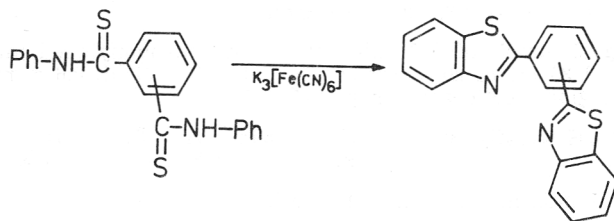


Fig. 2

bisthioanilides, like that of 2,5-furobis(carbothioanilides)¹² proceeded in a very good yield (80—85%)** and it seems to be useful as a general method. The structures were confirmed by elemental analyses and ir spectra.

EXPERIMENTAL

The melting points are uncorrected. The ir spectra were taken by an Model 521 Perkin-Elmer spectrophotometer in KBr pellets.

General Procedure

To the warm solution (50—80 °C) of appropriate bisthioamide in 10% aqueous sodium hydroxyde a warm 20% aqueous solution of potassium ferricyanide (2—16 mol pro mol thioamide) was added dropwise with concomitant stirring. The reaction mixture was heated at 50—85 °C for 10—120 min and left to stand at room temperature for 24 hr. The precipitate, carefully rinsed with water and dried, was purified by dissolving into a warm conc. hydrochloric acid and dilution of the filtered solution with 10 volumes of water. Finally the product was recrystallized from an appropriate solvent.

* Kiprianov and Mihailenko⁷ found the same band at 813 cm^{-1} for the angular 2,7-dimethylbenzo[1,2-d:4,3-d']bisthiazole, and this ir band was absent in linear isomer.

** Bonnier, Gelus and Papoz¹³ prepared 1,4-bis-(2-benzothiazolil)benzene by other route in a 40% yield.

2,7-Diphenylbenzo[1,2-d : 3,4-d']bisthiazole

From 1.74 g (5 mmol) of *N,N'*-bis(thiobenzoyl)-*m*-phenylenediamine⁴ in 100 ml of 10% NaOH and 33 ml of 20% potassium ferricyanide at 50 °C. Yield 0.85 g, m. p. 197—99 °C. After repeated recrystallization from dioxane, crystals melting at 199—200 °C* were obtained.

Anal. C₂₀H₁₂N₂S₂ (344.3) calc'd.: C 69.77; H 3.49; N 8.15%.
found: C 69.56; H 3.55; N 8.31%.

Characteristic ir bands at 1473, 1468 and 972 cm⁻¹.

2,7-Diphenylbenzo[1,2-d : 4,3-d']bisthiazole

From 1.0 g (2.8 mmol) of *N,N'*-bis(thiobenzoyl)-*p*-phenylenediamine⁴ in 40 ml of 10% NaOH and 75 ml of 20% ferricyanide at 80 °C in 2 hr. Yield: 0.45 g; m. p. 200—205 °C. The product was further purified by column chromatography (>Merck alumina, 25 g, Φ 10 mm.) with benzene as a solvent. The analytically pure sample m. p. 235—236 °C** was obtained by recr. from benzene. The melting point was undepressed with an authentic sample⁶.

Anal. C₂₀H₁₂N₂S₂ (344.3) calc'd.: C 69.77; H 3.49; N 8.15%.
found: C 69.47; H 3.71; N 8.05%.

Characteristic ir bands at 1480 and 960 cm⁻¹.

2,7-Di-(2-furyl)benzo[1,2-d : 3,4-d']bisthiazole

From 1.64 g (5 mmol) of *N,N'*-di-(2-thiofuroyl)-*m*-phenylenediamine⁴ in 100 ml of 10% NaOH and 33 ml of 20% ferricyanide at 50 °C. Yield: 0.6 g, m. p. 208—11 °C. After recr. from glac. acetic acid, m. p. 215—17 °C.

Anal. C₁₆H₈N₂O₂S₂ (324.4) calc'd.: C 59.24; H 2.48; N 8.64%.
found: C 59.10; H 2.69; N 8.88%.

Characteristic ir bands at 1498 and 1010 cm⁻¹.

1,3-Bis-(2-benzothiazolil)benzene

From 1.64 g (5 mmol) of *N,N'*-di-(2-thiofuroyl)-*m*-phenylenediamine⁴ in 100 ml and 75 ml of 20% potassium ferricyanide. The mixture was kept for 10 min. at 80 °C and for 24 hr at room temp. Yield: 0.8 g, m. p. 140—145 °C. After recrystallization from ethanol m. p. 151—53 °C.

Anal. C₂₀H₁₂N₂S₂ (344.3) calc'd.: C 69.77; H 3.49; N 8.15%.
found: C 69.69; H 3.79; N 8.05%.

Characteristic ir bands at 1480 and 960 cm⁻¹.

1,4-Bis-(2-benzothiazolil)benzene

From 1.0 g (2.8 mmol) 1,4-benzenebis(carbothioanilide)⁴ in 40 ml of 10% NaOH with 75 ml of 20% ferricyanide heating for 2 hr at 80 °C. Yield: 0.85 g, m. p. 259—61 °C*** from chlorobenzene.

* Finzi and Grandolini⁸ reported m. p. 196 °C for the compound prepared by melting 2-phenyl-5-benzalamino-benzothiazole with sulphur.

** Bogert and Abrahamson⁶ reported m. p. 235 °C for the comp. prepared by melting 2-phenyl-6-benzalamino-benzothiazole with sulphur. Green and Perkin⁵ prepared the same comp. with m. p. 232—234 °C from potassium *p*-phenylenediamine-dithiosulphonate and benzaldehyde.

*** Bonnier, Gelus and Papoz¹³ stated m. p. 261 °C for the same compound prepared by a different route.

Anal.: C₂₀H₁₂N₂S₂ (344.3) calc'd.: C 69.77; H 3.49; N 8.15%.
found: C 69.56; H 3.70; N 7.97%.

Characteristic ir bands at 1480 and 962 cm⁻¹.

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SAŽETAK

Tioamidi XIV. Oksidativna ciklizacija nekih supstituiranih bistioamida

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Oksidativnom ciklizacijom po Jacobsonu² nekoliko *N,N'*-bis(tioaroil)fenilendiamina⁴ i benzenbis(karbotioanilida)⁴ prevedeno je u odgovarajuće disupstituirane benzobistiazole (slika 1.) odnosno bisbenzotiazolilbenzene (slika 2.). Produkti su karakterizirani ir spektrima i elementarnom analizom. Utvrđena je angularna struktura dobivenih benzobistiazola (A, slika 1.), a rezultati su uspoređeni sa sličnim podacima iz literature.

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