

DETERMINATION OF THE STRUCTURE OF THE OXIDATIVE CYCLIZATION PRODUCTS OF 4-METHOXY-N,N'-DITHIOAROYL-*m*-PHENYLENDIAMINES BY SPECTROSCOPIC METHODS

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ABSTRACT

4-Methoxy-N,N'-dithiobenzoyl-*m*-phenyldiamine (dithioamide) has been subjected to oxidation with potassium ferricyanide. By using the equimolar amounts of dithioamide and ferricyanide only a partially cyclized compound has been obtained, whereas when the great amount of ferricyanide is used the cyclization is completed. The structures of the oxidative products as well as of the parent compounds are studied by spectroscopic methods.

INTRODUCTION

Many thioamides derived from phenyldiamines or benzen dicarboxylic acids have been synthesized in our laboratories and their reactions and vibrational spectra studied (1-4). The structural determination of the oxidative cyclization products of 4-methoxy-N,N'-dithioaroyl-*m*-phenyldiamines by spectroscopic methods is the main concern of this paper.

EXPERIMENTAL

4-Methoxy-N,N'-diaroyl-*m*-phenyldiamines (diamides) were obtained by action of aryl chlorides on 4-methoxy-*m*-phenyldiamine and then by treating with P_2S_5 converted into 4-methoxy-N,N'-dithioaroyl-*m*-phenyldiamines (dithioamides). The oxidation of dithioamides with potassium ferricyanide in the molar ratio 1:1 gave only partially cyclized compounds, but when great amount of ferricyanide was used the complete cyclization was performed.***

The ir spectra were recorded as KBr pressed discs on a Perkin Elmer 580 spectrophotometer. The NMR spectra were taken on Thomson Pickard (TPV 60) Wilmad (WCV 60) spectrometer.

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Detailed description for the preparation of the investigated compounds will be published elsewhere.

RESULTS AND DISCUSSION

Each step in the reaction process has been followed spectroscopically. The structures of prepared diamides and dithioamides have been confirmed by elemental analyses and ir spectra. The most characteristic bands of diamides are found at around 1650 (Amide I), 1510 (Amide II) and 1330 cm^{-1} (Amide III) for amide group and at about 1250 (ν_{as} C-O) and 1050 cm^{-1} (ν_{s} C-O) for methoxy group; and of dithioamides at about 1550 ($\bar{\nu}_{\text{NH}}/\nu_{\text{CN}}$), 1350 ($\nu_{\text{CN}}/\bar{\nu}_{\text{NH}}$) and 980 cm^{-1} (mainly $\nu_{\text{C=S}}$) for thioamide group

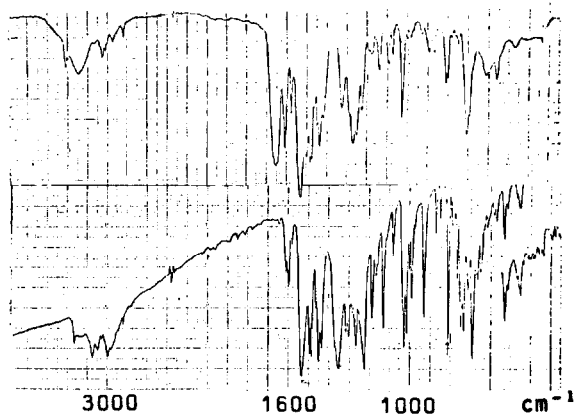


Fig.1. IR spectra of (a) 4-methoxy-N,N'-bisbenzoyl-*m*-phenyldiamine; (b) 4-methoxy-N,N'-bis(2-thiobenzoyl)-*m*-phenyldiamine

and at 1230 (ν_{as} C-O) and 1030 cm^{-1} (ν_{s} C-O) for methoxy group (Fig.1). When dithioamides are subjected to oxidation with potassium ferricyanide, using equimolar amount, only partially cyclized compounds are obtained. The structure of partially cyclized compound has been confirmed by its ir spectrum. In that spectrum, besides the bands of benzene rings, the characteristic bands at about 1570, 1420, 1220, 1105 and 920 cm^{-1} for benzothiazole ring, then at 1510, 1360 and 1020 cm^{-1} for thioamide group and at 1250 and 1020 cm^{-1} for methoxy group have been found (Fig.2). A question appears,

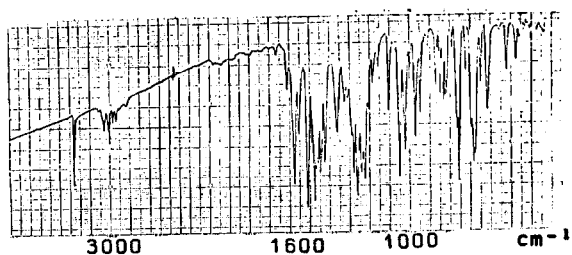


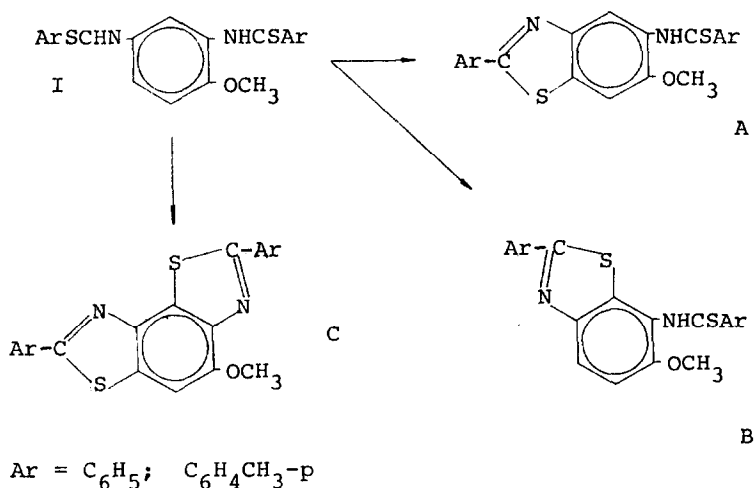
Fig.2. IR spectrum of 2-phenyl-5-thiobenzamido-6-methoxybenzothiazole

however, whether the thioamide group in *ortho*- or *para*-position takes part in the cyclization. For both dithioamide and diamide two ν_{NH} bands, sharp and broad ones, are found (Fig.1). For diamide sharp band appears at 3415 and broad at 3250 cm^{-1} while for dithioamide corresponding bands

are found (Fig.1). For diamide sharp band appears at 3415 and broad at 3250 cm^{-1} while for dithioamide corresponding bands

occur at 3360 and 3160 cm^{-1} . In the spectra of corresponding diamide and dithioamide, however, where there is no methoxy group, only one broad band appears in that region (at 3260 for *N,N'*-dibenzoyl-*m*-phenyldiamine and at 3190 cm^{-1} for *N,N'*-dithiobenzoyl-*m*-phenyldiamine). This indicates that the sharp band of both compounds might be due to the stretching vibration of the NH group in the *ortho*-position to the methoxy group, which probably owing to steric repulsion is very weak or not at all hydrogen bonded. In the spectrum of the partially cyclized compound (Fig.2) only single sharp band at 3360 cm^{-1} , occurs which certainly belongs to NH vibration of the thioamide group in the *ortho*-position to the methoxy group.

Two structures, however, could be attributed to the partially cyclized product. A question appears whether structure A or B is obtained.



If it were structure B then in its ir spectrum should appear strong or very strong band at about 810 cm^{-1} (out of plane deformation) which can be present only if two vicinal CH groups in the aromatic nucleus are present, as it is found in the spectrum of the parent dithioamide (Fig.1). Such band, however, is absent in the spectrum of the partially cyclized compound. This indicates that structure A is obtained.

A further proof that structure A is obtained is found in the NMR spectrum. The singlet of the proton between the methoxy group and

heterocyclic ring is found at δ 7.16 ppm, while the resonance of the proton between the two N atoms is observed at δ 9.69 ppm which unequivocally shows that partially cyclized compound has structure A

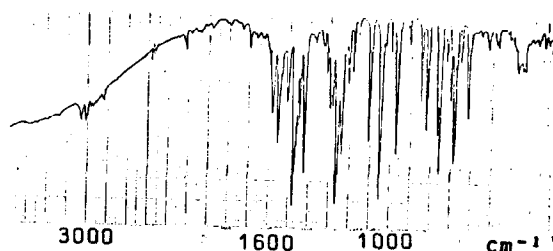


Fig.3. IR spectrum of 4-methoxy-2,7-diphenylbenzobis /1,2-d:3,4-d'/thiazole

(2-phenyl-5-thiobenzamido-6-methoxybenzothiazole).

The oxidative cyclization is completed when the great amount of potassium ferricyanide is used. In the ir spectrum there are no more bands of thioamide group.

In the NMR spectrum there is only a singlet for the proton between S and N

atoms, which indicates that the structure C is obtained (4-methoxy-2,7-diphenylbenzobis /1,2-d:3,4-d'/thiazole). (Fig.3)

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