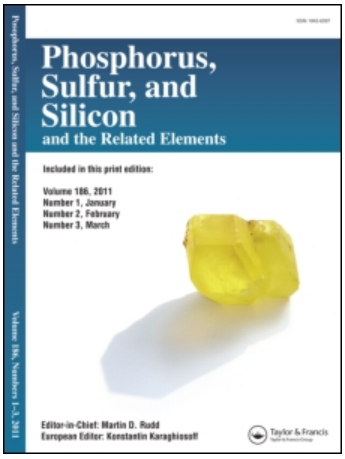

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REACTION OF 2-MERCAPTOBENZOTHIAZOLE WITH DIAMINES. SYNTHESIS OF O-AMINOBENZENETHIOL

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Heating of 2-mercaptobenzothiazole in an excess of hydrazine, ethylenediamine or propylenediamine leads to o-aminobenzenethiol. Moreover, with ethylenediamine, ethylenethiourea is isolated as secondary product. Successive addition-elimination steps rationalize these results.

Key words: 2-mercaptobenzothiazole; o-aminobenzenethiol; hydrazine; diamines.

INTRODUCTION

Ortho-aminobenzenethiol (OABT, **1**) is an important synthetic intermediate for pharmaceutical, rubber and dye industries. The synthesis of this relatively unstable compound (it is easily oxidized by air into its corresponding disulfide) has been the subject of several publications and patents.

The more usual but rather drastic preparative methods for the synthesis of compound **1** which start from benzothiazole or 2-substituted benzothiazoles are: fusion of 2-mercapto- or 2-aminobenzothiazole with sodium hydroxide, potassium hydroxide and sodium sulfide at 240–250°C,[1] treatment of benzothiazole by an aqueous solution of sodium hydroxide at refluxing temperature,[2] heating of 2-mercaptobenzothiazole in a concentrated solution of potassium hydroxyde at 210–220°C.[3] Other methods, often less selective, such as the reaction of hydrazine with benzothiazole[4] and desulfurization reactions of mercaptobenzothiazole[5,6] have also been described. OABT, contaminated with o-chloroaniline is obtained by the thiolation-reduction of o-chloronitrobenzene by sodium sulfide or hydrogenosulfide.[7]

Concerning the reaction of amines with 2-mercaptobenzothiazole **2**, the only result reported is the substitution of the mercapto group by an amino substituent. In particular with hydrazine (in refluxing ethanol), 2-hydrazinobenzothiazole **3** was isolated. No product resulting from the cleavage of the thiazole ring is mentioned.[8–10]

The results presented in this paper show that it is possible to prepare OABT by reaction of diamines, such as hydrazine, ethylenediamine and propylenediamine, with 2-mercaptobenzothiazole in conditions milder than "alkalin fusion." More-

over, with ethylenediamine, the CS group of **2** eliminated in this reaction is partially recovered as a by-product, ethylenethiourea, another useful industrial reagent.

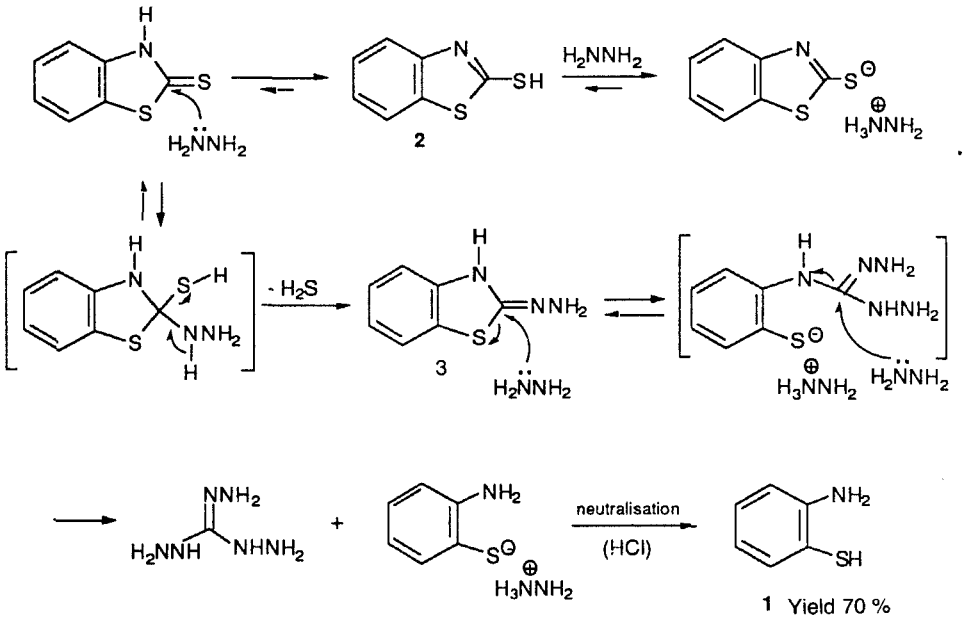
RESULTS AND DISCUSSION

2-Mercaptobenzothiazole **2** was heated under nitrogen at 105–110°C, in an excess of hydrazine for 76 h. The major product formed and isolated in 70% yield after distillation was OABT **1**. Evolution of H_2S was observed, with the disulfide of **1** and 2-hydrazinobenzothiazole **3** as by-products (Scheme 1). This result can be rationalized by three successive addition-elimination reactions involving three moles of hydrazine per mole of **2**. The formation of a guanidyl type compound $(H_2NNH)_2C{=}NNH_2$[11] is suggested by ^{13}C NMR analysis ($\delta_{C=N}$ [D_2O]: 162.8 ppm).

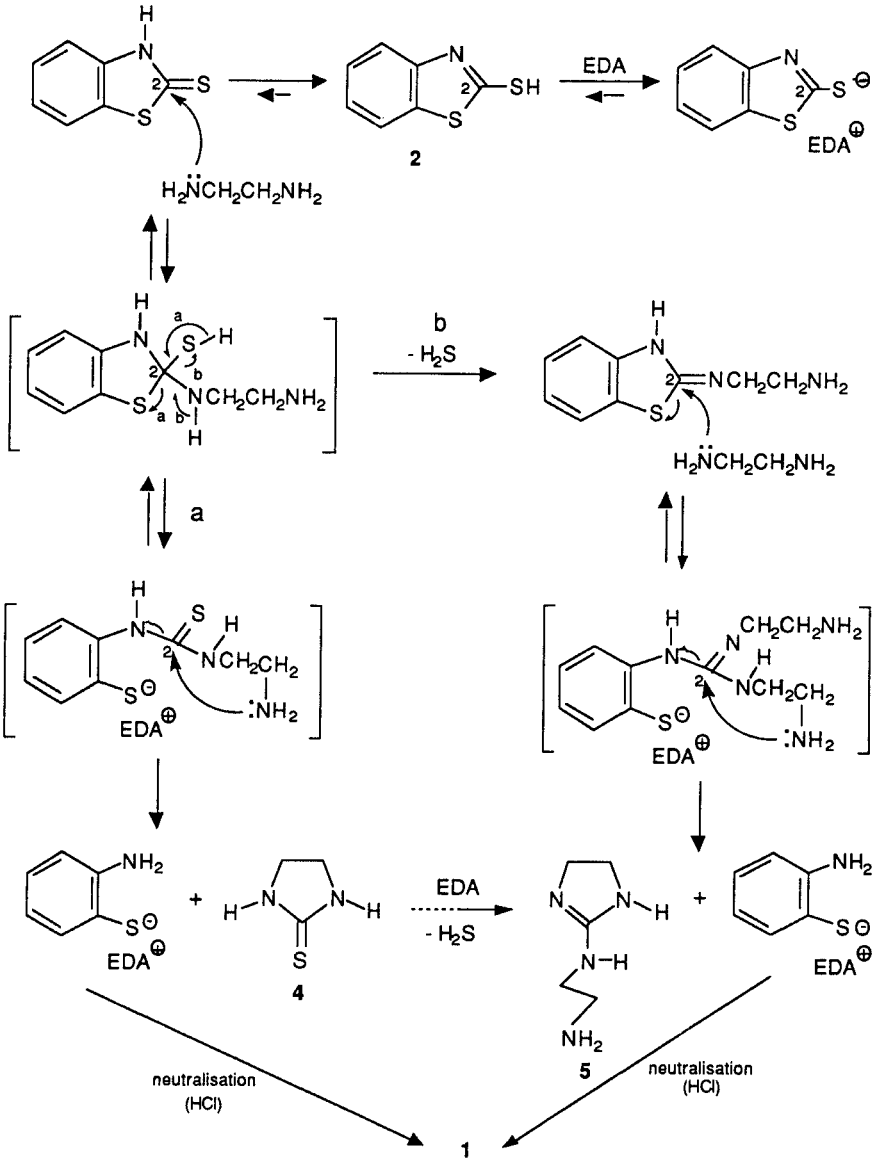
The reaction of excess ethylenediamine with **2**, was performed in a sealed tube at 150°C for 20 h. After cooling, water was added and crystalline and fairly pure ethylenethiourea **4** was readily separated from the reaction mixture in 56% yield (Scheme 2). Acidification of the mixture and distillation, led to the isolation of OABT in 80% yield and of its disulfide (10%). Complete evaporation of the aqueous phase gave a mixture of **4** and the guanidyl type compound **5** (yields: ca. 20% for each compound).

The same kind of reaction was observed with 2-mercapto-6-methylbenzothiazole. In this case, 2-amino-5-methylbenzenethiol[12] was isolated in 70% yield.

The proposed rationalization for the formation of these products is presented in Scheme 2. As usually observed with hydrazine and other amines, the first step must be the attack of ethylenediamine at C_2 of mercaptobenzothiazole. Two paths (a) and (b) are then possible. Path (a) begins by the cleavage of the cyclic C_2—S bond



SCHEME 1



SCHEME 2

followed by an intramolecular cyclisation and the cleavage of the C_2—N bond. This route which leads to ethylenethiourea is probably favoured, and the formation of the guanidyl compound **5** can result from the slow reaction[13] between **4** and ethylenediamine. Path (b), which cannot be excluded, consists of the elimination of H_2S (similarly to the reaction observed with hydrazine), addition of a second molecule of amine to the C_2=N bond and cleavage of the C_2—S bond. Then an intramolecular cyclisation with cleavage of the C_2—N bond leads to OABT **1** and to **5**.

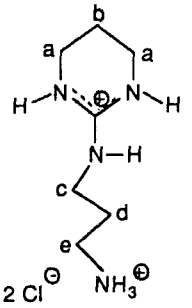
Under the same experimental conditions, propylenediamine reacted with mercaptobenzothiazole to give OABT in similar yield. However, no propylenethiourea was isolated and, after isolation of OABT, we were not able to separate the constituents of the viscous brown residue resulting from evaporation of the aqueous phase. From the NMR spectra of this crude oil, it seems to contain a large amount of a guanidyl type compound.

EXPERIMENTAL

Reaction of 2-mercaptobenzothiazole with hydrazine. Hydrazine monohydrate (150 mL, 3.09 mol) and 2-mercaptobenzothiazole (30 g, 0.18 mol) were stirred at 105–110°C, under a N_2 atmosphere, for 76 h. Evolution of H_2S was observed during the first 25 hours. After cooling to room temperature, the resulting white crystals of 2-hydrazinobenzothiazole (6.0 g, yield = 20%, F = 199–200°C[10]) were filtered off and dried. Evaporation of the filtrate under reduced pressure yielded hydrazine (50 mL) and a brown oily residue which was diluted with water (50 mL) and then carefully neutralized with 6N HCl at 0–5°C under nitrogen. Extraction with CH_2Cl_2, followed by distillation, gave OABT as a colourless liquid (16 g, yield = 70%, Eb_{10} = 110°C[7]).

Reaction of 2-mercaptobenzothiazole with ethylenediamine. Ethylenediamine (960 mL, 14.34 mol) and 2-mercaptobenzothiazole (800 g, 4.78 mol) were heated at 150°C, with stirring, for 20 h in an autoclave reactor. After cooling, the reaction mixture was poured into water (1000 mL) under N_2. Ethylenethiourea was filtered off, washed with cold water and dried (m = 273 g, yield = 56%, F = 197–198°C). The dark brown filtrate was then added dropwise to a 12N solution of HCl (1600 mL, 19.20 mol) and cooled with an ice bath. The resulting neutralised mixture was extracted twice with 500 mL of CH_2Cl_2. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. Distillation of the resulting oil gave OABT (479 g, yield = 80%). The disulfide of OABT was obtained in 10% yield by crystallization of the distillation residue. Evaporation of the aqueous layer led to a solid mixture which was shaken with ethanol. The insoluble ethylenediamine hydrochloride was filtered off and the ethanol was then evaporated. ^1H and ^{13}C NMR spectra of the resulting residue show it to be a 1/1 mixture of ethylenethiourea and (2-aminoethylimino)imidazolidine dihydrochloride, which were not separated. The latter compound was characterized by: ^1H NMR (D_2O-D_6DMSO) δ(ppm): 3.00 and 3.45 (2t, J = 6 Hz, 2 × 2H); 3.53 (s, 4H); 4.00 (bs). ^{13}C NMR (D_2O-D_6 DMSO) δ(ppm): 38.2; 39.8; 42.5; 159.0.

Reaction of 2-mercaptobenzothiazole with propylenediamine. Reaction between 2-mercaptobenzothiazole and propylenediamine, under the same experimental conditions, gave OABT (yield 70%). ^1H and ^{13}C NMR spectra of the resulting residue from the aqueous layer, show it to be the 2-(3-aminopropylimino)hexahydropyrimidine dihydrochloride.



RMN ^1H (D_2O) δ (ppm) : NH and $NH_3^{\oplus}$ (D_2O exchange) : 4,80 (broad singulet)
CH_2 (b and d) : 1,90 (multiplet, 4H)
CH_2 (a, c and e) : 3,20 (multiplet, 8H)

RMN ^{13}C (D_2O) δ (ppm) : CH_2 (b and d) : 19,7 ; 26,5
CH_2 (a, c and e) : 37,3 ; 37,9 ; 38,5
C=N : 153,3

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