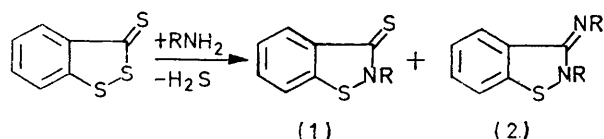


Reaction of 1,2-Benzodithiole-3-thione with Ethylene- and Trimethylene-diamines

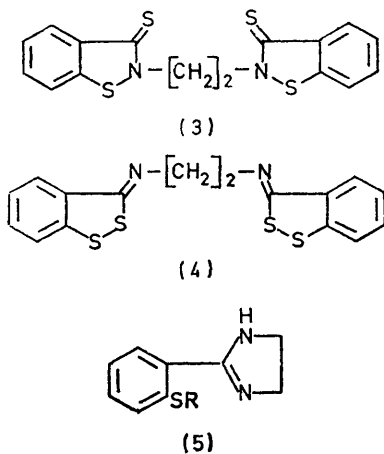
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In contrast to its reactions with monoamines, in which only one of its sulphur atoms is displaced, 1,2-benzodithiole-3-thione can react with ethylene- and trimethylene-diamines with displacement of two sulphur atoms; the products are probably *o*-mercaptophenyl-substituted nitrogen heterocycles.

BÖSHAGEN and his co-workers¹ found that aliphatic amines react with 1,2-benzodithiole-3-thione to give two series of interconvertible isomeric products: 1,2-benzoisothiazoline-3-thiones (1) and 1,2-benzodithiol-3-imines (2). No reports of compounds from reaction

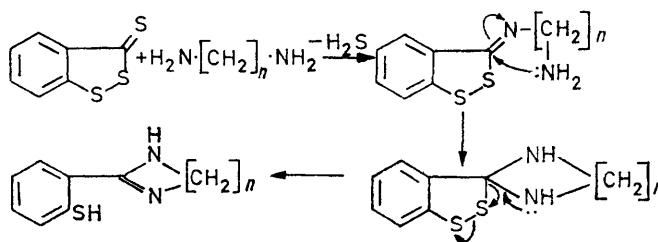


of two molecules of amine with one of the thione have been seen, so it was therefore expected that ethylenediamine would react with two molecules of thione to give the bis-compound (3), or its isomer (4). In fact, unchanged thione was recovered from the reaction and, together with a little of the expected bis-compound, a yellow compound, $C_9H_{10}N_2S$, was also isolated, evidently formed from one molecule of diamine and one molecule of thione, with loss of one molecule of hydrogen sulphide and one atom of sulphur.



The mass spectrum of the compound suggested the absence of C=S and the possible presence of SH. The n.m.r. spectrum was not helpful; different types of non-aromatic protons could not be distinguished. The i.r. spectrum indicated an NH group but there was no prominent band attributable to SH. The compound was soluble in hot water, the yellow solution instantaneously becoming colourless on acidification and almost colourless on basification. Structure (5; R =

H) is therefore tentatively suggested rather than the corresponding tricyclic benzisothiazoline structure originally favoured. The bicyclic structure was suggested by Dr. D. Leaver,² who postulates the illustrated mode of formation of this compound (see Scheme) and of a homologue, $C_{10}H_{12}N_2S$, with similar properties (except for differences in the i.r. spectrum, which include a prominent band attributed to SH) which has been made from trimethylenediamine. Both homologues react additively with one molecular proportion of ethyl iodide. There is no band attributable to SH



SCHEME

in the i.r. spectrum of either product. The simplest interpretation is that *S*-alkylation has occurred in each case, so that the products are bicyclic, *i.e.* the hydriodide of compound (5; R = Et) and the corresponding tetrahydropyrimidine.

EXPERIMENTAL

Reaction of 1,2-Benzodithiole-3-thione with Ethylenediamine.—A mixture of the thione (9.2 g), ethylenediamine (1.5 g), and ethanol (60 ml) was boiled for 4 h, then cooled, and the solid (6.4 g) was filtered off and slurried with warm benzene (50 ml) for 10 min to remove unchanged thione. The undissolved material was recrystallised from ethanol to give crude 2-mercaptophenyl- Δ^2 -imidazoline (5; R = H) (1.05 g). Recrystallisation from dimethylformamide gave bronze-yellow plates, m.p. 244° (Found: C, 61.0; H, 5.6; N, 15.9; S, 17.0. $C_9H_{10}N_2S$ requires C, 60.7; H, 5.6; N, 15.7; S, 18.0%), ν_{\max} (Nujol) 3200–3000, 1590, 1565, 1415, 1286, 1100, 1058, 725, and 664 cm^{-1} , m/e 178 (M^+). A little ethanol-insoluble material was recrystallised from dimethylformamide to give NN'-bis-(1,2-benzodithiol-3-ylidene)ethylenediamine (4) as bronze-yellow needles (0.19 g), m.p. 233–234° (Found: C, 53.3; H, 3.5; N, 7.9; S, 34.9. $C_{16}H_{12}N_2S_2$ requires C, 53.3; H, 3.3; N, 7.8; S, 35.6%), ν_{\max} (Nujol) 2865, 1605, 1440, 1292, 1012, 758, and 715 cm^{-1} .

Repetition of the experiment with twice the amount of

¹ H. Böshagen, H. Feltkamp, and W. Geiger, *Ber.*, 1967, **100**, 2435; A. Baruffini, P. Borgna, and L. Amoretti, *Il Farmaco*, 1968, **23**, 574.

² D. Leaver, Chemistry Department, University of Edinburgh, personal communication.

ethylenediamine gave a high yield (6.9 g) of compound (5). Use of a large excess of boiling diamine in the absence of solvent gave an intractable, brown gum.

Reaction of 1,2-Benzodithiole-3-thione with Trimethylenediamine.—A solution of the thione (4.55 g) in benzene (40 ml) was treated with trimethylenediamine (1.03 ml), added in five portions on successive days. After two more days, the benzene solution was decanted from a brown gum and evaporated. Recrystallisation of the residue from ethanol gave yellow prisms (0.56 g), m.p. 210–220° of the 1,4,5,6-tetrahydro-2-o-mercaptophenylpyrimidine (Found: C, 62.2; H, 6.3; N, 14.6; S, 16.7. $C_{10}H_{12}N_2S$ requires C, 62.5; H, 6.3; N, 14.6; S, 16.7%), ν_{\max} (KBr) 3150, 3045, 2610, 1600, 1320, 1044, and 737 cm^{-1} , m/e 192 (M^+).

Reaction of the Mercapto-compounds with Ethyl Iodide.—The imidazoline (0.5 g), partly dissolved in boiling ethanol

(10 ml), was treated with ethyl iodide (1 ml). The rest of the starting material rapidly dissolved. After 3 min boiling, the solution was concentrated to yield, on cooling, cream plates (0.48 g), m.p. 185–189° of the *hydriodide* of 2-o-ethylthiophenyl- Δ^2 -imidazoline (Found: C, 39.5; H, 4.7; N, 8.4. $C_{11}H_{15}IN_2S$ requires C, 39.5; H, 4.5; N, 8.4%), ν_{\max} 3000, 1605, 1580, 1475, 1360, 1280, 1030, 988, 763, 730, and 650 cm^{-1} . Similarly, the tetrahydropyrimidine (0.17 g) yielded the *hydriodide* of 2-o-ethylthiophenyl-1,4,5,6-tetrahydropyrimidine (0.08 g), m.p. 185° (Found: C, 41.2; H, 4.9; N, 7.9. $C_{12}H_{17}IN_2S$ requires C, 41.1; H, 4.9; N, 8.0%), ν_{\max} 3120, 3000, 1630, 1610, 1425, 1315, 1200, 970, 766, and 732 cm^{-1} .

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