Reactions of Heterocycles with Thiophosgene. Part 8.[1] Reactions of *NN'*-Bis-(2-isothiocyanatophenyl)-*NN'*-diformyl-1,2-diaminoethane

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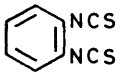
Reactions of *NN'*-bis-(2-isothiocyanatophenyl)-*NN'*-diformyl-1,2-diaminoethane (4), prepared by fission of 1,2-bis(benzimidazol-1-yl)ethane (3) with thiophosgene and base, are described with a variety of nucleophiles. Aliphatic diamines give rise to 16—20-membered rings. Some reactions of the 16-ring compound (8) are also described.

EARLIER studies of the action of thiophosgene and base on heterocycles have led to a large range of intermediates suitable for synthesis of novel heterocycles. Thus benzimidazole [2] affords *o*-phenylene bisisothiocyanate (1) and 1-substituted benzimidazoles [1] give rise to compounds of type (2).



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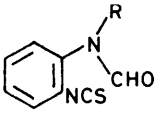

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RESULTS AND DISCUSSION

1,2-Bis(benzimidazol-1-yl)ethane (3) has been reported in the literature,[3,4] being obtained in low or unrecorded yields. We found that, with the aid of a phase-transfer catalyst,[5] tetrabutylammonium bromide, the desired product was isolated in good yield (50—60%). Thiophosgene and 1,2-bis(benzimidazol-1-yl)ethane in the presence of base gave the expected bisisothiocyanate (4). The bisisothiocyanate (4) formed the expected thioureas (5) when treated with primary or secondary amines (Table 1). The nature of the products from the bisisothiocyanate (4) with bidentate nucleophiles was unexpected. β-Aminoethanol gave the bis-thiourea (6), and similar bis-products (Table 1) were formed from *o*- and *p*-phenylenediamines and also from hydrazine (7).

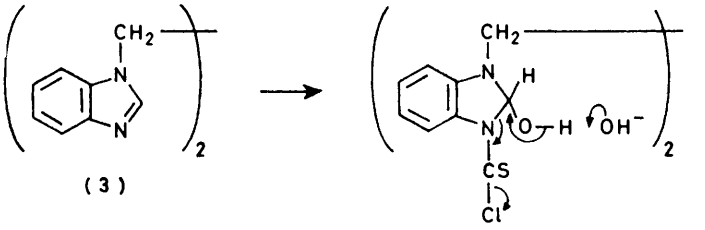
Ethylenediamine, however, yielded the 16-membered ring compound (8; $n = 2$).

This was found to be the normal addition of aliphatic diamines, wherein large rings were formed from the bisisothiocyanate. Thus with 1,3-diaminopropane, 1,4-diaminobutane, and 1,6-diaminohexane, 17-, 18-, and 20-membered rings, respectively, were obtained (Table 2).

The large ring compounds were hygroscopic, and drying at 40 °C *in vacuo* gave solids which analysed for a molecule containing half a molecule of water. It was found that in some cases, drying at 100 °C *in vacuo* for at least 1 d, it was possible to obtain the anhydrous compound.

Alkylation of ring compound (9) with methyl iodide in dimethyl sulphoxide (DMSO) gave the di-*S*-methyl derivative (10). Nucleophilic displacement of one of the *S*-methyl groups with morpholine led to (11).

The large rings could be compared to crown com-



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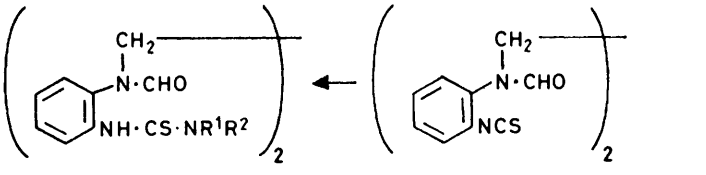

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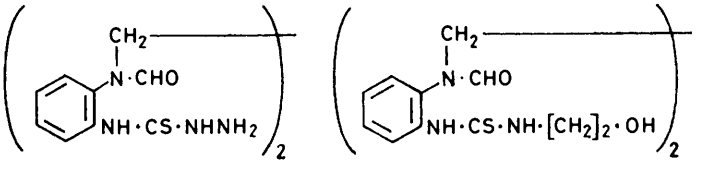

(7) (6)

pounds, but we found the thioureas to be highly insoluble in common solvents. They were soluble in DMSO, but did not increase the solubility of various metal halides in this solvent. No reaction was observed between the bisisothiocyanate (4) and urea, thiourea, semicarbazide, or thiosemicarbazide.

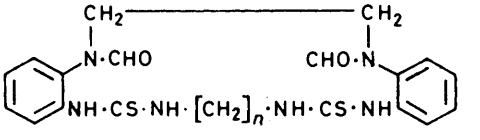

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TABLE 1

NN'-Bis-[2-(3-thioureido)phenyl]-*NN'*-diformyl-2,2-diaminoethanes (5)

NR^1R^2	M.p. (°C)	Crystallisation solvent	Yield (%)	Formula	Found (%) [Required]	^{1}H N.m.r. (δ) in [$(CD_3)_2SO$]
Morpholino	208	EtOH	91	$C_{26}H_{32}N_6O_4S_2$	C, 56.2; H, 5.8; N, 14.7; S, 11.4 [C, 56.1; H, 5.8; N, 15.1; S, 11.5]	3.0br (2 H, NH exch.), 3.2br (8 H, s, NCH_2), 3.8br (8 H, OCH_2), 4.0 (4 H, s, NCH_2CH_2-N), 7.2—7.4 (8 H, m, aromatic), 8.0 (2 H, s, CHO)
NH_2 *	150	EtOH	60	$C_{18}H_{20}N_6O_2S_2$	C, 51.5; H, 4.9; N, 19.8; S, 14.9	3.0br (2 H, NH exch.), 3.4br (4 H, NH_2, exch.), 4.0 (4 H, s, NCH_2CH_2N), 7.1—7.6 (8 H, m, aromatic), 8.2 (2 H, s, CHO)
	185		30		C, 51.6; H, 4.8; N, 20.0; S, 15.3 [C, 51.9; H, 4.8; N, 20.2; S, 15.4]	
NHPh	145	DMSO–water	78	$C_{32}H_{28}N_6O_2S_2$	C, 63.3; H, 5.0; N, 14.9; S, 11.3 [C, 63.4; H, 4.9; N, 14.8; S, 11.3]	3.5br (4 H, NH, exch.), 4.0 (4 H, s, NCH_2CH_2N), 7.3—7.8 (18 H, m, aromatic), 8.4 (2 H, s, CHO)
$NHMe_2$	209	DMSO–water	89	$C_{22}H_{30}N_8O_2S_2$	C, 52.7; H, 6.0; N, 21.9; S, 12.8 [C, 52.6; H, 6.0; N, 22.3; S, 12.8]	2.2br (2 H, NH, exch.), 2.6br (2 H, NH, exch.), 2.4 (12 H, s, Me), 4.8 (4 H, s, NCH_2-CH_2N), 7.2—7.7 (8 H, m, aromatic), 8.2 (2 H, s, CHO)
NPr^i_2	145	DMSO–water	89	$C_{30}H_{44}N_6O_2S_2$	C, 61.5; H, 7.7; N, 14.5; S, 10.9 [C, 61.6; H, 7.5; N, 14.4; S, 10.9]	1.3 (12 H, s, Me), 1.4 (12 H, s, Me), 2.5 (4 H, m, CH), 3.4br (2 H, NH, exch.), 3.9 (4 H, s, NCH_2CH_2N), 7.4 (8 H, m, aromatic), 8.3 (2 H, s, CHO)
$NH[CH_2]_2OH$	163	EtOH	84	$C_{22}H_{28}N_6O_4S_2$	C, 52.9; H, 5.7; N, 17.0; S, 12.6 [C, 52.4; H, 5.5; N, 16.7; S, 12.7]	3.0br (2 H, OH, exch.), 3.3br (4 H, NH, exch.), 4.0 (4 H, s, NCH_2CH_2N), 7.2–7.6 (8 H, m, aromatic), 8.4 (2 H, s, CHO)
$NHNH_2$	170	DMSO–water	90	$C_{18}H_{22}N_{12}O_2S_2$	C, 48.5; H, 4.5; N, 25.2; S, 14.2 [C, 48.7; H, 4.5; N, 25.2; S, 14.4]	2.2br (2 H, NH, exch.), 2.6br (2 H, NH, exch.), 4.0br (4 H, NH, exch.), 4.1 (4 H, s, NCH_2CH_2N), 7.2—7.8 (8 H, m, aromatic), 8.1 (2 H, s, CHO)
NHC_6H_4OH-*o*	169	DMSO–water	92	$C_{30}H_{28}N_6O_4S_2$	C, 59.7; H, 4.6; N, 14.0; S, 10.7 [C, 60.0; H, 4.7; N, 14.0; S, 10.7]	2.6br (2 H, NH, exch.), 3.0br (2 H, NH, exch.), 3.4br (2 H, OH, exch.), 4.4 (4 H, s, NCH_2CH_2N), 7.1—7.6 (16 H, m, aromatic), 8.2 (2 H, s, CHO)
$NHC_6H_4NH_2$-*o*	160	DMSO–water	83	$C_{30}H_{30}N_8O_2S_2$	C, 59.8; H, 5.0; N, 18.5; S, 10.9 [C, 60.2; H, 5.0; N, 18.7; S, 10.7]	2.4br (2 H, NH, exch.), 2.6br (2 H, NH, exch.), 3.5br (4 H, NH_2, exch.), 3.9 (4 H, s, NCH_2CH_2N), 6.5—7.7 (16 H, m, aromatic), 8.2 (2 H, s, CHO)
$NHC_6H_4NH_2$-*p*	164	DMSO–water	50	$C_{30}H_{30}N_8O_2S_2$	C, 60.3; H, 5.0; N, 18.6; S, 11.1 [C, 60.2; H, 5.0; N, 18.7; S, 10.7]	2.2br (2 H, NH, exch.), 2.6br (2 H, NH, exch.), 3.4br (4 H, NH_2, exch.), 3.9 (4 H, s, NCH_2CH_2N), 7.2—7.6 (16 H, m, aromatic), 8.2 (2 H, s, CHO)

I.r.: all compounds display similar bands at 3 100 (NH) and 1 660 (CO) cm^{-1}.

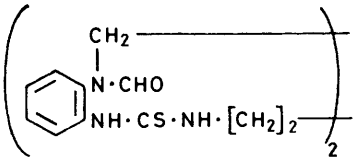
* The ammonia adduct exists in two distinct physical forms, one a crystalline solid insoluble in ethanol, and the other an amorphous powder soluble in ethanol. Their solid state i.r. spectra and their m.p.s are different, but their n.m.r. spectra are similar.

When refluxed in 4N hydrochloric acid, or methanolic hydrochloric acid, the bis-isothiocyanate (4) cyclised to 1,2-bis-(2-thioxobenzimidazolyl)ethane (12).

Reaction with alkyl halides in DMSO gave the corresponding benzimidazole derivatives (13), (Table 3).

We failed to obtain any nucleophilic displacement of the alkylthio-group in (13; R = Me) with morpholine or hydrazine. An attempt was made to enhance the nucleophilicity by oxidation of 1,2-bis-(2-methylthiobenzimidazol-1-yl)ethane with potassium permanganate to the corresponding sulphone (14). Nucleophiles were found to be inert to this compound also.

Treatment of the 1,2-bis-(2-thioxobenzimidazol-1-yl)-



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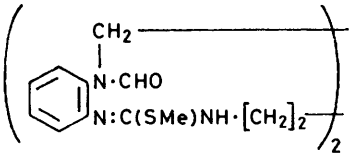

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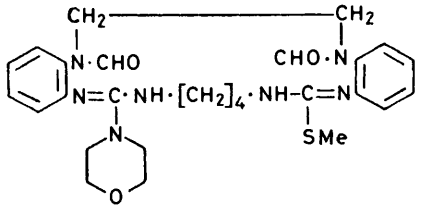
ethane (12) with 1,2-dibromoethane in propan-2-ol–sodium hydride gave the ring compound (15).



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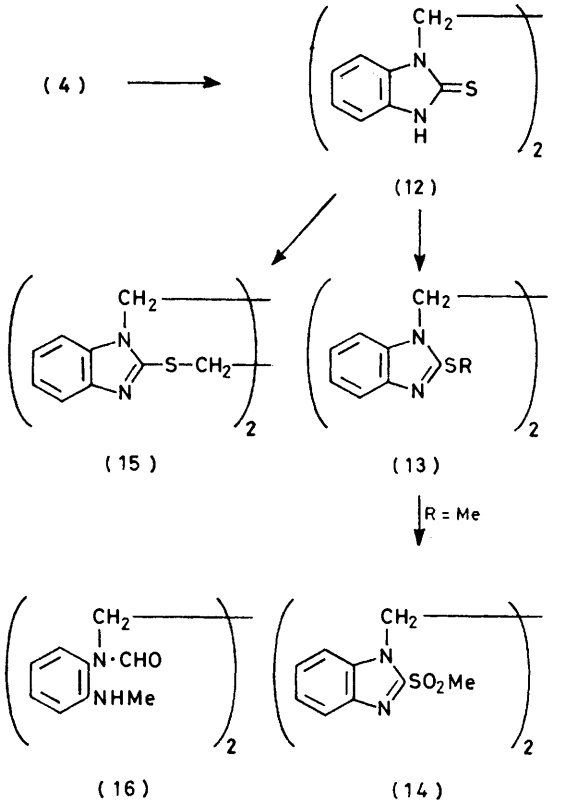
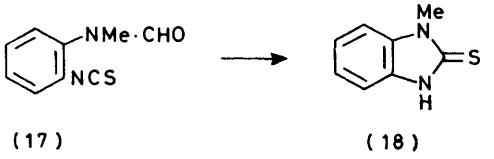
Finally, reduction of the bisisothiocyanate (4) with lithium aluminium hydride in THF gave the thione (12)



(15) (13) (16) (14)

and not the expected secondary amine (16). In a similar manner we found that the isothiocyanate (17) [1] gave the thione (18).[6]



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EXPERIMENTAL

1,2-*Bis*(*benzimidazol*-1-*yl*)*ethane* (3).—Benzimidazole (2.36 g, 0.02 mol), sodium hydroxide (10 g), and water (20 ml) were stirred until a homogeneous solution was obtained. Tetrabutylammonium bromide (0.4 g) was added followed by ethylene dibromide (1.9 g, 0.01 mol) (at 50 °C), and the mixture was allowed to cool to room temperature. After 2 h the product was collected, and recrystallisation from water gave the *benzimidazole* (1.4 g, 54%), m.p. 226 °C (lit.,[4] 227 °C); *m/e* 262 (M^+) (Found: C, 72.8; H, 5.4; N, 21.3; Calc. for $C_{16}H_{14}N_4$: C, 73.3; H, 5.3; N, 21.4%).

NN′-*Bis*(2-*isothiocyanatophenyl*)-NN′-*diformyl*-1,2-*diaminoethane* (4).—Thiophosgene (1.6 ml, 0.02 mol) in acetone (20 ml) was added dropwise to a stirred mixture of 1,2-bis-(*N*-benzimidazolyl)ethane (2.62 g, 0.01 mol) in acetone (100 ml) and water (50 ml) and barium carbonate (6 g). After stirring overnight at laboratory temperature the mixture was filtered, washed with acetone, and excess of reagent removed. Purification of the residue by column chromatography [ethyl acetate–light petroleum (60—80 °C)] and recrystallisation from ethyl acetate–light petroleum (60—80 °C) gave the *isothiocyanate* (2.6 g, 72%) as yellow crystals, m.p. 124 °C (Found: C, 57.0; H, 4.0; N, 14.3; S, 16.3. $C_{18}H_{14}N_4S_2O_2$ requires C, 56.6; H, 3.7; N, 14.7; S, 16.7%); *m/e* 382 (M^+); δ ($CDCl_3$) 4.6 (4 H, s, CH_2CH_2), 8.7 (8 H, m, aromatic), and 9.6 (2 H, s, 2 × CHO).

Reactions of Amines with the Bisisothiocyanate (4): *General Procedure*.—The amine (0.002 mol) in acetonitrile (5 ml) was added dropwise during 10 min to the bisisothiocyanate (4) (0.001 mol) in acetonitrile (20 ml) with stirring at room temperature. After 3 h the product was collected and recrystallised from ethanol or aqueous DMSO (Table 1).

Reactions of Diamines with the Bisisothiocyanate (4): *General Procedure*.—The diamine (0.001 mol) in acetonitrile (10 ml) was added dropwise during 30 min to the bisisothiocyanate (4) (0.001 mol) in acetonitrile (60 ml) with stirring at room temperature. After 3 h the product was collected and recrystallised from aqueous DMSO (Tables 1 and 2).

7,8,9,10,11,12,19,20,21,22-*Decahydro*-19,22-*diformyl*-6,13-*bis*(*methylthio*)-5,7,12,14,19,22-*hexa-azadibenzo*[d,j]*cyclo-octadecene* (10).—Methyl iodide (0.6 g, 0.004 mol) was added to a solution of 5,7,8,9,10,11,12,14,19,20,21,22-dodecahydro-19-22-diformyl-5,7,12,14,19,22-hexa-azadibenzo[*d,j*]-cyclo-octadecene-6,13-dithione (0.45 g, 0.001 mol) in DMSO (10 ml). After stirring for 3 h, 20% sodium hydroxide (10 ml) was added, and the product was collected and recrystallised from aqueous DMSO to give the *dimethylthio-derivative* (0.35 g, 75%) as cream crystals, m.p. 186 °C (Found: C, 57.0; H, 6.0; N, 17.0. $C_{24}H_{30}N_6S_2O_2$ requires C, 57.8; H, 6.1; N, 16.8%); δ [$(CH_3)_2SO$] 1.6 [4 H, br, CH_2CH_2], 2.3 (6 H, s, 2 × Me), 3.5 (4 H, br, 2 × CH_2NH), 4.0 (4 H, s, NCH_2CH_2N), 4.3 (2 H, br, NH, exchangeable), 7.0—7.6 (8 H, m, aromatic), and 8.4 (2 H, s, 2 × CHO).

7,8,9,10,11,12,19,20,21,22-*Decahydro*-19,22-*diformyl*-6-*methylthio*-13-*morpholino*-5,7,12,14,19,22-*hexa-azadibenzo*-[d,j]*cyclo-octadecene* (11).—Morpholine (0.18 g, 0.002 mol) was added with stirring to the dimethylthio-compound (10) (0.5 g, 0.001 mol) in DMSO (20 ml) at 80 °C. After 16 h the mixture was poured into water (100 ml), extracted with chloroform (3 × 25 ml), and washed with water (3 × 25 ml). After drying ($MgSO_4$) and evaporation of solvent the residue crystallised from chloroform–light petroleum (60—80 °C) to give the *mono-morpholino-derivative* (0.45 g, 86%) as cream crystals, m.p. 138 °C (Found: C, 60.5; H, 6.8; N, 18.7. $C_{27}H_{35}N_7S_2O_3$ requires C, 60.3; H, 6.6; N, 18.3%); δ ($CDCl_3$) 1.5 (4 H, br, CH_2), 2.3 (3 H, s, SMe), 3.2 (4 H, br, morpholine NCH_2), 3.4 (4 H, br, 2 × $HNCH_2$), 3.7 (4 H, br, morpholine OCH_2), 4.0 (4 H, s, NCH_2CH_2N), 4.2 (2 H, br, NH exchangeable), 7.0—7.6 (8 H, m, aromatic), and 8.4 (2 H, s, CHO).

1,2-*Bis*-(2-*thioxobenzimidazol*-1-*yl*)*ethane* (12).—The bisisothiocyanate (4) (0.382 g, 0.001 mol) was heated under

TABLE 2

17,20-Diformyl-5,7,8,9,10,12,17,18,19,20-decahydro-5,7,10,12,17,20-hexa-azadibenzo[*d*,*j*]cyclohexadecene-6,11-dithione (8; $n = 2$) and related compounds

n	M.p. (°C)	Yield (%)	Formula	Found (%) [Required]	^{1}H N.m.r. (δ) in [$(CD_3)_2SO$]
2	172	79	$C_{20}H_{22}N_6O_2S_2 \cdot 0.5H_2O$	C, 53.7; H, 5.1; N, 18.6; S, 14.1 [C, 53.2; H, 5.1; N, 18.6; S, 14.1]	2.1br (2 H, NH, exch.), 2.5br (2 H, NH, exch.), 3.6 (4 H, s, $NHCH_2CH_2NH$), 3.9 (4 H, s, NCH_2CH_2N), 7.1—7.6 (8 H, m, aromatic), 8.1 (2 H, s, CHO)
3	171	65	$C_{21}H_{24}N_6O_2S_2 \cdot 0.5H_2O$	C, 54.0; H, 5.4; N, 18.0; S, 13.6 [C, 54.2; H, 5.4; N, 18.1; S, 13.8]	1.3br (2 H, CH_2), 2.0br (2 H, NH, exch.), 2.4br (2 H, NH, exch.), 3.3br (4 H, CH_2), 3.8 (4 H, s, NCH_2CH_2N), 7.2—7.6 (8 H, m, aromatic), 8.2 (2 H, s, CHO)
4	180	84	$C_{22}H_{26}N_6O_2S_2 \cdot 0.5H_2O$	C, 55.0; H, 5.6; N, 17.6; S, 13.3 [C, 55.1; H, 5.6; N, 17.5; S, 13.4]	1.6br (4 H, CH_2), 2.3br (2 H, NH, exch.), 2.6br (2 H, NH, exch.), 3.6br (4 H, CH_2), 3.9 (4 H, s, NCH_2CH_2N), 7.3—7.7 (8 H, m, aromatic), 8.2 (2 H, s, CHO)
6	158	60	$C_{24}H_{30}N_6O_2S_2 \cdot 0.5H_2O$	C, 56.6; H, 6.0; N, 16.4; S, 12.9 [C, 56.8; H, 6.1; N, 16.5; S, 12.6]	1.6br (8 H, CH_2), 2.3br (2 H, NH, exch), 2.6br (2 H, NH, exch.), 3.6br (4 H, CH_2), 3.9 (4 H, s, $NCHCH_2N$), 7.3—7.8 (8 H, m, aromatic), 8.2 (2 H, s, CHO)
(CH_2·CHMe)	183	87	$C_{21}H_{24}N_6O_2S_2 \cdot 0.5H_2O$	C, 53.9; H, 5.3; N, 17.9; S, 13.8 [C, 54.2; H, 5.4; N, 18.1; S, 13.8]	1.4 (3 H, s, Me), 2.0br (2 H, NH, exch.), 2.4br (2 H, NH, exch.), 3.7 (3 H, m, CH), 3.9 (4 H, s, NCH_2CH_2N), 7.2—7.6 (8 H, m, aromatic), 8.1 (2 H, s, CHO)
($CH_2CHOHCH_2$)	167	78	$C_{21}H_{24}N_6O_3S_2 \cdot 0.5H_2O$	C, 52.2; H, 5.3; N, 17.3; S, 13.1 [C, 52.3; H, 5.2; N, 17.5; S, 13.3]	2.1br (2 H, NH, exch.), 2.6br (2 H, NH, exch.), 3.4 (5 H, m, CH), 3.8 (4 H, s, NCH_2CH_2N), 7.1—7.6 (8 H, m, aromatic), 8.1 (2 H, s, CHO), 9.2br (1 H, OH, exch.)

TABLE 3

1,2-Bis(2-alkylthiobenzimidazol-1-yl)ethanes (13)

R	Yield (%)	M.p. (°C)	M^+	Formula	Found (%) [Required]	^{1}H N.m.r. (δ) in $CDCl_3$
Me	81	188	356	$C_{18}H_{18}N_4S_2$	C, 60.9; H, 5.2; N, 15.8 [C, 61.0; H, 5.1; N, 15.8]	2.9 (6 H, s, Me), 5.0 (4 H, s, NCH_2CH_2N), 7.4—8.0 (8 H, m, aromatic)
Et	83	179	384	$C_{20}H_{22}N_4S_2$	C, 62.7; H, 5.8; N, 14.6 [C, 62.8; H, 5.8; N, 14.7]	1.5 (6 H, t, CH_2CH_3), 3.3 (4 H, q, CH_2CH_3), 4.4 (4 H, s, NCH_2CH_2N), 7.0—7.6 (8 H, m, aromatic)
$PhCH_2$	80	144	506	$C_{30}H_{26}N_4S_2$	C, 71.0; H, 5.3; N, 11.2 [C, 71.1; H, 5.3; N, 11.1]	4.2 (4 H, s, CH_2), 4.5 (4 H, s, NCH_2CH_2N), 7.0—7.6 (18 H, m, aromatic)

reflux in 4N hydrochloric acid for 6 h. After cooling the solid was collected. Recrystallisation from aqueous DMSO gave the *thione* (0.29 g, 84%) as cream crystals, m.p. >300 °C (Found: C, 58.4; H, 4.4; N, 16.8; S, 19.3. $C_{16}H_{14}N_4S_2$ requires C, 58.9; H, 4.3; N, 17.2; S, 19.6%); δ [$(CD_3)_2SO$] 3.56 (2 H, NH, exchangeable), 4.7 (4 H, s, NCH_2CH_2N), and 7.2 (8 H, m, aromatic); *m/e* 326 (M^+).

Preparation of 1,2-*Bis*-(2-*alkylthiobenzimidazol*-1-*yl*)*ethanes* (13) (Table 3).—The alkyl halide (0.004 mol) in DMSO (5 ml) was added dropwise with stirring to 1,2-bis-(2-thioxobenzimidazol-1-yl)ethane (0.33 g, 0.001 mol) in DMSO (10 ml). The resulting mixture was stirred for 3 h at room temperature. 20% Sodium hydroxide solution (10 ml) was added, and the mixture was extracted with chloroform (3 × 25 ml), the extract washed with water (3 × 25 ml), and dried over magnesium sulphate. After filtration and evaporation, the residue was recrystallised from acetonitrile to give the benzimidazole.

1,2-*Bis*-(2-*methylsulphonybenzimidazol*-1-*yl*)*ethane* (14).—Potassium permanganate (1.0 g) was added in portions over 1 h to a stirred solution of 1,2-bis-(2-methylthiobenzimidazol-1-yl)ethane (0.35 g, 0.001 mol) in acetone (36 ml) and acetic acid (4 ml) at 0 °C. After 3 h at 0 °C the solution was decolourised with aqueous sodium sulphite, evaporated *in vacuo*, and the residue extracted with chloroform (3 × 25 ml). Evaporation gave the *bis-sulphone* (0.35 g, 85%), m.p. 241—243 °C (Found: C, 51.8; H, 4.4; N, 13.1. $C_{18}H_{18}N_4O_4S_2$ requires C, 51.7; H, 4.3; N, 13.4%); δ ($CDCl_3$) 3.6 (6 H, s, 2 × SO_2Me), 5.1 (4 H, s, NCH_2CH_2N), and 7.1—7.7 (8 H, m, aromatic).

7,8,16,17-*Tetrahydrobisbenzimidazo*[2,1-b;1′,2′-f][1,8,3,6]-*dithiadiazecine* (15).—1,2-Dibromoethane (0.19 g, 0.001 mol) in propan-2-ol (10 mol) was added dropwise during 1 h to 1,2-bis-(2-thioxobenzimidazol-1-yl)ethane (0.33 g, 0.001 mol) in propan-2-ol (50 ml) and stirred at room temperature for 16 h. After filtration and evaporation, the residue recrystallised from acetonitrile to give the *ring compound* (15) (0.30 g, 84%), m.p. 200 °C; *m/e* 354 (M^+) (Found: C, 60.9; H, 5.0; N, 15.8. $C_{18}H_{18}N_4S_2$ requires C, 61.3; H, 4.6; N, 15.9%); δ ($CDCl_3$) 2.8 (4 H, s, SCH_2CH_2S), 5.0 (4 H, s, NCH_2CH_2N), and 7.3—7.9 (8 H, m, aromatic).

Reaction of the Bisisothiocyanate (4) *with Lithium Aluminium Hydride*.—Lithium aluminium hydride (0.4 g) was added, with stirring, to the bisisothiocyanate (0.38 g, 0.001 mol) in THF (50 ml) at room temperature. After 2 h acetone (5 ml), water (5 ml), and then 2N hydrochloric acid (5 ml) were added, and the whole was evaporated *in vacuo*. The residue was extracted with chloroform and the extract was chromatographed on alumina using chloroform as solvent. The product (0.3 g, 81%) was identical (i.r.) with 1,2-bis-(2-thioxobenzimidazol-1-yl)ethane (12). Similarly prepared from *o*-isothiocyanato-*N*-methylformanilide (17) (0.001 mol) was N-*methylbenzimidazoline*-2-*thione* (0.18 g, 92%), m.p. 196 °C (lit.,[6] 195 °C) (Found: C, 58.4; H, 5.1; N, 17.1. Calc. for $C_8H_8N_2S$: C, 58.5; H, 4.9; N, 17.1%).

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