Formation of 3-Substituted 2-Iminocyclopentanedithiocarboxylic Acids and *N*-[Amino(dimercapto)methyl]-2-methylcyclopentanimine from 2-Substituted Cyclopentanones. Some Reactions of the Imino-dithiocarboxylic Acids

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2-Ethyl, 2-isopropyl, 2-cyclopentyl, and 2-cyclopentylidenecyclopentanones, when treated with carbon disulphide and ammonia, gave the corresponding 3-substituted 2-iminocyclopentanedithiocarboxylic acids (5)—(7) and (9). Under the same conditions, 2-methylcyclopentanone gave 2-imino-3-methylcyclopentanedithiocarboxylic acid (2), and *N*-[amino(dimercapto)methyl]-2-methylcyclopentanimine (3), and 2-isopropylidenecyclopentanone gave 7a-amino-4,4-dimethylperhydrocyclopenta[*e*][1,3]thiazine-2-thione (8). Reactions of the 2-iminocyclopentanedithiocarboxylic acids with hydrazine, thiosemicarbazide, picryl chloride, and phenyl isothiocyanate have also been investigated.

WE have previously shown[1] that cyclopentanone, in the presence of aqueous ammonia, reacts with carbon disulphide to give 2-iminocyclopentanedithiocarboxylic acid (1) or its tautomer. The product (1) is stable and displays interesting properties. It is exceedingly sensitive to Ni^{II} and other metal ions, giving characteristic colourations or precipitates,[2] and reacts with carbonyl compounds to yield a series of 1,3-thiazines.[3,4] Recently, Matolcsy has reported its antifungal activity.[5]

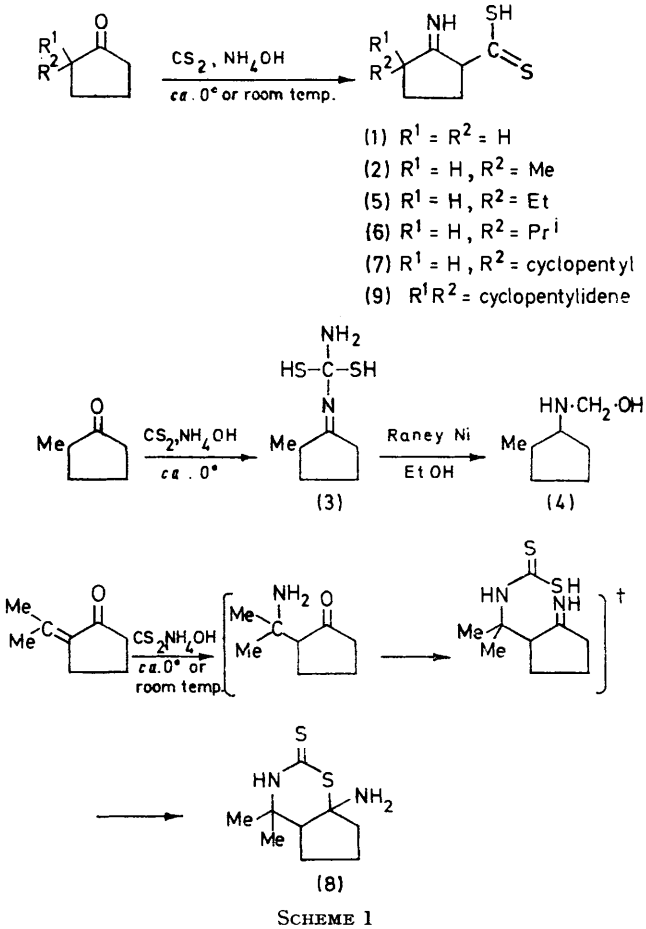
Several other ketones with α-hydrogen atoms were subjected to the reaction with carbon disulphide, but the corresponding imino-dithiocarboxylic acids were not isolated. Instead, 1,3-thiazine derivatives, which seemed to be formed *via* unstable imino-dithiocarboxylic acids, were obtained;[3,6] the product from acetone and one of the products from methyl ethyl ketone were yet another type of compound.[6]

Matolcsy and his co-workers have recently synthesised a crystalline imino-dithiocarboxylic acid of a five-membered heterocycle, 4,5-dihydro-5-imino-3-methyl-1-phenyl-1*H*-pyrazole-4-dithiocarboxylic acid.[5]

The present investigation was undertaken to extend the reaction with carbon disulphide to 2-substituted cyclopentanones, with the object of preparing a series of substituted imino-dithiocarboxylic acids. Unexpectedly, however, the mode of reaction was found to depend markedly upon the nature of the 2-substituent.

RESULTS

2-Methylcyclopentanone gave two types of compound, the imino-dithiocarboxylic acid (2), and *N*-[amino-(dimercapto)methyl]-2-methylcyclopentanimine (3). Compound (3) was obtained as the major product when the reaction was conducted below 0° in the presence of a large excess of aqueous ammonia. 2-Ethylcyclopentanone afforded only a trace of the thiourea-type compound; the greater part of the product was the imino-dithiocarboxylic acid (5). 2-Isopropylcyclopentanone and 2-cyclopentylcyclopentanone yielded the imino-dithiocarboxylic acids (6) and (7), respectively.



SCHEME 1

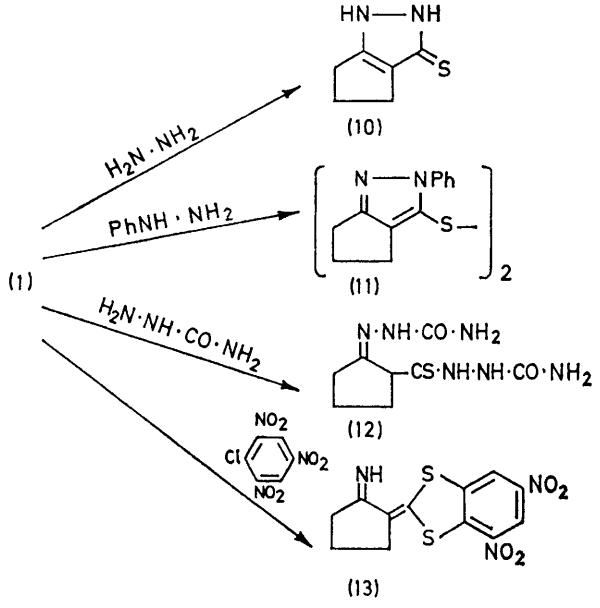
† Suggested mechanism.

[1] T. Takeshima, M. Yokoyama, T. Imamoto, M. Akano, and H. Asaba, *J. Org. Chem.*, 1969, **34**, 730.
[2] M. Yokoyama and T. Takeshima, *Analyt. Chem.*, 1968, **40**, 1344.
[3] T. Takeshima, T. Hayashi, M. Muraoka, and T. Matsuoka, *J. Org. Chem.*, 1967, **32**, 980.
[4] M. Muraoka, M. Yokoyama, K. Yamamoto, and T. Takeshima, *Bull. Chem. Soc. Japan*, 1970, **43**, 2134.
[5] G. Matolcsy, P. Sohár, and B. Bordás, *Chem. Ber.*, 1971, **104**, 1155; G. Matolcsy, M. Hamrán, and B. Bordás, *Acta Phys. Acad. Sci. Hung.*, 1970, **5**, 123; G. Matolcsy, B. Bordás, M. Hamrán, and M. Tiborcz, *ibid.*, 1971, **6**, 381.
[6] T. Takeshima, T. Imamoto, M. Yokoyama, K. Yamamoto, and M. Akano, *J. Org. Chem.*, 1968, **33**, 2877.

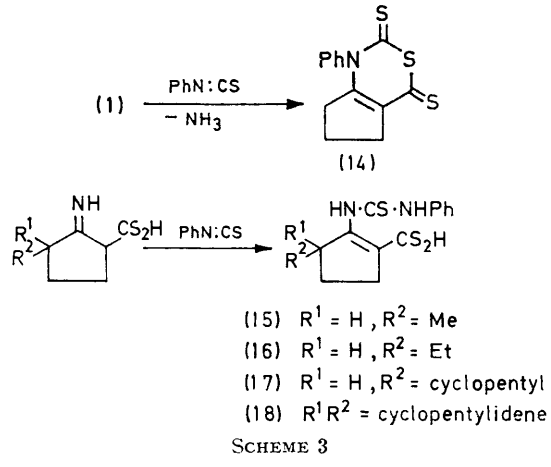
However, 2-isopropylidenecyclopentanone yielded the perhydrocyclopenta[*e*][1,3]thiazine (8), whereas 2-cyclopentylidenecyclopentanone gave 3-cyclopentylidene-2-iminocyclopentanedithiocarboxylic acid (9).

The products were identified on the basis of i.r., u.v., n.m.r., and mass spectra together with elemental analyses and chemical reactions (see Experimental section). Desulphuration of the thiourea analogue (3) with Raney nickel gave *N*-hydroxymethyl-2-methylcyclopentanamine (4).

Several derivatives of compounds (1), (2), (5), (7), and (9) were prepared with the object of investigating the nature of these imino-dithiocarboxylic acids (see Schemes 2—4 and Experimental section). Compound



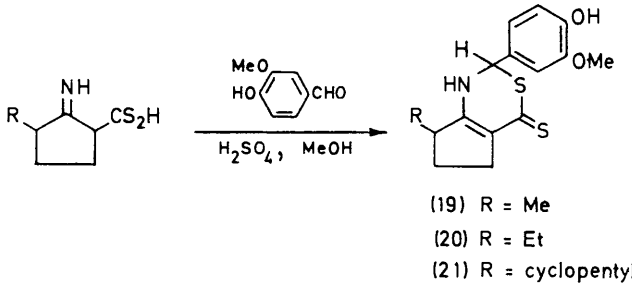
SCHEME 2



SCHEME 3

(1) apparently assumes the isomeric enedithiol structure in the reaction [7] with picryl chloride, which also involves denitration of the latter.

Compound (1) reacted with phenyl isothiocyanate to give the cyclopenta[*d*][1,3]thiazinedithione (14). In contrast, compounds (2), (5), (7), and (9) afforded the expected thiourea derivatives (15)—(18). The i.r. and u.v. spectra of compound (14) were similar to those of 5,6,7,8-tetrahydro-3,1-benzothiazine-2(1*H*),4-dithione.[3]



SCHEME 4

Compounds (15)—(17) are soluble in alkali and produce pink-red precipitates with Ni^{II} ion, in common with the foregoing imino-dithio-acids; this may be evidence for the presence of a free dithiocarboxy-group; green or bluish-green precipitates were produced in the case of compounds (9) and (18).

These derivatives were also identified on the basis of spectra, elemental analyses, and chemical reactions (see Experimental section).

The cycloaddition products of vanillin with compounds (2), (5), and (7) were also prepared [(19)—(21); see Table 3].[1,3,4]

EXPERIMENTAL

2-Imino-3-methylcyclopentanedithiocarboxylic Acid (2).—A mixture of 2-methylcyclopentanone (5 g, 0·051 mol), carbon disulphide (5 g, 0·066 mol), and aqueous 28% ammonia (10 ml) was shaken at room temperature for several hours and kept overnight in an ice-box. The yellow solid product was collected, washed with ether, and dried: yield *ca.* 3 g (34%). This crude ammonium salt was recrystallised from acetic acid to give yellow *crystals* (2) (2·1 g, 24%), m.p. 81°; $\nu_{max.}$ (KBr) 3240ms (NH), 2480w (SH), 1623vs (NH), and 1610vs (C=N) cm^{-1}; $\nu_{max.}$ ($CHCl_3$) 3445s (NH), 2570w (SH), and 1600vs (C=N) cm^{-1}; $\lambda_{max.}$ (EtOH) 303 (log ε 3·90) and 392 nm (4·26); δ [$(CD_3)_2SO$] 1·80 (3H, dd, *J* 6 Hz, CH_3), *ca.* 1·75 (2H, m, 4-H_2), 2·85 (2H, m. 5-H_2), 3·40 (1H, m, 3-H), 6·00br (1H, 1-H), 9·05br (1H, NH or SH), and 11·15br p.p.m. (1H, s, NH or SH); *m/e* 173 (83%), 140 (100), 125 (13), 96 (16), and 76 (28) (Found: C, 48·45; H, 6·35; N, 8·25; S, 37·05%; M^+ 173. $C_7H_{11}NS_2$ requires C, 48·55; H, 6·4; N, 8·1; S, 36·95%; *M*, 173), which gave a pink-red precipitate with Ni^{II} ion.

N-[Amino(dimercapto)methyl]-2-methylcyclopentanimine (3).—A mixture of 2-methylcyclopentanone (5 g, 0·051 mol), carbon disulphide (5 g, 0·066 mol), and aqueous 28% ammonia (25 ml) was shaken below 0° for 24 h. The yellow solid product was collected and washed with ether; yield 2 g (21%). Recrystallisation from acetic acid–water (1 : 1) gave yellow crystals of (3) *monohydrate* m.p. 145—146° (slow heating) and 180—182° (decomp.) (rapid heating); $\nu_{max.}$ (KBr) 3540m (OH), 3360sh, 3260s,br, 3060—3160s,br (NH_2), 2770sh,w (SH), and 1688vs (C=N) cm^{-1}; $\lambda_{max.}$ (EtOH) 222sh (log ε 3·98), 237sh (3·60), and 340 nm

[7] M. Yokoyama, *J. Org. Chem.*, 1970, **35**, 283.

(4·36); δ [$(CD_3)_2SO$] 1·07 (3H, d, *J* 6 Hz, CH_3), 1·56 (4H, m, 3- and 4-H_2), 2·32 (2H, t, *J* 6 Hz, 5-H_2), 3·26 and 3·34 (3H, m, H_2O and 2-H), and 8·45br p.p.m. (4H, s, NH_2 and SH); δ ($CF_3{\cdot}CO_2H$) 1·37 (3H, d, *J* 6 Hz, CH_3), 1·80br (4H, s), 2·60br (2H, s), 3·40 (1H, m), and 7·50br p.p.m. (4H, s); *m/e* 190 (3%, M^+), 156 (100, $M^+ - H_2S$), 96 (24, $M^+ - H_2S - NH_2CS$), 76 (38, $NH_2{\cdot}CS{\cdot}NH_2$), and 34 (100, H_2S) (Found: C, 40·4; H, 7·65; N, 13·65; S, 30·6. $C_7H_{16}N_2OS_2$ requires C, 40·4; H, 7·75; N, 13·45; S, 30·75%). Washing with ethanol, recrystallisation from dimethylformamide–ether or acetic acid–ether, or drying (P_2O_5 at 110°) gave anhydrous *material*, m.p. 153° (Found: C, 44·2; H, 7·3; N, 15·0; S, 33·3%; M^+ 190. $C_7H_{14}N_2S_2$ requires C, 44·2; H, 7·4; N, 14·75; S, 33·65%; *M*, 190), which gave a brown colouration (no precipitate) with Ni^{II} ion and did not react with benzaldehyde, phenyl isothiocyanate, monobromoacetic acid, picryl chloride, or 2,4-dinitrophenylhydrazine.

Desulphuration of Compound (3).—Compound (3) (3·8 g) was refluxed with Raney nickel (40 g) in ethanol (300 ml) for 3 h. The mixture was worked up in the usual manner, and distilled at *ca.* 20 mmHg. The white crystals of N-*hydroxymethyl*-2-*methylcyclopentanamine* (4) adhering to the wall of the condenser were collected, and purified by sublimation and recrystallisation from benzene; yield 0·5 g (19%), m.p. 105—106° (sealed tube); $\nu_{max.}$ (KBr) 3360s (OH), 3180m (NH), 1657vs, and 1630vs cm^{-1}; $\nu_{max.}$ ($CHCl_3$) 3530m (OH), 3405m (NH), and 1680vs (NH) cm^{-1}; no u.v. absorption; δ ($CDCl_3$) 0·85 (3H, d, *J* 6 Hz, CH_3), 0·90 (2H, s, $CH_2{\cdot}OH$), *ca.* 1·5 (6H, m, 3-, 4-, and 5-H_2), 2·20 (2H, m, 1- and 2-H), *ca.* 6·0br (1H, NH or OH), and *ca.* 6·4br p.p.m. (1H, NH or OH) [Found: C, 65·1; H, 11·6; N, 10·85%; *M*, 129 (osmometry in acetone). $C_7H_{15}NO$ requires C, 65·05; H 11·7; N, 10·85%; *M*, 129].

3-*Ethyl*-2-*iminocyclopentanedithiocarboxylic Acid* (5).—The preparation was similar to that of compound (2). The cooled reaction mixture was acidified with dilute acetic acid. The solid product was collected; yield *ca.* 15%. Recrystallisation from methanol gave yellow crystals, m.p. 88—90°, spectroscopic data similar to those of (2) (Found: C, 51·35; H, 6·9; N, 7·65; S, 34·2%; M^+ 187. $C_8H_{13}NS_2$ requires C, 51·35; H, 7·0; N, 7·5; S, 34·2%; *M*, 187]. Compound (5) with Ni^{II} produced a pink-red precipitate.

When a mixture of 2-ethylcyclopentanone (6 g, 0·054 mol), carbon disulphide (5 g, 0·066 mol), and aqueous 28% ammonia (25 ml) was shaken at *ca.* 0° for *ca.* 24 h, a few yellow crystals were obtained. The compound seemed to be *N*-[amino(dimercapto)methyl]-2-ethylcyclopentanimine from its i.r. spectrum, but was not investigated further owing to lack of material; $\nu_{max.}$ (KBr) 3320m, 3200br (NH_2), 2760w (SH), 1675vs (C=N), and 1590vs cm^{-1}.

2-*Imino*-3-*isopropylcyclopentanedithiocarboxylic Acid* (6).—A mixture of 2-isopropylcyclopentanone (10 g, 0·079 mol), carbon disulphide (15 g, 0·197 mol), and aqueous 28% ammonia (85 ml) was stirred at *ca.* 0° for 20 h. Dilute hydrochloric acid was then added until a heavy oil separated. The oil was treated with active charcoal in ether; the ethereal solution was filtered and evaporated and the yellow *crystals* which separated were washed with petroleum; yield *ca.* 0·5 g (3%), m.p. 105°; $\nu_{max.}$ (KBr) 3250s (NH), 2460m (SH), and 1610vs (C=N) cm^{-1}; $\lambda_{max.}$ (EtOH) 304 (log ε 3·93) and 392 nm (4·32) (Found: C, 53·6; H, 7·4; N, 6·8; S, 31·6. $C_9H_{15}NS_2$ requires C, 53·7; H, 7·5; N, 6·95; S, 31·8%). Compound (6) produced a pink-red precipitate with Ni^{II} ion.

3-*Cyclopentyl*-2-*iminocyclopentanedithiocarboxylic Acid* (7).—The preparation was similar to that of compound (2). Recrystallisation from ethanol gave yellow *crystals* (26%), m.p. 108—109° (decomp.), spectroscopic data similar to those of (2) (Found: C, 58·2; H, 7·55; N, 6·15; S, 28·05%; M^+ 227. $C_{11}H_{17}NS_2$ requires C, 58·15; H, 7·55; N, 6·15; S, 28·15%; *M*, 227).

7a-*Amino*-4,4-*dimethylperhydrocyclopenta*[e][1,3]*thiazine*-2-*thione* (8).—A mixture of isopropylidenecyclopentanone (6 g, 0·048 mol), carbon disulphide (8 g, 0·105 mol), and aqueous 28% ammonia (50 ml) was shaken at room temperature for 8 h, then kept for 4 days in an ice-box. The solid product was collected, washed with water, and dried (yield *ca.* 1·8 g, 17%), then recrystallised from ethanol to give light yellow *crystals* (1·2 g), m.p. *ca.* 140° (decomp.) (slow heating) and 151° (decomp.) (rapid heating); $\nu_{max.}$ (KBr) 3360m, 3270m (NH_2), 3120m (NH), and 1585s (NH_2) cm^{-1}; $\lambda_{max.}$ (EtOH) 244 (log ε 3·88) and 289 nm (4·22); * δ [$(CD_3)_2SO$] 1.23 (3H, s, CH_3), 1·38 (3H, s, CH_3), 1·78 (7H, m, CH_2, CH), 2·90 (2H, s, NH_2), and 10·00br p.p.m. (1H, NH); *m/e* 216 (72%), 183 (15), 124 (100), 83 (79), and 82 (62) (Found: C, 49·95; H, 7·4; N, 13·0; S, 29·5%; M^+, 216. $C_9H_{16}N_2S_2$ requires C, 50·0; H, 7·45; N, 12·95; S, 29·6%; *M*, 216).

3-*Cyclopentylidene*-2-*iminocyclopentanedithiocarboxylic Acid* (9).—A mixture of 2-cyclopentylidenecyclopentanone (10 g, 0·067 mol), carbon disulphide (30 g, 0·39 mol), and aqueous 28% ammonia (150 ml) was shaken at room temperature for 20 h. Ether was added and the mixture was shaken for an additional few minutes. The solid product was collected, washed with ether (yield *ca.* 3 g, 20%), and dissolved in pyridine. Ethanol–water (10 : 1) was then added dropwise to give yellow *crystals*, m.p. 105° (slow heating) and 116—118° (rapid heating); $\nu_{max.}$ (KBr) 3445m (NH), 2570w, 2490w (SH), 1640s (C=C), and 1590vs (C=N) cm^{-1}; $\nu_{max.}$ ($CHCl_3$) 3490s (NH), 2570w (SH), 1640s (C=C), and 1597vs (C=N) cm^{-1}; $\lambda_{max.}$ (EtOH) 260 (log ε 3·57), 306 (3·67), 322 (3·69), and 436 nm (4·11); δ ($CDCl_3$) 1·77 (4H, m, 3′ and 4′-H_2), 2·50 (8H, m, *J* 9 Hz, 4-, 5-, 2′-, and 5′-H_2), 4·30br (1H, 1-H), 6·10br (1H, SH), and 11·40br p.p.m. (1H, NH); *m/e* 225 (71%), 192 (100), 149 (21), 148 (21), and 76 (87) (Found: C, 58·45; H, 6·75; N, 6·3; S, 28·2%; M^+, 225. $C_{11}H_{15}NS_2$ requires C, 58·65; H, 6·7; N, 6·2; S, 28·4%; *M*, 225). Compound (9) produced a green or bluish-green precipitate with Ni^{II} and a reddish-brown precipitate with Cu^{II}. When refluxed with morpholine, it gave morpholinium morpholine-*N*-dithiocarboxylate,[1] and when warmed with methanolic 2,4-dinitrophenylhydrazine containing sulphuric acid for 30 min, it gave the 2,4-dinitrophenylhydrazone of cyclopentylidenecyclopentanone, m.p. and mixed m.p. 229—230°.

The oxidative *dimer* † of compound (9) (orange crystals) was obtained from recrystallisation of a second crop; m.p. 140° (slow heating) and 155° (rapid heating); $\nu_{max.}$ (KBr) 3455m, 3390m (NH_2), 1635s (exocyclic C=C), 1595sh (NH_2 or endocyclic C=C), and 1582vs (NH_2 or endocyclic C=C) cm^{-1} (Found: C, 58·95; H, 6·3; N, 6·35; S, 28·2. $C_{22}H_{28}N_2S_4$ requires C, 58·9; H, 6·3; N, 6·25; S, 28·55%).

* U.v. spectrum identical with that of 6-amino-3,4,5,6-tetrahydro-4,4,6-trimethyl-1,3-thiazine-2-thione.[6]

† $(C_{10}H_{14}N{\cdot}CS_2)_2$, see ref. 1.

Esters of Compounds (1),[1] (2), *and* (7).—These esters were made in the usual way (Table 1). The i.r., u.v., and n.m.r. spectra, and elemental analyses agreed with the proposed formulae.

TABLE 1

Esters of compounds (1), (2), and (7)

	M.p. (°C) Slow heating	Rapid heating	Solvent
Methyl 2-iminocyclopentanedithiocarboxylate [a]	74—75		HOAc–H_2O
Carboxymethyl 2-iminocyclopentanedithiocarboxylate	150—151	165—168	HOAc–H_2O
Hydrazinium salt of carboxymethyl 2-iminocyclopentanedithiocarboxylate	121—122	138—141	MeOH
2,4-Dinitrophenyl 2-iminocyclopentanedithiocarboxylate	141 (decomp.)	153—154 (decomp.)	EtOH
Carboxymethyl 3-methyl-2-iminocyclopentanedithiocarboxylate	127		EtOH–H_2O
Methyl 3-cyclopentylidene-2-iminocyclopentanedithiocarboxylate	148		EtOH–Me_2CO

[a] B. Bordás, P. Sohár, G. Matolcsy, and P. Berencsi, *J. Org. Chem.*, 1972, **37**, 1727.

1,4,5,6-*Tetrahydrocyclopenta*[c]*pyrazole*-3(2H)-*thione* (10). —*Method A*. To a mixture of the ammonium salt [1] of (1) (0·6 g, 0·0034 mol), ethanol (15 ml), and 80% hydrazine hydrate (10 g, 0·25 mol) was added a solution of acetic acid (20 ml) in water (10 ml) in an ice-bath. The mixture was kept at room temperature for 1 h. The solid *product* was collected, washed with water and methanol, dried (yield *ca.* 0·3 g, 63%), and recrystallised from ethylene glycol; m.p. 234—235° (decomp.) (slow heating) and 251—255° (decomp.) (rapid heating); $\nu_{max.}$ (KBr) 3150m (NH), 3060m (NH), and 1575s (C=C) cm^{-1}; $\lambda_{max.}$ (EtOH) 235 (log ε 3·42) and 286 nm (3·88); δ [$(CD_3)_2SO$] 2·40 (6H, m, CH_2), 3·40br (1H, NH), and 12·50br p.p.m. (1H, NH) (Found: C, 51·45; H, 5·7; N, 20·05; S, 22·55%; M^+, 140. $C_6H_8N_2S$ requires C, 51·4; H, 5·75; N, 20·0; S, 22·85%; *M*, 140).

Method B. A mixture of carboxymethyl 2-iminocyclopentanedithiocarboxylate (2 g, 0·0092 mol), water (50 ml), and 80% hydrazine hydrate (1 g, 0·025 mol) was refluxed at 140° for 4 h. After removing the solvent, the yellow solid product was collected, washed with water, dried (yield *ca.* 1 g, 78%), and was recrystallised from acetic acid; m.p. 231—233° (decomp.) (slow heating) and 255—259° (decomp.) (rapid heating), i.r. and u.v. spectra were identical with those of the sample prepared by method A (Found: C, 51·2; H, 5·75; N, 20·5; S, 22·7%).

Bis-(2,4,5,6-*tetrahydro*-2-*phenylcyclopenta*[c]*pyrazol*-3-*yl*) *Disulphide* (11).—A mixture of the ammonium salt of (1) (0·5 g, 0·0028 mol), phenylhydrazine (0·66 g, 0·006 mol), hydrochloric acid (0·3 ml), and water (5 ml) was warmed on a steam-bath at 50° for 2 h, then cooled. The yellow oil was collected and dissolved in ethanol. The crystalline product (0·25 g, 21%) that separated was recrystallised from pyridine–water to give light yellow *crystals*, m.p. 170—172°; $\nu_{max.}$ (KBr) 1590s, 1553sh, 1546m, and 1507vs (conj. C=N, C=C) cm^{-1}; $\lambda_{max.}$ (EtOH) 248 (log ε 4·25) and 275 nm (4·30); δ ($CDCl_3$) 2·65 (8H, m, 4- and 5-H_2), 2·90 (4H, t, *J* 7 Hz, 6-H_2), and 7·37 p.p.m. (10H, m, Ph) (Found: C, 67·0; H, 5·0; N, 13·25; S, 14·95. $C_{24}H_{22}N_4S_2$ requires C, 66·95; H, 5·15; N, 13·0; S, 14·8%).

2-*Semicarbazidothiocarbonylcyclopentanone Semicarbazone* (12).—To a mixture of the ammonium salt of (1) (0·3 g, 0·0017 mol), ethanol (20 ml), and water (4 ml) were added semicarbazide hydrochloride (1 g, 0·009 mol) in water (3 ml), and then piperidine (0·2 ml). The mixture was kept at room temperature for 2 days. The precipitate was collected, washed with pyridine and ethanol, and dried (yield of deep yellow *crystals ca.* 0·4 g, 92%); m.p. 178° (decomp.) (slow heating) and *ca.* 190° (decomp.) (rapid heating); $\nu_{max.}$ (KBr) 3420s, 3280m,br, 3220m,br, 3200m,br (NH_2, NH), 1687sh, 1670s (C=O), 1610sh, and 1594s (C=N, NH_2) cm^{-1}; $\lambda_{max.}$ (EtOH) 235 (log ε 3·79) and 274 nm (3·72); δ [$(CD_3)_2SO$], 2·15 (6H, m, CH_2), 3·73 (1H, m, CH), 6·40 (4H, s, NH_2), 9·03 (1H, s, NHCO), 9·07 (1H, s, NHCO), and 11·85br p.p.m. (1H, CSNH) (Found: C, 37·3; H, 5·7; N, 32·5; S, 12·65. $C_8H_{14}N_6O_2S$ requires C, 37·2; H, 5·45; N, 32·55; S, 12·4%).

2-(2-*Iminocyclopentylidene*)-4,6-*dinitro*-1,3-*benzodithiole* (13).—To a suspension of picryl chloride (0·5 g, 0·002 mol) in ethanol (10 ml) was added gradually a suspension of the ammonium salt of (1) (0·35 g, 0·002 mol) in ethanol (10 ml) in an ice-bath. The mixture was kept overnight at room temperature. The solid product was collected, washed several times with ethanol, and dried (yield of deep brown *crystals ca.* 0·4 g, 62%); m.p. >300°; $\nu_{max.}$ (KBr) 3260m (NH), 1630s (C=N), 1590m (C=C), 1580m (aromatic C=C), 1555s, and 1335vs (NO_2) cm^{-1}; $\lambda_{max.}$ (EtOH) 262 (log ε 4·09), 318 (4·33), and 470 nm (3·83) (Found: C, 44·95; H, 2·7; N, 12·85; S, 19·5. $C_{12}H_9N_3O_4S_2$ requires C, 44·6; H, 2·8; N, 13·0; S, 19·8%).

1,5,6,7-*Tetrahydro*-1-*phenylcyclopenta*[d][1,3]*thiazine*-2,4-*dithione* (14).—The ammonium salt of (1) (0·5 g, 0·0028 mol) was dissolved in hot ethanol and phenyl isothiocyanate (0·45 g, 0·0033 mol) was added. The mixture was warmed on a steam-bath and then cooled to room temperature. The precipitate (*ca.* 0·5 g, 61%) was recrystallised from acetone to give orange *crystals*, m.p. 212—215°; $\nu_{max.}$ (KBr) 1592w and 1547vs (conj. C=C, aromatic C=C) cm^{-1}; $\lambda_{max.}$ (EtOH) 242 (log ε 2·87), 308 (3·66), 320sh (3·57), 412 (3·38), and 425sh nm (3·31); δ [$(CD_3)_2SO$] 1·84 (2H, m, 6-H_2), 2·31 (2H, m, 5-H_2), 2·85 (2H, t, *J* 8 Hz, 7-H_2), and 7·50 p.p.m. (5H, s, Ph) (Found: C, 56·3; H, 4·0; N, 5·05; S, 34·6%; M^+, 277. $C_{13}H_{11}NS_3$ requires C, 56·3; H, 4·0; N, 5·05; S, 34·65%; *M*, 277).

Phenyl Isothiocyanate Derivatives of Compounds (2), (5), (7), *and* (9).—The preparation of these thiourea derivatives [(15)—(18)] followed the same method (Table 2). The

TABLE 2

Phenyl isothiocyanate derivatives of compounds (2), (5), (7), and (9)

	M.p. (°C) Slow heating	Rapid heating	Solvent
1-(2-Dithiocarboxy-5-methylcyclopent-1-enyl)-3-phenylthiourea (15)	97—98		EtOH
1-(2-Dithiocarboxy-5-ethylcyclopent-1-enyl)-3-phenylthiourea (16)	96—97		Et_2O
1-(5-Cyclopentyl-2-dithiocarboxycyclopent-1-enyl)-3-phenyl thiourea (17)	77—78	88—90	EtOH
1-(5-Cyclopentylidene-2-dithiocarboxycyclopent-1-enyl)-3-phenyl thiourea (18)	114—115		

TABLE 3

Cycloaddition products of vanillin with compounds (2), (5), and (7)

	M.p. (°C) Slow heating	Rapid heating	Solvent
1,5,6,7-Tetrahydro-2-(*p*-hydroxy-*m*-methoxyphenyl)-7-methylcyclopenta[*d*][1,3]thiazine-4(2*H*)-thione (19)	228—230	234—243 (gradual decomp.)	Me_2SO–H_2O
7-Ethyl-1,5,6,7-tetrahydro-2-(*p*-hydroxy-*m*-methoxyphenyl)cyclopenta[*d*][1,3]-thiazine-4(2*H*)-thione (20)	155—157		Me_2N·-CHO–H_2O
7-Cyclopentyl-1,5,6,7-tetrahydro-2-(*p*-hydroxy-*m*-phenyl)cyclopenta[*d*][1,3]-thiazine-4(2*H*)-thione (21)	202		Me_2CO

i.r., u.v., and n.m.r. spectra, and elemental analyses of these compounds agreed with the proposed structures. The products gave coloured precipitates with Ni^{II} ion [(15)—(17) pink-red; (18) green or bluish-green] indicating the presence of the free dithiocarboxy-group.

Cycloaddition Products of Vanillin with Compounds (2), (5), *and* (7).—For example, compound (2) (0·3 g, 0·0017 mol) and vanillin (0·3 g, 0·002 mol) were dissolved in methanol (7·2 ml) containing sulphuric acid (0·12 g) with cooling. The yellow precipitate of (19) was collected and washed with ethanol; yield 0·4 g (75%).

The m.p.s and solvents for recrystallisation of compounds (19)—(21) are shown in Table 3. The i.r., u.v., and n.m.r. spectra agreed with those of known similar 1,3-thiazines.[1,3,4] Elemental analyses were in good agreement with the proposed formulae.

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