

Reactions of β -Imino-nitriles and -esters with Carbon Disulphide. A New Synthesis and Some Reactions of 2-Cyano-3-imino-dithiocarboxylic Acids

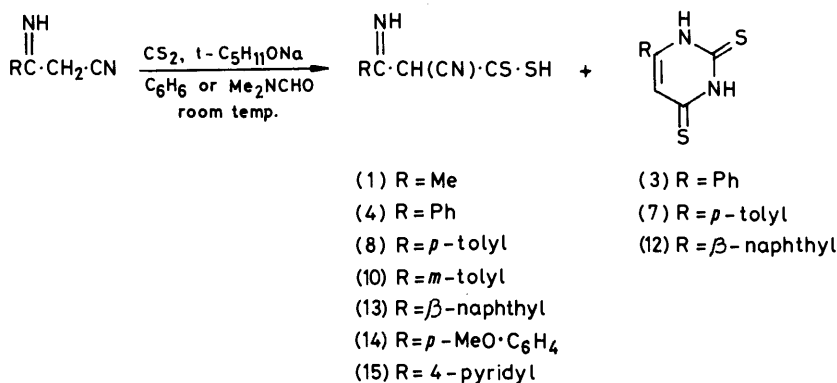
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Treatment of a series of β -imino-nitriles with carbon disulphide and sodium t-pentyl oxide at room temperature gave the corresponding 2-cyano-3-imino-dithiocarboxylic acids, accompanied in some cases by pyrimidine-2,4-dithiones. β -Imino- β -arylpropionitriles, when treated with carbon disulphide in dimethylformamide at low temperature, afforded 1,3-thiazine-2,6-dithiones. When an excess of sodium t-pentyl oxide was used in this reaction, β -iminobutyronitrile yielded pyrido[4,3-*d*][1,3]thiazine-2,4,5,7(1*H*,8*H*)-tetrathione. β -Imino- β -phenylpropionitrile, under the same conditions, gave a 1,5-diazocine-2,6(1*H*,5*H*)-dithione. β -Imino-esters in this reaction, afforded 1,3-thiazine-2,6-dithiones. Reactions of 2-cyano-3-imino-dithiocarboxylic acids with methyl and phenyl isocyanates, ethyl and phenyl isothiocyanates, picryl chloride, and hydrazine have also been studied.

We have previously shown that 2-iminocyclopentane-dithiocarboxylic acids can be synthesised by the reaction of cyclopentanones with carbon disulphide in the presence of ammonia.^{1,2} The method, however, is limited to the cyclopentanones. Free acyclic 3-imino-dithiocarboxylic acids have not been reported so far, and the 2-imino-cyclopentane-1-dithiocarboxylic acids are the only cyclic compounds of this type to have been described.

ture gave 3-imino-dithiocarboxylic acids as major products (Scheme 1). In addition, pyrimidine-2,4-dithiones [(3), (7), and (12)] could be obtained in some cases, apparently formed from the precursor dithiocarbamic acids *via* rearrangement of a 3,6-dihydro-6-imino-1,3-thiazine-2-thione. When the reaction was conducted in dimethylformamide at low temperature, the major products were the 1,3-thiazine-2,6-dithiones [(6), (9), and (11)]. The



SCHEME 1

Ketones such as ethyl methyl ketone, cyclohexanone, 4-methylcyclohexanone, cycloheptanone, phloroglucinol, and glutazines, on treatment with carbon disulphide in the presence of ammonia, afford 1,3-thiazine derivatives, apparently formed *via* unstable imino-dithiocarboxylic acids.^{1,3,4,5} Unisolable imino-dithiocarboxylic acids were reported by Miyauchi and his co-workers, who converted the acids into 1,3-thiazines by treatment with aldehydes.⁶ We now report a new synthesis of acyclic 2-cyano-3-imino-dithiocarboxylic acids, and the related formation of 1,3-thiazine-2,6-dithiones and some other new compounds.

β -Imino-nitriles when treated with carbon disulphide in the presence of sodium t-pentyl oxide at room tempera-

difference in results may be due to the dependence of the stability of the intermediate 3-imino-dithiocarboxylate dipole on both the polarity of the solvent and the reaction temperature. The imino-dithiocarboxylic acids themselves, except for 2-cyano-3-iminodithiobutyric acid, were reluctant to react with carbon disulphide. This type of intermediate has been proposed for the reactions of enamines with carbon disulphide in acetone-trile.⁷

β -Iminobutyronitrile, in contrast with other β -imino-nitriles, reacted with 3 mol. equiv. of carbon disulphide in the presence of an excess of sodium t-pentyl oxide to

¹ T. Takeshima, M. Yokoyama, T. Imamoto, M. Akano, and H. Asaba, *J. Org. Chem.*, 1969, **34**, 730.

² T. Takeshima, T. Miyauchi, N. Fukada, S. Koshizawa, and M. Muraoka, *J.C.S. Perkin I*, 1973, 1009.

³ T. Takeshima, T. Imamoto, M. Yokoyama, K. Yamamoto, and M. Akano, *J. Org. Chem.*, 1968, **33**, 2877.

⁴ T. Takeshima, T. Hayashi, M. Muraoka, and T. Matsuoka, *J. Org. Chem.*, 1967, **32**, 980.

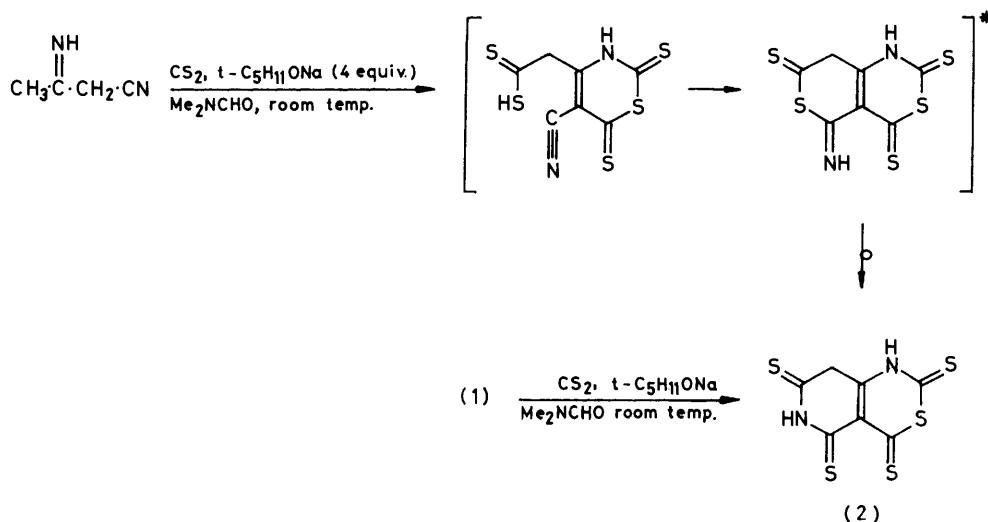
⁵ M. Muraoka, T. Yamamoto, and T. Takeshima, *Bull. Chem. Soc. Japan*, 1975, **48**, 2462.

⁶ T. Miyauchi, Y. Kadokura, N. Fukada, and T. Takeshima, *Bull. Chem. Soc. Japan*, 1974, **47**, 1678.

⁷ R. Gompper, B. Wetzell, and E. Wolfgang, *Tetrahedron Letters*, 1968, 5519.

give as the only product, pyrido[4,3-*d*][1,3]thiazine-2,4,5,7(1*H*,8*H*)-tetrathione (2), apparently formed *via*

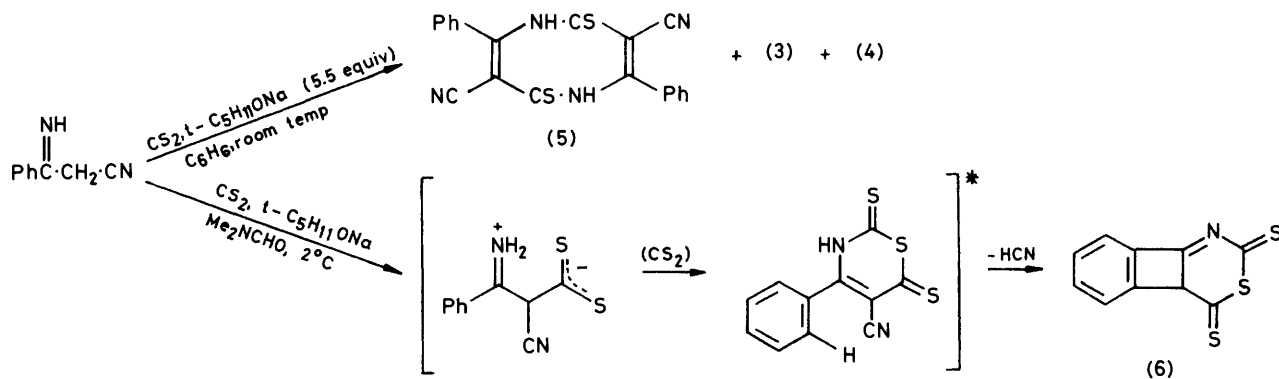
Experimental section). The i.r. spectrum of compound (2) had neither a C=N nor an SH band, and the u.v.



SCHEME 2 * Suggested mechanism

the isolable 2-cyano-3-dithiocarboxyamino-pent-2-enebis(dithioic) acid. Compound (2) was also obtained by the reaction of compound (1) with carbon disulphide.

spectrum displayed a marked resemblance to those of 5,6,7,8-tetrahydro-3,1-benzothiazine-2,4(1*H*)-dithiones^{4,5} and compounds (9), (11), and (16)—(18). Com-



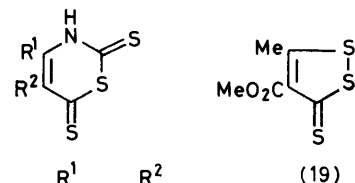
SCHEME 3 * Suggested mechanism

β -Imino- β -phenylpropionitrile, when treated with carbon disulphide in benzene in the presence of an excess of sodium *t*-pentyl oxide, gave the 1,5-diazocine-2,6-dithione (5), other imino-nitriles did not undergo this reaction.

β -Imino-esters in the present reaction produced 1,3-thiazine-2,6-dithiones [(16)—(18)]. The corresponding imino-dithiocarboxylic acids could not be isolated. Ethyl β -iminobutyrate and ethyl β -imino- β -(*m*-tolyl)-propionate were reluctant to undergo the reaction. Treatment of methyl β -iminobutyrate with carbon disulphide and sodium amide yielded 1,2-dithiole-3-thione (19).

The new compounds obtained here were identified on the basis of i.r., u.v., n.m.r., and mass spectra together with elemental analyses and chemical reactions (see

compounds (3), (7), and (12) exhibited i.r. and u.v. spectra resembling those of quinazoline-2,4(1*H*,3*H*)-dithione.⁸



R ¹	R ²
(9) <i>p</i> -tolyl	CN
(11) <i>m</i> -tolyl	CN
(16) Me	CO ₂ Me
(17) Ph	CO ₂ Et
(18) <i>p</i> -tolyl	CO ₂ Et

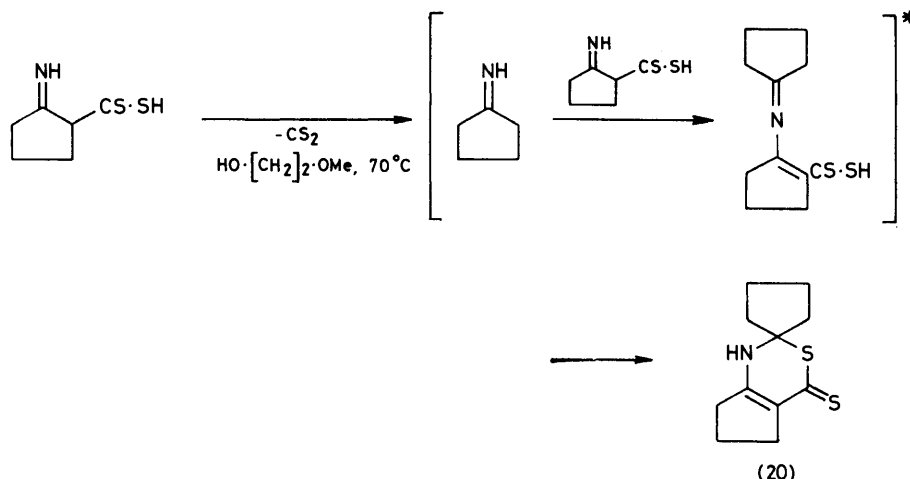
The i.r. spectrum of compound (6) has neither NH nor SH bands. A band at 750 cm⁻¹ may be due to the four adjacent aromatic CH groups. The u.v. spectrum was

⁸ E. C. Taylor, A. McKillop, and R. N. Warrener, *Tetrahedron*, 1967, **23**, 891.

similar to those of 5,6,7,8-tetrahydro-3,1-benzothiazine-2,4(1*H*)-dithiones^{4,5} and compounds (9) and (11).

The behaviour of the dithio-acids (1), (4), (8), (10),

acid (1) was much more sensitive to silver ion than *p*-dimethylaminobenzylidenerhodanine, forming a brilliant pinkish red complex.

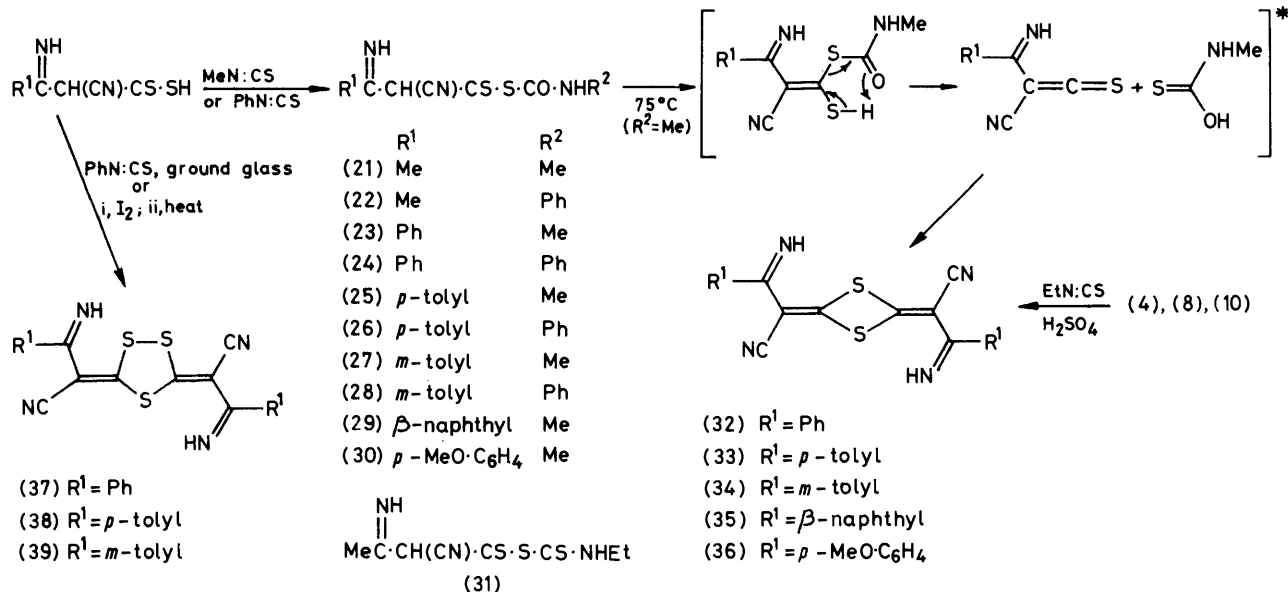


SCHEME 4 * Suggested mechanism

(13), and (14) towards methyl and phenyl isocyanates, ethyl and phenyl isothiocyanates, picryl chloride, and hydrazine was tested and compared with that of 2-imino- and 2-oxo-cyclopentanedithiocarboxylic acids and 3-methyl-5-oxo-1-phenyl- Δ^2 -pyrazoline-4-dithiocarboxylic acid (Schemes 4–6 and Experimental sec-

The dithio-acids (8) and (10) when heated at 70 °C in methylcellosolve gave the original β -imino-nitriles. In contrast, 2-iminocyclopentanedithiocarboxylic acid, under the same conditions, afforded the spiro-1,3-thiazine-2-thione (20).

The acids (1), (4), (8), (10), (13), and (14) reacted with



SCHEME 5 * Suggested mechanism

tion).^{1,2,9-11} The dithio-acids, like 2-iminocyclopentanedithiocarboxylic acids, were exceedingly sensitive to heavy metal ions, forming coloured complexes (see Experimental section). 2-Cyano-3-iminodithiobutyric

⁹ M. Muraoka, M. Yokoyama, K. Yamamoto, and T. Takeshima, *Bull. Chem. Soc. Japan*, 1970, **43**, 2134.

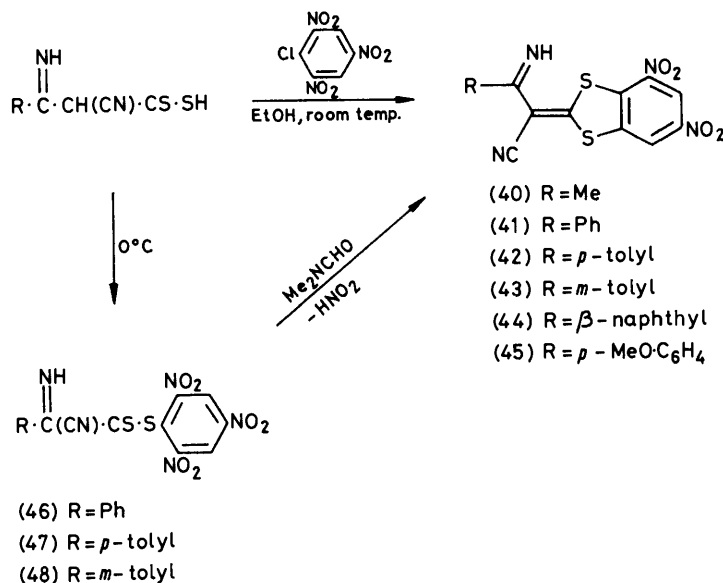
¹⁰ T. Takeshima, N. Fukada, E. Okabe, F. Mineshima, and M. Muraoka, *J.C.S. Perkin I*, 1975, 1277.

methyl and phenyl isocyanates to give the addition compounds (21)—(30), which were soluble in aqueous alkali. These compounds gradually produced violet precipitates with aqueous Ni^{II} . These facts, together with the absence of SH absorption in both i.r. and n.m.r.

¹¹ T. Takeshima, N. Fukada, T. Ishii, and M. Muraoka, *J.C.S. Perkin I*, 1976, 1706.

spectra and the conversion of these compounds into the corresponding 1,3-dithietan derivatives agreed with the assigned thioanhydride structures. The acid (1) reacted with ethyl isothiocyanate to give the addition product (31). Compounds (23), (25), (27), (29), and (30), when heated in dioxan, yielded the corresponding 1,3-dithietan derivatives. Some of these were also obtained by the reactions of the acids (4), (8), and (10) with ethyl or allyl isothiocyanate under acidic conditions.

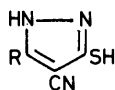
The acids (4), (8), and (10), when treated with iodine, gave 1,2,4-trithioles (37)—(39) *via* thermal decomposition



SCHEME 6

of bis-(1-cyano-2-iminoethylthiocarbonyl) disulphides (see footnote in Experimental section).¹¹ Compounds (37) and (38) could also be obtained in the presence of phenyl isocyanate and freshly prepared ground glass in place of iodine. N.m.r. spectra showed these products to have the *trans*-configuration (see Table 3).

The acids (1), (4), (8), (10), (13), and (14), like 2-imino- and 2-oxo-cyclopentanedithiocarboxylic acids, afforded



- (49) R = Me
 (50) R = Ph
 (51) R = *p*-tolyl
 (52) R = *m*-tolyl
 (53) R = *p*-MeO-C₆H₄

benzodithioles (40)—(45) when treated with picryl chloride.^{2,10} In the cases of compounds (4), (8), and (10), the intermediate esters (46)—(48) were isolated by performing the reaction at 0 °C, and were readily denitrated in dimethylformamide at room temperature to give the corresponding dithioles.

5-Mercapto-2*H*-pyrazoles (49)—(53) (Table 5) were prepared from the acids (1), (4), (8), (10), and (14) by reaction with hydrazine.²

EXPERIMENTAL

2-Cyano-3-iminodithiobutyric Acid (1).—To a solution of β -iminobutyronitrile (5 g, 0.061 mol) in benzene (300 ml) was added finely powdered sodium *t*-pentyl oxide (13.4 g, 0.12 mol); the mixture was stirred for 5 min, then carbon disulphide (9.3 g, 0.12 mol) was added. The mixture was stirred at room temperature for 3 h. Water (150 ml) was added and the aqueous layer was washed several

times with ether, and treated under diminished pressure to remove any remaining ether, and acidified with 2*N*-hydrochloric acid and ice (pH *ca.* 1). A yellowish orange solid which separated was dissolved in aqueous *N*-ammonia (70 ml); the solution was filtered and acidified. The resulting solid was collected, washed with water, and dried; yield 3.9 g (40%). Recrystallisation from acetone-water (3 : 1) gave yellow crystals, m.p. 97° (slow heating) or 98—99.5° (rapid heating); ν_{max} (KBr) 3 220m (NH), 2 515m (SH), 2 200s (CN), and 1 638s cm⁻¹ (C=N); λ_{max} (EtOH) 230 (log ϵ 4.14), 302 (3.88), and 359 nm (4.25); τ [(CD₃)₂SO] —3.43br and —0.33br (1 H, all s, NH), 3.83br (1 H, s, SH), 7.03br (1 H, s, 2-H), and 7.51 (3 H, s, Me) (Found: C, 38.1; H, 3.8; N, 17.9; S, 40.5%; M^+ , 158. C₅H₆N₂S₂ requires C, 37.95; H, 3.8; N, 17.7; S, 40.5%; M , 158). Compound (1) produced a reddish violet precipitate with Ni^{II} and a brilliant red precipitate with silver ion.

Pyrido[4,3-*d*][1,3]thiazine-2,4,5,7-(1*H*,8*H*)-tetrathione (2).—*Method A.* A mixture of β -iminobutyronitrile (1.5 g, 0.018 mol), sodium *t*-pentyl oxide (8 g, 0.073 mol), and dimethylformamide (10 ml) was shaken for 15 min, and to this was added carbon disulphide (5.6 g, 0.074 mol) below 0 °C. The mixture was set aside at 12 °C for 24 h. Water (20 ml) was added and the aqueous solution was washed several times with ether, treated under reduced pressure, and poured into 2*N*-hydrochloric acid (60 ml) and ice (20 g). The solid was collected, washed with water, and dried; yield 3 g (59%). Recrystallisation from dimethylform-

amide-water gave reddish brown crystals, m.p. $>300^\circ$; ν_{\max} (KBr) 3 275br, 3 170br, 3 040br, 2 920m, 2 880sh, 1 576s, 1 561vs, 1 520m, 1 447m, 1 415s, 1 364vs, 1 270s, and 1 237s cm^{-1} ; λ_{\max} (EtOH) 224 (log ϵ 4.16), 339 (4.42), 360 (4.39), 426sh (4.12), 446sh (4.44), and 469 nm (4.56); τ [$(\text{CD}_3)_2\text{SO}$] -2.78br (2 H, s, 2 NH) and 2.94 (2 H, s, 8- H_2); m/e 276 (M^+ , 62%), 243(18), 205(14), 200(40), 167(26), and 76(100) (Found: C, 30.6; H, 1.6; N, 10.3; S, 58.2). $\text{C}_7\text{H}_4\text{N}_2\text{S}_2$ requires C, 30.4; H, 1.5; N, 10.1; S, 58.0%).

Method B. To a mixture of compound (1) (1 g, 0.0063 mol), sodium t-pentyl oxide (2.2 g, 0.020 mol), and dimethylformamide (5 ml) was added carbon disulphide (1.5 g, 0.020 mol) below 0°C . The mixture was kept at 12°C for 20 h, then worked up as above (yield 1.1 g, 63%).

Reaction of β -Imino- β -phenylpropionitrile with Carbon Disulphide.—(A) *In benzene at room temperature: 6-phenylpyrimidine-2,4(1H)-dithione* (3). The molar ratio of reactants, conditions, and work-up procedure were similar to those for the preparation of compound (1). The crude yellowish orange solid was washed with ether-methanol (4:1) and dried; yield 13%. The crude product was recrystallised from dioxan-water to give pale yellow crystals, m.p. $277\text{--}278^\circ$; ν_{\max} (KBr) 3 200w, 3 100m, 2 940m, 2 890m, 1 612s, 1 570s, 1 403m, and 1 138s cm^{-1} ; λ_{\max} (EtOH) 266sh (log ϵ 4.32), 285 (4.43), and 379 nm (3.94); τ [$(\text{CD}_3)_2\text{NCD O}$] -3.79br and -3.20br (2 H, both s, $2 \times \text{NH}$), ca. 2.1 (5 H, m, Ph), and 3.04 (1 H, s, 5-H); m/e 220 (M^+ , 100%), 219(75), 187(68), 176(24), 163(84), 134(26), 128(42), 104(72), and 77(43) (Found: C, 54.5; H, 3.8; N, 12.5; S, 29.2). $\text{C}_{10}\text{H}_8\text{N}_2\text{S}_2$ requires C, 54.5; H, 3.7; N, 12.7; S, 29.1%).

2-Cyano-3-imino-3-phenyldithiopropionic acid (4). The morpholinium salt of the acid (4) separated on addition of morpholine to the ether-methanol washings. The salt was dissolved in dimethylformamide; the solution was neutralised with 2N-hydrochloric acid (1.3 equiv.) and diluted with water. The precipitate was collected, washed with water, and dried; overall yield 41%. Recrystallisation from acetone-water gave yellow crystals, m.p. $134\text{--}135^\circ$ (slow heating) or $142\text{--}144^\circ$ (rapid heating) [spectroscopic data similar to those of compound (1)] (Found: C, 54.4; H, 3.7; N, 12.5; S, 29.1). $\text{C}_{10}\text{H}_8\text{N}_2\text{S}_2$ requires C, 54.5; H, 3.7; N, 12.7; S, 29.1%). Compound (4) produced a violet precipitate with Ni^{II} , a green precipitate with Fe^{III} , and a dark brown precipitate with Cu^{II} .

(B) *In benzene in the presence of an excess of sodium t-pentyl oxide: 3,7-dicyano-4,8-diphenyl-1,5-diazocine-2,6-(1H,5H)-dithione* (5). A mixture of β -imino- β -phenylpropionitrile (2 g, 0.014 mol), sodium t-pentyl oxide (7.5 g, 0.068 mol), and benzene (25 ml) was shaken for 15 min, then carbon disulphide (6.5 g, 0.086 mol) was added dropwise and the mixture was shaken at room temperature for an additional 24 h. Water (25 ml) was added and the aqueous layer was washed with ether, and neutralised (pH ca. 7) with 2N-hydrochloric acid at 0°C to give a red viscous oil and a brown solid [compound (3) (26%)]. The oil was taken up in ether and the solution evaporated under reduced pressure to give a solid, which was collected, dried (yield 1.3 g, 50%), and recrystallised from acetone-water to give red crystals, m.p. 194° ; ν_{\max} (KBr) 3 200w, 3 020w, 2 230m, 1 583m, 1 562s, 1 490vs, 1 450vs, 1 412vs, and 1 224vs cm^{-1} ; λ_{\max} (EtOH) 274 (log ϵ 4.43), 324 (4.18), and 432 nm (4.10); τ [$(\text{CD}_3)_2\text{SO}$] 2.33 (10 H, m, $2 \times \text{Ph}$) and 5.53br (ca. 2 H, s, $2 \times \text{NH}$); m/e 372 (M^+ , 76%), 339(71), 308(42), 301(45), 235(100), 225(79), 202(85), and 128(88) (Found: C, 64.3;

H, 3.25; N, 14.8; S, 17.5). $\text{C}_{20}\text{H}_{12}\text{N}_4\text{S}_2$ requires C, 64.5; H, 3.25; N, 15.05; S, 17.2%).

(C) *In dimethylformamide at 2°C : benzo[3,4]cyclobuta-[1,2-d][1,3]thiazine-2,4(4aH)-dithione* (6). A mixture of β -imino- β -phenylpropionitrile (5 g, 0.035 mol), sodium t-pentyl oxide (11.5 g, 0.11 mol), and dimethylformamide (60 ml) was shaken for 30 min, carbon disulphide (8.1 g, 0.11 mol) was added, and the solution was kept for 48 h at 2°C . Water (60 ml) was added and the aqueous solution was washed with ether and poured into 2N-hydrochloric acid (55 ml) and ice (30 g). The precipitate was collected and washed several times with aqueous 2N-ammonia and then with water and dried; yield 3.5 g (43%). Recrystallisation from acetone-water (4:1) gave brownish red crystals, m.p. $171\text{--}172^\circ$; ν_{\max} (KBr) 1 595w, 1 500s, 1 474vs, 1 444s, and 750s cm^{-1} ; λ_{\max} (EtOH) 224 (log ϵ 4.09), 291 (4.23), 313 (4.12), and 422 (3.92); τ (CDCl_3) ca. 2.3 (4 H, m, C_6H_4) and 8.40 (1 H, s, 4a-H); m/e 235 (M^+ , 100%), 208(16), 202(88), 171(18), 170(21), 145(16), and 127(45) (Found: C, 51.1; H, 2.3; N, 6.2; S, 40.9). $\text{C}_{10}\text{H}_8\text{NS}_2$ requires C, 51.0; H, 2.1; N, 6.0; S, 40.9%).

Reaction of β -Imino- β -(p-tolyl)propionitrile with Carbon Disulphide.—(A) *In dimethylformamide at room temperature: 6-(p-tolyl)pyrimidine-2,4(1H)-dithione* (7). A mixture of β -imino- β -(p-tolyl)propionitrile (5 g, 0.032 mol), sodium t-pentyl oxide (8.7 g, 0.079 mol), and dimethylformamide (50 ml) was shaken for 30 min. Carbon disulphide (6 g, 0.079 mol) was added dropwise at 0°C and the mixture was shaken in air at 28°C for an additional 24 h. Water (50 ml) was added; the aqueous solution was washed with ether and acidified (pH 1) with dilute hydrochloric acid. The resulting yellow solid was collected and washed with water (yield 5.1 g). Isolation of compound (7) from this crude product was performed as for compound (3); yield 0.65 g (9%). Recrystallisation from dioxan-water (9:1) gave pale yellow crystals, m.p. $262\text{--}266^\circ$ (decomp.) [spectroscopic data similar to those of compound (3)] (Found: C, 56.1; H, 4.2; N, 11.8; S, 27.4). $\text{C}_{11}\text{H}_{10}\text{N}_2\text{S}_2$ requires C, 56.4; H, 4.3; N, 11.95; S, 27.4%).

2-Cyano-3-imino-3-(p-tolyl)dithiopropionic acid (8). Compound (8) was isolated as in the case of compound (4). The crude solid (4 g, 54%) was recrystallised from acetone-water (4:1) to give light yellow crystals, m.p. 156.5° [spectroscopic data similar to those of compound (4)] (Found: C, 56.55; H, 4.4; N, 11.8; S, 27.6). $\text{C}_{11}\text{H}_{10}\text{N}_2\text{S}_2$ requires C, 56.4; H, 4.3; N, 11.95; S, 27.4%), producing a violet precipitate with Ni^{II} .

(B) *In dimethylformamide at 2°C : 5-cyano-4-(p-tolyl)-1,3-thiazine-2,6(3H)-dithione* (9). The preparation was similar to that of compound (6). The reaction mixture, after water was added, was washed with ether, and the aqueous solution was poured into dilute hydrochloric acid and ice. The solid was collected, washed with water, and dissolved in aqueous N-ammonia. The solution was filtered and saturated with sodium chloride to precipitate the ammonium salt, which was collected [compound (8) was obtained from the mother liquor], washed with water saturated with sodium chloride, and dissolved in water. The aqueous solution was acidified with dilute hydrochloric acid to give a solid (60%), which was recrystallised from acetone-water (2:1) to afford brown crystals, m.p. $225.5\text{--}226^\circ$ (slow heating) or $249.5\text{--}251^\circ$ (rapid heating); ν_{\max} (KBr) 3 150m, 2 240m, 1 605m, 1 576m, 1 550s, 1 481vs, 1 460sh, 1 344s, 1 290m, and 1 218vs cm^{-1} ; λ_{\max} (EtOH) 236sh (log ϵ 3.86), 307 (4.54), 324 (4.46), 441sh (3.98), 450 (4.06), and 469 nm (4.14); τ [$(\text{CD}_3)_2\text{CO}$]

—1.73br (1 H, s, NH), 2.30 (4 H, q, C₆H₄), and 7.55 (3 H, s, Me) (Found: C, 52.05; H, 3.0; N, 10.2; S, 34.9. C₁₂H₈N₂S₃ requires C, 52.15; H, 2.9; N, 10.1; S, 34.8%).

2-Cyano-3-imino-3-(*m*-tolyl)dithiopropionic Acid (10).—The preparation * was similar to that of compound (8). Recrystallisation from acetone–water gave yellow crystals (62%), m.p. 123–123.5° [spectroscopic data similar to those of compound (4)] (Found: C, 56.6; H, 4.3; N, 11.9; S, 27.3. C₁₁H₁₀N₂S₂ requires C, 56.4; H, 4.3; N, 11.95; S, 27.4%), producing a violet precipitate with Ni^{II}.

5-Cyano-4-(*m*-tolyl)-1,3-thiazine-2,6(3H)-dithione (11).—The preparation was similar to that of compound (9). Recrystallisation from hot methanol gave red crystals (39%), m.p. 213° [spectroscopic data similar to those of compound (9)] (Found: C, 52.0; H, 3.0; N, 10.0; S, 34.9. C₁₂H₈N₂S₃ requires C, 52.15; H, 2.9; N, 10.1; S, 34.8%).

Reaction of β -Imino- β -(β -naphthyl)propionitrile † with Carbon Disulphide.—6-(β -Naphthyl)pyrimidine-2,4(1H)-dithione (12). The preparation was similar to that of compound (3). Recrystallisation from dioxan–water gave yellow crystals (14%), m.p. 283–286° (decomp.) [spectroscopic data similar to those of compound (3)] (Found: C, 62.1; H, 3.7; N, 10.3; S, 23.4. C₁₄H₁₀N₂S₂ requires C, 62.2; H, 3.7; N, 10.4; S, 23.7%).

2-Cyano-3-imino-3-(β -naphthyl)dithiopropionic acid (13). The method of isolation was the same as in the case of compound (4). The powder obtained was recrystallised from acetone–water to afford fine yellow crystals (36%), m.p. 161.5–162° [spectroscopic data similar to those of compound (4)] (Found: C, 62.25; H, 3.7; N, 10.3; S, 23.6. C₁₄H₁₀N₂S₂ requires C, 62.2; H, 3.7; N, 10.4; S, 23.7%), (13) producing a violet precipitate with Ni^{II}.

2-Cyano-3-imino-3-(*p*-methoxyphenyl)dithiopropionic Acid (14).—The preparation was similar to that of compound (8). To a suspension of the morpholinium salt in dimethylformamide was added 2*N*-hydrochloric acid (2 equiv.) and then water. The solid was collected and washed with water; yield 34%. Recrystallisation from acetone–water gave yellow crystals, m.p. 144° [spectroscopic data similar to those of compound (8)] (Found: C, 52.5; H, 4.0; N, 11.0; S, 25.7. C₁₁H₁₀N₂OS₂ requires C, 52.8; H, 4.0; N, 11.2; S, 25.6%).

Morpholinium Salt of 2-Cyano-3-imino-3-(4-pyridyl)dithiopropionic Acid (15).—The preparation ‡ was similar to that of compound (8). The compound was obtained as the morpholinium salt; the free acid was not stable enough to be isolated. The salt was recrystallised from dimethylformamide–ethanol (1:1) to give red crystals (15%), m.p. 174° (decomp.) (slow heating) or 184° (rapid heating) [spectroscopic data similar to those of compound (4)] (Found: C, 50.7; H, 5.2; N, 18.0; S, 20.8. C₁₃H₁₆N₄OS₂ requires C, 50.6; H, 5.2; N, 18.2; S, 20.8%). Compound (15) produced a violet precipitate with Ni^{II}.

Methyl 3,6-Dihydro-2,6-dithioxo-4-methyl-2H-1,3-thiazine-5-carboxylate (16).—To a mixture of methyl β -iminobutyrate (3 g, 0.026 mol), sodium *t*-pentyl oxide (5.5 g, 0.050 mol), and dimethylformamide (50 ml), was added dropwise carbon disulphide (3.8 g, 0.050 mol) at 0°. The mixture was shaken at room temperature for two days, and then water (50 ml) was added, washed with ether, and acidified (pH ca.

1) with hydrochloric acid (2*N*). The resulting red solid was collected, washed with water, and dried; yield 0.8 g (13%). The red solid was recrystallised from acetone–water to afford red crystals, m.p. 187–188°; ν_{\max} . (KBr) 3 165m, 1 730s, 1 597s, 1 207vs, and 1 120vs cm⁻¹; λ_{\max} . (EtOH) 236 (log ϵ 4.09), 295 (4.26), 309sh (4.20), 406sh (3.76), 430sh (3.91), and 457 nm (4.03); τ [(CD₃)₂SO] 2.20br (1 H, s, NH), 6.17 (3 H, s, OMe), and 7.79 (3 H, s, 4-Me) (Found: C, 35.7; H, 3.0; N, 5.7; S, 41.3%; *M*⁺, 233. C₇H₇NO₂S₃ requires C, 36.0; H, 3.0; N, 6.0; S, 41.2%; *M*, 233).

Methyl 3,6-Dihydro-2,6-dithioxo-4-phenyl-2H-1,3-thiazine-5-carboxylate (17).—The preparation was similar to that of compound (16). Recrystallisation from methanol–water gave red crystals (23%), m.p. 141–141.5° [spectroscopic data similar to those of compound (16)] (Found: C, 50.4; H, 3.6; N, 4.8; S, 31.2. C₁₃H₁₁NO₂S₃ requires C, 50.5; H, 3.6; N, 4.5; S, 31.1%).

Ethyl 3,6-Dihydro-2,6-dithioxo-4-(*p*-tolyl)-2H-1,3-thiazine-5-carboxylate (18).—The preparation was similar to that of compound (16). Recrystallisation from methanol–water gave red crystals (26%), m.p. 170–171° [spectroscopic data similar to those of compound (16)] (Found: C, 52.2; H, 4.0; N, 4.5; S, 29.7. C₁₄H₁₃NO₂S₃ requires C, 52.0; H, 4.1; N, 4.3; S, 29.7%).

Methyl 3-Methyl-5-thioxo-3H-1,2-dithiole-4-carboxylate (19).—To a mixture of methyl β -iminobutyrate (5 g, 0.043 mol), sodium amide (5.1 g, 0.13 mol), and ether (100 ml) was added carbon disulphide (9.9 g, 0.13 mol) at 0°C, and the mixture was stirred at 0°C for 24 h. Water (50 ml) was added and the ether layer was washed twice with water. The water layer and washings were combined and acidified with dilute hydrochloric acid; the solid was collected, washed with water, and dried; yield 0.6 g (6%). Recrystallisation from acetone–water gave yellow crystals, m.p. 95.5–96°; ν_{\max} . (KBr) 1 711vs, 1 500s, 1 249vs, and 1 153s cm⁻¹; λ_{\max} . (EtOH) 235 (log ϵ 3.97), 267 (3.83), 323 (3.68), and 405 nm (3.93); τ (CDCl₃) 6.02 (3 H, s, OMe) and 7.38 (3 H, s, Me) (Found: C, 34.8; H, 3.1; S, 46.4. C₆H₆O₂S₃ requires C, 34.9; H, 2.9; S, 46.65%).

Redithiocarboxylation of Compounds (8) and (10).—An example is as follows. A solution of compound (8) (2 g, 0.0091 mol) in methylcellosolve (10 ml) was refluxed at 80°C for 4 h. Water was added to the cooled mixture, which was kept for 30 min in an ice box to give a white solid; this was collected, washed with water, and dried (yield 0.8 g, 61%); m.p. 110–111.5° (lit.¹² 108°); i.r. spectrum identical with that of an authentic sample (Found: C, 75.8; H, 6.45; N, 17.9. Calc. for C₁₀H₁₀N₂: C, 75.9; H, 6.4; N, 17.7%).

Thermal Decomposition of 2-Iminocyclopentanedithiocarboxylic Acid: 6',7'-Dihydrospiro[cyclopentane-1,2'(1'H)-cyclopenta[d][1,3]thiazine]-4'(5'H)-thione (20).—A solution of 2-iminocyclopentanedithiocarboxylic acid (3 g, 0.019 mol) in methylcellosolve (10 ml) was refluxed at 70°C for 40 min. Water (80 ml) was added to the cooled mixture. The orange solid was collected, washed with ether, and dried; yield 2 g (94%), m.p. 188–189° (lit.¹ 189–190°), i.r. and u.v. spectra identical with those reported (Found: C, 58.45; H, 6.8; N, 6.5; S, 28.3. Calc. for C₁₁H₁₅NS₂: C, 58.6; H, 6.7; N, 6.2; S, 28.45%).

Thiocarboxylic Carbamic Thioanhydrides (21)–(30) from Compounds (1), (4), (8), (10), (13), and (14).—For example, a

* β -Imino- β -(*m*-tolyl)propionitrile was prepared from acetonitrile and *m*-toluonitrile by Meyer's method;¹² b.p. 130–135° at 0.1 Torr; m.p. 67–68° (from benzene).

† Prepared from acetonitrile and β -naphthonitrile by Meyer's method;¹² m.p. 98° [from benzene–petroleum (1:1)].

‡ β -Imino- β -(4-pyridyl)propionitrile was obtained from acetonitrile and γ -cyanopyridine by Meyer's method¹² as a viscous brown oil which was used without purification.

¹² E. V. Meyer, *J. prakt. Chem.*, 1895, [2]52, 110.

mixture of compound (4) (0.22 g, 0.001 mol), methyl isocyanate (0.06 g, 0.001 mol), and benzene (100 ml) was refluxed at 70 °C for 30 min, and set aside at room temperature for 3 h. The yellow product was collected, washed with benzene, and dried (see Table 1). The i.r. and n.m.r.

TABLE 1
Thiocarboxylic carbamic thioanhydrides (21)—(30)

Com- pound	Yield (%)	M.p. (°C)		Solvent *
		Slow heating	Rapid heating	
(21)	85	95—100		MeCO ₂ Et-n-C ₆ H ₁₄
(22)	95	149—150	145—147	MeCO ₂ Et-n-C ₆ H ₁₄
(23)	86	160—230	109—111	MeCO ₂ Et-THF-n-C ₆ H ₁₄
(24)	86	221—222 (decomp.)	127—128	MeCO ₂ Et
(25)	80	300 (decomp.)	146—147 (decomp.)	THF-n-C ₆ H ₁₄
(26)	71	251—252	235—236	C ₆ H ₆ -n-C ₆ H ₁₄
(27)	68	96—97 (decomp.)	96—98 (decomp.)	MeCO ₂ Et-THF-n-C ₆ H ₁₄
(28)	62	172		MeCO ₂ Et-n-C ₆ H ₁₄
(29)	74	224—225		Me ₂ N·CHO-EtOH
(30)	65	222—223		Me ₂ N·CHO-EtOH

THF = tetrahydrofuran.

spectra and elemental analyses of these compounds agreed with the proposed structures.

2-Cyano-3-iminothiobutyric Ethylthiocarbamic Thioanhydride (31).—A mixture of compound (1) (1 g, 0.0067 mol), ethyl isothiocyanate (2 g, 0.023 mol), sulphuric acid (96%, 0.05 g), and dioxan (10 ml) was shaken at room temperature for 3 h. The yellow crystalline solid was collected, washed several times with dioxan, and dried; yield 0.72 g (45%), m.p. 105—106° (decomp.). Recrystallisation from polar solvents such as methanol, ethanol, acetone, and dimethylformamide denatured the product; ν_{\max} (KBr) 3295m, 3250s, 3100m, 2195s, 1643s, 1542vs, 1450sh, 1420vs,

1,2,4-Trithioles (37)—(39).—*Method A.* For example, a mixture of compound (4) (0.7 g, 0.0032 mol), phenyl isothiocyanate (0.5 g, 0.0037 mol), ground glass (10 g), and dioxan (10 ml) was shaken at room temperature for 10 h. The yellow solid was collected and washed with dioxan; yield 0.19 g (50%). The i.r., u.v., and n.m.r. spectra and elemental analysis agreed with the proposed structure (see Table 3).

Method B. A solution of the oxidative dimer of compound (4), bis-(1-cyano-2-imino-2-phenylethylthiocarbonyl) disulphide* (0.7 g, 0.0032 mol) in methylcellosolve (2 ml)

TABLE 2
1,3-Dithietans (32)—(36)

Compound	Yield (%)	M.p. (°C)	Colour
(32)	54 (65)	299—300	Red
(33)	58 (68)	>300	Red
(34)	52 (71)	245—246	Red
(35)	56	>300	Dark red
(36)	88	>300	Orange

was refluxed for 6 min. The yellow product was collected and washed with ethanol; yield 0.29 g (45%), m.p. and i.r. spectrum identical with those of compound (37) obtained by method A.

Compound (38) was obtained directly in good yield on oxidation of compound (8) with iodine.

2-(2-Substituted 1-cyano-2-iminoethylidene)-1,3-benzodithioles (40)—(45).—For example, to a solution of picryl chloride (0.25 g, 0.001 mol) in ethanol (12 ml), cooled in ice, was added a solution of compound (4) (0.22 g, 0.001 mol) and triethylamine (0.1 g, 0.001 mol) in ethanol (18 ml). The mixture was kept at room temperature for 10 h. The crystalline solid was collected, washed with ethanol, dried (yield 0.31 g, 81%), and recrystallised from dimethylformamide-ethanol (1:2) to give orange crystals (see Table

TABLE 3
1,2,4-Trithioles (37)—(39)

Compound	Yield (%)	M.p. (°C)	τ [(CD ₃) ₂ SO]
(37)	50 (45)	225—226	-1.97br (1 H, s, NH), -0.90br (1 H, s, NH), ca. 1.8—2.5 (10 H, m, 2Ph)
(38)	54 (91) ^a	240—241	-1.93br (1 H, s, NH), -0.85br (1 H, s, NH), ca. 1.9—2.6 (8 H, m, 2C ₆ H ₄), 7.55 (3 H, s, CH ₃)
(39)	(49)	212—213	-1.97br (1 H, s, NH), -0.87br (1 H, s, NH), ca. 2.1—2.5 (8 H, m, 2C ₆ H ₄), 7.53 (3 H, s, CH ₃)

^a Yield obtained on direct oxidation of compound (8) with iodine.

1382m, 1242vs, 1192s, and 1140 cm⁻¹ (Found: C, 39.2; H, 4.35; N, 17.4; S, 39.3. C₈H₁₁N₃S₃ requires C, 39.2; H, 4.5; N, 17.1; S, 39.2%). Compound (31) was soluble in aqueous alkali and gradually displayed a violet colouration with Ni^{II}.

2,4-Bis-(2-substituted 1-cyano-2-iminoethylidene)-1,3-dithietans (32)—(36).—*Method A.* For example, a solution of compound (23) (0.3 g, 0.0011 mol) in dioxan (5 ml) was refluxed at 75 °C for 2 h. The red precipitate of compound (32) was collected, washed with dioxan (yield 0.11 g, 54%), and recrystallised from dimethylformamide-water. Yields, m.p.s, and colours of compounds (32)—(36) are shown in Table 2. The i.r., u.v., n.m.r., and mass spectra and elemental analyses agreed with the proposed structures.

Method B. For example, a mixture of compound (4) (0.55 g, 0.0025 mol), phenyl isothiocyanate (0.6 g, 0.0044 mol), sulphuric acid (96%, 0.05 g), and dioxan (10 ml) was shaken at room temperature for 10 h. The red solid product was collected and washed with dioxan; yield 0.3 g (65%). The m.p., i.r., and u.v. spectra were identical with those of compound (32) obtained by method A.

4). The i.r. and u.v. spectra and elemental analyses of these compounds agreed with the proposed structures.

Picryl 2-Cyano-3-imino-3-phenyldithiopropionate (46).—To a suspension of picryl chloride (0.25 g, 0.001 mol) in ethanol (10 ml) was added dropwise a solution of compound (4) (0.22 g, 0.001 mol) and triethylamine (0.1 g, 0.001 mol) in ethanol (5 ml) below 0 °C at such a rate the contents of the flask retained a pale yellow colour. The yellow crystalline solid was collected, washed with ethanol, and dried; yield 0.4 g (93%), m.p. 222—224° (decomp.) (slow heating) or 123—125° (decomp.) (rapid heating); ν_{\max} (KBr) 3380m, 3070m, 2870w, 2190m, 1618s, 1550vs, 1534vs, 1440sh, 1426s, 1341vs, and 1269vs cm⁻¹ (Found: C, 44.7; H, 2.3;

* Pale yellow crystals, prepared by the oxidation of compound (4) with iodine in the usual way; m.p. 153—166° (from dimethylformamide-ethanol) (Found: C, 54.6; H, 3.4; N, 12.8. Calc. for C₂₆H₁₄N₄S₄: C, 54.8; H, 3.2; N, 12.8%). Bis-[1-cyano-2-imino-(*m*-tolyl)ethylthiocarbonyl] disulphide [oxidative dimer of compound (10), (C₁₀H₉N₂CS₂)₂, pale yellow crystals] was similarly prepared; m.p. 222° (from dimethylformamide-ethanol) (Found: C, 56.4; H, 4.0; N, 11.9. Calc. for C₂₂H₁₈N₄S₄: C, 56.6; H, 3.9; N, 12.0%).

N, 15.9; S, 15.1. $C_{16}H_9N_5O_6S_2$ requires C, 44.55; H, 2.1; N, 16.2; S, 14.85%.

Picryl 2-Cyano-3-imino-3-(p-tolyl)dithiopropionate (47).—To a suspension of the morpholinium salt of compound (8) (0.35 g, 0.001 1 mol) in ethanol (25 ml) was added picryl chloride (0.3 g, 0.001 2 mol) at 0 °C. The mixture was

TABLE 4

1,3-Benzodithioles (40)—(45)		
Compound	Yield (%)	M.p. (°C)
(40)	53	213—214 (decomp.)
(41)	81	227—228
(42)	88	240—242
(43)	73	230
(44)	98	264—265 (decomp.)
(45)	81	233—234 (decomp.)

shaken at 0 °C for 3.5 h. The yellow solid was collected, washed with ethanol, and dried in the dark (yield 0.35 g, 74%), m.p. 124° (withering) (rapid heating) or 196—201° (slow heating), i.r. spectrum similar to that of compound (46) (Found: C, 46.1; H, 2.5; N, 15.25. $C_{17}H_{11}N_5O_6S_2$ requires C, 45.8; H, 2.5; N, 15.7%).

Picryl 2-Cyano-3-imino-3-(m-tolyl)dithiopropionate (48).—The preparation was similar to that of compound (47). The yellow product was washed with methanol and dried in the dark (yield 70%); m.p. 127° (withering) and 166—172° (decomp.) (rapid heating) or 167—177° (decomp.) (slow heating), i.r. spectrum similar to that of compound (46) (Found: C, 46.1; H, 2.6; N, 15.35. $C_{17}H_{11}N_5O_6S_2$ requires C, 45.8; H, 2.5; N, 15.7%).

Conversion of Compounds (46)—(48) into Compounds (41)—(43).—For example, a solution of compound (41) (0.4 g,

0.000 93 mol) in dimethylformamide (10 ml) was kept at room temperature for 5 min. Methanol (20 ml) was added and the precipitate was collected, washed with methanol, dried (yield 0.2 g, 56%), and recrystallised from dimethylformamide-methanol to give orange *crystals*. The m.p.s and i.r. spectra of these compounds were identical with those of the corresponding compounds (41)—(43).

5-Substituted 4-Cyano-3-mercapto-2H-pyrazoles (49)—(53).—For example, a mixture of compound (4) (1.1 g, 0.005 mol), hydrazine hydrate (1 g, 0.02 mol), and water (10 ml) was warmed to 70 °C for 30 min. 2N-Hydrochloric acid (15 ml) was added to the cooled mixture and the precipitate was collected, washed with water, and dried; yield 0.95 g (95%). Yields, m.p.s, and solvents for recrystallisation of compounds (49)—(53) are shown in Table 5. The

TABLE 5

Pyrazoles (49)—(53)			
Compound	Yield (%)	M.p. (°C)	Solvent
(49) ^a	91	242—243	EtOH
(50)	95	147—148	C_6H_6
(51)	97	163—165	C_6H_6
(52)	76	252—253	C_6H_6
(53)	73	203—204	C_6H_6

^a Isolated as pyridinium salt.

i.r. spectra of the compounds had an SH band near 2 450 cm^{-1} . The u.v. spectra and elemental analyses agreed with the proposed structures.

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