Reaction of Carbon Disulphide with Cyclic Amides and Related Compounds. Free *N*-Acyl- and *N*-Carbamoyl-dithiocarbamic Acids

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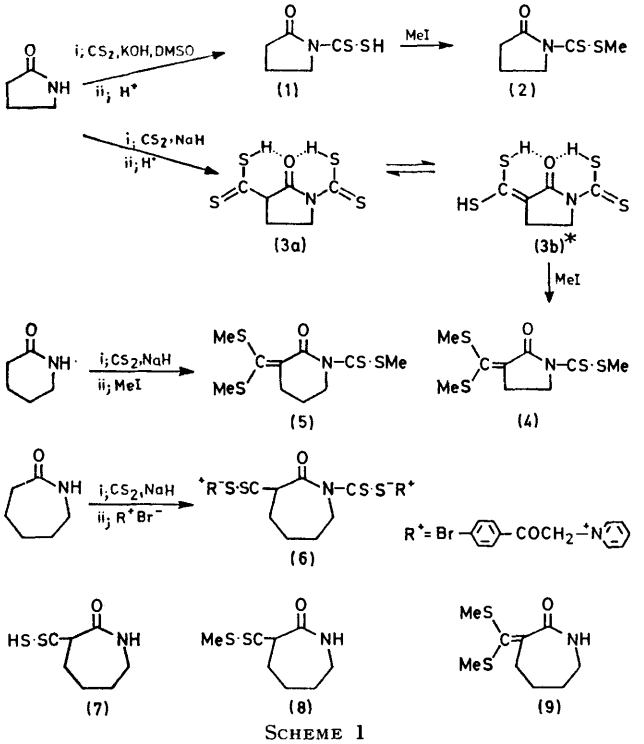
2-Pyrrolidone, 2-piperidone, ε-caprolactam, imidazolidin-2-one, imidazolidine-2,4-dione, and 2,5-dioxopiperazine, after treatment with sodium hydride or in the presence of alkali, reacted with carbon disulphide to give the respective 1-dithiocarboxylic acid and/or 1,3-bisdithiocarboxylic acid which were readily esterified. The stable crystalline free acids could be easily isolated in the case of the five-membered ring compounds.

No reports seem to have appeared concerning the isolation of free *N*-acyl- and *N*-carbamoyl-dithiocarbamic acids. Some have been reported, but these were obtained in the form of esters and were prepared *via* procedures different from ours.[1] Shahak and Sasson have proposed a *N*-acyldithiocarbamate anion as an intermediate in the mechanism of the formation of thiol acids from amides and carbon disulphide.[2]

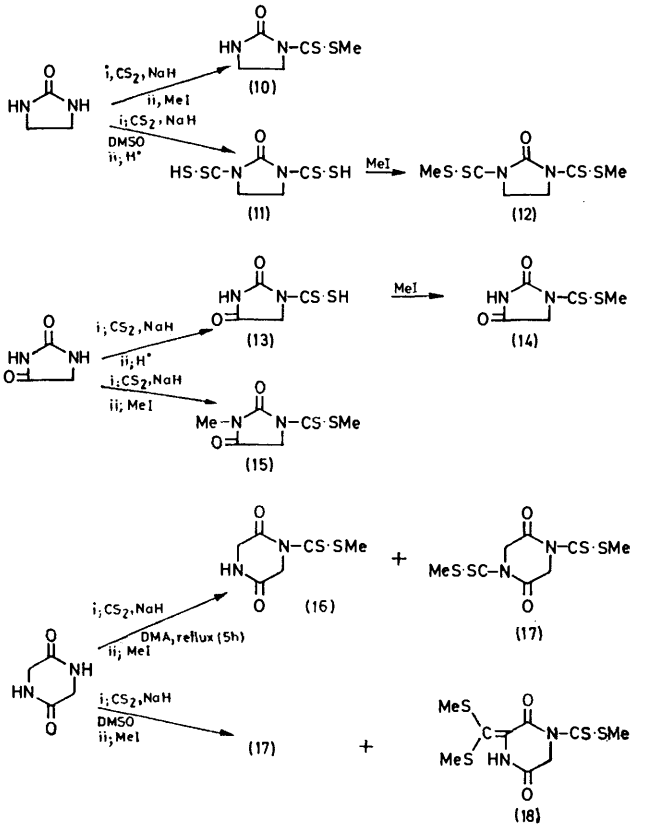
We have synthesized the title compounds by the reaction of cyclic amides and related compounds with carbon disulphide. The merit of the present method is the ready availability of cyclic amide type compounds. One limitation is that the imino-group flanked by two carbonyl groups, as in succinimide, fails to react.†



SCHEME 1

* Structure (3b) is considered to be in equilibrium with the tautomer (3a), as judged from n.m.r. (see Experimental section).

2-Pyrrolidone, in the presence of potassium hydroxide, reacted with carbon disulphide to give the dithiocarboxylic acid (1). When the amide was treated with sodium hydride and then with carbon disulphide the bisdithiocarboxylic acid (3) was produced. Imidazolidin-2-one, on similar treatment, afforded the impure 1-dithiocarboxylic acid which was identified as its ester (10). When treatment with sodium hydride was conducted in, for example, dimethyl sulphoxide, the 1,3-bisdithiocarboxylic acid (11) was isolated. Imidazolidine-2,4-dione (hydantoin) gave the 1-dithiocarboxylic acid (13); lack of dithiocarboxy-group at the 3-position is consistent with the fact that the imino-hydrogen of succinimide did not enter into the present reaction. This may



SCHEME 2

† H. Malissa and E. Schöffmann (*Mikrochim. Acta*, 1955, 187) have reported the syntheses of succinimide *N*-dithiocarboxylic acid sodium salt and related compounds. We have tried the same experiment but of the expected compounds, could only obtain the pyrrolidine-1-dithiocarboxylate.

be due to electron deficiency at the imino-group in question. These dithiocarbamic acids could be isolated as the crystalline free acids.

From 2-piperidone, the 1,3-bisdithiocarboxylic acid was produced as an unstable oily material, and was identified as the ester (5). Likewise, from dioxopiperazine were obtained the dithiocarboxylate (16) and the bisdithiocarboxylate (17) when the reaction was conducted in dimethylacetamide; in dimethyl sulphoxide containing tetrahydrofuran, (17) and the ester (18) were obtained. The 1,3-bisdithiocarboxylic acid of ε-caprolactam could be identified as its *p*-bromophenacylpyridinium salt (6). Acidification of the product resulted in the formation of the ε-caprolactam-3-dithiocarboxylic acid (7).

All these free acids or their salts were extremely reactive towards heavy-metal ions producing coloured complexes.[3] The new compounds obtained were identified by i.r., n.m.r., and mass spectra together with elemental analyses and chemical reactions (see Experimental section).

That the five-membered ring acids in particular had enhanced stability and easily crystallized may be due to lack of skeletal inversion, which may also facilitate intramolecular hydrogen bonding between dithiocarboxy hydrogen and carbonyl oxygen. This trend applies to the cases of 2-imino-[3,4] and 2-oxocyclopentanedithiocarboxylic acids as well.[4,5]

Cyclic *N*-acyl- and *N*-carbamoyl-dithiocarbamic acids and related compounds

Compound	M.p./°C	$\lambda_{max.}$/nm (log ε) [a]	Yield (%)	Formula	Found (%) C	H	N	S	Required (%) C	H	N	S
(1)	101—102 [b,c]	229sh (3.63) 276 (4.09) 341 (4.01)	20	$C_5H_7NOS_2$	37.4	4.3	8.7	39.4	37.2	4.4	8.7	39.8
(2)	97—98	269 (4.22) 304 (4.05)	80	$C_6H_9NOS_2$	41.1	5.2	7.9	36.85	41.1	5.2	8.0	36.6
(3)	105 [b,c]	262 (3.75) 311 (3.96) 408 (4.40)	35	$C_6H_7NOS_4$	30.2	3.1	5.7	53.4	30.4	3.0	5.9	54.0
(4)	112—113	216 (3.29) 249 (3.46) 285sh (3.67) 364 (4.29)	89	$C_9H_{13}NOS_4$	38.1	4.7	5.0	45.05	38.7	4.7	5.0	45.9
(5)	103—105	213 (4.22) 281 (4.13) 322 (4.39) 355 (4.39)	75	$C_{10}H_{15}NOS_4$	40.9	5.2	4.6	43.05	41.0	5.15	4.8	43.7
(6)	136—137 [b,c]	263 (4.62) 346 (4.10) 426 (4.22)	49	$C_{34}H_{31}N_3O_3S_4Br_2$	49.6	3.8	5.1	15.5	49.9	3.8	5.1	15.7
(7)	103—105	345 (4.30)	57 [d] 35 [e]	$C_7H_{11}NOS_2$	44.1	6.1	7.3	32.9	44.4	5.9	7.4	33.9
(8)	144—145	310 (4.01)	5	$C_8H_{13}NOS_2$	47.2	6.5	6.7	31.3	47.3	6.4	6.9	31.5
(9)	152—153	250 (3.98)	75	$C_9H_{15}NOS_2$	49.8	7.1	6.6	29.2	49.7	7.0	6.45	29.5
(10)	213—215	214 (3.75) 268 (4.26) 289 (4.14)	23	$C_5H_8N_2OS_2$	34.3	4.65	15.7	35.9	34.1	4.6	15.9	36.4
(11)	119—120 [b,c]	283 [f,g] 309 315sh 420	85	$C_5H_6N_2OS_4$	25.1	2.6	11.8	53.2	25.2	2.5	11.75	53.8
(12)	304—305	303 (4.76) [h]	78 [i]	$C_7H_{10}N_2OS_4$	31.7	3.8	10.6	48.2	31.55	3.8	10.5	48.1
(13)	222—225 [b,c]	254 (4.21) 298 (4.07) 331sh (3.46)	47	$C_4H_4N_2O_2S_2$	27.6	2.5	15.6	36.0	27.3	2.3	15.9	36.4
(14)	243—245	265 (4.20) [h] 298 (3.99)	76	$C_5H_6N_2O_2S_2$	31.7	3.2	14.9	33.8	31.6	3.2	14.7	33.7
(15)	206	242 (3.40) 265 (4.34) 301 (4.09)	32	$C_6H_8N_2O_2S_2$	35.4	3.9	13.8	31.5	35.3	3.95	13.7	31.4
(16)	197—198	267 (4.04) 310 (3.90)	12	$C_6H_8N_2O_2S_2$	35.2	4.0	13.6	31.4	35.3	3.95	13.7	31.4
(17)	270—272 [b]	274 [g,h] 311	19 21 [j]	$C_8H_{10}N_2O_2S_4$	32.8	3.4	9.6	43.0	32.6	3.4	9.5	43.6
(18)	200—202	250sh (3.99) 286 (4.13) 313sh (4.04) 384 (4.11)	32	$C_9H_{12}N_2O_2S_4$	35.1	3.8	9.2	40.9	35.0	3.9	9.1	41.6

[a] In EtOH. [b] With decomposition. [c] Rapid heating. [d] Based on ε-caprolactam. [e] Based on the salt (5). [f] In $CHCl_3$. [g] The measurement of ε was impossible because of low solubility. [h] In dioxan. [i] Based on imidazolidine. [j] In the reaction in which dimethyl sulphoxide was used.

EXPERIMENTAL

Two model preparative methods are described below.

2-Pyrrolidone-1-carbodithioic Acid (1).—To a solution of 2-pyrrolidone (6 g, 0.071 mol) in dimethyl sulphoxide (30 ml) were added carbon disulphide (6 g, 0.079 mol) at *ca.*

15 °C and then aqueous 33% potassium hydroxide (12 ml) below 35 °C with stirring. After being stirred at 15—20 °C for an additional 20 min the mixture was slowly poured into a mixture of conc. hydrochloric acid (40 ml), water (200 ml), and ice (200 g). The yellow precipitate was collected, washed with water and then ether, and recrystallised from acetone; $\nu_{max.}$(KBr) 2 540s (SH) and 1 726vs cm^{-1} (C=O).

2-Pyrrolidone-1,3-bis(carbodithioic Acid) (3).—To a mixture of sodium hydride (3.75 g; 50% dispersion in oil; 0.078 mol) and tetrahydrofuran (40 ml) was gradually added a solution of 2-pyrrolidone (6.5 g, 0.076 mol) in tetrahydrofuran (5 ml) with stirring in a water-bath. A solution of carbon disulphide (14 g, 0.18 mol) in tetrahydrofuran (10 ml) was added dropwise over a period of 1.5 h at 6—7 °C in an ice-bath and the mixture was stirred for 20 min. To decompose the excess of sodium hydride, water (20 ml) was added dropwise to the reaction mixture under nitrogen. The whole was washed with benzene and the aqueous portion was separated and acidified with 2N-hydrochloric acid (50 ml) with cooling. The yellow precipitate was collected, washed with water and ethanol, and dried; $\nu_{max.}$(KBr) 2 500m, 2 440m (SH), and 1 675vs cm^{-1} (C=O); δ($CDCl_3$) 2.50br [1/2 H, s, CH (2a)], 2.78 (2 H, t, 4-H_2), 3.42br [1/2 H, s, no hydrogen-bonding SH (2a)], 4.18 (2 H, t, 5-H_2), and 6.30br [2 H, m, hydrogen-bonding SH (2a, b)]. Methyl esters were prepared by adding methyl iodide directly to each reaction mixture. One exception is the methyl ester of (1); this is described below.

Methyl 2-Pyrrolidone-1-carbodithioate (2).—The acid (1) (1.15 g, 0.007 mol) was added to a solution of potassium hydroxide (0.4 g, 0.007 mol) in ethanol (25 ml), and the mixture was stirred for 30 min with cooling. The orange potassium salt of (1) was collected, 1.3 g (91.5%); m.p. 155—156 °C, $\nu_{max.}$(KBr) 1 679vs cm^{-1} (C=O). The mixture of the salt (0.5 g, 0.002 5 mol), methyl iodide (0.7 g, 0.005 mol), and ethanol (10 ml) was stirred for 20 min with cooling and then kept in a refrigerator for 1 h. The solid product was collected, washed with water and ethanol, and recrystallised from ethanol; $\nu_{max.}$(KBr) 1 719vs cm^{-1} (C=O).

Methyl 3-[bis(methylthio)methylene]-2-pyrrolidone-1-carbodithioate (4) was recrystallised from benzene–n-hexane (1 : 2) and then acetone; $\nu_{max.}$(KBr) 1 689vs cm^{-1} (C=O); δ($CDCl_3$) 2.47, 2.50 [each 3 H, s, =C($SMe)_2$], 2.60 (3 H, s, CS_2Me), 2.94 (2 H, t, 4-H_2), and 4.20 (2 H, t, 5-H_2).

Methyl 3-[bis(methylthio)methylene]-2-piperidone-1-carbodithioate (5) was recrystallised from isopropanol; $\nu_{max.}$(KBr) 1 637vs cm^{-1} (C=O); δ($CDCl_3$) 1.96 (2 H, quint, 5-H_2), 2.42, 2.44 [each 3 H, s, =C($SMe)_2$], 2.57 (3 H, s, CS_2Me), 2.88 (2 H, t, 4-H_2), and 4.37 (2 H, t, 6-H_2).

Bis-(p-bromophenacylpyridinium) ε-Caprolactam-1,3-biscarbodithioate (6).—To the aqueous layer from work-up of the reaction mixture was added aqueous *p*-bromophenacylpyridinium bromide [from *p*-bromophenacylbromide (7 g, 0.025 mol) and pyridine (35 ml) in water (70 ml)] and the whole was kept overnight in an ice-box. The orange-yellow crystals were collected, washed with ethanol, and dried. Recrystallisation of the salt (6) brought about partial decomposition and a pure sample could only be obtained when pyridine was used in excess (70 ml) in the preparation of the *p*-bromophenacylpyridinium bromide solution; the resulting *precipitate* was collected after standing at room temperature for a few hours; $\nu_{max.}$(KBr) 1 683vs (*p*-bromophenacyl C=O) and 1 622vs cm^{-1} (C=O).

ε-Caprolactam-3-carbodithioic Acid (7).—The aqueous portion of the reaction mixture from the preceding preparation was cooled in an ice-bath and 2N-hydrochloric acid (60 ml) was added. A red tarry material separated; this was left at room temperature until crystallisation accompanied by evolution of a gas occurred. Recrystallisation from ethanol yielded *orange crystals*; $\nu_{max.}$(KBr) 3 280s, 3 220s, 3 070s (NH), 2 460vs (SH), and 1 635vs cm^{-1} (C=O); δ($CDCl_3$) *ca.* 1.36—1.94 (4 H, m, 5- and 6-H_2), *ca.* 1.94—2.36 (2 H, m, 4-H_2), 3.25 (2 H, m, 7-H_2), 4.30 (1 H, m, 3-H), 5.60br (1 H, s, NH), and 7.20br (1 H, s, SH). The acid (7) was also obtained from the salt (6) by acidification of a suspension of the latter in ethanol.

Methyl ε-caprolactam-3-carbodithioate (8) was recrystallised from ethanol; $\nu_{max.}$(KBr) 3 270s, 3 200vs, 3 060s (NH), and 1 644vs cm^{-1} (C=O); *m/e* 203 (M^+). Use of excess of methyl iodide followed by crystallisation from ethanol yielded *3-[bis(methylthio)methylene]-ε-caprolactam* (9); $\nu_{max.}$(KBr) 3 275s, 3 195vs, 3 070s (NH), 1 654vs, and 1 648vs cm^{-1} (C=O); δ($CDCl_3$) *ca.* 1.45—2.05 (4 H, m, 5- and 6-H_2), 2.25, 2.28 [each 3 H, s, =C($SMe)_2$], 2.55 (2 H, m, 4-H_2), 3.07 (2 H, m, 7-H_2), and 6.50br (1 H, s, NH).

Methyl 2-oxoimidazolidine-1-carbodidithioate (10) was prepared as for (5), washed with ethanol, and dried; it showed $\nu_{max.}$(KBr) 3 210vs, 3 120s (NH), and 1 738vs cm^{-1} (C=O); δ[$(CD_3)_2SO$] 2.48 (3 H, s, Me), 3.42 (2 H, t, 4-H_2), 4.20 (2 H, t, 5-H_2), and 8.08br (1 H, s, NH). 2-Oxoimidazolidine-1-carbodithioic acid was obtained by acidification of the above aqueous mixture. The crude cream solid was washed with ethanol and dried, yield 0.7 g (25%), m.p. *ca.* 70 °C (decomp.); $\nu_{max.}$(KBr) 3 160s (NH), 2 430s (SH), and 1 733 cm^{-1} (C=O). Further purification of the acid was difficult.

2-Oxoimidazolidine-1,3-bis(carbodithioic Acid) (11).—Use of dimethyl sulphoxide–tetrahydrofuran as the reaction medium and recrystallisation from acetic acid yielded the *acid*, $\nu_{max.}$(KBr) 2 500w, 2 450s (SH), and 1 730vs cm^{-1} (C=O).

Dimethyl 2-oxoimidazolidine-1,3-bis(carbodithioate) (12) was recrystallised from dimethyl sulphoxide; $\nu_{max.}$(KBr) 1 722vs cm^{-1} (C=O); *m/e* 266 (M^+).

2,4-Dioxoimidazolidine-1-carbodithioic Acid (13).—The acid (13) was prepared by the method used for (3). Ligroin–dimethyl sulphoxide was used as solvent. Recrystallisation from acetone yielded the *acid*, $\nu_{max.}$(KBr) 3 150vs, 3 070s (NH), 2 435s (SH), 1 765s, and 1 708vs cm^{-1} (C=O); *m/e* 176 (M^+).

Methyl 2,4-dioxoimidazolidine-1-carbodithioate (14) was recrystallised from tetrahydrofuran and acetone to yield pale yellow crystals; $\nu_{max.}$(KBr) 3 160vs, 3 060vs (NH), 1 778vs, and 1 712vs cm^{-1} (C=O); δ[$(CD_3)_2SO$] 2.54 (3 H, s, Me), 4.54 (2 H, s, CH_2), and 11.80br (1 H, s, NH).

Methyl 3-methyl-2,4-dioxoimidazolidine-1-carbodithioate (15) was recrystallised from pyridine to give crystals tinged green–yellow; $\nu_{max.}$(KBr) 1 778s and 1 700vs cm^{-1} (C=O); δ[$(CD_3)_2SO$] 2.61 (3 H, s, SMe), 2.94 (3 H, s, NMe), and 4.61 (2 H, s, CH_2); *m/e* 204 (M^+).

Methyl 2,5-Dioxopiperazine-1-carbodithioate (16), *Dimethyl 2,5-Dioxopiperazine-1,4-biscarbodithioate* (17), *and Methyl 3-[Bis(methylthio)methylene]-2,5-dioxopiperazine-1-carbodithioate* (18).—Compounds (16), (17), and (18) were prepared in the usual way (see Scheme 2). From the crude products, (16) and (17) were separated by using hot methyl cellosolve; (17) was the less soluble. Recrystallisation of

(17) from pyridine gave yellow *crystals*; $\nu_{max.}$(KBr) 1 675vs cm^{-1} (C=O); *m/e* 294 (M^+). The crude (16) was recrystallised from acetone to afford the *methyl carbodithioate*; $\nu_{max.}$(KBr) 3 280m (NH), 1 692vs, and 1 633vs cm^{-1} (C=O). The yellow–orange solid [the crude esters (17) and (18)] was treated with pyridine. The residue of (17) was filtered off. To the filtrate, water (100 ml) was added and the mixture stored overnight in a refrigerator. The yellow solid (18) was recrystallised from benzene (charcoal) to give light yellow *crystals*; $\nu_{max.}$(KBr) 3 150m (NH), 1 675vs, and 1 660s cm^{-1} (C=O); $\delta(CDCl_3)$ 2.40, 2.52 [each 3 H, s, $=C(SMe)_2$], 2.64 (3 H, s, CS_2Me), 5.09 (2 H, s, CH_2), and 8.66br (1 H, s, NH); *m/e* 308 (M^+).

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