

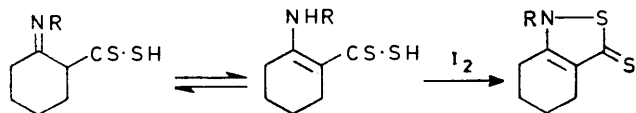
Oxidation and Bimolecular Condensation Reactions of 2-Alkyliminocyclopentanedithiocarboxylic Acids, 2-Oxocyclopentanedithiocarboxylic Acids, and 3-Methyl-5-oxo-1-phenyl- Δ^2 -pyrazoline-4-dithiocarboxylic Acid

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The 2-oxocyclopentanedithiocarboxylic acids (9) and (10) and 3-methyl-5-oxo-1-phenyl- Δ^2 -pyrazoline-4-dithiocarboxylic acid (13), on oxidation, gave the 3,5-bis-(2-oxocyclopentylidene)-1,2,4-trithioles (11) and (12) and 3,5-bis-(3-methyl-5-oxo-1-phenyl- Δ^2 -pyrazolin-4-ylidene)-1,2,4-trithiole (14), respectively. The 2-alkyliminocyclopentanedithiocarboxylic acids (1)—(4), under similar conditions, underwent normal oxidation to the bis-(2-alkyliminocyclopentylthiocarbonyl) disulphides (5)—(8). The acid (9) afforded 6,7-dihydro-2-(2-oxocyclopentylidene)cyclopenta[*d*][1,3]dithiin-4(5*H*)-thione (15) when treated with dimethylformamide alone, and 2,4-bis-(2-oxocyclopentylidene)-1,3-dithietan (16) when treated with dimethylformamide and an acyl chloride. 2,4-Bis-(3-methyl-5-oxo-1-phenyl- Δ^2 -pyrazolin-4-ylidene)-1,3-dithietan (17) was likewise obtained from the acid (13).

It is well known that many dithiocarboxylic acids are susceptible to oxidation to bithiocarbonyl disulphides. We have previously¹ described the corresponding oxidation of 2-iminocyclopentanedithiocarboxylic acids. Mayer and Jentzsch² have reported, however, that 2-alkyliminocyclohexanedithiocarboxylic acids, on oxidation with iodine, suffer intramolecular cyclization to give isothiazoline-5-thiones (Scheme 1).



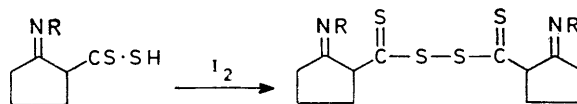
SCHEME 1

We now report the oxidation of the *N*-substituted 2-iminocyclopentanedithiocarboxylic acids (1)—(4), the 2-oxocyclopentanedithiocarboxylic acids (9) and (10), and 3-methyl-5-oxo-1-phenyl- Δ^2 -pyrazoline-4-dithiocarboxylic acid (13). The products from these two types of acid (imino- and oxo-) were different in nature (Schemes 2 and 3). The imino-acids gave the thiocarbonyl disulphides (5)—(8), whereas the oxo-acids (9) and (10) yielded trithioles³ (11) and (12). The products were identified on the basis of spectroscopic data, elemental analyses, and molecular weights (see Experimental section). These oxidation reactions did not always require an oxidising agent. In many cases the reaction took place simply on dissolution in a solvent.

The i.r. carbonyl absorptions of the acids (9) and (13) are unusually weak;⁴ this may be due to intramolecular hydrogen bonding. The derived trithioles, however, showed distinct carbonyl absorption.

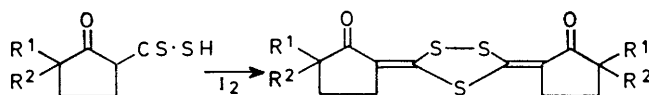
In the absence of oxidising agent, the acid (9), in dimethylformamide, tetramethylene sulphone, or hexamethylphosphoric triamide, underwent a bimolecular condensation to give 6,7-trihydro-2-(2-oxocyclopentylidene)cyclopenta[*d*][1,3]dithiin-4(5*H*)-thione (15). Use of

acetone or dimethyl sulphoxide as the solvent, however, gave the trithiole derivative (11). The condensation reaction appeared to involve both the enedithiol and the enol form of the acid, with elimination of one molecule

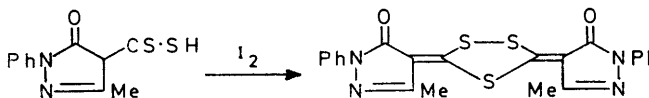


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|--|--|
| (1) R = Pr ⁱ | (5) R = Pr ⁱ |
| (2) R = Bu ^s | (6) R = Bu ^s |
| (3) R = n-C ₆ H ₁₃ | (7) R = n-C ₆ H ₁₃ |
| (4) R = cyclo-C ₆ H ₁₁ | (8) R = cyclo-C ₆ H ₁₁ |

SCHEME 2



- | | |
|--|--|
| (9) R ¹ = R ² = H | (11) R ¹ = R ² = H |
| (10) R ¹ R ² = [CH ₂] ₄ C | (12) R ¹ R ² = [CH ₂] ₄ C |



- | | |
|------|------|
| (13) | (14) |
|------|------|

SCHEME 3

each of water and hydrogen sulphide (Scheme 4). When a large excess of an acyl chloride was added the enedithiol form alone contributed to the condensation, giving 2,4-bis-(2-oxocyclopentylidene)-1,3-dithietan (16) (Scheme 4). The use of less than 1 equiv. of acyl chloride resulted in compound (15). A dithiin-type could not be obtained from the acid (13) under the influence of a solvent, but 2,4-bis-(3-methyl-5-oxo-1-phenyl- Δ^2 -pyrazolin-4-ylidene)-

¹ T. Takeshima, M. Yokoyama, T. Imamoto, M. Akano, and H. Asaba, *J. Org. Chem.*, 1969, **34**, 730; T. Takeshima, T. Miyauchi, N. Fukada, S. Koshizawa, and M. Muraoka, *J.C.S. Perkin I*, 1973, 1009.

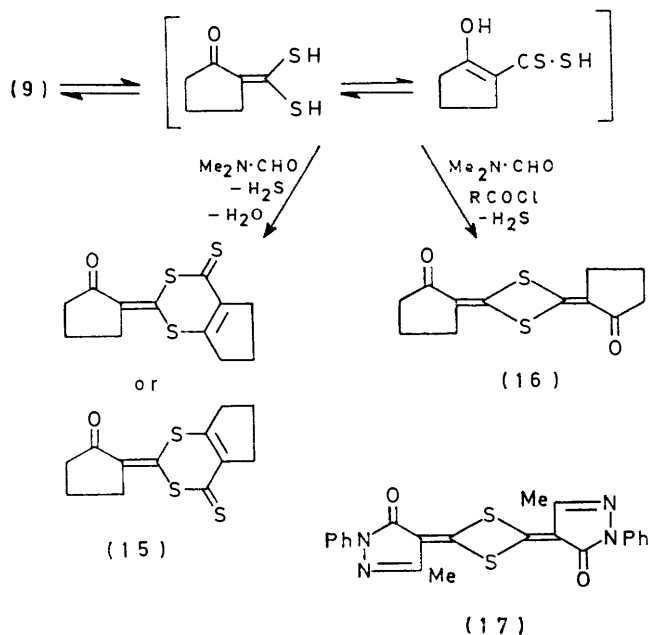
² R. Mayer and J. Jentzsch, *J. prakt. Chem.*, 1964, **23**, 113.

³ T. Takeshima, M. Yokoyama, N. Fukada, and M. Akano, *J. Org. Chem.*, 1970, **35**, 2438; A. J. Kirby, *Tetrahedron*, 1966, **22**, 3001; Y. Hayashi, T. Akazawa, K. Yamamoto, and R. Oda, *Tetrahedron Letters*, 1971, 1781.

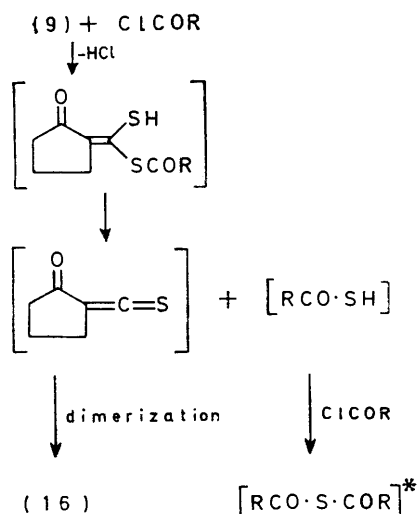
⁴ T. Takeshima, N. Fukada, E. Okabe, F. Mineshima, and M. Muraoka, *J.C.S. Perkin I*, 1975, 1277.

1,3-dithietan (17), was formed on treatment with 1 equiv. of an acyl chloride. 1-Chloro-2,4-dinitrobenzene had an effect similar to that of the acyl chloride. Compounds (15)—(17) were identified on the basis of spectroscopic data and elemental analyses (see Experimental section).

The formation of the dithietans can be explained in terms of a thioketen intermediate (Scheme 5).



SCHEME 4



SCHEME 5

* When 1-chloro-2,4-dinitrobenzene was employed in place of an acyl chloride, 2,4-dinitrophenyl sulphide could be occasionally isolated as sparingly soluble crystals.

EXPERIMENTAL

2-Alkyliminocyclopentanedithiocarboxylic Acids (1)—(4).—The acids (2)—(4) were prepared as reported.⁵ 2-Isopropyliminocyclopentanedithiocarboxylic acid (1) was similarly obtained from cyclopentanone, isopropylamine, and carbon

disulphide,⁵ as yellow crystals (from Me₂CO), m.p. 111—112° (decomp.); ν_{\max} (KBr) 2 460s cm⁻¹ (SH); λ_{\max} (EtOH) 304 (log ϵ 4.06) and 398 nm (4.39) (Found: C, 53.8; H, 7.4; N, 7.05; S, 31.7. C₉H₁₅NS₂ requires C, 53.7; H, 7.5; N, 7.0; S, 31.8%).

Bis-(2-alkyliminocyclopentylthiocarbonyl) Disulphides (5)—(8).—The disulphides (5)—(8) were prepared from the dithiocarboxylic acids (1)—(4) respectively as follows. To a solution of iodine (0.001—0.002 mol) in ethanol (2.5—5 ml) and dimethylformamide (or dimethylsulphoxide) (2.5—5 ml) was added a solution of the acid (1 g, 0.004—0.005 mol) in hot ethanol (20 ml). The mixture was kept overnight at room temperature. The precipitate was collected, washed with ethanol, and recrystallised to give orange crystals (see Table).

2-Oxocyclopentanedithiocarboxylic Acids (9) and (10) and 3-Methyl-5-oxo-1-phenyl- Δ^2 -pyrazoline-4-dithiocarboxylic Acid (13).—The acids (9) and (13) were prepared as reported.⁴ 3-Cyclopentylidene-2-oxocyclopentanedithiocarboxylic acid (10) was obtained similarly from 2-cyclopentylidenecyclopentanone and carbon disulphide,⁴ as yellow crystals (from EtOH), m.p. 117—118°; ν_{\max} (KBr) 2 570s (SH) and 1 635vs cm⁻¹ (C=C); λ_{\max} (EtOH) 245sh (log ϵ 3.63), 252 (3.66), 284sh (2.12), 296 (2.20), 329sh (3.63), 340 (3.70), and 424 nm (4.42) (Found: C, 58.4; H, 6.2; S, 28.55. C₁₁H₁₄OS₂ requires C, 58.4; H, 6.2; S, 28.3%).

The 1,2,4-Trithioles (11), (12), and (14).—These were prepared from the dithiocarboxylic acids (9), (10), and (13), respectively, as follows. To a solution of iodine (0.01 mol) in dimethylformamide (10 ml) was added a solution of the acid (0.016 mol) in dimethylformamide (20 ml). The mixture was kept overnight at room temperature. The precipitate was collected, washed with ethanol, and recrystallised to give orange crystals (see Table). The 1,2,4-trithioles showed ν_{\max} 1 640—1 660s cm⁻¹ (C=O).

6,7-Dihydro-2-(2-oxocyclopentylidene)cyclopenta[d][1,3]dithiin-4(5H)-thione (15).—The acid (9) (1 g, 0.0063 mol) was dissolved in dimethylformamide (or tetramethylene sulphone or hexamethylphosphoric amide) (3 ml) and kept at room temperature for several hours. The red solid product was collected, washed with ethanol, and dried (yield ca. 0.7 g, 83%). Recrystallisation from ethanol gave orange-red crystals, m.p. ca. 160° (decomp.) (slow heating) or ca. 190° (decomp.) (rapid heating); ν_{\max} (KBr) 1 670vs (C=O), 1 542sh, and 1 529vs cm⁻¹ (C=C); λ_{\max} (EtOH) 258 (log ϵ 3.73), 345 (4.43), and 429 nm (3.54); δ (CDCl₃) ca. 2.00 (4 H, m, 6- and 4'-H₂) and ca. 2.40—3.10 (8 H, m, 5-, 7-, 3', and 5'-H₂) [Found: C, 53.8; H, 4.5; S, 35.7%; *M*, 242 (in C₆H₆). C₁₂H₁₂OS₃ requires C, 53.7; H, 4.5; S, 35.8%; *M*, 268.2].

2,4-Bis-(2-oxocyclopentylidene)-1,3-dithietan (16).—To a solution of benzoyl chloride (3 g, 0.021 mol) (or acetyl chloride) in dimethylformamide (2 ml) was added gradually a solution of the acid (9) (1 g, 0.0063 mol) in dimethylformamide (4 ml), and the mixture was kept at room temperature for several hours. The orange solid product was collected, washed with ethanol, dried (yield ca. 0.7 g, 89%), and recrystallised from dimethylformamide to give ochre, yellow crystals, m.p. ca. 210—230° (decomp.); ν_{\max} (KBr) 1 677vs (C=O) and 1 584vs cm⁻¹ (C=C); λ_{\max} (EtOH) 226 (log ϵ 3.82), 360sh (4.31), and 373 nm (4.38); δ (CDCl₃) 2.00 (4 H, quint, 4- and 4'-H₂), 2.36 (4 H, t, 5- and 5'-H₂),

⁵ T. Takeshima, N. Fukada, T. Miyauchi, M. Muraoka, T. Yamamoto, and T. Hayashi, *J.C.S. Perkin I*, 1974, 914.

Oxidation products (5)—(8), (11), (12), and (14)

Com- pound	Yield (%)	M.p. (°C) ^a	$\lambda_{\max.}/\text{nm}(\log \epsilon)$	Formula	Found					Required				
					C	H	N	S	<i>M</i> ^b	C	H	N	S	<i>M</i>
(5)	70	149—150 ^c (Me ₂ CO—C ₆ H ₆)	313 (3.88), 414 (4.74) ^d	C ₁₈ H ₂₆ N ₂ S ₄	54.2	7.0	6.9	31.7	415 ^e	54.0	7.05	7.0	32.0	400.4
(6)	90	146—147 ^c (Me ₂ CO—C ₆ H ₆)	307 (3.95), 407 (4.83) ^f	C ₂₀ H ₃₂ N ₂ S ₄	56.4	7.6	6.5	29.7	429 ^e	56.1	7.5	6.5	29.9	428.5
(7)	85	143—144 ^c (Me ₂ CO—C ₆ H ₆)	308 (4.18), 410 (4.91) ^d	C ₂₄ H ₄₀ N ₂ S ₄	59.5	8.2	6.2	26.4	487 ^e	59.5	8.3	5.8	26.4	484.6
(8)	70	187—188 (CHCl ₃)	240 (4.11), 310 (4.14), 410 (4.91) ^d	C ₂₄ H ₃₆ N ₂ S ₄	59.7	7.5	5.75	26.4	471 ^g	60.0	7.55	5.8	26.6	480.5
(11)	75	221—222 (Me ₂ N·CHO)	250 (3.95), 342 (4.33) ^f	C ₁₂ H ₁₂ O ₂ S ₃	50.8	4.3		33.5	285 ^g	50.7	4.3		33.8	284.2
(12)	82	251—252 (CHCl ₃ —EtOH)	232 (3.50), 239 (3.48), 250sh (3.40), 288 (3.40), 296 (3.40), 384 (3.97) ^f	C ₂₂ H ₂₄ O ₂ S ₃	63.4	5.8		22.75	426 ^g	63.45	5.8		23.05	416.4
(14)	93	250—251 (PhNO ₂)	277 (3.64), 363 (3.94) ^d	C ₂₂ H ₁₆ N ₄ O ₂ S ₃	56.6	3.4	11.7	20.9		56.9	3.5	12.1	20.7	

^a With decomposition; solvent in parentheses. ^b Vapour pressure osmometry. ^c Rapid heating, *ca.* 160° (decomp.). ^d In C₆H₆. ^e In Me₂CO. ^f In EtOH. ^g In CHCl₃.

and 2.64 (4 H, t, 3- and 3'-H₂) [Found: C, 57.4; H, 4.8; S, 25.8%; *M*, 276 (in CHCl₃). C₁₂H₁₂O₂S₂ requires C, 57.1; H, 4.8; S, 25.4%; *M*, 252.2].

2,4-Bis-(3-methyl-5-oxo-1-phenyl- Δ^2 -pyrazolin-4-ylidene)-1,3-dithietan (17).—To a solution of benzoyl chloride (3 g, 0.002 mol) (or acetyl chloride) in dimethylformamide (2 ml) was added gradually a solution of the acid (13) (0.5 g, 0.002 mol) in dimethylformamide (2 ml), and the mixture was kept at room temperature for several hours. The red precipitate was collected, washed several times with ethanol, and dried

(yield *ca.* 0.4 g, 93%); m.p. *ca.* 250° (decomp.); ν_{\max} (KBr) 1 690s (C=O), 1 580vs, and 1 547s cm⁻¹ (C=N and C=C); λ_{\max} (EtOH) 252, 308, 360sh, 380, and 444 nm (the measurement of ϵ was impossible because of low solubility) (Found: C, 61.1; H, 3.7; N, 12.9; S, 15.1%; *M*⁺, 432. C₂₂H₁₆N₄O₂S₂ requires C, 61.1; H, 3.7; N, 13.0; S, 14.8%; *M*, 432).

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