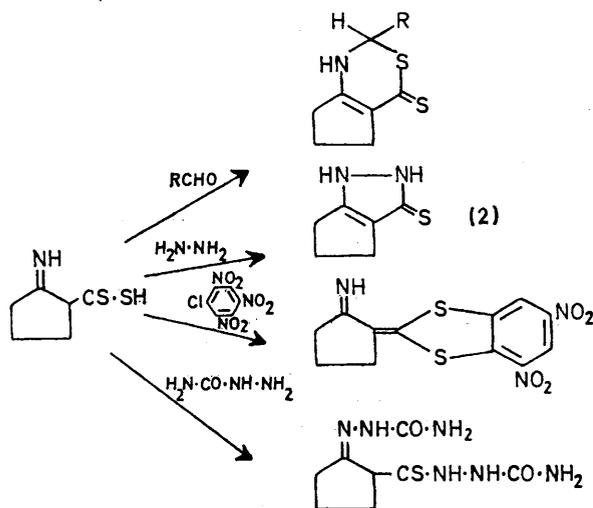


Some Reactions of 2-Oxocyclopentanedithiocarboxylic Acid and 3-Methyl-5-oxo-1-phenyl- Δ^2 -pyrazoline-4-dithiocarboxylic Acid

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The title dithiocarboxylic acids, (1) and (6) respectively, were obtained by substitution reactions of the corresponding cyclic ketones with carbon disulphide in the presence of aqueous alkali. The acid (1) reacted with hydrazine to give 1,4,5,6-tetrahydrocyclopenta[c]pyrazole-3(2*H*)-thione (2); the acid (6) simply afforded the hydrazide (11). Treatment of the acid (6) with aldehydes yielded the 1,3-dithietan-2-ylidenepyrazolines, (7)—(10). The acids (1) and (6) both gave benzodithiol-2-ylidene derivatives [(3), (4), and (12)] when treated with 2,4-dinitrochlorobenzene or similar reagents.

We have previously reported the reactions of 2-iminocyclopentanedithiocarboxylic acid with carbonyl compounds, hydrazine, picryl chloride, and other reagents to give 1,3-thiazines, a pyrazole, a benzodithiole, *etc.* (Scheme 1).¹⁻³



SCHEME 1

We have now studied the reactions of 2-oxocyclopentanedithiocarboxylic acid (1) and 3-methyl-5-oxo-1-phenyl- Δ^2 -pyrazoline-4-dithiocarboxylic acid (6) towards

¹ T. Takeshima, T. Miyauchi, N. Fukada, S. Koshizawa, and M. Muraoka, *J.C.S. Perkin I*, 1973, 1009.

² M. Muraoka, M. Yokoyama, K. Yamamoto, and T. Takeshima, *Bull. Chem. Soc. Japan*, 1970, **43**, 2134.

³ T. Takeshima, M. Yokoyama, T. Imamoto, M. Akano, and H. Asaba, *J. Org. Chem.*, 1969, **34**, 730.

the same reagents and report that the dithiocarboxy-groups of these acids differ in their behaviour.

The acid (1), previously obtained only as the ester,⁴ was easily prepared in fairly stable crystalline form by the reaction of cyclopentanone with carbon disulphide in the presence of aqueous potassium hydroxide. The acid (6) was similarly readily obtained from 3-methyl-1-phenyl- Δ^2 -pyrazolin-5-one and carbon disulphide, even in the presence of aqueous potassium carbonate or aqueous ammonia. Both acids (1) and (6), like 2-iminocyclopentanedithiocarboxylic acids,^{1,3,5,6} were exceedingly sensitive to heavy metal ions, forming coloured complexes; the characteristic reaction with Ni¹¹ produced an orange-red or a pink-red precipitate.

The acid (6) reacted with aldehydes to give dithietans, (7)—(10). The corresponding reaction of the acid (1), however, gave only tarry material. The i.r. spectra of compounds (7)—(10) showed that the carbonyl group was retained, thus excluding the 4*H*-1,3-oxathiin structures analogous to the 1,3-thiazines^{2,3} obtained from 2-iminocyclopentanedithiocarboxylic acid.

When treated with hydrazine, the acid (1) gave 1,4,5,6-tetrahydrocyclopenta[c]pyrazole-3(2*H*)-thione (2), also formed from 2-iminocyclopentanedithiocarboxylic acid by the same method.¹ In contrast, the acid (6) yielded simply the hydrazide (11).

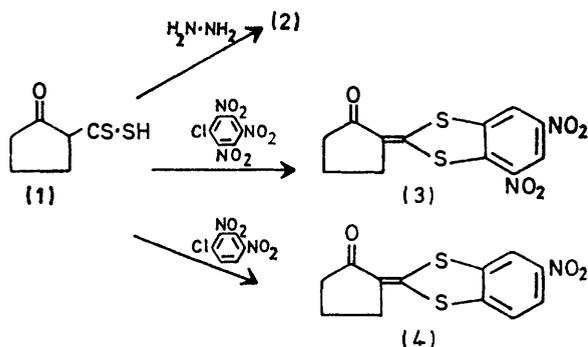
Both acids (1) and (6) gave dithioles[(3), (4), and (12)]

⁴ A. Thuillier and J. Vialle, *Bull. Soc. chim. France*, 1962, 2194.

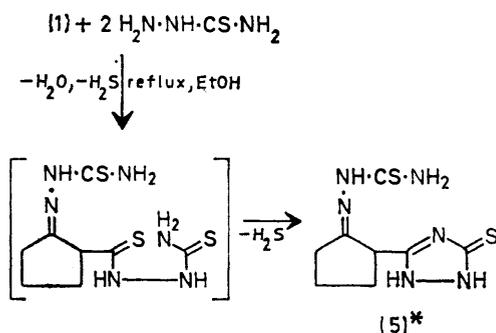
⁵ M. Yokoyama and T. Takeshima, *Analyt. Chem.*, 1968, **40**, 1344.

⁶ T. Takeshima, N. Fukada, T. Miyauchi, and M. Muraoka, *J.C.S. Perkin I*, 1974, 914.

when treated with picryl chloride, 2,4-dinitrochlorobenzene, or 2,4-dinitrofluorobenzene (Schemes 2 and 4).

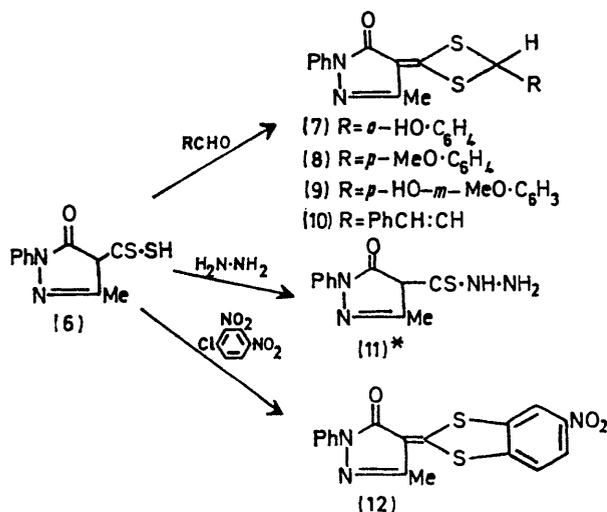


SCHEME 2



SCHEME 3

* Other tautomers possible.



SCHEME 4

Further, thiosemicarbazide reacted only with the acid (1) to give 2-(5-thioxo-1,2,4-triazolin-3-yl)cyclopentanone thiosemicarbazide (5), identified mainly on the basis of n.m.r. and i.r. spectra. The course of this reaction was suggested by analogy with that of thiosemicarbazide with formic acid.⁷

EXPERIMENTAL

2-Oxocyclopentanedithiocarboxylic Acid (1).—To potassium hydroxide (30 g) in water (30 ml) were added cyclopentanone

(5 g, 0.06 mol) and carbon disulphide (5.2 g, 0.068 mol). The mixture was shaken at room temperature for 1 h, washed twice with benzene, and slowly poured into a mixture of concentrated hydrochloric acid (50 ml), water (200 ml), and ice (200 g). The reddish-brown precipitate was collected, washed with water, and dried; yield ca. 7.5 g (79%). The crude acid was recrystallised from ethanol (charcoal) to give orange crystals, m.p. 90–91°; ν_{\max} (KBr) 2480s (SH) and 1700w (C=O) cm⁻¹; λ_{\max} (EtOH) 308 (log ϵ 4.15) and 371 nm (4.15); δ (CDCl₃) ca. 1.90 (2H, m, 4-H₂), ca. 2.70 (5H, m, 1-H, 3- and 5-H₂), and 5.24 (1H, s, SH) (Found: C, 45.05; H, 5.0; S, 39.7%; M^+ , 160. C₆H₈OS₂ requires C, 45.0; H, 5.0; S, 40.0%; M , 160). Compound (1) produced an orange-red precipitate with Ni^{II} ions.

Triethylammonium 2-Oxocyclopentanedithiocarboxylate.—The acid (1) (3.2 g, 0.02 mol) was dissolved in ethanol (75 ml) and triethylamine (2.5 g, 0.025 mol) was added. The mixture was shaken at room temperature for 5 min. The orange solid was collected, washed several times with ether, and dried; yield ca. 3.2 g (62%); m.p. 109–110°; λ_{\max} (EtOH) 358 nm (log ϵ 4.22) (Found: C, 55.05; H, 8.75; N, 5.3; S, 24.5. C₁₂H₂₃NOS₂ requires C, 55.15; H, 8.9; N, 5.4; S, 24.5%), which gave an orange precipitate with Ni^{II} ions.

Hexamethylenetetramine Salt of 2-Oxocyclopentanedithiocarboxylic Acid.—To a solution of the acid (1) (1 g, 0.0063 mol) in ethanol (50 ml) was added hexamethylenetetramine (0.9 g, 0.0064 mol), followed by acetic acid (ca. 0.15 ml). The mixture was shaken at room temperature for 40 min. The reddish brown solid was collected, washed several times with ethanol, and dried; yield ca. 1.2 g (64%); m.p. 86–87° (slow heating) or ca. 100° (rapid heating); λ_{\max} (EtOH) 360 nm (log ϵ 4.21) (Found: C, 48.0; H, 6.7; N, 18.6; S, 21.0. C₁₂H₂₀N₄OS₂ requires C, 48.0; H, 6.7; N, 18.7; S, 21.3%), which gave an orange precipitate with Ni^{II} ions.

1,4,5,6-Tetrahydrocyclopenta[c]pyrazole-3(2H)-thione (2).—To a suspension of the acid (1) (2 g, 0.013 mol) in ethanol (20 ml) was added 80% hydrazine hydrate (1 g, 0.016 mol). The mixture was shaken at room temperature for 10 min. The solid product was collected, washed with water and ethanol (yield ca. 1 g, 55%), dissolved in aqueous 28% ammonia, and cooled in an ice-bath. Acetic acid was then added dropwise to give a white powder, which was washed with water and ethanol, and dried; m.p. 231–233° (decomp.) (slow heating) or ca. 260° (decomp.) (rapid heating). The i.r. and u.v. spectra were identical with those reported¹ (Found: C, 51.1; H, 5.8; N, 20.3; S, 22.7. Calc. for C₆H₈N₂S: C, 51.4; H, 5.75; N, 20.0; S, 22.85%).

2-(2-Oxocyclopentylidene)-4,6-dinitro-1,3-benzodithiole (3).—To a solution of the acid (1) (1 g, 0.0063 mol) in dimethylformamide (2 ml), cooled in ice, was added a solution of picryl chloride (1.6 g, 0.0065 mol) in dimethylformamide (2 ml). The mixture was kept at room temperature for 2 h. Ethanol (20 ml) was added and the precipitate was collected, washed with ethanol and ether, and dried (yield ca. 0.8 g, 39%). Recrystallisation from pyridine gave reddish brown crystals, m.p. ca. 210° (decomp.) (rapid heating); ν_{\max} (KBr) 1660vs (C=O), 1590m, 1580s (C=C and aromatic C=C), 1535vs, and 1335s cm⁻¹ (NO₂); λ_{\max} (EtOH) 255 (log ϵ 3.82), 325sh (3.97), 337 (4.01), and 436 nm (3.62) (Found: C, 44.6; H, 2.5; N, 8.35; S, 19.9. C₁₂H₈N₂O₅S₂ requires C, 44.45; H, 2.3; N, 8.6; S, 19.7%).

2-(2-Oxocyclopentylidene)-6-nitro-1,3-benzodithiole (4).—To

⁷ L. F. Fieser and M. Fieser, 'Reagents for Organic Synthesis,' Wiley, New York, 1967, p. 1188.

a solution of the acid (1) (0.8 g, 0.005 mol) in dimethylformamide (2 ml) was added a solution of 2,4-dinitrochlorobenzene (1.1 g, 0.0054 mol) in dimethylformamide (2 ml). The mixture was kept overnight at room temperature. Ethanol (20 ml) was added and the precipitate was collected, washed with ethanol and ether, dried (yield *ca.* 0.7 g, 50%), and recrystallised from ethanol to give reddish brown *crystals*, m.p. *ca.* 165° (decomp.) (rapid heating); ν_{\max} (KBr) 1 670s (C=O), 1 590s (C=C and aromatic C=C), 1 530vs, and 1 345vs cm^{-1} (NO_2); λ_{\max} (EtOH) 257 (log ϵ 4.03), 325sh (4.43), 344 (4.49), and 430sh nm (3.67) (Found: C, 51.3; H, 3.5; N, 4.8; S, 23.3. $\text{C}_{12}\text{H}_9\text{NO}_3\text{S}_2$ requires C, 51.6; H, 3.25; N, 5.0; S, 22.9%).

2-(5-Thioxo-1,2,4-triazolin-3-yl)cyclopentanone Thiosemicarbazone (5).—A mixture of the acid (1) (2 g, 0.013 mol), thiosemicarbazide (2.3 g, 0.025 mol), and ethanol (50 ml) was

(1H, SH) (Found: C, 52.9; H, 4.0; N, 11.3; S, 25.5. $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_2\text{S}_2$ requires C, 52.8; H, 4.0; N, 11.2; S, 25.6%), which produced a pink-red precipitate with Ni^{II} ions.

4-Substituted 2-(3-Methyl-5-oxo-1-phenyl- Δ^2 -pyrazolin-4-ylidene)-1,3-dithietans (7)–(10).—The 1,3-dithietans (7)–(10) were prepared from the acid (6) by reaction with salicylaldehyde, *p*-anisaldehyde, vanillin, or cinnamaldehyde, respectively.

To a suspension of (6) (3 g, 0.012 mol) in ethanol (30 ml) was added a solution of the aldehyde (0.012 mol) in ethanol (10 ml) followed by concentrated sulphuric acid (0.5 ml). The mixture was shaken at room temperature for 3 h and kept overnight. The solid product was collected, washed with ethanol, and recrystallised to give yellow *crystals* (see Table), ν_{\max} 1 640–1 655 cm^{-1} (C=O); all the products showed molecular ions in their mass spectra.

Compound	1,3-Dithietans (7)–(10)		λ_{\max}/nm (log ϵ)*	Formula	Found (%)				Required (%)			
	Yield (%)	M.p. (°C)			C	H	N	S	C	H	N	S
(7)	85	196–198 (C ₆ H ₄)	251 (4.09), 275sh (3.63), 285sh (3.66), 321 (4.33)	C ₁₈ H ₁₄ N ₂ O ₂ S ₂	61.3	4.1	8.0	18.0	61.0	4.0	7.9	18.1
(8)	27	162–163 (EtOH)	253 (4.13), 276sh (3.45), 286sh (3.51), 320 (4.14)	C ₁₉ H ₁₆ N ₂ O ₂ S ₂	62.0	4.4	7.65	17.2	61.95	4.4	7.6	17.4
(9)	63	145–147 (C ₆ H ₄)	251 (4.21), 275sh (3.66), 285sh (3.68), 321 (4.25)	C ₁₉ H ₁₄ N ₂ O ₂ S ₂ .H ₂ O	56.8	4.6	6.9	15.8	56.7	4.5	7.0	15.9
(10)	55	197–198 (C ₆ H ₄)	252 (3.66), 276sh (3.00), 286sh (3.04), 343 (3.77)	C ₂₀ H ₁₄ N ₂ O ₂ S ₂ .EtOH	64.2	5.35	6.6	15.7	64.4	5.4	6.8	15.8

* In EtOH.

refluxed on a steam-bath for 1.5 h, and cooled to room temperature. The solid product (*ca.* 1.2 g, 36%) was recrystallised from dimethyl sulphoxide–water to give light yellow *crystals*, m.p. 208–209° (decomp.) (slow heating) or *ca.* 225° (decomp.) (rapid heating); ν_{\max} (KBr) 3 410s, 3 240s, and 3 140s (NH and NH₂), 1 635m, and 1 590vs cm^{-1} (C=N and NH₂); λ_{\max} (EtOH) 235 (log ϵ 3.96) and 278 nm (4.37); δ [(CD₃)₂SO] *ca.* 2.00 (7H, m, CH and CH₂), 7.15br (4H, NH and NH₂), and 1.83br (1H, NH) (Found: C, 37.5; H, 4.65; N, 32.6; S, 24.8. $\text{C}_8\text{H}_{12}\text{N}_6\text{S}_2$ requires C, 37.5; H, 4.7; N, 32.8; S, 25.0%).

3-Methyl-5-oxo-1-phenyl- Δ^2 -pyrazoline-4-dithiocarboxylic Acid (6).—To a solution of potassium hydroxide (15 g) in water (15 ml)* were added 3-methyl-1-phenyl- Δ^2 -pyrazolin-5-one (5 g, 0.029 mol) and carbon disulphide (2.2 g, 0.029 mol). The mixture was shaken at room temperature for 6h, washed twice with benzene, and slowly poured into a mixture of concentrated hydrochloric acid (25 ml), water (100 ml), and ice (100 g). The yellow precipitate was collected, washed with water, and dried; yield *ca.* 6 g (83%). Recrystallisation from ethanol gave yellow *crystals*, m.p. 109–110°; ν_{\max} (KBr) 2 490s cm^{-1} (SH); λ_{\max} (EtOH) 240 (log ϵ 4.15), 298 (4.03), and 353 nm (4.26); δ (CDCl₃) 2.58 (3H, s, CH₃), *ca.* 7.50 (6H, m, Ph and 4-H), and *ca.* 13.00br

3-Methyl-5-oxo-1-phenyl- Δ^2 -pyrazoline-4-dithiocarboxylic acid (11).—A mixture of the acid (6) (5 g, 0.02 mol), 80% hydrazine hydrate (2 g, 0.032 mol), and ethanol (20 ml) was refluxed for 2 h, cooled to room temperature, and treated with ice-cold dilute acetic acid to give a solid product, which was washed with water and dried (yield *ca.* 4 g, 76%). Recrystallisation from ethanol gave *crystals*, m.p. 172–174°; ν_{\max} (KBr) 3 542m (H₂O), 3 454m, 3 240, 3 145w (NH and NH₂), and 1 630s cm^{-1} (C=O); λ_{\max} (EtOH) 240 (log ϵ 4.00) and 289 nm (3.93) (Found: C, 50.1; H, 4.8; N, 21.3; S, 12.1. $\text{C}_{11}\text{H}_{10}\text{N}_4\text{OS}$, H₂O requires C, 50.0; H, 4.6; N, 21.2; S, 12.1%).

2-(3-Methyl-5-oxo-1-phenyl- Δ^2 -pyrazolin-4-ylidene)-6-nitro-1,3-benzodithiole (12).—A mixture of the acid (6) (5 g, 0.02 mol), 2,4-dinitrofluorobenzene (3.8 g, 0.02 mol), and ethanol (150 ml) was stirred at room temperature for 3 h and kept overnight. The solid product was collected, washed with ethanol, dried (yield *ca.* 6 g, 81%), and recrystallised from acetone–benzene (1:1) to give light orange *crystals*, m.p. 253–255°; ν_{\max} (KBr) 1 640s (C=O), 1 590s (C=C and aromatic C=C), 1 492vs, and 1 320vs cm^{-1} (NO_2); λ_{\max} (C₆H₆) 301 (log ϵ 4.08) and 360 nm (4.34) (Found: C, 55.6; H, 2.9; N, 11.3; S, 17.4. $\text{C}_{17}\text{H}_{11}\text{N}_3\text{O}_3\text{S}_2$ requires C, 55.3; H, 3.0; N, 11.4; S, 17.3%).

* Or aqueous potassium carbonate or ammonia.