Addition Reaction of β-Imino- and β-Oxodithiocarboxylic Acids with Methyl Propiolate and with Strongly Electrophilic Olefins

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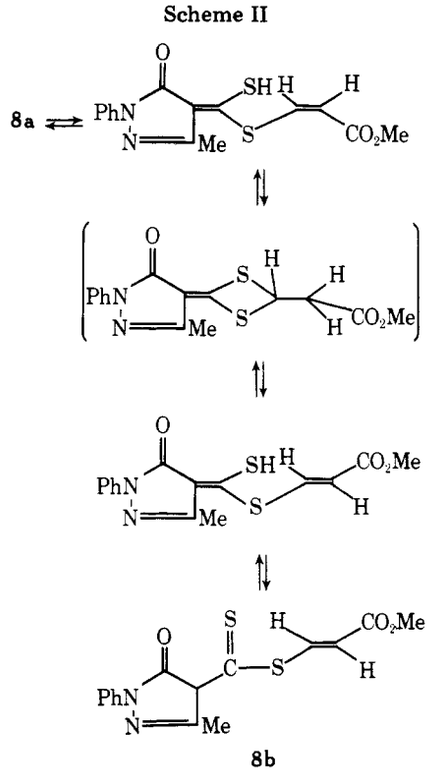
2-Iminocyclopentanedithiocarboxylic acid (**1**), 2-cyclohexyliminocyclopentanedithiocarboxylic acid (**2**), 2-oxocyclopentanedithiocarboxylic acid (**3**), and 3-methyl-5-oxo-1-phenyl-Δ^2-pyrazoline-4-dithiocarboxylic acid (**4**) reacted with methyl propiolate to give the cis adducts of normal ester type, **5, 6, 7,** and **8a.** Phenylacetylene and propargyl alcohol did not react with these acids. On dissolution in a solvent such as dimethyl sulfoxide, compound **8a** converted into the trans isomer **8b.** The acids 1–4 added only to the strongly electrophilic olefins. The iminodithio acids were much more reactive than the oxodithio acids in this addition reaction.

In the course of our studies of the dithio acids, 2-iminocyclopentanedithiocarboxylic acid (**1**), 2-cyclohexyliminocyclopentanedithiocarboxylic acid (**2**), 2-oxocyclopentanedithiocarboxylic acid (**3**), and 3-methyl-5-oxo-1-phenyl-Δ^2-pyrazoline-4-dithiocarboxylic acid (**4**)[2], we have now investigated the addition to methyl propiolate and to certain alkenes. Dithio acids **1, 2,** and **4** added to methyl propiolate simply on dissolution in a solvent; in the case of **3,** a small amount of a base such as triethylamine was necessary for the reaction to proceed (Scheme I). All the adducts assumed the cis configuration (see NMR data in the Experimental Section). Thus, the mode of the addition is the same as in the case of addition of thiols to carbon–carbon triple bond.[3] The new adduct esters obtained are listed in Table I. The acids 1–4 did not react with phenylacetylene and propargyl alcohol.

Among the adducts obtained, only **8a** rearranged to the trans isomer simply on dissolution in a solvent such as dimethyl sulfoxide. The transformation could be followed by the NMR spectra. It seems that the rearrangement occurs through the transient dithietan form shown (Scheme II), of the acids, only **4** is capable of forming a dithietane by addition to a carbonyl compound.[4]

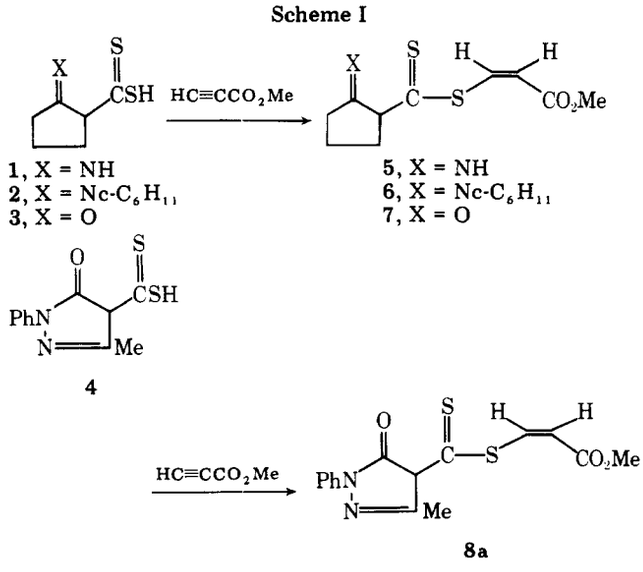
In reference to the above addition reaction, we have examined the addition of the acids, **1–4,** to olefins. Concerning the addition of dithioacids to olefins, dithiocarbamic acids with olefins[5] and *p*-benzoquinone[6] and dithioacetic acid with a variety of olefins[7] have been reported. It is stated that dithioacetic acid reacts with both electrophilic and nucleophilic olefins to give the corresponding ester type adducts (Schemes III and IV).

Scheme II



8b

Scheme I



1, X = NH
2, X = Nc-C_6H_{11}
3, X = O

5, X = NH
6, X = Nc-C_6H_{11}
7, X = O

4

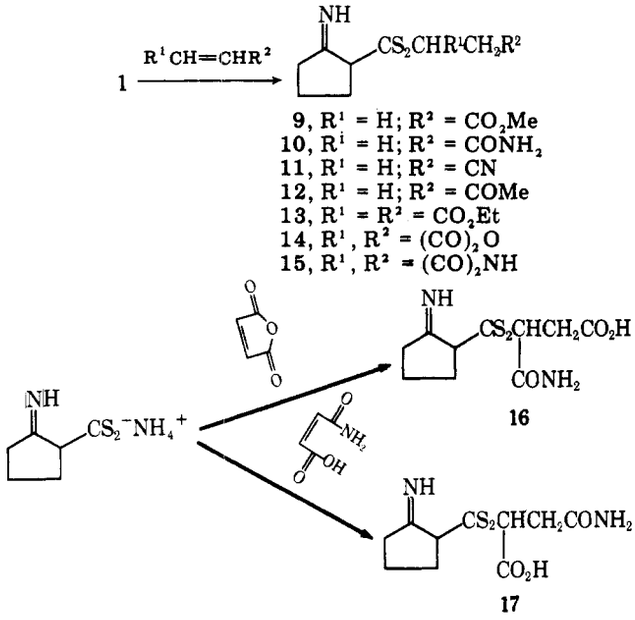
8a

In our present experiment, it was found that the acids, **1–4,** differed from dithioacetic acid in that they reacted only with strongly electrophilic olefins to give the distinct crystalline adducts (Table II; Scheme V). The reaction was conducted in a solvent such as ethanol at room temperature. The presence of an excess of a base or an acid retarded the reaction. There was considerable difference in reactivity between the iminodithio acids and the oxodithio acids. The latter acids, **3** and **4,** were much less reactive and reacted only with maleic anhydride and maleimide.

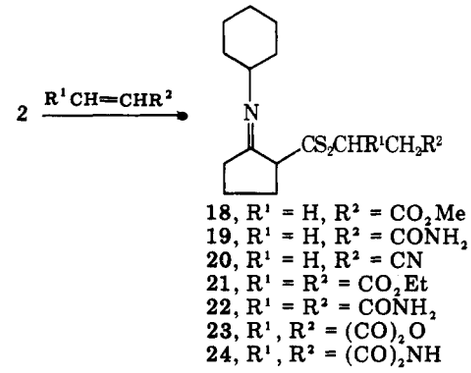
The β position of the olefins was the site of attack of the dithiocarboxyl group. It is of interest that tetracyanoethylene did not afford adducts with the dithio acids; instead, the same as those obtained on oxidation of the dithio acids were produced.[8] This behavior resembled the reaction of thiols with tetracyanoethylene.[9]

When the ammonium salt of acid **1** was subjected to reaction with maleic anhydride, adduct **16** was obtained rather than **14.** The ammonium salt reacted with maleic monoamide

Scheme III



Scheme IV



Scheme V

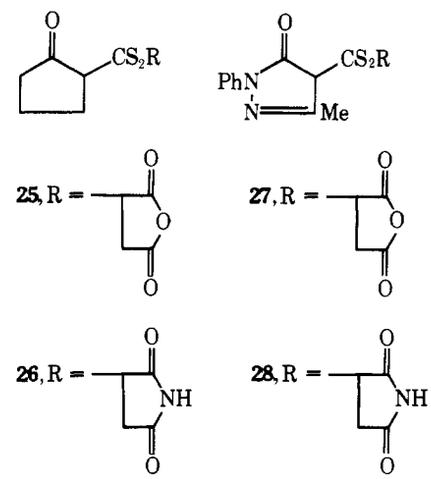


Table I. Adduct Esters 5–8[a]

Registry no.	Adduct ester	Yield, %	Mp, °C	Recryst. solvent
63018-07-5	5	82	240–241	DMF–EtOH
63018-06-4	6	39	130–131	DMF–EtOH
63018-08-6	7	79	113–115	DMF–EtOH
63018-09-7	8a	80	170–171	Dioxane
63058-89-9	8b		156–158	Me_2SO

[a] Satisfactory analytical data (±0.3% for C, H, N, S) were reported for all compounds listed in this table.

Table II. Adduct Esters 9–28[a]

Registry no.	Starting olefin[b]	Registry no.	Adduct ester	Yield, %[c]	Mp, °C	Recryst. solvent
96-33-3	Methyl acrylate	6301810-0	9	77	71–72	EtOH
79-06-1	Acrylamide	63058-86-6	10	65	175 dec	EtOH–DMF
107-13-1	Acrylonitrile	63018-11-1	11	45	104–106	EtOH–DMF
78-94-4	Methyl vinyl ketone	63018-12-2	12	98	122–123	EtOH–DMF
141-05-9	Diethyl maleate (diethyl fumarate)	63018-13-2	13	39 (72)	108–109	EtOH–DMF
108-31-6	Maleic anhydride	63018-14-4	14	75	136–137[d]	EtOH–C_6H_6
541-59-3	Maleimide	63018-15-5	15	93	200–201[e] dec	EtOAc–C_6H_6
	Maleic anhydride	63018-16-6	16	70	189[f]	DMF–H_2O
557-24-4	Maleic monoamide	63018-17-7	17	40	147–148[g]	MeOH
	Methyl acrylate	63018-18-8	18	46	75–76	EtOH
	Acrylamide	63018-19-9	19	64	117–119	EtOH–DMF
	Acrylonitrile	63018-20-2	20	58	89–90	EtOH
	Diethyl maleate (diethyl fumarate)	63018-21-3	21	35 (55)	70–71	EtOH–C_6H_6
928-01-8	Maleic diamide	63018-22-4	22	64	267–268[h]	DMF–H_2O
	Maleic anhydride	63018-23-5	23	89	145–146[i]	EtOAc–C_6H_6
	Maleimide	63018-24-6	24	99	203–204	
	Maleic anhydride	63018-25-7	25	60	198–200	EtOH
	Maleimide	63018-26-8	26	30	144–145	EtOH–H_2O
	Maleic anhydride	63018-27-9	27	93	186–189	
	Maleimide	63018-28-0	28	84	181–182	

[a] Satisfactory analytical data (±0.3% for C, H, N, S) were reported for all compounds listed in this table. [b] Olefins which did not react are: 1-hexene, cyclohexene, methyl crotonate, methyl methacrylate, mesityl oxide, citraconic anhydride, crotonaldehyde, cinnamaldehyde, methyl cinnamate, styrene, crotononitrile, methacrylonitrile, tetracyanoethylene, vinyl acetate, vinyl *n*-butyl ether, vinyl bromide, trichloroethylene, and tetrachloroethylene. [c] By using free dithiocarboxylic acids except for 16 and 17. [d] Rapid heating, 152–156 °C. [e] Rapid heating, 214–216 °C dec. [f] Rapid heating, 200–202 °C. [g] Rapid heating, 156–157 °C. [h] Rapid heating, 277–280 °C. [i] Rapid heating, 161–163 °C.

to give the isomeric adduct **17**. The reaction of the ammonium salt of acid **1** with maleic anhydride thus seems to involve initial attack of the dithiocarboxyl group, followed by ammonolysis of the anhydride. Structure **16** is based on the close correspondence of the chemical shift for the SC**H**($CONH_2$) peak (δ 4.87 dd) in **16** and the corresponding peak (δ 4.90 dd) in the spectrum of **22**. The isomeric structure **17** then follows for the product from maleamic acid.

All the adducts obtained were identified on the basis of IR, NMR, and UV spectra together with elemental analyses (see Experimental Section). The adduct esters of acid **1** with methyl propiolate and olefins showed UV absorptions at ca. 310 and ca. 380–390 nm, which were in good agreement with the spectra of methyl and carboxymethyl 2-iminocyclopentanedithiocarboxylates (ca. 312 and 384 nm).[10]

Experimental Section

Ammonium 2-iminocyclopentanedithiocarboxylate was prepared by modification of previously described method.[11] A mixture of cyclopentanone (25 g, 0.30 mol), carbon disulfide (30 g, 0.39 mol), and 70 mL of aqueous ammonia (28%) was stirred below 0 °C for ca. 8 h. The yellow solid product was collected, washed with ether, and dried over $CaCl_2$; yield ca. 26 g (50%). The crude ammonium salt of **1** was recrystallized from EtOH; mp 135–137 °C dec (lit.[11] mp 135–137 °C dec).

2-Iminocyclopentanedithiocarboxylic Acid (1). The crude ammonium salt of **1** was dissolved in water. The solution was cooled in ice, and 2 N HCl was added to the solution. The yellow solid material separated from the solution was collected, washed with water, and dried over $CaCl_2$. The crude **1** was saturated with MeOH at 40–50 °C, and the solution was filtered. To the filtrate was added water (a quarter of the volume of the filtrate), and the solution was allowed to stand below 10 °C. The yellow solid was collected, washed with H_2O–EtOH (1:1), and dried over $CaCl_2$; mp 106–108 °C dec (rapid heating) and 99–101 °C dec (slow heating) (lit.[11] mp 101–102 °C dec and 96 °C dec).

2-Cyclohexyliminocyclopentanedithiocarboxylic acid (2) was prepared as previously reported.[12]

2-Oxocyclopentanedithiocarboxylic acid (3) was prepared by modification of a previously described method.[4] A mixture of sodium hydride (2 g, 50% oil dispersion) in THF (10 mL) and carbon disulfide (3.2 g, 0.042 mol) was stirred below 0 °C. To the mixture was added cyclopentanone (3 g, 0.036 mol) and then dropwise water (0.7 mL, 0.039 mol) in THF (10 mL). After an additional 30 min of stirring EtOH was added. The mixture was acidified with dilute acetic acid and kept overnight in an ice box. The orange solid product was collected, washed with water and EtOH, and dried; yield ca. 4 g (70%). The crude acid was recrystallized from EtOH; mp 91–92 °C (lit.[4] mp 90–91 °C).

3-Methyl-5-oxo-1-phenyl-Δ²-pyrazoline-4-dithiocarboxylic acid (4) was prepared as previously reported.[2]

***cis*-2-Methoxycarbonylvinyl 2-Iminocyclopentanedithiocarboxylate (5).** To a solution of acid **1** (0.4 g, 0.0025 mol) in EtOH (20 mL) was added methyl propiolate (0.22 g, 0.0026 mol). The mixture was kept overnight at room temperature. The yellow solid product was collected, washed with EtOH, dried, and recrystallized: IR (KBr) 3060 w (=CH), 1692 vs (C=O), 1627 vs cm^{-1} (C=C); UV max (EtOH) 307 (log ε 4.06), 383 nm (4.49); NMR (Me_2SO-d_6) δ ca. 1.90 (2 H, m, 4-H_2), ca. 2.80 (4 H, m, 3-, 5-H_2), 3.74 (3 H, s, CH_3), 6.31 (1 H, d, J = 11 Hz, CHCO), 8.85 (1 H, d, J = 11 Hz, SCH), 9.77 br, 11.40 br (each 1 H, s, tautomeric 2-NH_2).

***cis*-2-Methoxycarbonylvinyl 2-Cyclohexyliminocyclopentanedithiocarboxylate (6).** To a solution of acid **2** (0.5 g, 0.0021 mol) in EtOH (80 mL) was added methyl propiolate (0.18 g, 0.0021 mol). The mixture was left at room temperature for several days until the whole turned red and then kept for 2 days at ca. −18 °C in a refrigerator. The ocher yellow solid product was collected, washed with EtOH, dried, and recrystallized: IR (KBr) 2985 m (=CH), 1709 vs (C=O), 1595 br cm^{-1} (C=C); UV max (EtOH) 245 (log ε 3.60), 261 (3.70), 340 (4.33), 412 nm (4.46); NMR ($CDCl_3$) δ 1.15–2.10 (12 H, m, 4-,2′-3′-,4′-,5′-,6′-H_2), 2.55–3.00 (5 H, m, 3-,5-H_2 and 1′-H), 3.67 (3 H, s, CH_3), 5.93 (1 H, d, J = 11 Hz, CHCO), 8.63 (1 H, d, J = 11 Hz, SCH), ca. 13.10 br (1 H, s, tautomeric 2-NH).

***cis*-2-Methoxycarbonylvinyl 2-Oxocyclopentanedithiocarboxylate (7).** To a mixture of acid **3** (0.97 g, 0.0061 mol), methyl propiolate (0.53 g, 0.0063 mol), and dioxane (6 mL) was added triethylamine (0.04 g) at 0 °C. After an additional cooling for 30 min, the mixture was kept overnight in an ice box. To this was gradually added water, and the orange-red solid product was collected, washed with MeOH, dried, and recrystallized: IR (KBr) 3000 m (=CH), 1693 vs (C=O), 1585 vs cm^{-1} (C=C); UV max (EtOH) 260 (log ε 3.56), 322 sh (4.17), 350 (4.24), 380 nm (4.35); NMR (Me_2CO-d_6) δ ca. 2.90 (7 H, m, 1-H and 3-,4-,5-H_2), 3.80 (3 H,, s, CH_3), 6.40 (1 H, d, J = 11 Hz, CHCO), 8.65 (1 H, d, J = 11 Hz, SCH).

***cis*-2-Methoxycarbonylvinyl 3-Methyl-5-oxo-1-phenyl-Δ²-pyrazoline-4-dithiocarboxylate (8a).** To a solution of acid **4** (0.5 g, 0.002 mol) in EtOH (60 mL) was added methyl propiolate (0.18 g, 0.0021 mol). The mixture was kept overnight at room temperature. The yellow needles were collected, washed with EtOH, dried, and recrystallized: IR (KBr) 3030 w (=CH), 1696 vs (C=O), 1592 vs cm^{-1} (C=C and C_6H_5); UV max (EtOH) 248 (log ε 4.03), 266 sh (3.98), 336 (4.34), 390 nm (4.16); NMR (Me_2SO-d_6) δ 2.60 (3 H, s, 3-CH_3), 3.70 (3 H, s, OCH_3), 6.25 (1 H, d, J = 11 Hz, CHCO), 7.20–7.80 (5 H, m, C_6H_5), 8.54 (1 H, s, enol OH or enethiol SH), 8.85 (1 H, d, J = 11 Hz, SCH).

Isolation of *trans*-2-Methoxycarbonylvinyl 3-Methyl-5-oxo-1-phenyl-Δ²-pyrazoline-4-dithiocarboxylate (8b). 8a (0.5 g, 0.0015 mol) was dissolved in Me_2SO (14 mL) at 40 °C and filtered. The solution was warmed at 70 °C in a water bath for a few minutes and allowed to stand at room temperature for 24 h. The red precipitate [3,5-bis(3-methyl-5-oxo-1-phenyl-Δ²-pyrazolin-4-ylidene)-1,2,4-trithiole[8]] was filtered off and to the filtrate was added MeOH–H_2O (2:1). The yellow solid (0.2 g, 40%) was collected, washed with MeOH, and dried. From the filtrate the mixture of **8a** and **8b** was precipitated by adding water. The crude **8b** was recrystallized twice from Me_2SO to give yellow crystals of **8b**: IR (KBr) 3005 w (=CH), 1718 vs (C=O), 1590 vs cm^{-1} (C=C and C_6H_5); UV max (EtOH) 248 (log ε 4.20), 267 (4.22), 336 (4.44), 388 nm (4.25); NMR (Me_2SO-d_6) δ 2.60 (3 H, s, 3-CH_3), 3.75 (3 H, s, OCH_3), 6.37 (1 H, d, J = 16 Hz, CHCO), 7.20–7.80 (5 H, m, C_6H_5), 8.96 (1 H, d, J = 16 Hz, SCH), 9.75 (1 H, s, enol OH or enethiol SH).

2-Iminocyclopentanedithiocarboxylic Acid Esters (9–15). General Procedure. A mixture of acid **1** (1.59 g, 0.01 mol), olefin (0.01 mol), and EtOH (10–20 mL) was shaken at room temperature for 0.5–1.5 h and kept overnight in an ice box. The yellow solid product was collected, washed with EtOH, dried, and recrystallized.

2-Methoxycarbonylethyl 2-Iminocyclopentanedithiocarboxylate (9). IR (KBr) 1730 cm^{-1} (C=O); UV max (EtOH) 226 (log ε 4.61), 314 (4.72), 388 nm (4.93).

2-Carbamoylethyl 2-Iminocyclopentanedithiocarboxylate (10). IR (KBr) 3383 m, 3260, 3200 m (NH_2 and NH), 1638 vs, 1620 vs cm^{-1} (C=O and NH_2); UV max (EtOH) 218 (log ε 4.15), 315 (4.28), 388 nm (4.58); NMR (Me_2SO-d_6) δ 1.88 (2 H, quint, 4-H_2), 2.24 (6 H, m, 3-,5-H_2 and CH_2CO), 3.32 (2 H, t, SCH_2), 6.79 br, 7.28 br (each 1 H, s, $CONH_2$), 8.82 br, 10.86 br (each 1 H, s, tautomeric 2-NH_2).

2-Cyanoethyl 2-Iminocyclopentanedithiocarboxylate (11). IR (KBr) 2240 w, 2260 w cm^{-1} (C≡N); UV max (EtOH) 220 (log ε 3.93), 310 (4.04), 387 nm (4.34).

3-Oxobutyl 2-Iminocyclopentanedithiocarboxylate (12). IR (KBr) 1710 s cm^{-1} (C=O); UV max (EtOH) 315 (log ε 3.63), 387 nm (3.97).

1,2-Diethoxycarbonylethyl 2-Iminocyclopentanedithiocarboxylate (13). IR (KBr) 1720 vs, 1710 vs cm^{-1} (C=O); UV max (EtOH) 310 (log ε 3.59), 388 nm (3.94); NMR ($CDCl_3$) δ 1.28 (6 H, t, 2 × CH_3), 1.93 (2 H, m, 4-H_2), 2.73 (5 H, m, 3-,5-H_2 and 1-H), 3.05 (2 H, d, CH_2CO), 4.20 (2 H, quart, OCH_2), 4.27 (2 H, quart, OCH_2), 5.34 (1 H, t, SCH), 10.91 br (1 H, s, 2-NH).

3-(2,5-Dioxo)tetrahydrofuryl 2-Iminocyclopentanedithiocarboxylate (14). IR (KBr) 1860 sh, 1850 s, 1785 vs cm^{-1} (C=O); UV max (EtOH) 307 (log ε 3.81), 389 nm (4.23); NMR (Me_2SO-d_6) δ 1.90 (2 H, m, 4-H_2), 2.75 (4 H, m, 3-,5-H_2), 3.15–4.10 (2 H, m, CH_2CO), 5.40 (1 H, dd, SCH), 9.45 br, 10.75 br (each 1 H, s, tautomeric 2-NH_2); *m/e* 257 (M^+).

3-(2,5-Dioxo)pyrrolidinyl 2-Iminocyclopentanedithiocarboxylate (15). IR (KBr) 3330 s, 3120 br (NH), 1765 m, 1736 w, 1705 vs, 1684 sh (C=O), 1635 m cm^{-1}; UV max (EtOH) 220 sh (log ε 3.93), 309 (4.05), 388 nm (4.51); NMR (C_5D_5N) δ 1.60 (2 H, quint, 4-H_2), 2.70 (4 H, m, 3-,5-H_2), 2.90–4.10 (2 H, m, CH_2CO), 5.00 br (1 H, s, NH), 5.93 (1 H, dd, SCH), 10.17 br, 11.50 br (each 1 H, s, tautomeric 2-NH_2).

1-Carbamoyl-2-carboxyethyl 2-Iminocyclopentanedithiocarboxylate (16). The ammonium salt of **1** (3 g, 0.017 mol) and maleic anhydride (1.7 g, 0.017 mol) were dissolved in DMF (30 mL) in an ice bath, and the mixture was kept at room temperature for 20 h. Water (200 mL) was added, and the mixture was kept for an additional 3 h. The solid product was collected, washed with water, dried, and recrystallized: IR (KBr) 3580 sh (OH), 3380 br, 3200 m (NH_2 and NH), 1705 vs, 1650 m cm^{-1} (C=O); UV max (EtOH) 310 (log ε 4.04), 382

nm (4.44); NMR (Me_2SO-d_6) δ 1.80 (2 H, quint, 4-H_2), 2.50–3.70 (6 H, m, 3-,5-H_2 and CH_2CO), 4.87 (1 H, dd, SCH), 7.20 br, 7.43 br (each 1 H, s, $CONH_2$), 9.23 br, 10.90 br (each 1 H, s, tautomeric 2-NH_2), 12.30 br (1 H, s, COOH).

2-Carbamoyl-1-carboxyethyl 2-Iminocyclopentanedithiocarboxylate (17). A mixture of the ammonium salt of 1 (3 g, 0.017 mol), maleic monoamide (2 g, 0.017 mol), and DMF (70 mL) was kept at room temperature for 24 h. Ether was added to the oil which separated out. The resulting solid product was collected, washed with ether, dried, and recrystallized: IR (KBr) 3650 (s (OH), 3400 vs, 3375 vs, 3300 vs, 3230 s (NH_2 and NH), 1690 vs, 1640 vs cm^{-1} (C=O); UV max (EtOH) 311 (log ε 4.03), 381 nm (4.41); NMR (Me_2SO-d_6) δ ca. 1.70 (2 H, m, 4-H_2), ca. 2.70 (4 H, m, 3-,5-H_2), ca. 4.00 br (3 H, s, CH_2CO and COOH), 5.03 (1 H, t, SCH), 7.00 br, 7.47 br (each 1 H, s, $CONH_2$), 9.18 br, 10.93 br (each 1 H, s, tautomeric 2-NH_2); NMR (C_5D_5N) δ 3.70 (2 H, d, CH_2CO), 6.38 (1 H, t, SCH).

2-Cyclohexyliminocyclopentanedithiocarboxylic Acid Esters (18–24). General Procedure. A mixture of acid **2** (2.4 g, 0.01 mol), olefin (0.01 mol), and EtOH or EtOH–DMF (10–20 mL) was worked up according to the preparation of **9–15.**

2-Methoxycarbonylethyl 2-Cyclohexyliminocyclopentanedithiocarboxylate (18). IR (KBr) 1720 vs cm^{-1} (C=O); UV max (EtOH) 252 sh (log ε 3.84), 314 (3.90), 398 nm (4.18); NMR ($CDCl_3$) δ 1.44 (6 H, m, 3′-,4′-,5′-H_2), 1.84 (6 H, m, 4-, 2′-, 6′-H_2), 2.75 (6 H, m, 3-,5-H_2 and CH_2CO), 3.50 (3 H, m, 1′-H and SCH_2), 3.66 (3 H, s, CH_3), 12.50 br (1 H, s, tautomeric 2-NH).

2-Carbamoylethyl 2-Cyclohexyliminocyclopentanedithiocarboxylate (19). IR (KBr) 3380 s, 3305 sh, 3190 s (NH_2), 1653 vs, 1647 vs cm^{-1} (C=O and NH_2); UV max (EtOH) 227 sh (log ε 3.70), 315 (3.82), 398 nm (4.26).

2-Cyanoethyl 2-Cyclohexyliminocyclopentanedithiocarboxylate (20). IR (KBr) 2240 w cm^{-1} (C≡N); UV max (EtOH) 227 sh (log ε 3.74), 310 (3.87), 398 nm (4.26).

1,2-Diethoxycarbonylethyl 2-Cyclohexyliminocyclopentanedithiocarboxylate (21). IR (KBr) 1737 vs, 1725 vs cm^{-1} (C=O); UV max (EtOH) 311 (log ε 4.15), 399 nm (4.53).

1,2-Dicarbamoylethyl 2-Cyclohexyliminocyclopentanedithiocarboxylate (22). IR (KBr) 3380 s, 3300 sh, 3160 s (NH_2), 1650 vs cm^{-1} (C=O); UV max (DMF) 313 (log ε 4.00), 393 nm (4.46); NMR (Me_2SO-d_6) δ ca. 1.50 br (10 H, m, 2′-,3′-,4′-,5′-,6′-H_2), ca. 1.80 (2 H, m, 4-H_2), ca. 2.80 (5 H, m 3-,5-H_2 and 1′-H), 2.60–3.70 (2 H, m, CH_2CO), 4.90 (1 H, dd, SCH), 6.75 br (2 H, s, $CONH_2$), 7.17 br (2H, s, $CONH_2$), 12.50 (1 H, d, tautomeric 2-NH).

3-(2,5-Dioxo)tetrahydrofuryl 2-Cyclohexyliminocyclopentanedithiocarboxylate (23). IR (KBr) 1783 m cm^{-1} (C=O); UV max (EtOH) 309 (log ε 3.45), 400 nm (4.15); *m/e* 339 (M^+).

3-(2,5-Dioxo)pyrrolidinyl 2-Cyclohexyliminocyclopentanedithiocarboxylate (24). IR (KBr) 3160 m (NH), 1785 s, 1719 vs, 1708 vs cm^{-1} (C=O); UV max (EtOH) 225 sh (log ε 4.02), 309 (4.07), 398 nm (4.54).

3-(2,5-Dioxo)tetrahydrofuryl 2-Oxocyclopentanedithiocarboxylate (25). A mixture of acid **3** (1.6 g, 0.01 mol), maleic anhydride (1 g, 0.01 mol), and EtOH (10 mL) was warmed on a steam bath and then kept at room temperature for 2 h. The solid product was collected, washed with EtOH, dried, and recrystallized: IR (KBr) 1705 s, 1684 sh, 1671 vs cm^{-1} (C=O); UV max (EtOH) 320 (log ε 3.92), 370 nm (3.82); NMR (Me_2SO-d_6) δ 1.60–2.87 (7 H, m, 1-H and 3-,4-,5-H_2), 2.95–3.45 (2 H, m, CH_2COO), 4.82 (1 H, dd, SCH).

3-(2,5-Dioxo)pyrrolidinyl 2-Oxocyclopentanedithiocarboxylate (26). A mixture of acid **3** (1 g, 0.0062 mol), maleimide (1 g, 0.01 mol), and EtOH (15 mL) was worked up according to the preparation of **25:** IR (KBr) 3180 w (NH), 1784 w, 1700 vs cm^{-1} (C=O); UV max (EtOH) 318 (log ε 3.40), 374 nm (3.82); *m/e* 257 (M^+).

3-(2,5-Dioxo)tetrahydrofuryl 3-Methyl-5-oxo-1-phenyl-Δ²-pyrazoline-4-dithiocarboxylate (27). A mixture of acid **4** (1.5 g, 0.006 mol), maleic anhydride (0.6 g, 0.006 mol), and EtOH (15 mL) was shaken at room temperature for 20 min. The solid product was collected, washed with benzene, and dried: IR (KBr) 1718 sh, 1705 vs, 1655 vs cm^{-1} (C=O); UV max (EtOH) 245 (log ε 4.41), 270 sh (4.19), 306 (4.30), 372 nm (4.49).

3-(2,5-Dioxo)pyrrolidinyl 3-Methyl-5-oxo-1-phenyl-Δ²-pyrazoline-4-dithiocarboxylate (28). A mixture of acid **4** (1.5 g, 0.006 mol), maleimide (0.6 g, 0.006 mol), and EtOH (13 mL) was warmed on a steam bath and then shaken at room temperature for 10 min. The solid product was collected, washed with EtOH, and dried: IR (KBr) 3500 m (enol 5-OH), 3160 m(NH), 1777 s, 1718 vs, 1705 vs cm^{-1} (C=O); UV max (EtOH) 246 (log ε 4.10), 270 sh (3.85), 305 (3.90), 372 nm (4.24).

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Registry No.—**1,** 18521-91-0; **1** NH_3, 36388-19-9; **2,** 54235-79-9; **3,** 57624-68-7; **4,** 57624-79-0; carbon disulfide, 75-15-0; cyclopentanone, 120-92-3; methyl propiolate, 922-67-2; 3,5-bis(3-methyl-5-oxo-1-phenyl-4²-pyrazolin-4-ylidene)-1,2,4-trithiole, 61656-33-5; diethyl fumarate, 623-91-6.

References and Notes

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