The Reaction of Cyclopentanone with Carbon Disulfide and Glycine Esters

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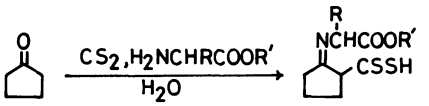
Synopsis. 2-(Methoxy- and ethoxycarbonylmethylimino)cyclopentanecarbodithioic acids were synthesized from cyclopentanone, carbon disulfide, and glycine esters. In the presence of sulfur, glycine, alanine, and phenylalanine esters reacted to give the corresponding oxidatively coupled products of dithiocarboxylic acid.

In the previous paper,[1] we have reported a convenient, one-step synthesis of 2-(alkylimino)-cyclopentanecarbodithioic acids by reaction of cyclopentanone with carbon disulfide in an aqueous amine medium. Earlier reports described the preparation of 2-imino-[2,3] and 2-(alkylimino)cycloalkanecarbodithioic acids.[4-6]

In this note, we wish to report the reaction of cyclopentanone with carbon disulfide in an aqueous solution of glycine esters. While the reaction of alkylamine was carried out below 10 °C for 0.5—2 h,[1] the present reaction required 6—8 h at room temperature. Although the yields were inferior, 2-(methoxy- and ethoxycarbonylmethylimino)cyclopentanecarbodithioic acids **1a** and **1b** were obtained from the corresponding glycine methyl and ethyl esters, respectively. In the case of alanine or phenylalanine ethyl ester, the reaction proceeded to give a crude unstable product in lower yield. However, it was difficult to isolate the corresponding pure dithiocarboxylic acid. The oxidatively coupled products **2a—d** were also directly obtained by the above reaction involving addition of sulfur to the starting materials.



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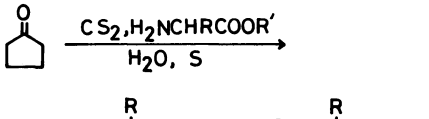

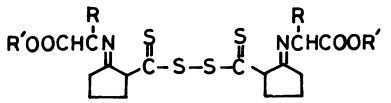

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The UV spectra of **1** and **2** as shown in Table 1 were similar to those of 2-(alkylimino)cyclopentanecarbodithioic acids (λ_{max} 304—306 and 393—398 nm in ethanol) and their oxidative dimers (λ_{max} 312—315 and 407—416 nm in chloroform).[1] Both the dithiocarboxylic acids **1a** and **1b** were exceedingly sensitive to Ni(II) ion, giving a pink red precipitate.[2,7]

Experimental

2-(Methoxycarbonylmethylimino)cyclopentanecarbodithioic Acid (1a). To a cooled mixture of cyclopentanone (5.7 g, 0.068 mol) and carbon disulfide (7.3 g, 0.096 mol) were added a solution of glycine methyl ester hydrochloride (9 g, 0.072 mol) in water (15 ml) and then a solution of sodium hydroxide (3 g, 0.075 mol) in water (15 ml). The mixture was shaken under nitrogen at room temperature for 6 h and allowed to stand overnight. The oily product was collected and washed with a small amount of ethanol. The yellow solid was purified by reprecipitation with acetone— a 2M HCl aqueous (1M=1 mol dm^{-3}) solution, IR (KBr), 2435 s (SH) 1740 *vs.* (C=O), and 1595 *vs.* cm^{-1} (C=N). Found: C, 46.87; H, 5.75; N, 6.00; S, 27.25%. Calcd for $C_9H_{13}NO_2S_2$: C, 46.73; H, 5.66; N, 6.05; S, 27.72%.

2-(Ethoxycarbonylmethylimino)cyclopentanecarbodithioic Acid (1b): Reprecipitated with acetone— a 2M HCl aqueous solution. IR (KBr), 2435 s (SH), 1740 *vs.* (C=O), and 1600 *vs.* cm^{-1} (C=N). Found: C, 48.99; H, 6.07; N, 5.74; S, 25.48%. Calcd for $C_{10}H_{15}NO_2S_2$: C, 48.95; H, 6.16; N, 5.71; S, 26.14%.

The Oxidatively Coupled Products of Dithiocarboxylic Acid (2). General Procedure. To a cooled mixture of cyclopentanone (1.5 g, 0.018 mol), carbon disulfide (2 g, 0.026 mol), and sulfur (0.1 g, 0.0031 mol) were added a solution of amino acid (glycine, alanine, or phenylalanine) ester hydrochloride (0.018 mol) in water (5 ml) and then a solution of sodium hydroxide (0.75 g, 0.019 mol) in water (4 ml). The mixture was shaken at room temperature for

Table 1. Yield and UV spectra

Compd	R	R′	Yield %	Mp θ_m/°C	UV nm (log ε)
1a	H	CH_3	32	142—144	308 (3.89), 398 (4.34)[a]
1b	H	C_2H_5	29	113—114	307 (4.01), 397 (4.34)[a]
2a	H	CH_3	31	173—174 (decomp)	317 (4.02), 414 (4.68)[b]
2b	H	C_2H_5	45	163—164 (decomp)	318 (4.06), 415 (4.68)[b]
2c	CH_3	C_2H_5	43	133—134 (decomp)	316 (4.03), 412 (4.67)[b]
2d	$CH_2C_6H_5$	C_2H_5	13	140—141 (decomp)	317 (3.98), 416 (4.66)[b]

a) In EtOH. b) In $CHCl_3$.

7—11 h and kept for 2 days at 4—18 °C. The oily product was collected, washed with ethanol and then carbon disulfide, and recrystallized or reprecipitated.

*Bis[2-(methoxycarbonylmethylimino)cyclopentyl(thiocarbonyl)] Disulfide (**2a**)*: Recrystallized with aniline–ethanol. IR (KBr), 1743 *vs.* (C=O) and 1580 *vs.* cm^{-1} (C=N). Found: C, 47.00; H, 5.25; N, 6.06; S, 27.40%. Calcd for $C_{18}H_{24}N_2O_4S_4$: C, 46.93; H, 5.25; N, 6.08; S, 27.84%.

*Bis[2-(ethoxycarbonylmethylimino)cyclopentyl(thiocarbonyl)] Disulfide (**2b**)*: Recrystallized with ethanol. IR (KBr), 1740 *vs.* (C=O) and 1582 *vs.* cm^{-1} (C=N). Found: C, 48.99; H, 5.80; N, 5.48; S, 25.99%. Calcd for $C_{20}H_{28}N_2O_4S_4$: C, 49.15; H, 5.78; N, 5.73; S, 26.24%.

*Bis[2-[ethoxycarbonyl(methyl)methylimino]cyclopentyl(thiocarbonyl)] Disulfide (**2c**)*: Reprecipitated with chloroform–hexane. IR (KBr), 1739 *vs.* (C=O) and 1578 *vs.* cm^{-1} (C=N). Found: C, 51.10; H, 6.21; N, 5.30; S, 24.45%. Calcd for $C_{22}H_{32}N_2O_4S_4$: C, 51.13; H, 6.24; N, 5.42; S, 24.82%.

*Bis[2-[benzyl(ethoxycarbonyl)methylimino]cyclopentyl(thiocarbonyl)] Disulfide (**2d**)*: To the resulting reaction mixture was added a 2M HCl aqueous solution (15 ml) and the mixture was extracted with chloroform. After the solvent was evaporated, ether (15 ml) was added to the orange red oil and a small amount of light yellow solid was removed by filtration. From the filtrate yellow solid **2d** was obtained and reprecipitated with chloroform–hexane. IR (KBr), 1740 *vs.* (C=O) and 1580 *vs.* cm^{-1} (C=N). Found: C, 60.85; H, 6.02; N, 4.14; S, 18.96%. Calcd for $C_{34}H_{40}N_2O_4S_4$: C, 61.05; H, 6.03; N, 4.19; S, 19.17%.

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References

1) N. Fukada, K. Arai, and T. Takeshima, *Synthesis*, **1980**, 566.

2) T. Takeshima, M. Yokoyama, T. Imamoto, M. Akano, and H. Asaba, *J. Org. Chem.*, **34**, 730 (1969). For the improved preparative method, see: T. Takeshima, M. Muraoka, N. Fukada, A. Takayama, and T. Yamamoto, *J. Org. Chem.*, **42**, 3383 (1977).

3) T. Takeshima, A. Yano, N. Fukada, Y. Hirose, and M. Muraoka, *J. Chem. Res. (S)*, **1979**, 140; *J. Chem. Res. (M)*, **1979**, 1732.

4) R. Mayer and J. Jentzsch, *J. Prakt. Chem.*, **23**, 83 (1964).

5) B. Bordás, P. Sohár, G. Matolcsy, and P. Berencsi, *J. Org. Chem.*, **37**, 1727 (1972).

6) T. Takeshima, N. Fukada, T. Miyauchi, M. Muraoka, T. Yamamoto, and T. Hayashi, *J. Chem. Soc., Perkin Trans. 1*, **1974**, 914.

7) N. K. Dutt and T. Seshadri, *Anal. Chim. Acta*, **47**, 571 (1969); P. Thomas and A. Poveda, *Z. Chem.*, **11**, 153 (1971).