[Chem. Pharm. Bull. 20(8)1824—1826(1972)]

UDC 547.7.04 : 547.556.8.04

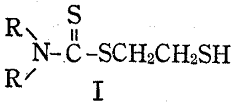
Reaction of Cyclic Trithiocarbonate with Amine and Phenylhydrazine

Mitsuru Furukawa, Kenji Nagato, Yoko Kojima,
and Seigoro Hayashi

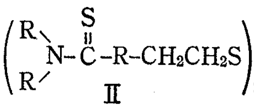
Faculty of Pharmaceutical Sciences, Kumamoto University[1]

(Received February 4, 1972)

Delaby[2] has reported that ethylene trithiocarbonate reacts with various secondary amines at room temperature to yield N,N-disubstituted 2-mercaptoethyldithiocarbonate (I). On the contrary, Durden[3] has repeated this reaction using morpholine and piperidine as secondary amine and found that the actual product is the disulfide (II) but not the thiol (I). Moreover, he has shown that the reaction of ethylene trithiocarbonate with two moles of *n*-butylamine in refluxing ethanol gives 1,3-dibutylthiourea.


$\mathrm{RR'N{-}\overset{S}{\overset{\|}{C}}{-}SCH_2CH_2SH}$

I


$\left(\mathrm{RR'N{-}\overset{S}{\overset{\|}{C}}{-}R{-}CH_2CH_2S}\right)_2$

II

We attempted to repeat and extend this condensation using 1-substituted propylene-2,3-trithiocarbonates. This paper concerned with the reaction of 1-morpholinopropylene- and 1-(β-naphthoxy)propylene-2,3-trithiocarbonates (III)[4,5] with several amines, such as cyclohexylamine, piperidine, and morpholine, and phenylhydrazine.

When these trithiocarbonates were heated with five moles of cyclohexylamine under reflux, 1,3-dicyclohexylthiourea (IV) was obtained in 62.4% and 81.1% yields, respectively, as only crystalline product. This was identified by mixed melting point determination and infrared (IR) comparison with an authentic sample.[6] Attempts to prepare the corresponding piperidine- and morpholine-substituted thiourea under the similar conditions using five moles of piperidine and morpholine, however, gave piperidinium piperidinoxanthate (V) and morpholinium morpholinoxanthate (VI), which were identified by mixed melting point determination and IR comparison with an authentic samples prepared by the reaction of

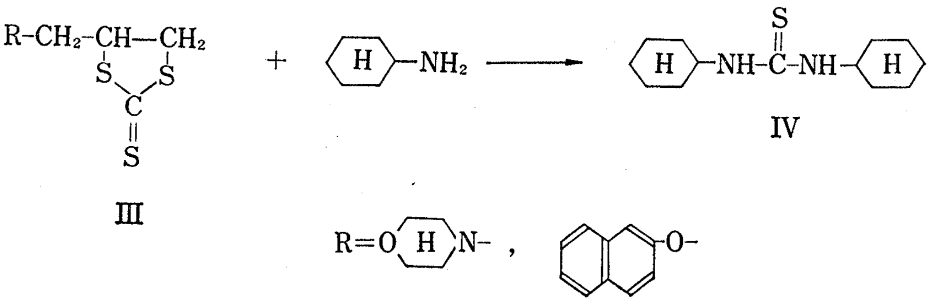


Chart 1

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[1] Location: *Oe-hon-machi, Kumamoto.*

[2] R. Delaby, P. Piganiol, and C. Warolin, *Compt. rend.*, **230**, 1671 (1950) [*C.A.*, **44**, 8870*b* (1950)].

[3] J.A. Durden, H.A. Stansbury, and W.H. Catlette, *J. Am. Chem. Soc.*, **82**, 3082 (1960).

[4] S. Hayashi, M. Furukawa, Y. Fujino, T. Nakao, and K. Nagato, *Chem. Pharm. Bull.* (Tokyo), **19**, 1594 (1971).

[5] R.F. Homer, *J. Chem. Soc.*, **1950**, 3690.

[6] A. Skita and H. Rolfes, *Chem. Ber.*, **53**, 1242 (1920).

piperidine and morpholine with carbon disulfide.[7] The same reaction in alcohol under reflux also gave the same products, no trace of any expected dithiocarbamates being isolated as crystalline.

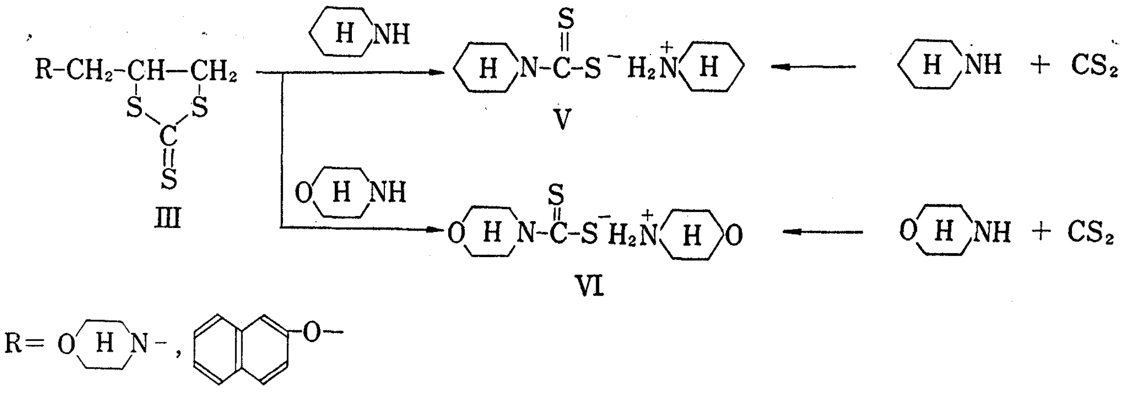
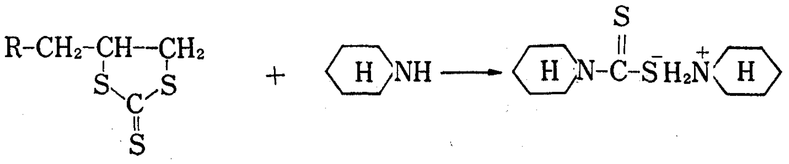
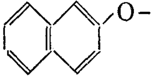


Chart 2

In this reaction, variation of amounts of piperidine reacting with the trithiocarbonates was examined. Table I showed the relationship between the amount of piperidine and the yield of the corresponding xanthate.

Table I. Relationship between the Amount of Piperidine and the Yield of Piperidinium Piperidinoxanthate



Piperidine (mole)		5.0	3.0	2.0	1.0
Yield (%)	R = 	69.9	51.9	21.6	16.0
	R = 	60.9	39.8	27.6	4.0

As shown in the Table I, the yield of the xanthate was considerably decreased with the deminution of the amount of piperidine. The reaction would probably proceed through the formation of dithiocarbamate intermediate, though it failed to isolate.

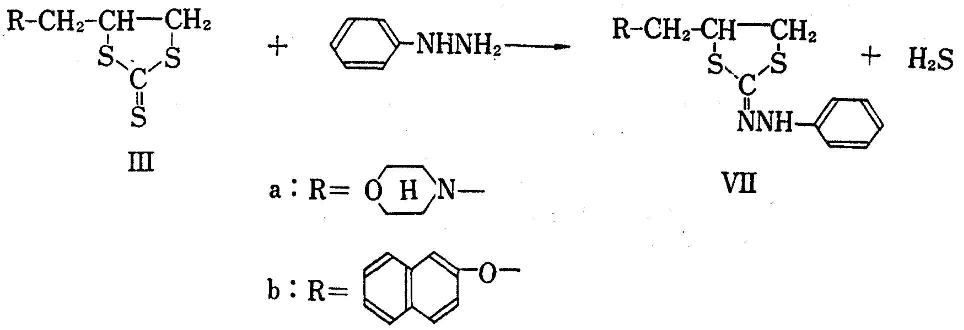


Chart 3

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[7] A. Wohs, *Chem. Ber.*, 1, 25 (1860).

Heating of 1-morpholinopropylene- and 1-(β-naphthoxy)propylene-2,3-trithiocarbonates (III) with an equivalent amount of phenylhydrazine in ethanol under reflux for 3 hr gave the corresponding phenylhydrazone (VII) in 74.3% and 84.6% yields, respectively, liberating hydrogen sulfide. Same results were obtained when a great excess of phenylhydrazine was employed, no ring cleavage occuring. The structures of the phenylhydrazones (VII) were confirmed by the elementary analyses and spectral data.

Experimental

1,3-Dicyclohexylthiourea (IV)——a) A mixture of 2.35 g (0.01 mole) of 1-morpholinopropylene-2,3-trithiocarbonate and 4.95 g (0.05 mole) of cyclohexylamine was heated for 30 min under reflux. The mixture was distilled under reduced pressure to remove cyclohexylamine unchanged. The residue was recrystallized from acetone to give 1.5 g (62.4%) of colorless prisms melting at 178—179°, which was identified by mixed melting point determination and IR comparison with an authentic sample. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3290 (NH). Mass Spectrum *m/e*: 240 (M^+).

b) A mixture of 2.92 g (0.01 mole) of 1-(β-naphthoxy)propylene-2,3-trithiocarbonate and 4.95 g (0.05 mole) of cyclohexylamine was treated by the procedure described above to yield 1.95 g (81.1%) of colorless prims melting at 178—179°.

Piperidinium Piperidinoxanthate (V)——a) A mixture of 2.35 g (0.01 mole) of 1-morpholinopropylene-2,3-trithiocarbonate and 4.26 g (0.05 mole) of piperidine was heated for 2 hr under reflux. After cooling, AcMe–ether (1:1) was added to the mixture and the precipitates deposited were collected by filtration, washed with AcMe–ether, recrystallized from EtOH and then sublimed to give 1.75 g (69.9%) of colorless prisms subliming at 171—173°, which was identified by IR comparison with an authentic sample. *Anal.* Calcd. for $C_{11}H_{22}N_2S_2$: C, 53.64; H, 9.00; N, 11.37. Found: C, 53.63; H, 8.82; N, 11.35. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 2755, 2680, 2500, 2417, 1583 ($>\overset{+}{N}H_2$).

b) A mixture of 2.92 g (0.01 mole) of 1-(β-naphthoxy)propylene-2,3-trithiocarbonate and 4.26 g (0.05 mole) of piperidine was treated by the procedure described above to give 1.50 g (60.9%) of colorless prisms subliming at 171—173°.

Morpholinium Morpholinoxanthate (VI)——a) A mixture of 2.35 g (0.01 mole) of 1-morpholinopropylene-2,3-trithiocarbonate and 4.35 g (0.05 mole) of morpholine was heated at 130° for 2 hr. After cooling, AcMe-ether was added to the solution and the mixture was stood overnight. Precipitated deposited were collected by filtration and sublimed to give 2.20 g (88.0%) of colorless needles subliming at 177—180°, which was identified by IR comparison with an authentic sample. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 2726, 2475, 2350, 2210, 1587 ($>\overset{+}{N}H_2$). *Anal.* Calcd. for $C_9H_{18}O_2N_2S$: C, 43.19; H, 7.25; N, 11.20. Found: C, 43.14; H, 7.03; N, 11.02.

b) A mixture of 2.92 g (0.01 mole) of 1-(β-naphthoxy)propylene-2,3-trithiocarbonate and 4.35 g (0.05 mole) of morpholine was treated by the procedure described above to give 2.07 g (82.8%) of colorless needles subliming at 177—180°.

2-Phenylhydrazono-4-morpholinomethyl-1,3-dithiolane (VIIa)——A solution of 2.35 g (0.01 mole) of 1-morpholinopropylene-2,3-trithiocarbonate and 5.40 g (0.05 mole) of phenylhydrazine in 50 ml of EtOH was heated for 3 hr under reflux. The solution was evaporated to dryness under reduced pressure and the residue was recrystallized from CCl_4 to give 2.38 g (74.3%) of colorless prisms melting at 147—148°. *Anal.* Calcd. for $C_{14}H_{19}ON_3S_2$: C, 54.36; H, 6.19; N, 13.59. Found: C. 54.20; H, 6.07; N, 13.42. NMR ($CDCl_3$) τ: 7.55—7.05 (6H, multiplet, $\genfrac{}{}{0pt}{}{H_2C}{H_2C}\!>\!N\text{–}CH_2$), 6.57 (2H, doublet, ring CH_2), 6.20 (4H, triplet, CH_2-O-CH_2), 5.98—5.50 (1H, multiplet, CH), 3.40—2.35 (5H, multiplet, phenyl hydrogen). Mass Spectrum *m/e*: 309 (M^+).

2-Phenylhydrazono-4-(β-naphthoxy)methyl-1,3-dithiolane (VIIb)——A mixture of 2.92 g (0.01 mole) of 1-(β-naphthoxy)propylene-2,3-trithiocarbonate and 5.40 g (0.05 mole) of phenylhydrazine was treated by the procedure described above to yield 3.10 g (84.6%) of colorless prisms melting at 132—134°. *Anal.* Calcd. for $C_{20}H_{18}ON_2S_2$: C, 65.52; H, 4.95; N, 7.64. Found: C, 65.28; H, 4.80; N, 7.76. NMR ($CDCl_3$) τ: 6.37 (2H, doublet, ring CH_2), 5.85—5.44 (3H, multiplet, CH_2-CH), 3.05—1.95 (12H, multiplet, aromatic hydrogen). Mass Spectrum *m/e*: 366 (M^+).

Acknowlegdement We are grateful to Mr. K. Takeda for measurements of NMR and Mass Spectra and to Miss M. Sato for IR data. We also thank Mrs. K. Shiraki and Yoshitomi Seiyaku Co. Ltd. for microanalytical data.