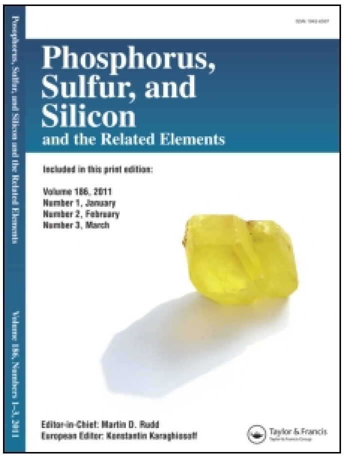

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Synthesis of Mixed Thiuram Disulfides

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SHORT COMMUNICATION

Synthesis of Mixed Thiuram Disulfides

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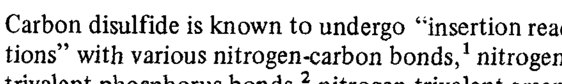
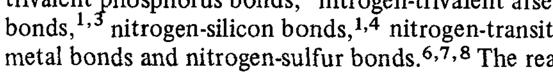
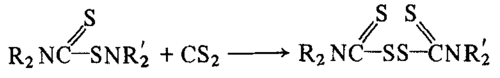
Carbon disulfide is known to undergo "insertion reactions" with various nitrogen-carbon bonds,[1] nitrogen-trivalent phosphorus bonds,[2] nitrogen-trivalent arsenic bonds,[1,3] nitrogen-silicon bonds,[1,4] nitrogen-transition metal bonds and nitrogen-sulfur bonds.[6,7,8] The reaction of carbon disulfide with secondary amine sulfides or alkyl sulfenamides furnished tetralkyl thiuram disulfides[6] and trithiopercarbamates,[7,8] respectively (Eq. I and II).


$$R_2NSNR_2 + 2CS_2 \longrightarrow R_2N\overset{S}{\overset{\|}{C}}{-}SS{-}\overset{S}{\overset{\|}{C}}NR_2 + S \qquad \text{(I)}$$


$$RSNR'_2 + CS_2 \longrightarrow RSS\underset{S}{\underset{\|}{C}}NR'_2 \qquad \text{(II)}$$

Although bis(disubstitutedthiocarbamoyl) disulfides [thiuram disulfides] have been known for sometime, the synthesis of mixed thiuram disulfides have never been reported. We wish to report that the reaction of thiocarbamoylsulfenamides with carbon disulfide afforded either the symmetrical or previously unknown asymmetrical thiuram disulfides (eq. III).


$$R_2N\overset{S}{\overset{\|}{C}}{-}SNR'_2 + CS_2 \longrightarrow R_2N\overset{S}{\overset{\|}{C}}{-}SS{-}\overset{S}{\overset{\|}{C}}NR'_2 \qquad \text{(III)}$$

$R = R'$ or $R \neq R'$

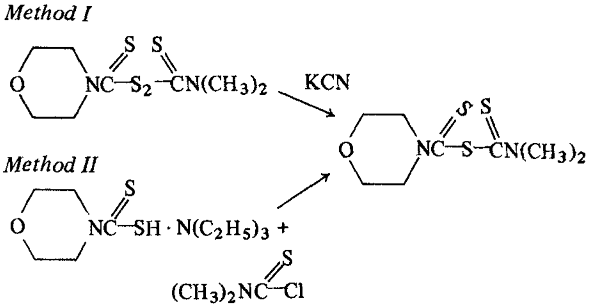
The thiocarbamoylsulfenamides[9,10] may be prepared by the oxidative condensation of a salt of a dithiocarbamic acid and a secondary amine or by the reaction of a salt of a dithiocarbamic acid with a N-chloro secondary amine.

All compounds obtained are listed in Table I, along with reaction conditions, yields, nmr spectral and physical data.

A general procedure is as follows: A stirred mixture containing 0.1 mol of the appropriate *freshly prepared* thiocarbamoylsulfenamide,[9,10] 0.11 to 0.15 mol of carbon disulfide in 100 ml of methyl alcohol was heated at reflux for the time period specified in Table I. After stirring at 25-30° for 18 hours, the reaction mixture was cooled to 0°, the solids collected by filtration and air-dried at 25-30°.

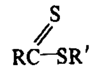
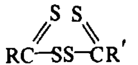
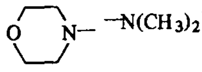
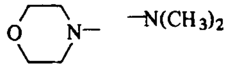
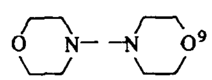
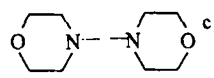
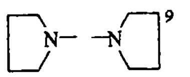
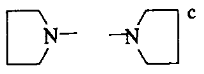
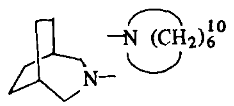
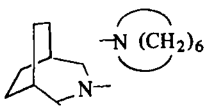
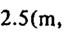
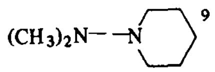
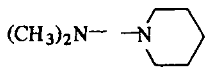
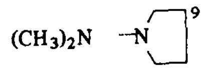
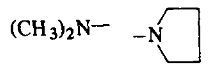
The structures for all disulfides were consistent with their nmr spectra and all compounds gave satisfactory elemental analyses. N,N-Dimethylthiocarbamoyl morpholinothiocarbonyl disulfide was further characterized by the sequence outlined in Chart I.

CHART I



Method I A stirred mixture containing 0.1 mol of above disulfide, 0.11 mol of potassium cyanide in 400 ml of methyl alcohol was heated under reflux for 5 hours. After cooling to 30°, 500 ml of water was added and stirring continued at 25-30° for 18 hours. The precipitate was collected by filtration, washed with water and air-dried at 25-30°. The product, mp 135-137°, was obtained in 80% yield. After recrystallization from toluene, it melted at 143-144°, nmr ($CDCl_3$) δ 3.47 (s,6,N(CH_3)$_2$), 3.8 (m,4,CH_2OCH_2), 4.1 (m,4,CH_2NCH_2).

TABLE I

 $R\overset{S}{\overset{\parallel}{C}}-SR'$ R R'	% Excess CS_2	Reflux Time (hrs)	 $R\overset{S}{\overset{\parallel}{C}}-SS-\overset{S}{\overset{\parallel}{C}}R'$ R R'	mp, °C	% Yield crude	nmr δ(ppm) $CDCl_3$—TMS
 [9]	50	6		112-113[a]	96	3.6(s,6,$(CH_3)_2N$) 3.8(m,4,CH_2OCH_2) 4.3(m,4,CH_2NCH_2)
 [9]	20	5	 [c]	147-148[a]	87	3.8(m,8,CH_2OCH_2) 4.3(m 8,CH_2NCH_2)
 [9]	10	2	 [c]	145-146[b]	98	2.1(m,8,CH_2CH_2) 3.9(m,8,CH_2NCH_2)
 [10]	50	6		145-146[a]	98	1.4-2.5(m,18,  + $(CH_2)_4$) 4.0-4.1(m,4,CH_2NCH_2 of R') 4.4(d,4,CH_2NCH_2 of R)
 [9]	50	6		98-99[d]	90	1.78(br.s,6,$(CH_2)_3$) 3.6(s,6,$(CH_3)_2N$) 4.2(br.s,4,CH_2NCH_2)
 [9]	50	6		96-97[d]	93	2.1(m,4,CH_2CH_2) 3.6(s,6,$(CH_3)_2N$) 4.0(m,4,CH_2NCH_2)

[a] Recrystallized from ethyl acetate.
[b] Recrystallized from toluene.
[c] A mixed melting point with an authentic sample was not depressed and nmr spectral data were identical.
[d] Recrystallized from isopropyl alcohol.

Anal. Calcd. for $C_8H_{14}N_2OS_3$: C, 38.37; H, 5.64; N, 11.19, S,38.42. Found: C, 38.54; H, 5.64; N, 10.99; S, 38.23.

Method II A mixture containing 0.2 mol of triethyl amine salt of morpholinodithiocarbamic acid, and 0.2 mol of dimethylthiocarbamoyl chloride in 300 ml of acetone was stirred at 25-30° for 24 hours. After the addition of 800 ml of water, the product was collected by filtration and air-dried at 25-30°. The product, mp 143-144°, was obtained in 90% yield. After recrystallization from toluene the melting point remained unchanged. A mixed melting point with the product derived by Method I was not depressed and the nmr spectral data were identical.

It is seen that either symmetrical or asymmetrical thiuram disulfides are readily and cleanly prepared in excellent yield by the reaction of thiocarbamoylsulfenamides with carbon disulfide.

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