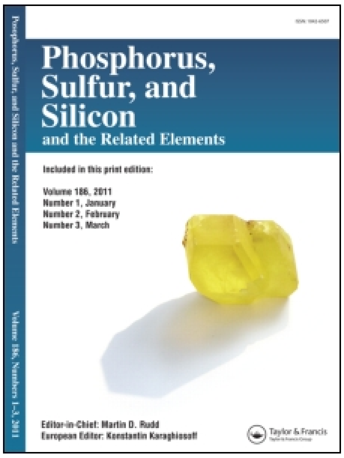

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INTERACTION OF THIOUREA WITH SULFUR DIVALENT COMPOUNDS: DESULFURIZATION OF THIOUREA BY *N,N'*-THIOBISMORPHOLINE

C. Díaz[a]; O. Bustos[a]; N. Yutronic[a]
[a] Facultad de Ciencias, Departamento de Química, Universidad de Chile, Santiago, Chile

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INTERACTION OF THIOUREA WITH SULFUR DIVALENT COMPOUNDS: DESULFURIZATION OF THIOUREA BY *N,N'*-THIOBISMORPHOLINE

C. DÍAZ, O. BUSTOS† and N. YUTRONIC
Facultad de Ciencias, Departamento de Química, Universidad de Chile,
Casilla 653, Santiago, Chile

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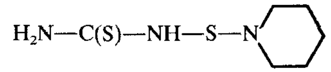
The reaction of thiourea with several sulfur (II)-nitrogen compound as well as thioethers and thiphenol have been investigated. At room temperature reaction of thiourea with *N,N'*-dithiobisamines afford compounds of composition $H_2N—C(S)—NH—S—S—NR_2$ while at high temperature sulfur and a complex mixture of S—N compounds are formed. *N,N'*-thiobismorpholine undergoes sulfuration with thiourea, to give *N,N'*-tetrathiomorpholine while from the reaction of *N,N'*-thiobis(piperidine) with thiourea the compound



was identified. From the reaction of thiourea with sulfenamides, dithioethers and thiophenol the unaltered reactives were isolated.

Key words: Thiourea reactions; thiobisamines reactivity; sulfur divalent.

INTRODUCTION

In a general study of the chemistry of sulfur(divalent)-nitrogen compounds we have found several types of reactivities:

i) sulfur coordination to transition metal in low oxidation state.[1–3]
ii) desulphurization with ion metal and with some organometallic fragments,[4] and
iii) hydrolysis[5] and alcoholysis[6] reactions in presence of Lewis acids.

In view of the recent interest of thiourea inclusion complexes[7] it was of interest to investigate the reactions of several sulfur divalent compounds with thoiurea. This matrix form inclusion compounds with a wide range of organic molecules although not inclusion compounds with sulfur compounds as guest have been reported.

In spite of that the expected inclusion compounds were not obtained, an interesting chemical reactivity between thiourea and the S—N compounds, is described here and discussed in comparison to earlier results.

RESULTS AND DISCUSSION

The reactions of thiourea with sulfur divalent compounds are summarized in Table I.

The reaction between thiourea and *N,N'*-dithiobisamines afford solid products that can be formulated as $H_2N—C(S)—NH—S—S—NR_2$,

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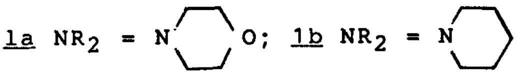
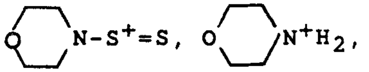
†Undergraduate research participant.



in basis of their elemental analysis and ^{1}H-NMR, IR and mass spectroscopy. The ^{1}H-NMR spectrum of the morpholine derivative show the two typical signals corresponding to the morpholine group protons with the chemical shifts values characteristic for morpholine-S—S compounds.[8] The expected NH and NH_2 protons were observed as a broad signal centered at 6.6 ppm in agreement with data for similar systems.[9,10] The insolubility of the piperidine derivative precludes a ^{1}H-NMR identification for this compound.

The IR spectra of the compounds exhibit, the characteristic $\nu(C{=}S)$ band[11] at 712 cm^{-1} as well as the $\nu(S—N)$ band[8] at 932 cm^{-1} (NR_2 = morpholine) and 925 cm^{-1} (NR_2 = piperidine). The $\nu(N—H)$ and $\delta(NH_2)$ bands are observed in the normal position.[11]

The mass spectrum of 1a does not show the presence of the molecular ion due probably to thermal decomposition of the compound. The spectrum is dominated by ion peaks assigned to $(S)n^+$ n = 1, 2, 4, 5, 6, 8 species and



$H_2N-C(S)-NH_2^+$.

The base peak was then ion $\cdot CH_2—CH_2—NH{=}CH_2$ at m/e = 57 characteristic for morpholine compounds.[12] These ion fragments are consistent with the thermal decomposition of the compound 1a in the mass spectrometer, to give—among other—octasulfur and some S—N compounds. Regeneration of thiourea indicated by the peak at m/e = 76 can arise from a thermal rearrangement of 1a. Consistently

TABLE I

Summary of the reactions of thiourea with sulfur divalent compounds at room temperature

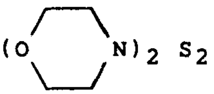
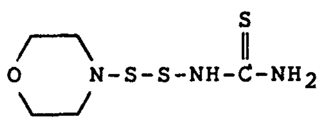
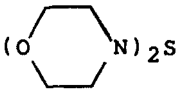
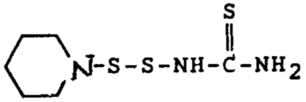
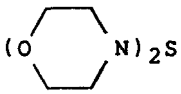
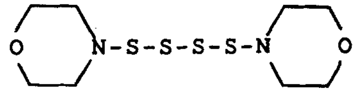
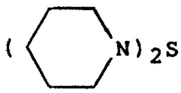
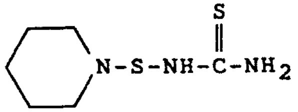
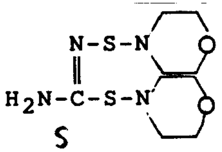
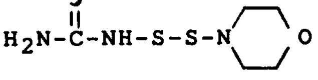
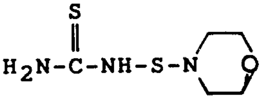
SULFUR DIVALENT REAGENT		PRODUCT
	1a	
	1b	
	2	
	3	

TABLE II

Probable S—N compounds present in the products obtained from the reaction of *N,N'*-dithiobisamines and *N,N'*-thiobisamines with thiourea at 65°C

Compound	MS (m/e)	ν(S—N)[c]	ν(C═S)[c]	ν(N═C═S)
	M+(278)[a]	921,980		
	M+(225)[a]	921,980	707	
	M+(193)[a]	922,981	707	
R-N=C=S	b			2150,2185

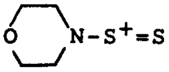
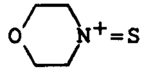
[a] This peak was observed with low intensity in the high resolution spectrum.

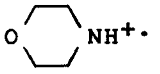
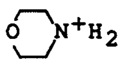
[b] The presence of this type of compounds was inferred from the peak in the mass spectrum at m/e = 59 assigned to $H\overset{+}{N}=C=S$.

[c] ν in cm^{-1}.

with this the reactions of *N,N'*-dithiobisamines with thiourea at 65°C in methanol afford sulfur and a complex mixture containing—among other—sulfur-nitrogen and isothiocyanat species. Some of this S—N compounds were identified by mass and IR data. See Table II.

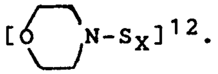
The molecular peak for the S—N species was observed with low intensity due probably to the unstability of the fragment. However in the mass spectrum was observed the peaks expected from their fragmentation:

 at m/e = 151;  at m/e = 118;

 at m/e = 87;  at me = 86;

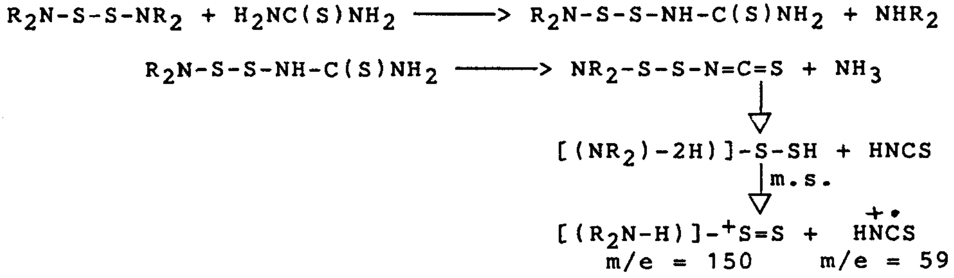
CH_2 = $^+N{=}S$ at m/e = 60; and $C_3H_7N^{+\cdot}$ at m/e = 56.

These last four fragments are very intense and typical of compounds containing the moiety



The presence of isothiocyanate compounds was suggested by the ν(N═C═S) bands at 2185 and 2150 cm^{-1} in the IR spectrum of the solid mixture and by the formation of hydrogen isothiocyanate (m/e = 59) in the mass spectrum.[13]

Some products found in the thermal decomposition as well as in the mass fragmentation can be explained by the scheme:



$$R_2N\text{-}S\text{-}S\text{-}NR_2 + H_2NC(S)NH_2 \longrightarrow R_2N\text{-}S\text{-}S\text{-}NH\text{-}C(S)NH_2 + NHR_2$$

$$R_2N\text{-}S\text{-}S\text{-}NH\text{-}C(S)NH_2 \longrightarrow NR_2\text{-}S\text{-}S\text{-}N{=}C{=}S + NH_3$$

$$\downarrow$$

$$[(NR_2)\text{-}2H)]\text{-}S\text{-}SH + HNCS$$

$$\downarrow \text{m.s.}$$

$$[(R_2N\text{-}H)]\text{-}{}^{+}S{=}S + \overset{+\bullet}{HNCS}$$

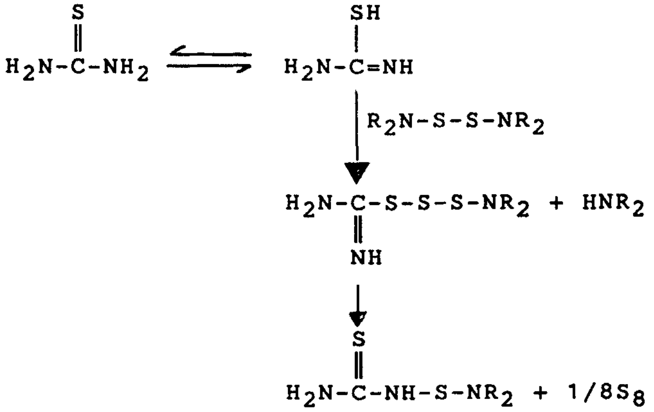
$$m/e = 150 \qquad m/e = 59$$

Similar thermal decomposition paths have been proposed for 1,1-disubstituted thioureas.[14]

At high temperature the reaction proceeds according to:

$$R_2N\text{—}S\text{—}S\text{—}NR_2 + H_2N\text{—}C(S)\text{—}NH_2 \rightarrow S_8 + S\text{—}N \text{ (products).}$$

The liberation of sulfur from this reaction requires some unsubstituted nitrogen; tetramethylthiourea with *N*,*N*′-dithiobismorpholine does not afford sulfur, while *N*,*N*′-dimethylthiourea reacts slowly with *N*,*N*-dithiobismorpholine and with loss of sulfur. Then a plausible mechanism of the reactions giving sulfur and involving N—H bonds could be:



$$H_2N\text{-}C({=}S)\text{-}NH_2 \rightleftharpoons H_2N\text{-}C(SH){=}NH$$

$$\downarrow R_2N\text{-}S\text{-}S\text{-}NR_2$$

$$H_2N\text{-}C({=}NH)\text{-}S\text{-}S\text{-}S\text{-}NR_2 + HNR_2$$

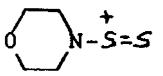
$$\downarrow$$

$$H_2N\text{-}C({=}S)\text{-}NH\text{-}S\text{-}NR_2 + 1/8S_8$$

Pathway leading other S—N compounds could be similar.

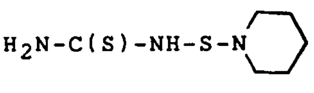
The proposition of this pathway was based in the mechanism of desulphurization of unalkylated thioureas by metallic salts.[15] The pyrolytic formation of sulfur does not occur at temperatures lower than 40°C; from the reaction in CH_2Cl_2 reflux formation of sulfur was not observed.

Several of the thermal cleavage reactions of the products obtained from the reaction of *N*,*N*′-dithiobisamines with thiourea at 65°C appears to resemble the electron impact induced fragmentation of the products obtained from the reaction at room temperature. For example the pyrolytic formation of sulfur find an analogy in the peak at m/e 255.8; 191.8; 159.8; 127.9; 95.9 and 64.0, corresponding to the species Sn^+ $n = 1 \ldots 8$ recorded in the mass spectrum of 1a. Formation of S—N species evidenced by the intense peak at m/e 150 assigned to a

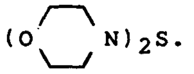


present, in the mass spectra of the product from reaction at room temperature, and at 65°C, appears to follow a similar pathway.

The reaction of *N,N′*-thiobisamines with thioureas at room temperature affords different products depending on the NR_2 substituent. With *N,N′*-thiobismorpholine the known compound *N,N′*-tetrathiomorpholine[16] 2 was obtained while with *N,N′*-thiobispiperidine the compound 3



was, identified by IR and ^{1}H-NMR spectroscopy. Similarly to other —NH—S—N— compounds[10] this compound is somewhat unstable. The formation of this S—N compound can be viewed as a cleavage of the S—N bond induced by thiourea acting as an acid reagent. Thus the rupture of S—N bond in *N,N′*-thiobisamines has been also observed with other acidic reagents.[2,4–6] Formation of *N,N′*-tetrathiomorpholine from *N,N′*-thiobismorpholine can be viewed as a desulphurization of thiourea by



In contrast thiobismorpholine itself undergoes desulphurization towards iron organometallic compounds.[4] This dual behaviour of *N,N′*-thiobismorpholine indicate that this sulfur compound can be regarded as a sulfur transfer compound. On the other hand, oxidative desulphurization reaction of thiourea have been informed with Pb and Hg salts,[15] and recently by Cu(II) salts.[17,18] Similarly to the reaction of dithiobisamines with thiourea, at temperature of reflux of MeOH, the reaction of thiobisamines with thiourea occurs with formation of sulfur and with formation of a complex mixture of S—N species as is indicated by mass and IR spectroscopy data. See Table II.

Thiourea is unreactive towards sulfenamides under mild conditions. Precipitation of thiourea or the sulfenamide unaltered was observed. This can be due to a more reactive S—N bond in *N,N′*-polythioamines than sulfenamides. Sulfenamides did not react with thiourea even at reflux of methanol. Its appears to be that the formation of sulfur as product in the reaction of thiourea with S—N compounds require two conditions: the presence of N—H bond in the thiourea, and sulfur reagents with at least two S—N bond.

These two conditions can be involved in the formation of some intermediate containing S—N and C=S bond as precursor in the formation of sulfur.

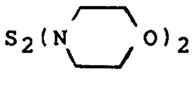
Thioethers and thiphenol are also unreactive towards thiourea. With the liquid dimethyldisulfide and thiophenol precipitation of thiourea was obtained while that with dibenzyl-disulfide their precipitation was observed.

EXPERIMENTAL

Infrared, proton NMR and mass spectra data were obtained as described elsewhere.[8,12] Thioureas commercially available (Merck) were purified by two recrystallizations. Thiobisamines *N,N′*-dithiobisamines and sulfenamides were prepared as described previously.[8,19] Thiophenol and disulfides of commercial grade were used without purification.

Methanol, CH_2Cl_2, pentane, *n*-hexane and acetone dried by standard procedure were used. Because of the instability of the —S—NH— compounds, the elemental analyses for 1a–b and 3 could not be very good. This is not rare in this type of compounds; for instance the related compounds X—C_6H_4—NH—S—NH—C_6H_4—X, X = H, OMe, Br, Cl and *m*—NO_2 were only spectroscopically characterized.[10]

Reaction of thiourea with N,N′-dithiobisamines. a) Reaction of thiourea with *N,N′*-dithiobismorpholine at room temperature.



(0.2 g 0.85 mmol) and thiourea (0.084 g, 1.1 mmol) were stirred in MeOH 20 ml at room temperature. Slow evaporation of the solvent afford plate crystals yield 90% m.p. 96–100°C Dec. Anal. Found: C 26.9%, H 4.63; N 18.62. Calc. for $C_5H_{11}N_3OS_3$; C 26.66 H 4.88; N 18.66. ^1H—NMR (($(CD_3)_2CO$): 6.6 (*s*, 3H, NH), 3.7 (*m*, 4H, OCH_2), 3.0 (*m*, 4H, NCH_2). IR (KBr): 3280–3360 br, vs. 3170 vs, 2985 *m*, 2860 *m*, 2840 *m*, 1610 vs, 1450 *w*, 1285 *m*, 1250 *s*, 1105 vs, 1070 *m*, 1055 *m*, 932 vs, 900 *w*, 840 *w*, 712 *m*, 789 *m*. Mass spectrum m/e (int./rel.): 255.7 (22), 191.8 (18), 159.8 (13), 150 (50), 127.9 (17), 118.1 (14.7), 95.9 (7), 87.71 (73), 86 (58.4), 76 (34), 64 (47), 60 (17), 57 (100), 44 (82.1), 32 (8).

b) At 65°C. *N,N′*-dithiobismorpholine (0.5 g 2.1 mmol) and thiourea (0.32 g, 4.2 mmol) were refluxed in methanol for 4.5 hrs. The yellow needles of sulfur (0.05 g) (m.p. 114–116°C and does not show ^1H—NMR signal in CS_2) were filtered off and the solution was evaporated. The resulting solid was washed with CS_2 to eliminate some sulfur and dried in vacuum. The white solid residue was insoluble in any of the usual organic solvent m.p. 118–120°C dec. Anal. Found: C 20.89, H 4.92, N 28.44. IR (KBr): 3400–3290 (vs, br), 3165 (vs, br) 2182 *m*, 1605 vs, 1478 *m*, 1390 *m*, 1245 *w*, 1100 *m*, 1075 *m*, 980 *m*, 920 *m*, 710 vs, 600 (vs, br). Mass spectrum m/e (rel. int., %): 257.8 (11), 256.8 (2), 255.9 (32), 191.95 (15), 159.9 (22), 150 (16), 130.05 (12), 127.9 (26), 116 (14), 95.9 (16), 87 (48), 86 (38), 76 (100). Other, less intense peaks were also observed. See Table I.

Reaction of *N,N′*-dithiobismorpholine with *N,N′*-dimethyl thiourea. *N,N′*-dithiobismorpholine, 0.3 g (1.3 mmol) and *N,N′*-dimethylthiourea, 0.13 g (1.2 mmol) were in 30 ml methanol refluxed for 30 hrs. The yellow needles of sulfur formed (0.04 g) were filtered off and the solvent evaporated from the filtrate. An oil uncharacterizable product was obtained.

Reaction of *N,N,N′,N′*-tetramethylthiourea with *N,N′*-dithio-bismorpholine. 0.28 g (2.1 mmol) of *N,N,N′,N′*-tetramethylthiourea and 0.5 g (2.1 mmol) of *N,N′*-dithio-bismorpholine in 50 ml MeOH were refluxed for 25 hrs. No formation of sulfur was observed.

a) Reaction of thiourea with *N,N′*-dithiobispiperidine at room temperature. Thiourea (0.09 g, 1.18 mmol) were stirred in MeOH at room temperature. After slow evaporation solvent, the yellow pale solid formed was filtered of and dried under vacuum. Anal. Found: C 33.45. H 5.96, N 19.9. Calcd. for $C_6H_{13}N_3S_3$. C 32.28, H 5.82, N 18.8. This compound was insoluble in common solvent therefore no ^1H—NMR was possible to obtain. IR (KBr) 3400–3290 (*s*, br), 3160 *s*, 2490 *s*, 2859 *w*, 2082 *w*, 2150 *w*, 1615 (vs), 1488 *m*, 1445 (m), 1400 *m*, 1360 *m*, 1215 *m*, 1180, 1035 *m*, 925 *s*, 855 *m*, 830 (m), 712 *s*, 680 *w*, 645 *m*, 615 *m*.

b) At 65°C. Dithiobispiperidine (0.3 g, 1.3 mmol) and thiourea (0.33 g, 4.3 mmol) were refluxed in 50 ml MeOH for 4 hrs. After the sulfur was filtered (0.06 g) the solvent was evaporated from the solution to give an light yellow oil. Attempts to crystallize this material were unsuccessful. No further work was done on this.

Reactions of thiourea with N,N′-thiobisamines. Reaction of thiourea with *N,N′*-thiobismorpholine at room temperature. Thiourea (0.24 g, 3 mmol) and *N,N′*-thiobismorpholine (0.5 g, 2.4 mmol) were stirred at room temperature in MeOH. Slow evaporation of solvent afford white solid m.p. 78°C (Dec.). Anal. Found: C 31.24, H 5.43, N 10.75. Calc. for $C_8H_{16}N_2O_2S_4$. C 31.96, H 5.32, N. 9.32. ^1H—NMR ($(CD_3)_2CO$) 3.7 (*m*, 2H, OCH_2), 3.0 (*m*, 2H, NCH_2). IR (KBr): 3500–3290 (br, *m*), 3170 *m*, 2960 *m*, 2859 *m*, 2838 *m*, 2060 *w*, 1615 *m*, 1445 *m*, 1355 *m*, 1282 *s*, 1255 vs, 1105 vs, 1055 *m*, 931 vs, 840 *m*, 690 *s*. Mass spectrum m/e (intensity): 300.1 (1) (M^+) 268.1 (19.5), 236.1 (3.1), 204.1 (64.7), 150 (100), 118.1 (13.9), 116 (44.3), 86.1 (19.38), 56 (10.6), 55.1 (12).

b) At 65°C. *N,N′*-thiobismorpholine (0.5 g, 2.4 mmol) and thiourea (0.37 g, 4.9 mmol) were refluxed in methanol for 14 h. The yellow needles formed were filtered off and the solution was evaporated to dryness. The solid residue obtained was washed with CS_2 and dried under vacuum. This solid was insoluble in any of the usual organic solvent m.p. 112–115°C dec. Anal. C 23.38, H 5.17, N 26.63. IR (KBr) 3400–3300 (vs, br), 3200–3100 (vs, br), 2185 *m*, 2150 *m*, 1510 vs, 1545 *m*, 1480 *m*, 1440 *m*, 1390 *s*, 1250 *m*, 1210 *s*, 1100 *s*, 1080 sh, 1015 *w*, 980 *m*, 930 *m*, 842 *m*, 710 (vs), 640 sh, 600 (*m*, br), 540 *w*. Mass spectrum m/e (intensity): 255.8 (21.9), 191.8 (29), 159.8 (25.8), 150.9 (27), 127.9 (15.7), 87 (21.78), 84 (18.9), 75.9 (100), 64 (26.4), 60 (31), 59 (12.9), 57 (26.5).

a) *Reaction of thiourea with N,N'-thiobispiperidine.* Thiourea 0.15 g, 2.0 mmol and the thioamine (0.2 g, 1 mmol) were stirred at room temperature in methanol. The yellow pale solid formed by slow evaporation of solvent was washed with *n*-hexane and vacuum dried. M.p. 99–103°C dec. Anal. Found: C 36.94, H 6.30, N 25.5. Calc. for $C_6H_{13}N_3S_2$ C 37.69, H 6.80, N 23.4. ^1H—NMR 3.4 (*s*, br, 3H, N) 2.9 [*m*. 4H, $(CH_2)_2N$], 1.54 (*m*, 6H, $(CH_2)_3N$). IR (KBr): 3330 (*s*, br), 3170 *s*, 2940 *m*, 2858 *m*, 2151 *m*, 1615 vs, 1475 (*m*), 1400 *m*, 1280 *m*, 1255 *w*, 1085 *m*, 1021 *m*, 980 *m*, 950 *w*, 850 *m*, 715 *m*.

b) *Reaction of thiourea with N,N'-thiobispiperidine at 65°C.* Thiourea 0.38 g 5 mmol and the thiobispiperidine 0.5 g, 2.5 mmol were refluxed in methanol for 4 h. The yellow solid formed (0.09 g) was filtered and dried in vacuum. Then the solvent was evaporated and the oil residue was washed with CS_2 to give a brown light solid which was dried in vacuum. This was insoluble in any of the usual organic solvents including CS_2 m.p. 98–103°C dec. IR (KBr): 3380 br, 3320 (br), 3190 (br), 2940 *m*, 2855 *m*, 2190 *m*, 2150 *m*, 1510 st, 1540 sh, 1400 *s*, 1230 *m*, 1210 *m*, 1100 br, 960 *w*, 875 *m*, 840 *m*, 620 *s*.

Reaction of thiourea with sulfenamides. Reaction of thiourea with triphenylmethanesulfenamide. Thiourea (0.14 g, 1.8 mmol) and [$(C_6H_5)_3C$—S—NH_2] (0.4 g, 1.4 mmol) were stirred in a mixture MeOH-acetone at room temperature. The solution was placed in the freezer overnight and the formed orange solid filtered off and dried in vacuum ^1H—NMR ($(CD_3)_2CO$) 7.18 (*s*, 15 H, C_6H_5); 3.2 (*s*, 2H, NH_2). IR of this compound was similar to those authentic sample of $(C_6H_5)_3C$—S—NH_2.

Reaction of thiourea with bencene(morpholine)sulfenamide. Thiourea (0.28 g, 3.6 mmol) and the sulfenamide (0.47 g, 2.4 mmol) were stirred at room temperature in a mixture MeOH-Acetone. Slow evaporation of the solvent affords an orange solid which contain primarily thiourea as deduced from their ^1H—NMR spectrum ($(CD_3)_2CO$ δ = 6.8 ppm broad) and IR spectrum (KBr, 3380 vs, 3280 vs, 3185, 1615 *m*, sh, 1590 vs, 1469 vs, 1431 *m*, 1085 *m*, 730 *m*, 625 *m*, 500 *s*, br).

Reaction of thiourea with bencene (N,N'-dicyclohexyl)sulfenamide. Thiourea (0.2 g, 2.65 mmol) and the sulfenamide (0.5 g, 1.03 mmol) were stirred in a mixture CH_3OH-$(CH_3)_2CO$ at room temperature. The orange solid isolated was identified by IR and ^1H—NMR as thiourea with traces of the sulfenamide.

Reaction of thiourea with disulfides and thiophenol. Reaction of thiourea with dimethyldisulfide. Thiourea (0.4 g, 5.3 mmol) and dimethyldisulfide (0.33 g, 3.5 mmol) were stirred in a mixture CH_3OH-acetone at room temperature. The white crystals isolated were identified as thiourea by their IR and ^1H—NMR spectra.

Reaction of thiourea with dibenzyldisulfide. Thiourea (0.5 g, 6.6 mmol) and the disulfide (1.08 g, 4.4 mmol) were stirred in MeOH at room temperature. The isolated colourless crystals were identified as dibenzyldisulfide by IR and ^1H—NMR spectroscopy by comparison with an authentic sample.

Reaction of thiourea with thiophenol. Thiourea (0.4 g, 5.3 mmol) and thiphenol (0.33 g, 3 mmol) were stirred at room temperature in MeOH. The white solid isolated showed an identical IR and ^1H—NMR of that thiourea.

Reaction of thiourea with triphenylmethanesulfenamide at 65°C. Thiourea (0.13 g, 1.7 mmol) and the sulfenamide (0.5 g, 1.7 mmol) were refluxed in 50 ml methanol. After 22 h no formation of sulfur was observed.

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