# THE PREPARATION OF SOME THIOSEMICARBAZONES AND THEIR COPPER COMPLEXES

## PART III<sup>1</sup>

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# ABSTRACT

Reactions of some diketones with thiosemicarbazide have been studied under various conditions. Monothiosemicarbazones, dithiosemicarbazones, and cyclization products can be obtained. It was found that dithiosemicarbazones form 1:1 complexes with Cu(II) but failed to react with Cu(I). Dithiosemicarbazones in which the N<sup>2</sup>-hydrogen atom has been replaced by Me do not form complexes, confirming our views about the importance of this hydrogen atom in the thione  $\leftrightarrow$  thiol tautomerism necessary for complex formation. 4,4-Dimethyldithiosemicarbazones behave like the unsubstituted parent compounds in forming 1:1 complexes with Cu(II). Infrared spectra provide evidence for the structure of a cyclization product, 5,6-diphenyl-3-thio-1,2,4-triazine, which had been erroneously described by various authors as the thiol tautomer, 5,6-diphenyl-3-mercapto-1,2,4-triazine.

In previous publications (1, 2), the reactions of thiosemicarbazones (tscs) with Cu(I) and Cu(II) ions were reported. A polymeric structure was suggested for the insoluble 1:1 complexes obtained from these reactions (2), and the antifungal activity of both free tscs and their copper complexes was also reported (3). The present work describes the reactions of mono- and di-tscs with a number of metals. It was found that monotscs which form complexes readily with copper in alkaline or neutral solution fail to react similarly with the following metals: Ag(I), Hg(II), Ni(II), Mn(II), Zn(II), Sn(II), Co(II), Fe(II), and Fe(III). Guha-Sircar *et al.* (4) obtained solid precipitates from tscs and several of these metals at pH from 3 to 7, and suggested that this reaction could be used for the quantitative determination of cations. In the present work, precipitates were obtained with the cations mentioned above but no definite products were isolated. The high metal content (approx. 50%) indicated that these solid materials were mostly inorganic, consisting probably of the metal sulphides.

The fact that tscs form definite complexes with copper only, coupled with our previous finding that antifungal activity is usually limited to the free tscs, the complexes being inactive (3), is believed to be quite significant in the study of the mechanism of antifungal action of these compounds. The role and the nature of the metal in biological processes involving metal-binding substances is of great importance (5) and work is currently being carried out along this line and will be reported elsewhere.

A number of dithiosemicarbazones (ditscs) were prepared from dicarbonyl compounds in order to examine their reaction with metals and eventually to study their antifungal properties. The reaction of dicarbonyl compounds with thiosemicarbazide is not simple and mixtures of products are usually obtained. The separation of these mixtures is complicated by the low solubility of the various components and the discrepancies encountered in the literature concerning their melting points.

Glyoxal (I) (R = R' = H) and diacetyl (I) (R = R' = CH<sub>3</sub>) gave readily the ditscs (III), but benzil (I) (R = R' = C<sub>6</sub>H<sub>5</sub>) afforded a mixture of monotscs (II), ditscs (III), and the cyclization product 5,6-diphenyl-3-thio-1,2,4-triazine (IV) (R = R' = C<sub>6</sub>H<sub>5</sub>).

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$$R-C = NNHCSNH_{2}$$
(II)
$$R'-C = 0$$

$$\downarrow alk.$$

$$R-C = N$$

$$R'-C = N$$

$$\downarrow R'-C = N$$

$$\downarrow R'-C = N$$

$$\downarrow R'-C = N$$

$$\downarrow R'-C = S$$

$$R-C = NNHCSNH_{2}$$

$$R'-C = NNHCSNH_{2}$$
(III)

$$\begin{array}{cccc} R-C=0 & R-C=N \\ & & H_2NNHCSNH_2 & H_2NNHCSNH_2 \\ & & CH_2 & CH_2 \\ & & CH_2 \\ R'-C=0 & R'-C=N \\ & & (V) & (VI) \end{array}$$

In the case of 1,3-diphenyl-1,3-propanedione (V) ( $\mathbf{R} = \mathbf{R}' = C_6 \mathbf{H}_5$ ), the monotsc and a cyclization product, 3,5-diphenyl pyrazole (VI) ( $\mathbf{R} = \mathbf{R}' = C_6 \mathbf{H}_5$ ), were obtained, while many attempts to isolate the ditsc were unsuccessful. Pyrazoles are usually obtained from reaction of 1,3-dicarbonyl compounds with hydrazine or semicarbazides (6), so it is not surprising that thiosemicarbazide should give rise to similar compounds. 1-Phenyl-1,3-butanedione (V) ( $\mathbf{R} = C\mathbf{H}_3$ ,  $\mathbf{R}' = C_6\mathbf{H}_5$ ) gave the expected ditsc plus an unidentified product,  $C_{20}\mathbf{H}_{19}\mathbf{N}_5\mathbf{S}$ . 2,5-Hexanedione, 2,3-heptanedione, and 2,3-octanedione gave the expected ditscs and no other tractable products. We failed to isolate the mono- or di-tsc from acetyl acetone, and part of the diketone must have been broken down since acetyl thiosemicarbazide was identified from the reaction mixture.

The preparation of Cu(II) and Ni(II) complexes with a few ditscs (diacetyl, 2,3pentanedione, 2,3-bexanedione, 1-phenyl-1,2-propanedione ditscs) has been previously described (7–9). Later, Górski *et al.* (10) obtained metal complexes with the ditsc of the diethyl ester of 2,3-dioxobutane-1,4-dicarboxylic acid, but did not isolate the compounds. We found that ditscs examined in this work formed 1:1 complexes readily with Cu(II)\* but no definite products were obtained using Cu(I) in ammoniacal solution, or with Fe(II), Fe(III), Zn(II), Sn(II), Co(II), Hg(II), or Ag(I) in neutral or alkaline solution.

Substituted ditscs were prepared from 2-methyl and 4,4-dimethyl thiosemicarbazide with glyoxal, and their reaction with copper was studied. The 2-methyl derivative did not form a complex, confirming our previous findings (2) that the N<sup>2</sup>-hydrogen atom is a requirement of the tautomeric equilibrium illustrated below, which is necessary for the formation of complexes.

\*2,5-Hexanedione and 2,3-heptanedione ditses gave solid precipitates with Cu(II) but no definite products could be identified.

-C=0

-Ċ=0

(I)

R-

R′

H<sub>2</sub>NNI

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On the other hand, both glyoxal and diacetyl di(4,4-dimethyl)tscs readily formed 1:1 copper complexes, as did the unsubstituted ditscs. Considering that ditscs contain two thiosemicarbazide residues, the 1:1 complexes described here may be regarded as 2:1 with respect to the thiosemicarbazide-copper ratio, for the important species here is the thiosemicarbazide residue,  $==N-NH-CS-NH_2$ , which alone is responsible for complex formation. On this basis, ditsc-copper complexes are quite different from monotsc-copper complexes, in which the ratio of thiosemicarbazide to copper is unity. The structure of ditsc-copper complexes is probably best represented by the conventional formula (VII), previously suggested by Bähr (7).



The compounds discussed in this work are listed in Table I together with their infrared spectra. Only two regions of the spectrum are of particular interest, the 3500–3000 cm<sup>-1</sup>

TABLE I								
Compounds and	their infrar	ed spectra	. in	two	regions			

Compounds		$3500-3000 \text{ cm}^{-1}$	1700–1500 cm <sup>-1</sup>	
Glyoval ditse		3380 m 3230 m 3130 m	1650 w 1605 s	
Givoral di(2-methyl)tsc		3420  s, $3240  s$ , $3120  m$	1685 w 1675 w	
Glyoxal di(4 4-dimethyl)tsc		3425 s. 3200 m. 3045 w	1575 m, 1550 m	
Giveral ditse-Cu(H)		3440 w. 3390 m. 3250 w	1655 m, 1630 m 1570 m	
Glyoxal di(4 4-dimethyl)tsc-Cu(H)		3420 m	1625 w. 1570 w	
Diacetyl ditsc		3425 s, 3200 s, 3260 w, 1695 w, 1600 w 3160 w		
Diacetyl di(4.4-dimethyl)tsc		3280 m	1525 s	
Diacetyl ditsc-Cu(II)		3400 s. 3290 s. 3140 s	1630 s. 1595 s	
Diacetyl di(4 4-dimethyl)tsc-Cu(II)		3410 m	1500 s	
2.5-Hexanedione ditsc		3400 s. 3200 s. 3140 w	1585 s. 1515 s	
2.3-Heptanedione ditsc		3440 m, 3280 m, 3160 m	1600 s	
2.3-Octanedione ditsc		3400 m, 3240 w, 3140 w	1690 w, 1600 s	
2.3-Octanedione ditsc-Cu(II)		3290 w, 3140 m	1615 m, 1585 m, 1530 m	
1-Phenyl-1.3-butanedione ditsc		3410 w, 3220 m, 3120 w	1585 s, 1540 w	
1.3-Diphenyl-1.3-propa	nedione	, ,	,	
nionotsc		3440 m, 3300 s, 3150 w	1590 s, 1575 w	
3.5-Diphenyl pyrazole		· ·	1610 w, 1590 w, 1575 w	
Benzil monotsc		3150–3120 b	1555 s, 1500 w	
Benzil ditsc		3420 w, 3220 m, 3140 m	1660 s, 1600 s	
5.6-Diphenyl-3-thio-				
1.2.4-triazine	(KBr)	3120 m	1585 w, 1565 m, 1540 s	
	(Soln.)	3380 m	1585 w, 1550–1500 b	
5-6-Diphenyl-3-oxy-				
1,2,4-triazine	(KBr)	3400 m	1680–1650 b, 1600 m, 1585 m, 1565 s	
	(Soln.)	3400 m	1700-1650 b, 1590 s, 1565 s	
5.6-Diphenvl-3-thio-	• •			
1,2,4-triazine-Cu(II)		3400 m, 3060 w	1625 w, 1600 m	

NOTE: s, strong; m, medium; w, weak; b, broad. Unless otherwise noted, the spectra were taken from KBr pellets.

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(N-H stretching) and the 1700-1500 cm<sup>-1</sup> (double-bond region). The spectra of ditscs resemble those of monotscs discussed earlier (2). Due to the overlapping of the bands in the N-H region, it has not been possible to ascribe the various absorptions to definite vibrations. It can be seen that the copper complexes have one more band in the double-bond region than the original compounds and this is in agreement with the suggested formula for the complexes.

As can be seen from the table, the spectrum of benzil monotsc shows a broad NH absorption at  $3120-3150^{-1}$  and the band at  $1555 \text{ cm}^{-1}$  is a little low for the free carbonyl group. Considering the spectrum of benzil ditsc, which has no carbonyl, the bands in the double-bond region due to C=N are at 1660 and 1600 cm<sup>-1</sup>. The lack of a carbonyl absorption in the case of benzil monotsc can be explained by a conjugate chelation between the carbonyl and the NH group of the thiosemicarbazide residue:

$$\begin{array}{cccc} C_{6}H_{5}-C=N-NH-CSNH_{2} \\ C_{6}H_{5}-C=0 \\ C_{6}H_{5}-C=0 \end{array} \rightleftharpoons \begin{array}{cccc} C_{6}H_{5}-C-N=N-CSNH_{2} \\ H \\ C_{6}H_{5}-C-O \\ \ominus \end{array}$$

This phenomenon has been observed before with dicarbonyl compounds (11) and the presence of the broad NH band, due to the hydrogen bridge, lends support to this theory. This agrees with the findings of Sadler (12) that in  $\alpha$ -diketone monotscs, strong intramolecular NH······O=C bonds predominate.

The spectrum of 5,6-diphenyl-3-thio-1,2,4-triazine (IVa) is particularly interesting in that it shows one sharp NH band at 3120 cm<sup>-1</sup> (KBr), 3380 cm<sup>-1</sup> (chloroform solution), and no SH band could be observed in either media. This triazine has been described before (8, 13, 14) and its structure was assumed to be (IVb) and not (IVa). On the basis



of its infrared spectrum, structure (IVa) is to be preferred and the tautomer (IVb) probably does not exist in the solid state nor in solution in chloroform. This is in agreement with similar findings that open-chain tscs exist only in the thiono form in the solid state (15), and 3-mercapto-5-oxo-1,2,4-triazines were recently shown to exist in the keto and thiono forms in neutral solution (16). However, there is little doubt that in the presence of a base, the thione  $\leftrightarrow$  thiol tautomerism takes place since both tscs and thiotriazine dissolve in alkali, and the S-Na salt of acetone tsc has already been described (17). As a comparison, the analogous 3-oxy-1,2,4-triazine (VIII) was prepared and its infrared



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spectrum taken both in the solid state and in chloroform solution. The same behavior was found in this case and no OH bands were detected. The weak peak at 3450 cm<sup>-1</sup> (KBr) and 3350 cm<sup>-1</sup> (chloroform) is due to N—H stretching. Furthermore, there is no doubt about the strong carbonyl absorption at 1685 cm<sup>-1</sup>, both in KBr and chloroform.

Chemical evidence also supports the ketonic structure of the oxytriazine, since all attempts to methylate the O atom failed, the product being the N-CH<sub>3</sub> derivative (IX) (18).

The structure of 3,5-diphenyl pyrazole (VI) ( $R = R' = C_6H_5$ ) is confirmed by its infrared spectrum, which is of requisite character, the lack of NH bands being its most significant feature.

### EXPERIMENTAL

The diketones and thiosemicarbazide were reagent grade material. Glyoxal was a 30% aqueous solution. 2-Methyl and 4,4-dimethyl thiosemicarbazides were prepared in this laboratory as previously described (19, 20). All melting points were taken on a Fisher-John apparatus and are corrected.

#### Glyoxal ditsc

Glyoxal (30% aq. soln.) (20 g, 0.1 mole) was dissolved in ethyl alcohol (250 ml) and the solution heated on a steam bath. To this was added a solution of thiosemicarbazide (18.2 g, 0.2 mole) in water (600 ml) containing acetic acid (40 ml). A solid precipitated out and heating was continued for 15 minutes. The mixture was cooled and the solid was collected by filtration and washed with hot alcohol and hot acetone; m.p. > 300° C decomp.; lit. m.p. > 300° C (1), 17.2 g, 84.6%.

### Glyoxal Di(2-methyl)tsc

Glyoxal (30% aq. soln.) (20 g, 0.1 mole) was added dropwise to a solution of 2-methyl thiosemicarbazide (4.75 g, 0.045 mole) in water (150 ml), and the mixture heated at 50° C for 10 minutes. A yellow solid precipitated out which, after cooling of the mixture, was separated by filtration, washed, and dried; m.p. 276° C, 1.83 g, 35%. Calc. for C<sub>6</sub>H<sub>12</sub>N<sub>6</sub>S<sub>2</sub>: C, 31.00; H, 5.17; N, 36.2; S, 27.6%. Found: C, 31.20; H, 5.11; N, 36.00; S, 27.6%.

# Glyoxal Di(4,4-dimethyl)tsc

Glyoxal di(4,4-dimethyl)tsc was prepared similarly using glyoxal (11.83 g, 0.025 mole) in alcohol (100 ml) and 4,4-dimethyl thiosemicarbazide (5.95 g, 0.05 mole) in water (100 ml) containing acetic acid (10 ml). A yellow precipitate was collected and washed with boiling alcohol; m.p. 203° C, 5.05 g, 77%. Calc. for  $C_8H_{16}N_6S_2$ : C, 36.9; H, 6.16; N, 32.3; S, 24.6%. Found: C, 36.83; H, 6.13; N, 32.45; S, 25.0%.

## Glyoxal ditsc-Cu(II)

To a gently refluxing solution of glyoxal ditsc (2 g, 0.01 mole) in N,N-dimethylformamide (100 ml) was added dropwise, with stirring, a hot solution of cupric acetate (2 g, 0.01 mole) in 40 ml of aqueous alcohol (50%). Heating was continued for 15 minutes and the black precipitate was collected; m.p. 236° C, 1.9 g, 71.4%. Calc. for  $C_4H_6N_6S_2$ . Cu: C, 18.07; H, 2.26; N, 31.62; S, 24.1; Cu, 23.96%. Found: C, 18.77; H, 2.87; N, 30.90; S, 24.3; Cu, 23.96%.

# Glyoxal Di(4,4-dimethyl)tsc-Cu(II)

Cupric acetate (3.4 g, 0.017 mole) in alcohol (100 ml) was added to a hot solution of glyoxal di(4,4dimethyl)tsc (4 g, 0.017 mole) in dimethyl sulphoxide (450 ml), and heating on the steam bath was continued for 15 minutes. The resulting purple solution was allowed to cool, and after addition of water, the crystals that formed were collected, washed with water and hydrochloric acid (3%), and recrystallized from alcohol. The 1:1 copper complex had m.p. 244° C, 3.86 g, 70%. Calc. for C<sub>8</sub>H<sub>14</sub>N<sub>6</sub>S<sub>2</sub>·Cu: C, 29.78; H, 4.65; N, 26.05; S, 19.84; Cu, 19.7%. Found: C, 30.12; H, 4.36; N, 26.10; S, 19.78; Cu, 19.9%.

#### Diacetyl ditsc

This was prepared by adding a warm solution of thiosemicarbazide (3.6 g, 0.04 mole) in water (120 ml) containing 6 ml of acetic acid to a warm solution of diacetyl (1.72 g, 0.02 mole) in ethyl alcohol (200 ml). The yellow precipitate obtained was collected and washed with boiling alcohol and acetone; m.p. 272° C, lit. m.p. 255° C (9), 4.5 g, 97%. Calc. for  $C_6H_{12}N_6S_2$ : C, 31.05; H, 5.18; N, 36.2; S, 27.6%. Found: C, 31.50; H, 5.35; N, 36.05; S, 27.24%.

### Diacetyl Di(4,4-dimethyl)tsc

This was prepared as above using diacetyl (1.72 g, 0.02 mole) in ethyl alcohol (100 ml) and 4,4-dimethyl thiosemicarbazide in water (100 ml) and acetic acid (8 ml). The compound obtained had m.p. 198° C, 1.9 g, 32.9%. Calc. for  $C_{10}H_{20}N_6S_2$ : C, 41.7; H, 6.95; N, 29.2; S, 22.2%. Found: C, 42.3; H, 7.5; N, 28.8; S, 22.15%.

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## Diacetyl ditsc-Cu(II)

To a hot solution of diacetyl ditsc (2.4 g, 0.01 mole) in dimethylformamide (240 ml) was added copper acetate (2 g, 0.01 mole) in water (50 ml), and the mixture was heated and stirred for an additional 15 minutes. A dark colored precipitate was formed which, after cooling of the mixture, was collected and washed with hydrochloric acid (3%), water, hot alcohol, and acetone; m.p. 267° C decomp., 2.09 g, 71%. Calc. for  $C_6H_{10}N_6S_2$ ·Cu: C, 24.55; H, 3.41; N, 28.63; S, 21.8; Cu, 21.6%. Found: C, 24.04; H, 3.59; N, 28.7; S, 21.8; Cu, 21.2%.

#### Diacetyl Di(4,4-dimethyl)tsc-Cu(II)

A solution of cupric acetate (1.04 g, 0.005 mole) in alcohol (100 ml) was added dropwise to a refluxing solution of diacetyl di(4,4-dimethyl)tsc (1.5 g, 0.005 mole) in chloroform (150 ml) and heating was continued for 15 minutes, during which time a solid precipitated out. After cooling of the mixture, the precipitate was collected, washed, and crystallized from acetone; m.p. 300° C, 0.32 g, 17.4%. Calc. for  $C_{10}H_{19}N_6S_2$ ·Cu: C, 34.25; H, 5.43; N, 23.95; S, 18.25; Cu, 18.12%. Found: C, 35.17; H, 5.25; N, 24.2; S, 18.6; Cu, 17.93%.

## 2,5-Hexanedione ditsc

This was prepared by adding a warm solution of thiosemicarbazide (3.6 g, 0.04 mole) in water (120 ml) containing acetic acid (16 ml) to a solution of 2,5-hexanedione (2.28 g, 0.02 mole) in alcohol (200 ml). The white precipitate obtained had m.p. 272° C, 4.5 g, 86.5%. Calc. for  $C_8H_{16}N_6S_2$ : C, 36.95; H, 6.15; N, 32.3; S, 24.6%. Found: C, 37.13; H, 6.54; N, 32.0; S, 24.5%.

#### 2,3-Heptanedione ditsc

This was obtained as above using 2,3-heptanedione (12.8 g, 0.1 mole) in alcohol (200 ml) and thiosemicarbazide (18.2 g, 0.2 mole) in water (600 ml) containing acetic acid (40 ml). The product, after recrystallization from aqueous ethyl cellosolve, had m.p. 218° C; lit. m.p. 222° C (9), 10.5 g, 40%.

### 2,3-Octanedione ditsc

This was made by the usual method starting with 2,3-octanedione (4.26 g, 0.03 mole) in alcohol (200 ml) and thiosemicarbazide (5.47 g, 0.06 mole) in water (200 ml) and acetic acid (10 ml). The product, 4.75 g, 55%, had m.p. 230° C. Calc. for  $C_{10}H_{20}N_6S_2$ : C, 41.7; H, 6.94; N, 29.15; S, 22.20%. Found: C, 41.93; H, 7.28; N, 28.6; S, 22.10%.

## 2,3-Octanedione ditsc-Cu(II)

Copper acetate (2 g, 0.01 mole) in water (80 ml) was added dropwise to a refluxing solution of 2,3-octanedione ditsc (2.88 g, 0.01 mole) in N,N-dimethylformamide (100 ml). The mixture was stirred and heating was continued for 15 minutes, during which time a brown precipitate was formed. This was collected, washed with water, and recrystallized from alcohol; m.p. 225° C, 0.65 g, 18.6%. Calc. for  $C_{10}H_{18}N_6S_2 \cdot Cu$ : C, 34.38; H, 5.16; N, 24.01; S, 18.3; Cu, 18.17%. Found: C, 34.81; H, 5.75; N, 23.95; S, 17.92; Cu, 17.9%.

#### 1-Phenyl-1,3-butanedione ditsc

The usual procedure of adding an aqueous solution of thiosemicarbazide to the diketone in alcohol afforded only an unidentified product of m.p. 106° C:  $C_{20}H_{19}N_5S$ . The required ditsc was obtained by using the following method:

Thiosemicarbazide (1.9 g, 0.02 mole) in boiling alcohol (150 ml) was added to the previously molten 1-phenyl-1,3-butanedione (1.62 g, 0.01 mole). The resulting solution was refluxed for 30 minutes and allowed to cool. The ditsc crystallized out and, after recrystallization from *n*-hexane, had m.p. 131° C, 0.39 g, 12.6%. Calc. for  $C_{12}H_{16}N_6S_2$ : C, 46.7; H, 5.2; N, 27.28; S, 20.78%. Found: C, 46.85; H, 5.23; N, 27.20; S, 20.40%.

#### Reaction of 1,3-Diphenyl-1,3-propanedione with Thiosemicarbazide

A solution of thiosemicarbazide (1.8 g, 0.02 mole) in water (60 ml) and acetic acid (8 ml) was added to the diketone (4.49 g, 0.02 mole) in alcohol (110 ml), and the resulting mixture was heated for 15 minutes on the steam bath and allowed to cool. 3,5-Diphenyl pyrazole crystallized out, and after filtration, it was recrystallized from benzene-hexane; m.p. 197° C, 1.55 g, 35.4%; lit. m.p. 197-200° C (21). Calc. for  $C_{15}H_{12}N_2$ : C, 81.8; H, 5.45; N, 12.7%. Found: C, 82.0; H, 5.45; N, 12.55%.

The mother liquor, after addition of water, yielded the monotsc (0.85 g, 14.3%), which, after recrystallization from benzene-hexane, and from alcohol, had m.p. 128° C. Calc. for  $C_{16}H_{15}N_3OS$ : C, 64.6; H, 5.05; N, 14.13; S, 10.78%. Found: C, 64.57; H, 5.38; N, 14.78; S, 10.58%.

## Reaction of Benzil with Thiosemicarbazide

As the conventional method of condensation gave mixtures of products, the following modified procedure was used:

Benzil (2.1 g, 0.01 mole) and thiosemicarbazide (1.8 g, 0.02 mole) were dissolved in N,N-dimethylformamide, and concentrated hydrochloric acid (3 ml) was added. After being heated on the steam bath for 4 hours, the solution was allowed to evaporate slowly until benzil ditsc had precipitated out. The product

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was collected and washed with water followed by hot alcohol. It had m.p. 217° C, 1.15 g, 42.4%. Calc. for C<sub>16</sub>H<sub>16</sub>N<sub>6</sub>S<sub>2</sub>: C, 53.9; H, 4.49; N, 23.6; S, 17.99%. Found: C, 52.98; H, 4.58; N, 23.4; S, 17.40%.

5,6-Diphenyl-3-thio-1,2,4-triazine was obtained in a 67% yield by a method described previously (22). The compound, after recrystallization from acetone, had m.p. 220° C; lit. m.p. 233° C (22), 226° C (23). Calc. for C15H11N3S: C, 67.9; H, 4.15; N, 15.84; S, 12.08%. Found: C, 67.31; H, 3.92; N, 16.12; S, 12.28%.

A small amount of benzil monotsc was identified as a by-product, and after recrystallization from acetone, had m.p. 190° C; lit. m.p. 188° C (23). Calc. for C15H13N3OS; C, 63.7; H, 4.6; N, 14.84; S, 11.3%. Found: C, 64.14; H, 5.48; N, 14.50; S, 10.93%.

### 5,6-Diphenyl-3-thio-1,2,4-triazine-Cu(II)

A small amount (200 mg) of copper complex was obtained from the addition of copper acetate (10 g, 0.05 mole) in water (200 ml) to a boiling solution of the triazine (13.8 g, 0.05 mole) in a large excess of acetone (500 ml). The complex precipitated out and was separated by filtration, washed successively with water, hydrochloric acid (3%), alcohol, acetone, and finally recrystallized from pyridine, m.p. 302° C. There was not sufficient material for further purification, but the elementary analysis is in fair agreement with the calculated values. Calc. for  $C_{15}H_{10}N_3S$  Cu: C, 54.9; H, 3.06; N, 12.82; S, 9.77; Cu, 19.38%. Found: C, 53.2; H, 3.12; N, 13.19; S, 10.02; Cu, 18.1%.

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