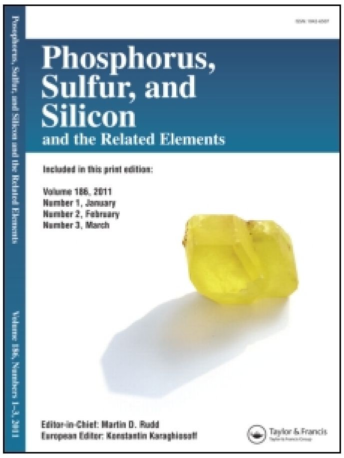

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REACTION OF SULFUR CHLORIDE WITH ACETOPHENONE. II

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REACTION OF SULFUR CHLORIDE WITH ACETOPHENONE. II

by

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ABSTRACT

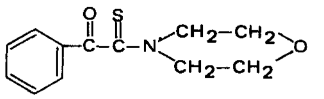
In a previous paper,[1] we reported the formation of a resinous material (1) from the reaction of sulfur chloride with acetophenone which, upon treatment with DMF, yielded phenylglyoxylthiodimethylamide (4). We now report two additional resinous materials (5, 6), resulting from bromination of sodium phenacylthiosulfate (3) and diphenacyl disulfide (7) respectively, both of which not only resemble resinous 1 in appearance, but also yield 4 upon treatment with DMF in aqueous alkali.

Resinous 1, 5, and 6 appear to have the same common basic structure and differ only in the number of sulfur atoms bonded between the common units. Cleavage at the sulfur-sulfur bonds and elimination of hydrogen halide then yields identical oxothioamides from 1, 5, or 6. The latter appears to be a general reaction, and several oxothioamides were prepared by this synthetic method from 1, 5, and 6 and various amides and amines.

Results and Discussion

In the first paper[1] of this series, it was shown that oxothioamides are formed by treating the resinous reaction products of sulfur chloride and substituted acetophenones with DMF. Resinous 1, obtained from sulfur chloride and acetophenone, exhibited a molecular weight of 780–815, and analyses showed sulfur, 33.5% and chlorine, 17.7%. Treatment of 1 with DMF gave 4 in 67.8% yield.

Milligan and Swan[2] obtained phenylglyoxylthiomorpholide (2) from sodium phenacylthiosulfate (3) and morpholine.



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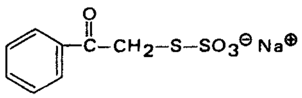
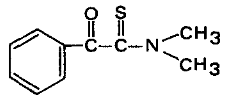


3

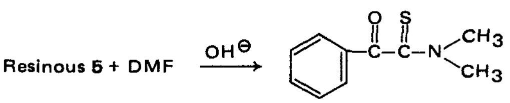
In an extension of the reaction, 3 and dimethylamine in our hands gave phenylglyoxylthiodimethylamide (4) in only 35% yield.



4

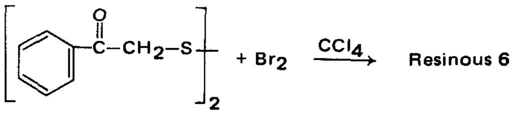
However, when 3 was brominated in carbon tetrachloride solution, a resinous material (5) was obtained which resembled resinous 1 and gave 4 in 72% yield when treated with DMF in aqueous alkali:

$$3 + Br_2 \xrightarrow{CCl_4} \text{Resinous 5} \qquad (1)$$



4 (2)

Similarly, diphenacyl disulfide[3] (7) and dimethylamine gave 4 in low yield (27%), but bromination of 7 in carbon tetrachloride gave resinous 6 which, upon treatment with DMF in aqueous alkali, afforded 4 in 82% yield:



(3)

$$\text{Resinous 6} + DMF \xrightarrow{OH^{\ominus}} 4 \qquad (4)$$

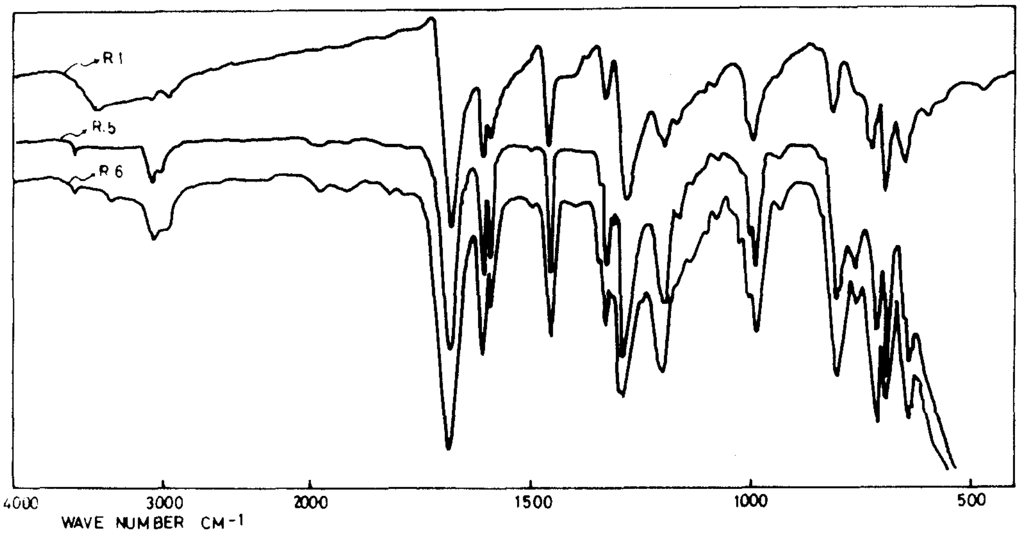
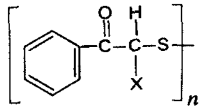


FIGURE I

Infrared Absorption Spectra of Resinous 1, 5 and 6 Resinous 1 (KBr disc); Resinous 5 and 6 (NaCl disc)

The infrared spectra of resinous 1, 5, and 6 are shown in Figure I. As can be seen, they each agree well in their absorption peaks. In the localized infrared spectra shown in Figure II, a comparison of the absorption peaks of Bunte Salt, 7, resinous 1, 5, and 6 indicates that 1, 5, and 6 all contain S–S bonds^4 in their molecular structures.

The nature of the starting materials in the preparation of resinous 1, 5, and 6, the resulting identical oxothioamides upon treatment with DMF in aqueous alkali, and the similar infrared spectra shown above all suggest that these three resinous materials have the approximate structure 8 shown below:



8

X = halogen n = 2, 3, 4

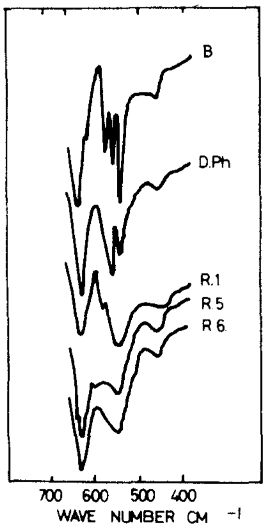


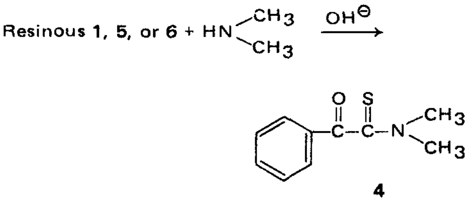
FIGURE II

Localized IR Absorption Spectra of Disulfides and Resinous Materials. B: Bunte salt, DPh: Diphenacyldisulfide, R.1: Resinous 1, R.5: Resinous 5 and R.6: Resinous 6

Analytical results obtained for resinous 1, 5, and 6 along with those calculated for the suggested structures are shown in Table I.

Agreement between the calculated and found values for resinous 5 and 6 is within the usual variation limits. Although some deviation is apparent in the calculated and found values for resinous 1, better agreement might be obtained if the suggested structure shown were actually a mixture of di- and polysulfides.

On the bases of the above conclusions, it appeared that DMF could be replaced by other amides or amines to form oxothioamides from resinous 1, 5, or 6. These reactions occurred, as expected, and resulted in good yields of oxothioamides. Reaction 5 is a typical example.

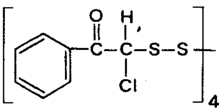
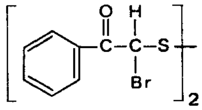
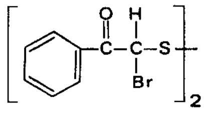


4 (5)

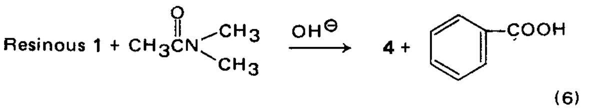
However, the reaction of dimethylacetamide with resinous 1 gave benzoic acid as a byproduct.

TABLE I

Analytical Results for Resinous 1, 5, and 6

Resin	Halogen, %	Sulfur, %	MW	Suggested Structure
1	17.7 (16.3)	33.9 (29.3)	780–815 (870)	
5	34.9 (34.7)	14.9 (13.9)	440–453 (460)	
6	35.8 (34.7)	13.1 (13.9)	467–468 (460)	

( ) Calculated for the suggested structures.



(6)

The reactions of amides and amines with resinous **1**, **5**, or **6** appear to be general and afford three new synthetic routes to oxothioamides, in addition to those previously reported.[2,5] In Table II are shown five oxothioamides synthesized *via* the reactions of amides or amines with resinous **1**, **5**, or **6**.

A proposed reaction mechanism for the formation of oxothioamides from amines and resinous **1**, **5**, or **6** is presented in Scheme I. The first step in the reaction of sulfur dichloride with acetophenone to form resinous **1** is being studied.

Experimental Section

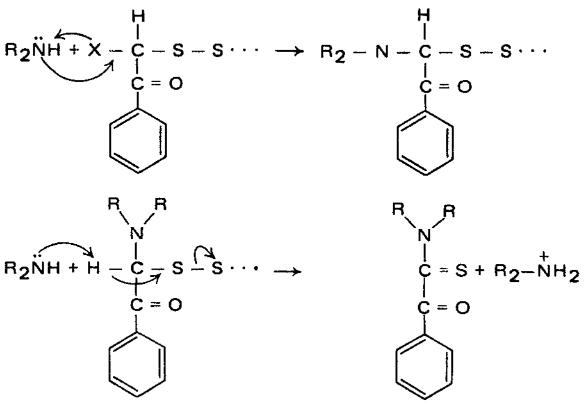
Preparation of Resinous 1

Preparation of resinous **1** was reported in the previous paper[1] of this series as Preparation of Resinous Material 7.

Preparation of Phenacylthiosulfate[3] (3)

Into a 300 ml round-bottomed flask was placed 40 g (0.2 mol) of phenacyl bromide[6] dissolved in 100 ml of alcohol. To the vigorously stirred solution was added 50 g (0.2 mol) of sodium thiosulfate in 100 ml of water and the mixture was refluxed on the water bath for approximately one hour. The reaction mixture was treated with activated carbon and evaporated to dryness, resulting in a crude white crystalline mass from which **3** was extracted with 200 ml of ethanol. Crystalline **3** obtained: 37.8 g (74.4%).

Anal. Calc. for $C_8H_7O_4S_2Na$: S, 25.22. Found: S, 24.64.



SCHEME I

Reaction Mechanism for the Formation of Oxothioamides from Resinous 1, 5, or 6

Phenylglyoxylthiodimethylamide (4) *from* 3 *and Dimethylamine*

Into a 15 ml Pyrex glass tube were placed 2.5 g (0.01 mol) of **3** and 5 ml of a 40% aqueous solution of dimethylamine. The reaction mixture was then heated on a hot water bath for approximately five hours. After removal of the solvent under vacuum, 0.95 g of crude crystalline **4** was obtained. Recrystallization from alcohol gave 0.68 g (35%) of **3**, mp 86.5–87.5°.

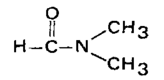
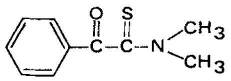
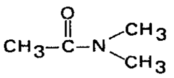
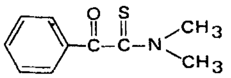
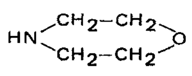
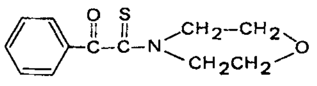
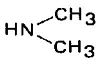
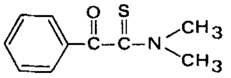
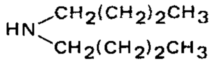
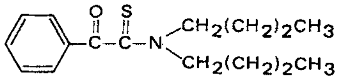
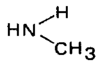
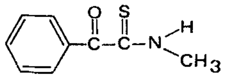
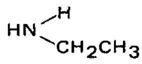
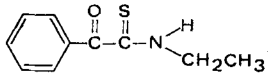
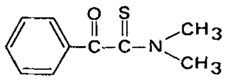
Anal. Calc. for $C_{10}H_{11}OSN$: S, 16.58; N, 7.26. Found: S, 16.20; N, 7.23.

Preparation of Resinous 5 *from* 3

A solution of bromine in carbon tetrachloride (48 ml 0.47 *N*) was added dropwise to a suspension of 5.0 g (0.02 mol) of **3** in 10 ml of chloroform. Soon, white lumps of sodium bromide–bromosulfonic acid began to separate along with evolution of hydrogen bromide. After gas evolution ceased, solid product was removed by suction filtration and washed several times with chloroform. The combined solution

TABLE II

Oxothioamides obtained

Starting material	Amide or amine	Structure	Yield %	mp. °C
Resinous 1	 $H-C(=O)-N(CH_3)_2$		72	86.5-87.5
Resinous 1	 $CH_3-C(=O)-N(CH_3)_2$		46	86.5-87.5
Resinous 1	 $HN(CH_2-CH_2)_2O$		68	114-115
Resinous 1	 $HN(CH_3)_2$		72	86.5-87.5
Resinous 1	 $HN(CH_2(CH_2)_2CH_3)_2$		54	67.5-68.5
Resinous 1	 $HN(H)(CH_3)$		54	137-139
Resinous 1	 $HN(H)(CH_2CH_3)$		58	106-107
Resinous 5	DMF		72	
	$HN-(CH_3)_2$		73	
				86.5-87.5
Resinous 6	DMF		82	
	$HN-(CH_3)_2$		84	

of filtrate and washings was extracted with water to remove acidic impurities. Evaporation of the chloroform solution gave resinous 5 as a very viscous yellow-red oil. Yield: 4.1 g (79%).

Phenylglyoxylthiodimethylamide (4) *from Resinous* 5

Resinous 5, obtained by bromination of 2.5 g (0.01 mol) of 3 in carbon tetrachloride, was dissolved in 5 ml of DMF and poured into 10 ml of alkali solution (2.0 g NaOH). The resulting product was recrystallized from ethanol. Yield: 1.38 g (71%), mp 86.5-87.5°.

Anal. Calc. for $C_{10}H_{11}OSN$: S, 16.58; N, 7.26. Found: S, 16.20; N, 7.20.

Preparation of Diphenacyl Disulfide (7)

A solution of 5.0 g (0.02 mol) of 3 in 5 ml water was oxidized with approximately 250 ml of bromine water. The solid product was removed by suction filtration and the filtrate was extracted with two 30 ml portions of chloroform. The solid and extracts were combined and evaporated to dryness. Crude 7 obtained: 2.8 g (92%). Recrystallization from alcohol gave 2.5 g (82%), mp 78.5-80°. (lit.[7] 81°).

Anal. Calc. for $C_{16}H_{14}O_2S_2$: S, 21.20. Found: S, 21.30.

Phenylglyoxylthiodimethylamide (4) *from* 7 *and Dimethylamine*

In a 50 ml round-bottomed flask equipped with a reflux condenser, 3.0 g (0.01 mol) of 7 and 10 ml of a 40% aqueous solution of dimethylamine were heated on a water bath at 40° for four hours. The reaction mixture was then evaporated under vacuum and the residue recrystallized from ethanol. Yield of Crystalline 7: 1.0 g (27%), mp 86-87°.

Anal. Calc. for $C_{10}H_{11}OSN$: S, 16.58; N, 7.26. Found: S, 16.65; N, 7.23.

Preparation of Resinous 6 *from* 7

A solution of 3.0 g (0.01 mol) of 7 in 6 ml of chloroform was mixed with 48 ml of 0.47 *N* bromine in carbon tetrachloride. After the evolution of hydrogen bromide ceased, the yellow solution was diluted with 20 ml of chloroform, extracted with water to remove acidic impurities, dried over anhydrous sodium sulfate and evaporated to dryness. Yield of resinous 6: 4.3 g (93%).

Phenylglyoxylthiodimethylamide (**4**) *from Resinous* **6**

A solution of 4.3 g of resinous **6** in 10 ml of DMF was poured into 20 ml of aqueous alkali (2.0 g NaOH). The crude product obtained was recrystallized twice from alcohol. Yield: 3.2 g (82%), mp 86.5–87.5°.

Anal. Calc. for $C_{10}H_{11}OSN$: S, 16.58; N, 7.26. Found: S, 16.62; N, 7.26.

Phenylglyoxylthiodimethylamide (**4**) *from Resinous* **1** *and Dimethylacetamide*

Resinous **1**, obtained from the reaction of 13.5 g (0.1 mol) of sulfur dichloride and 12 g (0.1 mol) of acetophenone was dissolved in 20 ml of dimethylacetamide and the solution was mixed with 200 ml of aqueous alkali (15 g NaOH). Solid **4** was removed by filtration. Benzoic acid was recovered from the filtrate and identified by comparison with an authentic sample. Yield of **4** was 8.8 g (45%).

Anal. Calc. for $C_{10}H_{11}OSN$: S, 16.58; N, 7.26. Found: S, 16.36; N, 7.10.
Benzoic acid recovered weighed 2.5 g (approximately 20% based on amount of acetophenone used), mp 121–122° (lit.[8] 121°).

Phenylglyoxylthiomorpholide[9] *from Resinous* **1** *and Morpholine*

Resinous **1**, obtained as above, was poured hot into 18 g (0.2 mol) of morpholine diluted with three volumes of water under vigorous stirring. The precipitated product was removed by suction filtration, washed with water, and recrystallized twice from ethanol. Yield: 16.0 g (68%), mp 114–115°.

Anal. Calc. for $C_{12}H_{13}O_2SN$: mw, 235.3; C, 61.25; H, 5.57; S, 13.63; N, 5.95.
Found: mw, 236.8; C, 59.37; H, 5.61; S, 13.70; N, 5.62.

Phenylglyoxylthiodimethylamide (**4**) *from Resinous* **1** *and Dimethylamine*

Resinous **1**, obtained as above, was poured into 30 ml of 40% aqueous dimethylamine solution with vigorous stirring. After evaporation of the solvent, **4** was recrystallized twice from alcohol. Yield: 13,9 g (72%), mp 86.5–87.5°.

Anal. Calc. for $C_{10}H_{11}OSN$: S, 16.58; N, 7.26. Found: S, 16.79; N, 7.15.

Preparation of Phenylglyoxylthiodibutylamide

Phenylglyoxylthiodibutylamide was obtained in a similar manner from resinous 1 and dibutylamine. The crystalline product obtained weighted 15 g (54%), mp 67.5–68.5°.

Anal. Calc. for $C_{16}H_{23}OSN$: mw, 277.4; C, 69.26; H, 8.36; S, 11.56; N, 5.05.
Found: mw, 276.2; C, 69.32; H, 8.24; S, 11.82; N, 5.00.

Preparation of Phenylglyoxylthiomethylamide

Resinous **1**, prepared in the usual manner, was mixed with 30 ml of 30% aqueous methylamine solution. The yellow needle-like crystalline solid which precipitated was recrystallized from ethanol. Yield: 9.6 g (64%), mp 137–139°.

Anal. Calc. for C_9H_9OSN: mw, 179.2; S, 17.88; N, 7.81.
Found: mw, 180.1; S, 18.00; N, 7.85.

Phenylglyoxylthiodimethylamide (**4**) *from Resinous* **5** *and Dimethylamine*

Resinous **5**, obtained by bromination of 2.5 g (0.01 mol) **3** in carbon tetrachloride, was mixed with 10 ml of 40% aqueous dimethylamine solution to yield 1.41 g (73%) of crystalline **4**,mp 86–87°.

Anal. Calc. for $C_{10}H_{11}OSN$: S, 16.58; N, 7.26. Found: S, 16.40; N, 7.28.

Phenylglyoxylthiodimethylamide (**4**) *from Resinous* **6** *and Dimethylamine*

Resinous **6**, from bromination of 3.0 g (0.01 mol) **7**, was mixed with 20 ml of 40% aqueous dimethylamine solution to yield 3.25 g (84%) crystalline **4**, mp 86–87°.

Anal. Calc. for $C_{10}H_{11}OSN$: S, 16.58; N, 7.26.
Found: S, 16.82; N, 7.20.

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