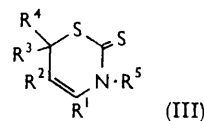
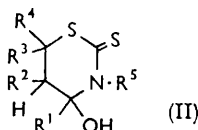
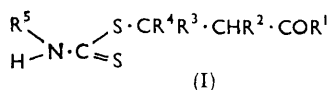


## 759. Derivatives of Dithiocarbamic Acids.

By J. L. GARRAWAY.

The preparation of a number of  $\beta$ -(thiocarbamoylthio)-substituted aldehydes and ketones is described. The ultraviolet spectra, stability, and structure of these compounds are discussed.

A NUMBER of  $\beta$ -substituted aldehyde and ketone derivatives (I) of dithiocarbamic and *N*-methylthiocarbamic acids have been prepared (Tables 1 and 2) for investigation as fungicides. The formation of 2,3-dihydro-2-thio-1,3-thiazines (III) from these compounds will be discussed in a later Paper.<sup>1</sup>



The preparation of a number of these compounds by the addition of dithiocarbamic acid to  $\alpha\beta$ -unsaturated aldehydes or ketones has already been reported.<sup>2</sup> The same method was used here and extended to include a wider range of  $\alpha\beta$ -unsaturated aldehydes and ketones and their addition compounds with *N*-methylthiocarbamic acid. The

TABLE I.  
Derivatives of dithiocarbamic acid (I or II; R<sup>5</sup> = H).

No.	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	Yield (%)	M. p.	Formula	Nitrogen (%)		$\lambda_{\text{max}}$ ( $\mu\mu$ ) and log $\epsilon$	
								Found	Reqd.	in water	in alcohol
1	H	H	H	H	16	128—129°	C <sub>4</sub> H <sub>7</sub> NOS <sub>2</sub>	9.42	9.39	242 3.85	240 3.84
										287 4.07	292 4.05
2	H	Me	H	H	30	97—98	C <sub>5</sub> H <sub>9</sub> NOS <sub>2</sub>	8.56	8.58	242 3.93	240 3.88
										287 4.10	292 4.10
3	H	H	Me	H	26	116—117 *	C <sub>5</sub> H <sub>9</sub> NOS <sub>2</sub>	8.77	8.58	242 3.82	240 3.86
										287 4.10	292 4.09
4	H	Me	Me	H	21	116—117	C <sub>6</sub> H <sub>11</sub> NOS <sub>2</sub>	7.81	7.89	243 3.72	241 3.85
										286 4.10	291 4.09
5	Me	H	H	H	43	65—90 †	C <sub>5</sub> H <sub>9</sub> NOS <sub>2</sub>	8.61	8.58	241 3.87	240 3.81
										284 4.09	288 4.00
6	Me	H	Me	H	7	126—127	C <sub>6</sub> H <sub>11</sub> NOS <sub>2</sub>	8.21	7.89	241 3.92	240 3.87
										284 4.17	290 4.12
7	Me	Me	Me	H	4	147—148	C <sub>7</sub> H <sub>13</sub> NOS <sub>2</sub>	7.55	7.32	242 3.90	240 3.87
										283 4.17	289 4.13
8	Me	H	Me	Me	7	133—134 *	C <sub>7</sub> H <sub>13</sub> NOS <sub>2</sub>	7.25	7.32	242 3.80	241 3.88
										285 4.24	290 4.15
9	H	H	Ph	H	9	139—142 †	C <sub>10</sub> H <sub>11</sub> NOS <sub>2</sub>	6.01	6.22	S241 ~3.93	233 4.16
										288 4.13	294 4.10
10	Me	H	Ph	H	29	137—138 *	C <sub>11</sub> H <sub>13</sub> NOS <sub>2</sub>	5.99	5.86	S243 ~3.87	238 4.15
										289 4.11	295 4.08
11	Me	Me	Ph	H	27	168 <sup>d</sup>	C <sub>12</sub> H <sub>15</sub> NOS <sub>2</sub>	5.52	5.53	S244 — †	235 4.12
										288 —	294 4.14
12	Ph	H	Ph	H	22	135—136 * †	C <sub>16</sub> H <sub>15</sub> NOS <sub>2</sub>	4.89	4.65	S246 4.04	240 4.19
										288 4.16	293 4.17
13	Me	H	CCl <sub>3</sub>	H	14	132—135 †	C <sub>6</sub> H <sub>8</sub> Cl <sub>3</sub> NOS <sub>2</sub>	5.14	4.99	236 3.79	233 3.96
										286 4.14	290 4.09
14	Me	Me	CCl <sub>3</sub>	H	39	152—153 †	C <sub>7</sub> H <sub>10</sub> Cl <sub>3</sub> NOS <sub>2</sub>	4.94	4.75	237 3.80	235 3.97
										286 4.14	290 4.09
15	Ph	H	CCl <sub>3</sub>	H	24	121—122	C <sub>11</sub> H <sub>10</sub> Cl <sub>3</sub> NOS <sub>2</sub>	3.99	4.09	241 3.99	243 4.17
										287 4.14	292 4.22

\* Jansen and Mathes (*J. Amer. Chem. Soc.*, 1955, **77**, 2866) give the following melting points: 3, 115—116°; 8, 128—129°; 10, 123—124°; 12, 150—151°. † Solubility in water too low.  
‡ Melting with decomposition.

<sup>1</sup> Garraway, following Paper.

<sup>2</sup> Jansen and Mathes, *J. Amer. Chem. Soc.*, 1955, **77**, 2866.

ultraviolet absorption spectra (220—400  $m\mu$ ,  $\log \epsilon > 3$  only) in alcohol and water were investigated (Tables 1 and 2). The effects of small quantities of inorganic acids and bases

TABLE 2.  
Derivatives of *N*-methyldithiocarbamic acid (I or II;  $R^5 = \text{Me}$ ).

No.	$R^1$	$R^2$	$R^3$	$R^4$	Yield (%)	M. p.	Formula	Nitrogen (%)		$\lambda_{\text{max.}}$ ( $m\mu$ ) and $\log \epsilon$			
								Found	Reqd.	in water		in alcohol	
16	H	H	H	H	35	101—102°	$\text{C}_5\text{H}_9\text{NOS}_2$	8.51	8.58	245	3.98	244	3.98
										282	4.10	285	4.10
17	H	Me	H	H	18	95—96	$\text{C}_6\text{H}_{11}\text{NOS}_2$	8.02	7.89	246	3.91	245	3.95
										282	4.13	286	4.09
18	H	H	Me	H	23	110—111	$\text{C}_6\text{H}_{11}\text{NOS}_2$	7.71	7.89	246	3.96	244	3.95
										282	4.12	285	4.09
19	H	Me	Me	H	18	154 d	$\text{C}_7\text{H}_{13}\text{NOS}_2$	7.04	7.32	247	3.93	245	3.96
										281	4.12	286	4.11
20	Me	H	Me	Me	14	76—77	$\text{C}_8\text{H}_{15}\text{NOS}_2$	6.72	6.83	248	3.95	248	4.01
										280	4.12	286	4.08
21	H	H	Ph	H	21	118—119 †	$\text{C}_{11}\text{H}_{13}\text{NOS}_2$	5.90	5.86	S243	~4.05	245	4.21
										283	4.15	287	4.11
22	Me	H	Ph	H	41	78—79 †	$\text{C}_{12}\text{H}_{15}\text{NOS}_2$	5.25	5.53	252	3.99	252	4.05
										273	3.98	281	4.06
23	Me	Me	Ph	H	5	97—98	$\text{C}_{13}\text{H}_{17}\text{NOS}_2$	5.24	5.24	253	4.00	252	4.02
										275	3.98	276	3.90
24	Ph	H	Ph	H	17	117—118	$\text{C}_{17}\text{H}_{17}\text{NOS}_2$	4.66	4.44	253	—*	248	4.35
										~283	—	~272	~4.01
										~315	vw	~310	vw
										246	3.91	245	3.93
25	Me	H	$\text{CCl}_3$	H	25	88—89	$\text{C}_7\text{H}_{10}\text{Cl}_3\text{NOS}_2$	4.50	4.75	275	3.93	284	3.88
										248	3.88	246	3.92
26	Me	Me	$\text{CCl}_3$	H	31	103—104 †	$\text{C}_8\text{H}_{12}\text{Cl}_3\text{NOS}_2$	4.58	4.54	273	3.90	284	3.85
										251	—*	245	4.30
27	Ph	H	$\text{CCl}_3$	H	36	126—127	$\text{C}_{12}\text{H}_{12}\text{Cl}_3\text{NOS}_2$	4.05	3.93	278	—	284	4.12

\* Solubility in water too low. † Melting with decomposition.

on the absorption spectra and stability of these compounds in alcohol were also studied; the detailed results are not included in this Paper but will be referred to briefly. These investigations were undertaken to assess the effect of various substituents and environment on chemical reactivity, and stability, and their relationship to *fungitoxic* action. For convenience the discussion of the absorption spectra and stability of these compounds is divided into two parts.

*Derivatives of Dithiocarbamic Acid* (I;  $R^5 = \text{H}$ ; Table 1).—This group of compounds in alcoholic solution exhibited two maxima at approximately 291 (band 1) and 240  $m\mu$  (band 2). Jansen and Mathes<sup>2</sup> have concluded that the structure of these compounds in the crystalline state is best represented by a cyclic formula (II;  $R^5 = \text{H}$ ). The existence of a cyclic structure in alcoholic and aqueous solutions also is indicated by the displacement of band 1 and the stability of a number of these compounds in the presence of alkali, in contrast to the usual absorption spectra<sup>3,4</sup> and instability<sup>5</sup> of other esters of dithiocarbamic acid.

Derivatives of aliphatic and aromatic aldehydes (1—4, 9) exhibited similar absorption spectra in neutral and acid solution (Fig. 1) except for a broadening of band 2 in the case of the aryl-substituted compound (9). Alkali produced a pronounced change, presumably due to base interaction at the  $>\text{NH}$  group or thione—thiol tautomeric change. These compounds were stable in neutral, acid, and alkaline solutions.

The absorption spectra of derivatives of aliphatic ketones (5—8) differed from the aldehydes above in the presence of acid and alkali (Fig. 2). Since similar behaviour in alkaline solution is shown by compounds possessing a *N*-methyl group (16—20), it must

<sup>2</sup> Janssen, *Rec. Trav. chim.*, 1960, **79**, 454.

<sup>4</sup> Garraway, *J.*, 1962, 4072.

<sup>5</sup> Chabrier and Nachmias, *Bull. Soc. chim. France*, 1950, **17**, D51.

be assumed that these substances do not follow the expected course of thione-thiol tautomeric change. They also appeared to decompose slowly in the presence of alkali, whilst acids caused highly-substituted derivatives (7 and 8) to form 2,3-dihydro-2-thio-1,3-thiazines (III;  $R^5 = H$ ).

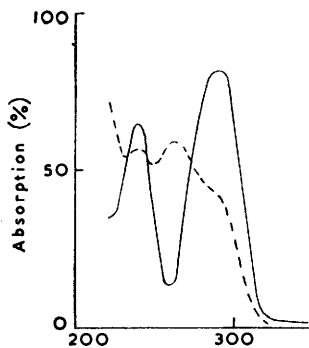


FIG. 1.

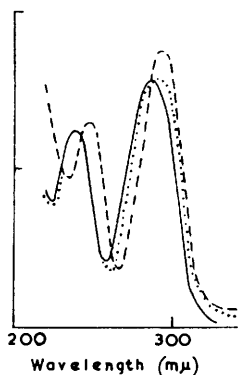


FIG. 2.

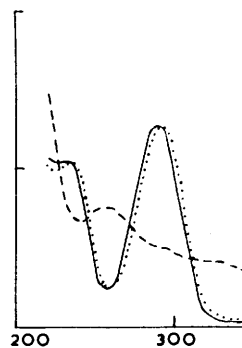


FIG. 3.

FIG. 1. Spectra of  $\beta$ -(thiocarbamoylthio)propionaldehyde (1) in alcohol in the presence of acid (—) and alkali (----).

FIG. 2. Spectra of 4-(thiocarbamoylthio)butan-2-one (5) in alcohol (—) and in the presence of acid (· · · ·) and alkali (----).

FIG. 3. Spectra of 5,5,5-trichloro-4-(thiocarbamoylthio)pentan-2-one (13) in alcohol (—) and in the presence of acid (· · · ·) and alkali (----).

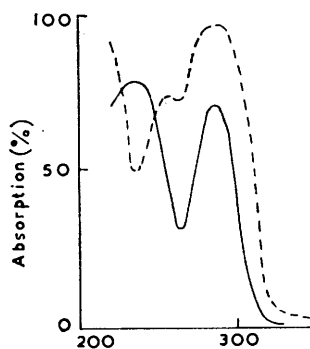


FIG. 4.

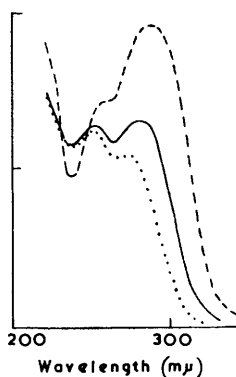


FIG. 5.

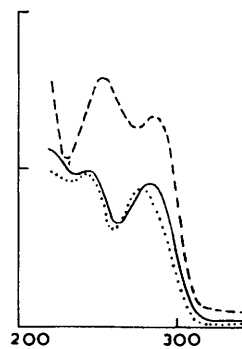


FIG. 6.

FIG. 4. Spectra of 3-(*N*-methylthiocarbamoylthio)-3-phenylpropanal (21) in alcohol in the presence of acid (—) and alkali (----).

FIG. 5. Spectra of 4-(*N*-methylthiocarbamoylthio)-4-phenylbutan-2-one (22) in alcohol (—) and in the presence of acid (· · · ·) and alkali (----).

FIG. 6. Spectra of 5,5,5-trichloro-4-(*N*-methylthiocarbamoylthio)pentan-2-one (25) in alcohol (—), and in the presence of acid (· · · ·) and alkali (----).

Aryl-substituted ketone derivatives (10, 11) exhibited the same absorption spectra as the aldehyde (9) considered above. They resembled the aliphatic ketones, however, in tending to form 2,3-dihydro-2-thio-1,3-thiazines (III;  $R^5 = H$ ) in acid solution and being unstable in the presence of alkali.

Compounds having a trichloromethyl group (13—15) had absorption spectra (Fig. 3) which differed only from those of other ketones (5—8) by the position of band 2 and their behaviour in alkaline solution. They were stable in neutral and alkaline solutions, but acids catalysed the formation of 2,3-dihydro-2-thio-1,3-thiazines (III;  $R^5 = H$ ).

Derivatives of *N*-Methyldithiocarbamic Acid (I;  $R^5 = \text{Me}$ ; Table 2).—Though all the  $\alpha\beta$ -unsaturated aldehydes and ketones that were tried formed adducts with *N*-methyldithiocarbamic acid, derivatives of certain ketones could not be purified satisfactorily and so were not used in this investigation.

Derivatives of aliphatic aldehydes and one ketone (16—20) in alcohol exhibited two bands at 286 (band 1) and 244  $m\mu$  (band 2). In the presence of acid and alkali the spectra behaved as those of certain ketone derivatives of dithiocarbamic acid (5—8; Fig. 2). In alkaline solution the compounds appeared to react slowly, with the appearance of a band at 320  $m\mu$ . The reaction did not follow the usual course of alkaline decomposition expected of esters of methyldithiocarbamic acid,<sup>6</sup> and this, together with the slightly different absorption spectra, would seem to support the cyclic structure (II;  $R^5 = \text{Me}$ ) for these compounds in solution.

The spectrum of the aryl-substituted aldehyde derivative (21) was the same in both neutral and acid solutions (Fig. 4). The spectra of aryl-substituted ketones (22—24), on the other hand, in both acid alcoholic (Fig. 5) and aqueous solutions, appeared to be closer to those normally exhibited by esters of *N*-methyldithiocarbamic acid.<sup>3,4</sup> This suggests that the cyclic form of these derivatives (22—24) is not favoured by the presence of acids or polar solvents. The spectra of all aryl-substituted compounds in alkaline solution were the same (Figs. 4 and 5). The ketone derivatives (22—24) underwent unidentified spectral changes in neutral, acid, and alkaline solutions.

Compounds having a trichloromethyl group (25—27) exhibited spectra (Fig. 6) which behaved in a similar way to those of the aryl-substituted derivatives (22—24) discussed above. The same conclusions, therefore, would seem to apply. These compounds also exhibited unidentified spectral changes in neutral and alkaline solutions.

The results of fungitoxicity tests will be published elsewhere.

#### EXPERIMENTAL

$\alpha\beta$ -Unsaturated aldehydes and ketones not obtainable from commercial sources were prepared by well known methods. The following preparations are examples of the addition reactions performed with dithiocarbamic and *N*-methyldithiocarbamic acids.

$\beta$ -(*Thiocarbamoylthio*)propionaldehyde (1).—Ammonium dithiocarbamate (11.0 g.) dissolved in a minimum amount of water was added to a solution of rectified spirit (50 ml.), water (10 ml.), and concentrated hydrochloric acid (10 ml.) at 0—5° with stirring. Acraldehyde (8.0 ml.) was then added slowly at 0—5° and the resulting solution stirred for 1½ hr. at room temperature. After cooling in ice-water, the *product* was filtered off and recrystallised as plates from rectified spirit.

1-(*N*-Methylthiocarbamoylthio)-1-phenylbutan-3-one (22).—Benzylideneacetone (14.5 g.) was dissolved in rectified spirit (100 ml.) and cooled to +5°. Concentrated hydrochloric acid (12.5 ml.) was added, followed by a solution of *N*-methyldithiocarbamate (35 ml.; 1 mole/350 ml.) with stirring, maintaining the temperature at +5°. After stirring at room temperature for 5 hr. and cooling in ice-water, the product was filtered off and recrystallised from 50% acetic acid in water.

The ultraviolet spectra of all compounds in alcohol and water were plotted with a S.P. 500 Unicam ultraviolet spectrophotometer. The effects of acid and alkali were studied by recording the spectra after the addition of 2*N*-hydrochloric acid and 2*N*-sodium hydroxide to neutral solutions of the compound in alcohol, the amount of acid or alkali being 0.2 ml. per 25 ml. of solution. Stability was assessed by recording the absorption spectra of solutions after 48 hr. at 25°.

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<sup>6</sup> Seyden-Penne, *Ann. chim.*, 1958, **3**, 599.