

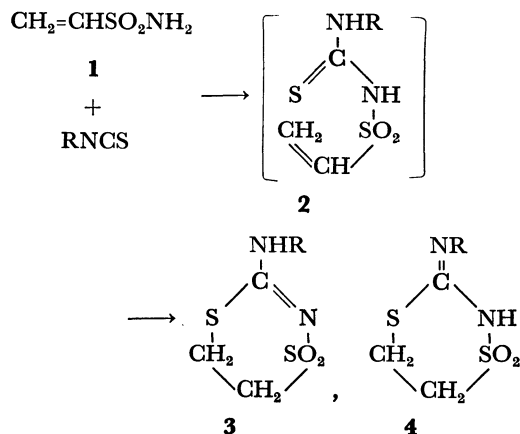
Synthesis of the New 1,4,2-Dithiazine 1,1-Dioxides<sup>1)</sup>

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Previously, the synthesis of *N*-(2-phenylethene-1-sulfonyl)-*N'*-alkylthioureas and their intramolecular cycloadducts, 3-alkylamino-5-phenyl-1,1-dioxo-5,6-dihydro-1,4,2-dithiazines, from 2-phenylethene-1-sulfonamides was reported.<sup>2)</sup>



The present paper will describe the reaction of vinylsulfonamide (**1**) with isothiocyanates to give new heterocyclic compounds, 3-alkylamino-1,1-dioxo-5,6-dihydro-1,4,2-dithiazines (**3**) and 3-phenylimino-1,1-dioxo-2,3,5,6-tetrahydro-1,4,2-dithiazines (**4**), which are the intramolecular Michael cycloadducts of the probable intermediates, vinylsulfonyl thioureas (**2**).

The reaction of **1** with carbon disulfide and dimethyl sulfate in DMF in the presence of sodium hydroxide yielded 3-methylthio-1,1-dioxo-5,6-dihydro-1,4,2-dithiazine (**5**). The treatment of **5** with chlorine in chloroform gave the 3-chloro derivative (**6**), and the

reaction of **6** with alcohol or amines afforded 3-alkoxy (**7**) or 3-amino derivatives (**8**), respectively.

Analogous syntheses starting from 2-phenylethene-1-sulfonamides were reported in a previous work,<sup>3)</sup> but the ethylenic bond in vinylsulfonamide is very reactive and we failed to secure the vinylsulfonylated thioureas **2** and dithiocarbamate, which are the non-cyclic intermediates between **1** and **3**, and between **1** and **5**, respectively.

## Experimental

3-Methylamino-1,1-dioxo-5,6-dihydro-1,4,2-dithiazine (**3a**).

To vinylsulfonamide (2.6 g, 0.025 mol) in acetone (15 ml), we added methyl isothiocyanate (2.2 g, 0.03 mol) and anhydrous potassium carbonate (4.2 g, 0.03 mol); the reaction mixture was then refluxed for 10–15 hr with stirring and subsequently filtered. The acetone layer was concentrated *in vacuo*, and the crude residue was cooled to give 3.0 g of a solid. Recrystallization from methanol gave colorless crystals. IR (KBr): 3260 ( $\nu_{\text{NH}}$ ), 1550–1570 ( $\nu_{\text{C=N}}$ ), 1200–1300, 1120–1160 ( $\nu_{\text{SO}_2}$ )  $\text{cm}^{-1}$ . NMR (DMSO- $d_6$ ):  $\delta$  2.710 (s, =NCH<sub>3</sub>), 2.713 (d,  $J_{\text{NHCH}_3}=4.6$  Hz), 3.16–3.56 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>), 8.56 (broad, 0.53H, NH). Ms:  $m/e$  45 (CHS), 180.061 (calculated molecular weight, 180.059).

3-Phenylimino-1,1-dioxo-2,3,5,6-tetrahydro-1,4,2-dithiazine (**4c**).

To vinylsulfonamide (1.0 g, 0.009 mol) in acetone (10 ml), we added phenyl isothiocyanate (1.4 g, 0.010 mol) and anhydrous potassium carbonate (1.4 g, 0.010 mol); the reaction mixture was then refluxed for 10–15 hr with stirring and subsequently filtered; the potassium salt of **4c** thus obtained was dissolved in water, and the resulting solution was acidified to give 2.2 g of **4c**. Although crude **3c** was obtained by concentrating the acetone layer *in vacuo*, it was converted to **4c**

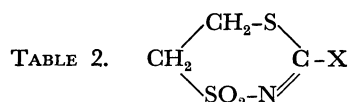
TABLE 1. **3** or **4**

Compd	R	Yield (%)	Ratio <sup>a)</sup> (%)	Mp (°C)	Found (%)				Calcd (%)				Solvent of recrystn
					C	H	N	S	C	H	N	S	
<b>3a</b> <b>4a</b>	CH <sub>3</sub>	68	100 0	146–147	26.69	4.52	15.31	35.01	26.65	4.47	15.54	35.57	methanol
<b>3b</b> <b>4b</b>	C <sub>6</sub> H <sub>11</sub>	73	94 6 <sup>b)</sup>	186–187	43.24	6.66	11.15	25.62	43.52	6.49	11.28	25.82	methanol
<b>3c</b> <b>4c</b>	C <sub>6</sub> H <sub>5</sub>	91	45 <sup>c)</sup> 55	161–163	44.31	4.14	11.48	26.30	44.61	4.16	11.56	26.48	methanol
<b>3d</b> <b>4d</b>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	90	0 100	170–171	47.15	4.81	11.05	24.87	46.85	4.72	10.93	25.01	methanol
<b>3e</b> <b>4e</b>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	79	100 0	233–235	39.16	3.23	10.17	22.96	39.06	3.28	10.12	23.17	ethanol

a) Ratio of **3** vs. **4** before recrystallization. b) **4b** could not be recrystallized. c) **4c** was given by recrystallization from methanol.

1) Presented at the 25th Annual Meeting of the Chemical Society of Japan, Tokyo, October, 1971.

2) K. Hasegawa and S. Hirooka, This Bulletin, **45**, 525 (1972),  
3) K. Hasegawa and S. Hirooka, *ibid.*, **45**, 1567 (1972).



Compd	X	Yield (%)	Mp (°C)	Found (%)					Calcd (%)				
				C	H	N	S	Cl	C	H	N	S	Cl
<b>5</b>	SCH <sub>3</sub>	84	126—127	24.30	3.62	7.08	48.43	—	24.35	3.58	7.10	48.75	—
<b>6</b>	Cl	80	131—132	19.24	2.29	7.44	34.28	19.64	19.41	2.17	7.55	34.54	19.10
<b>7</b>	OCH <sub>3</sub>	51 <sup>a)</sup>	139—140	26.47	3.84	7.81	35.07	—	26.51	3.89	7.73	35.38	—
<b>8a</b>	N(CH <sub>3</sub> ) <sub>2</sub>	68 <sup>a)</sup>	171—172	30.89	4.98	14.38	32.60	—	30.91	5.19	14.42	33.01	—
<b>8b</b>	NH <sub>2</sub>	97	196—197	21.96	3.64	16.64	—	—	21.68	3.64	16.86	38.58	—

a) Yield after recrystallization.

when recrystallized from methanol.

IR (KBr): 3240 ( $\nu_{\text{NH}}$ ), 1590 ( $\nu_{\text{phenyl}}$ ), 1540 ( $\nu_{\text{C=N}}$ ), 1300—1310, 1260—1270 ( $\nu_{\text{SO}_2}$ )  $\text{cm}^{-1}$ . NMR (acetone- $d_6$ ):  $\delta$  3.17—3.80 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>), 7.00—7.73 (m, 5H, phenyl CH), 9.25 (broad, 0.63H, NH). Ms:  $m/e$  46 (CH<sub>2</sub>S), 242 (M).

The **5**, **6**, **7**, **8a**, and **8b** compounds were prepared and confirmed in an analogous manner,<sup>3)</sup> starting from vinyl-sulfonamide.

*3-Methylthio-1,1-dioxo-5,6-dihydro-1,4,2-dithiazine (5)*.

IR (KBr): 1505 ( $\nu_{\text{C=N}}$ ), 1260—1310 and 1110—1170 ( $\nu_{\text{SO}_2}$ )  $\text{cm}^{-1}$ . NMR (CDCl<sub>3</sub>):  $\delta$  2.52 (s, 3H, SCH<sub>3</sub>). Ms:  $m/e$  197 (M).

*3-Chloro-1,1-dioxo-5,6-dihydro-1,4,2-dithiazine (6)*. IR

(KBr): 1570 and 1550 ( $\nu_{\text{C=N}}$ ), 1270—1325 and 1140—1180 ( $\nu_{\text{SO}_2}$ )  $\text{cm}^{-1}$ . Ms:  $m/e$  185 (M).

*3-Methoxy-1,1-dioxo-5,6-dihydro-1,4,2-dithiazine (7)*. IR (KBr): 1560 ( $\nu_{\text{C=N}}$ ), 1250—1320 and 1110—1170 ( $\nu_{\text{SO}_2}$ )  $\text{cm}^{-1}$ . Ms:  $m/e$  181 (M). NMR (CDCl<sub>3</sub>):  $\delta$  3.95 (s, 3H, OCH<sub>3</sub>).

*3-Dimethylamino-1,1-dioxo-5,6-dihydro-1,4,2-dithiazine (8a)*.

IR (KBr): 1545 ( $\nu_{\text{C=N}}$ ), 1310, 1270, and 1110—1140 ( $\nu_{\text{SO}_2}$ )  $\text{cm}^{-1}$ . NMR (CDCl<sub>3</sub>):  $\delta$  3.12 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>). Ms:  $m/e$  194 (M).

*3-Amino-1,1-dioxo-5,6-dihydro-1,4,2-dithiazine (8b)*. IR

(KBr): 3330, 3250, and 3160 ( $\nu_{\text{NH}}$ ), 1610 ( $\nu_{\text{NH}}$ ), 1515 ( $\nu_{\text{C=N}}$ ), 1140, 1110, and 1100 ( $\nu_{\text{SO}_2}$ )  $\text{cm}^{-1}$ .