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Synthesis of the New 1,4,2-Dithiazine 1,1-Dioxides[1)]

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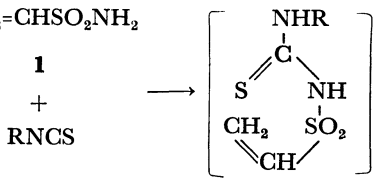
Previously, the synthesis of *N*-(2-phenylethene-1-sulfonyl)-*N'*-alkylthioureas and their intramolecular cycloadducts, 3-alkylamino-5-phenyl-1,1-dioxo-5,6-dihydro-1,4,2-dithiazines, from 2-phenylethene-1-sulfonamides was reported.[2)]



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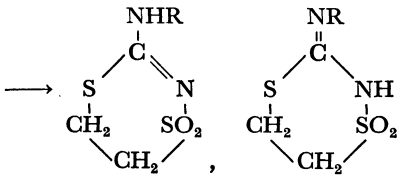


3 , **4**

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**).

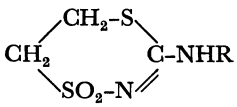
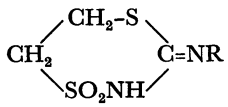
The reaction of **1** with carbon disulfide and dimethyl sulfate in DMF in the presence of sodium hydroxide yielded 3-methylthio-1,1-dioxo-5,6-dihydro-1,4,2-dithiazine (**5**). The treatment of **5** with chlorine in chloroform gave the 3-chloro derivative (**6**), and the reaction of **6** with alcohol 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,[3)] 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 m*l*), 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 (ν_{NH}), 1550—1570 ($\nu_{C=N}$), 1200—1300, 1120—1160 (ν_{SO_2}) cm^{-1}. NMR (DMSO-d_6): δ 2.710 (s, $=NCH_3$), 2.713 (d, J_{NHCH_3}=4.6 Hz), 3.16—3.56 (m, 4H, CH_2CH_2), 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 m*l*), 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[a)] (%)	Mp (°C)	Found (%) C	H	N	S	Calcd (%) C	H	N	S	Solvent of recrystn
3a / **4a**	CH_3	68	100 / 0	146—147	26.69	4.52	15.31	35.01	26.65	4.47	15.54	35.57	methanol
3b / **4b**	C_6H_{11}	73	94 / 6[b)]	186—187	43.24	6.66	11.15	25.62	43.52	6.49	11.28	25.82	methanol
3c / **4c**	C_6H_5	91	45[c)] / 55	161—163	44.31	4.14	11.48	26.30	44.61	4.16	11.56	26.48	methanol
3d / **4d**	*p*-$CH_3C_6H_4$	90	0 / 100	170—171	47.15	4.81	11.05	24.87	46.85	4.72	10.93	25.01	methanol
3e / **4e**	*p*-ClC_6H_4	79	100 / 0	233—235	39.16	3.23	10.17	22.96	39.06	3.28	10.12	23.17	ethanol

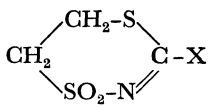
a) Ratio of **3** *vs.* **4** before recrystallization. b) **4b** could not be recrystallized. c) **4c** was given by recrystallization from methanol.

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).

TABLE 2.



Compd	X	Yield (%)	Mp (°C)	Found (%)					Calcd (%)				
				C	H	N	S	Cl	C	H	N	S	Cl
5	SCH_3	84	126—127	24.30	3.62	7.08	48.43	—	24.35	3.58	7.10	48·75	—
6	Cl	80	131—132	19.24	2.29	7.44	34.28	19.64	19.41	2.17	7.55	34.54	19.10
7	OCH_3	51[a)]	139—140	26.47	3.84	7.81	35.07	—	26.51	3.89	7.73	35.38	—
8a	$N(CH_3)_2$	68[a)]	171—172	30.89	4.98	14.38	32.60	—	30.91	5.19	14.42	33.01	—
8b	NH_2	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 (ν_{NH}), 1590 (ν_{phenyl}), 1540 ($\nu_{C=N}$), 1300—1310, 1260—1270 (ν_{SO_2}) cm^{-1}. NMR (acetone-d_6): δ 3.17—3.80 (m, 4H, CH_2CH_2), 7.00—7.73 (m, 5H, phenyl CH), 9.25 (broad, 0.63H, NH). Ms: *m/e* 46 (CH_2S), 242 (M).

The **5**, **6**, **7**, **8a**, and **8b** compounds were prepared and confirmed in an analogous manner,[3)] starting from vinylsulfonamide.

*3-Methylthio-1,1-dioxo-5,6-dihydro-1,4,2-dithiazine (**5**).*
IR (KBr): 1505 ($\nu_{C=N}$), 1260—1310 and 1110—1170 (ν_{SO_2}) cm^{-1}. NMR ($CDCl_3$): δ 2.52 (s, 3H, SCH_3). Ms: *m/e* 197 (M).

*3-Chloro-1,1-dioxo-5,6-dihydro-1,4,2-dithiazine (**6**).* IR (KBr): 1570 and 1550 ($\nu_{C=N}$), 1270—1325 and 1140—1180 (ν_{SO_2}) cm^{-1}. Ms: *m/e* 185 (M).

*3-Methoxy-1,1-dioxo-5,6-dihydro-1,4,2-dithiazine (**7**).* IR (KBr): 1560 ($\nu_{C=N}$), 1250—1320 and 1110—1170 (ν_{SO_2}) cm^{-1}. Ms: *m/e* 181 (M). NMR ($CDCl_3$): δ 3.95 (s, 3H, OCH_3).

*3-Dimethylamino-1,1-dioxo-5,6-dihydro-1,4,2-dithiazine (**8a**).* IR (KBr): 1545 ($\nu_{C=N}$), 1310, 1270, and 1110—1140 (ν_{SO_2}) cm^{-1}. NMR ($CDCl_3$): δ 3.12 (s, 6H, $N(CH_3)_2$). Ms: *m/e* 194 (M).

*3-Amino-1,1-dioxo-5,6-dihydro-1,4,2-dithiazine (**8b**).* IR (KBr): 3330, 3250, and 3160 (ν_{NH}), 1610 (ν_{NH}), 1515 ($\nu_{C=N}$), 1140, 1110, and 1100 (ν_{SO_2}) cm^{-1}.