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Michael Cycloaddition of 2-Phenylethene-1-sulfonamide with Carbon Disulfide[1)]

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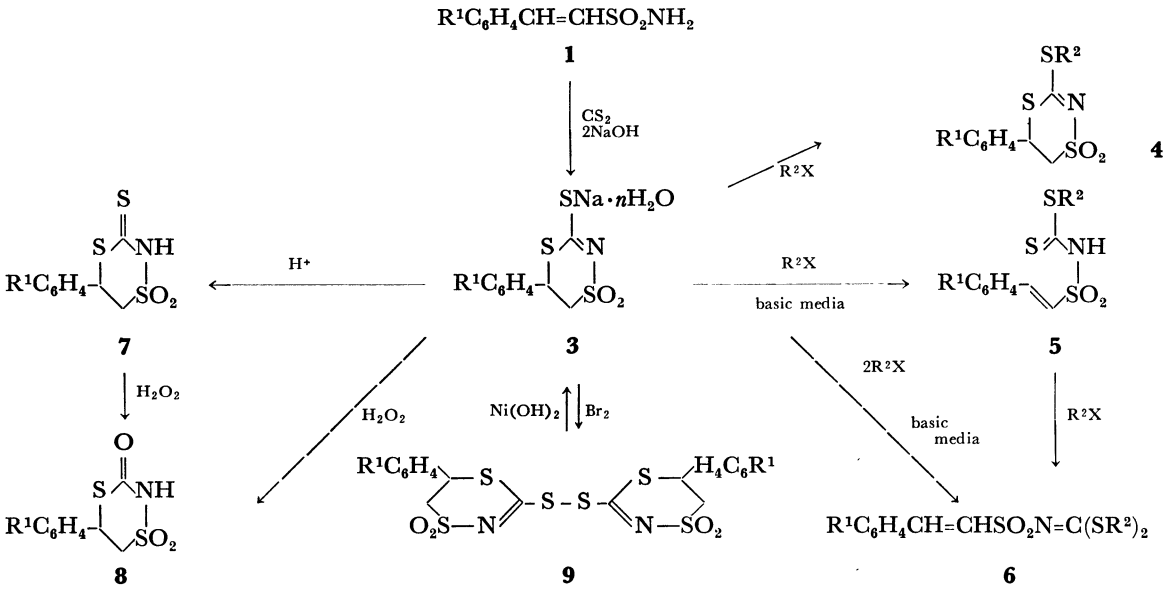
In the preceding paper,[2)] we reported that 2-phenylethene-1-sulfonamide **1** reacts with carbon disulfide and alkyl halide in the presence of base giving 3-alkylthio-5-phenyl-1,1-dioxo-5,6-dihydro-1,4,2-dithiazines **4**. The postulated mechanism for the formation of **4** involves an intermediary sodium salt of

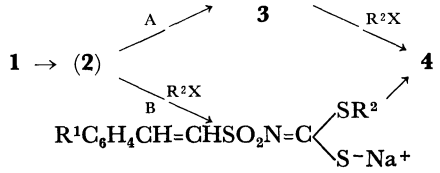


Scheme 1.

1) Presented at the 27th Annual Meeting of the Chemical Society of Japan, Nagoya, 12, October(1972). No. 2NO2.

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

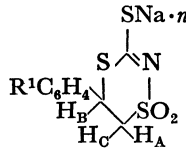
3-mercapto-5-phenyl-1,1-dioxo-5,6-dihydro-1,4,2-dithiazine **3**, which is intramolecular Michael cycloadduct of 2-phenylethene-1-sulfonyliminodithiocarbonate **2** ($R^1C_6H_4CH{=}CHSO_2N{=}C(S^-Na^+)_2$). This paper describes the isolation of **3** and the syntheses of some new derivatives from **3**. The process is outlined in Scheme 1.



Results

The hydrates of the Michael cycloadducts **3** (n= 1,2) were isolated from the reaction mixture of **1**, sodium hydroxide and carbon disulfide. The results are given in Table 1. As regards the mechanism for the formation of **4**, the following two paths A and B are conceivable.

Isolation of **3** supports path A in which highly reactive intermediate **2** undergoes rapid ring-closure giving **3** followed by alkylation. The C–S bond in **3** could not be cleaved by strong bases, **3** being recrystallized from a 1 N sodium hydroxide solution. The structure of **3** was determined on the basis of analytical and spectral data. In the NMR pattern of **3a**, ring protons, $H_AH_CH_B$, showed an ABX spin system consisting of three quartets of H_A centered at δ 3.06, H_C 3.39 and H_B 4.79 (J_{AC}=13.5 Hz, J_{AB}=13.0 Hz, J_{BC}=3.6 Hz). Monoalkylation of **3** in 50% ethanol afforded **4** in a yield greater than 89% (R^1=H, p-Cl, p-Br, p-CH_3, R^2=CH_3), but the reverse Michael cycloadducts of **4**, N-(2-phenylethene-1-sulfonyl)-dithiocarbamates **5** were obtained in a strong alkali (R^1=H, p-Cl, p-CH_3, R^2=CH_3). Dialkylation of **3** in strongly basic media afforded alkyl 2-phenylethene-1-sulfonyliminodithiocarbonates **6** which were the same

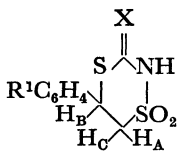
Table 1.  **3**

Compd.	R^1	Weight loss (%)[a] Found	Weight loss (%)[a] Calcd	n	Yield (%)	Mp (°C)	Found (%) C	Found (%) H	Found (%) N	Calcd (%) C	Calcd (%) H	Calcd (%) N
3a	H	12.1	11.3	2	67	245—247	33.92	3.70	4.37	34.06	3.81	4.41
3b	p-Cl	5.1	5.4	1	58	250—252	32.12	3.01	3.93	32.38	2.72	4.20
3c	p-Br	4.4	4.7	1	55	245—247	28.80	2.66	3.44	28.57	2.40	3.70
3d	p-CH_3	5.0	5.4	1	95	241—243	38.34	3.98	4.20	38.33	3.96	4.47

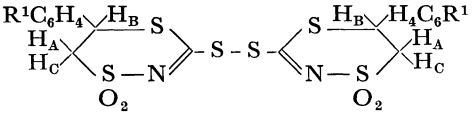
a) Mitamura 2-100-S type DTA apparatus was used and weight loss (%) was determined by heating hydrates **3** above 130°C.

Table 2. $R^1C_6H_4CH_B{=}CH_ASO_2N{=}C(SR^2)_2$ **6**

Compd.	R^1	R^2	Yield (%)	Mp (°C)	Found (%) C	Found (%) H	Found (%) N	Calcd (%) C	Calcd (%) H	Calcd (%) N
6a	H	CH_3	70	95— 96	45.76	4.42	4.97	46.00	4.56	4.88
6b	p-Cl	CH_3	72	129—130	41.35	3.77	4.50	41.10	3.76	4.36
6c	p-CH_3	CH_3	69	134—135	48.10	4.91	4.89	47.84	5.02	4.65

Table 3.  **7, 8**

Compd.	R^1	X	Yield (%)	Mp (°C)	Found (%) C	Found (%) H	Found (%) N	Calcd (%) C	Calcd (%) H	Calcd (%) N
7a	H	S	81	67— 69	41.49	3.40	5.38	41.71	3.50	5.40
7b	p-Cl	S	77	102—105	36.96	3.01	3.93	36.79	2.72	4.20
7c	p-CH_3	S	75	69— 71	44.23	3.98	5.02	43.96	4.06	5.13
8a	H	O	67	164—165	44.26	3.65	5.70	44.45	3.73	5.76
8b	p-Cl	O	68	172—173	39.03	2.91	5.30	38.92	2.90	5.04
8c	p-Br	O	73	159—161	33.82	2.51	4.43	33.56	2.50	4.35
8d	p-CH_3	O	83	170—171	46.98	4.29	5.32	46.70	4.31	5.45

TABLE 4.  **9**

Compd.	R^1	Yield (%)	Mp (°C)	Found (%)			Calcd (%)		
				C	H	N	C	H	N
9a	H	98	215—218	41.86	3.29	5.35	41.84	3.12	5.42
9b	*p*-CH_3	93	208—210	44.34	3.89	5.30	44.09	3.60	5.14

as alkylation products of **5** (Table 2). Acidification of aqueous solution of **3** under cooling gave yellow analytically pure crystals of 3-thio-5-phenyl-2,3,5,6-tetrahydro-1,1-dioxo-1,4,2-dithiazines **7** (Table 3). Cycloadducts **3** and **7** were desulfurized with alkaline hydrogen peroxide to give 5-phenyl-2,3,5,6-tetrahydro-1,1,3-trioxo-1,4,2-dithiazines **8** (Table 3). Oxidation of **3** with bromine afforded 3,3′-bis(5-phenyl-1,1-dioxo-5,6-dihydro-1,4,2-dithiazinyl)disulfides **9** (Table 4) whose S–S bonds were cleaved by reduction with nickel hydroxide[3] in basic media to give **3** again. The structures of the new compounds **6**, **7**, **8**, and **9** were determined on the basis of analytical and spectral data.

Experimental

Sodium Salt of 3-Mercapto-5-phenyl-1,1-dioxo-5,6-dihydro-1,4,2-dithiazine ***3a***. To a stirred solution of **1** (5.50 g, 0.030 mol) in DMF (60 ml) was added a solution of NaOH (2.40 g, 0.060 ml) in water (4.0 ml) and then CS_2 (3.40 g, 0.045 mol) at 20—30°C. The reaction mixture was stirred for 2 hr at room temperature. Evaporation of the DMF *in vacuo* left a dark red residue, into which 1N NaOH solution (100 ml) was added, and the solution was cooled overnight. The crystal was collected to give 6.30 g (67%) of **3a** as dihydrate. Recrystallization from 1N NaOH solution gave a colorless crystal. IR(KBr): 3570 and 3440 (dihydrate), 1385, 1135, and 1110 (SO_2) cm^{-1}. NMR (acetone-d_6): δ 3.06 (q, 1H, H_A), 3.39 (q, 1H, H_C), 4.79 (q, 1H, H_B), J_{AC}=13.5 Hz, J_{AB}=13.0 Hz, J_{BC}=3.6 Hz, 7.35 (s, 5H, phenyl).

Dimethyl N-(2-p-chlorophenylethene-1-sulfonyl)iminodithiocarbonate ***6a***. To a stirred solution of **3b** (0.33 g, 0.0010 mol) in methanol (8 ml) and 0.5 N NaOH solution (4 ml) was added drop by drop two equivalents of dimethyl sulfate (0.28 g, 0.0022 mol) at 0—10°C, after which the reaction mixture was stirred for 2 hr at 0—10°C. The precipitate was collected to give 0.23 g (72%) of **6b**. IR (KBr): 3040 (=CH), 1620 (C=C), 1460 (N=C), 1305 and 1140 (SO_2) cm^{-1}. NMR ($CDCl_3$): δ 2.59 (6H, SCH_3), 6.88 (1H, H_A), 7.52 (1H, H_B), J_{AB}=15.2 Hz, 7.34 (s, 4H, phenyl). When one equivalent of dimethyl sulfate (0.14 g, 0.0011 mol) *vs* **3b** was used, 0.18 g (59%) of the dithiocarbamate was obtained on acidification of the alkaline aqueous layer. mp 113—116°C (lit.[3]), 114—117°C).

3-Thio-5-phenyl-1,1-dioxo-2,3,5,6-tetrahydro-1,4,2-dithiazine ***7a***. IR (KBr): 3080 (NH, broad), 1330 and 1140 (SO_2) cm^{-1}. NMR (acetone-d_6): δ 3.81 (q, 1H, H_A), 3.98 (q, 1H, H_C), 5.09 (q, 1H, H_B), J_{AC}=13.8 Hz, J_{AB}=11.0 Hz, J_{BC}=5.8 Hz, 6.62 (1H, NH), 7.43±0.07 (5H, phenyl). MS *m/e*: 258.9783 (M^+, calculated for $C_{10}H_9NO_2S_3$: 258.9765).

5-Phenyl-1,1,3-trioxo-2,3,5,6-tetrahydro-1,4,2-dithiazine ***8a***. To a stirred solution of **3a** (0.48 g, 0.0015 mol) in acetone (2.0 ml) was added drop by drop a 30% hydrogen peroxide solution (0.21 g, 0.0060 mol) at 0—10°C, after which the reaction mixture was stirred for 3 hr at room temperature. The acetone was evaporated *in vacuo*, and the solution was acidified with concentrated hydrochloric acid to afford 0.24 g (67%) of **8a**. Analogously, **8a** was also formed in 59% yield from **7a** (0.26 g, 0.0010 mol), 0.5 N NaOH solution (6.0 ml) and 30% hydrogen peroxide solution (0.47 g, 0.0040 mol). IR (KBr): 2960 (NH), 1630 (C=O), 1330 and 1150 (SO_2) cm^{-1}. NMR (DMSO-d_6): δ 4.06 (q, 1H, H_A), 4.22 (q, 1H, H_C), 4.99 (q, 1H, H_B), J_{AC}=13.0 Hz, J_{AB}=10.8 Hz, J_{BC}=5.8 Hz, 5.77 (1H, NH), 7.46± 1.20 (5H, phenyl). MS *m/e*: 243 (M^+).

3,3′-Bis(5-phenyl-1,1-dioxo-5,6-dihydro-1,4,2-dithiazinyl) disulfide ***9a***. To a stirred solution of **3a** (0.66 g, 0.0021 mol) in DMF (5.0 ml) was added bromine (0.19 g, 0 0012 mol) at 0—10°C. After being stirred for 3 hr at 0—10°C, the reaction mixture was poured into ice water (100 ml) and kept overnight. The precipitate was collected to give 0.53 g (98%) of an analytically pure crystal. IR (KBr): 1520 (N=C), 1320 and 1140 (SO_2) cm^{-1}. NMR (DMSO-d_6): δ 4.09 (q, 2H, H_A), 4.41 (q, 2H, H_C), 5.43 (q, 2H, H_B), J_{AC}=14.0 Hz, J_{AB}=12.0 Hz, J_{BC}=4.1 Hz, 7.54± 0.03 (10H, phenyl).

3) S. Hirooka, K. Hasegawa, T. Kodama, K. Hisada, and H. Kodama, *Nippon Kagaku Zasshi*, **91**, 270 (1970).