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## The Synthesis of the New 1,4,2-Dithiazine Ring<sup>1)</sup>

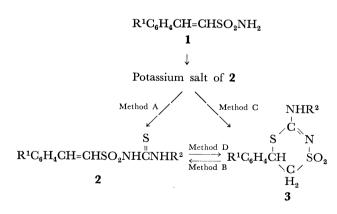
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Some derivatives of N-(2-phenylethene-1-sulfonyl)-N'-alkylthioureas of the  $R^1C_6H_4CH$ = $CHSO_2NHCSNHR^2$  type were synthesized by a reaction between 2-phenylethene-1-sulfonamides 1 and isothiocyanates in acetone in the presence of  $K_2CO_3$ . A new heterocyclic system, 3-alkylamino-5-phenyl-1,1-dioxo-5,6-dihydro-1,4,2-dithiazine 3, was obtained by the intramolecular Michael cycloaddition of 2 in weakly basic media, and also by the thermal cyclization of 2. The carbon-sulfur bond in 3 could be cleaved to give 2 again in strongly basic media.

A previous study<sup>2)</sup> in this laboratory has dealt with N-benzenesulfonyl-N'-alkylthioureas obtained from benzenesulfonamides and alkyl isothiocyanates. When 2-phenylethene-1-sulfonamide<sup>3)</sup> 1, in which the  $\alpha$ ,  $\beta$  double bond is activated by a neighboring sulfonyl group,<sup>4)</sup> was used, either the corresponding sulfonylthioureas 2 or the intramolecular cycloadducts, 3-alkylamino-5-phenyl-1,1-dioxo-5,6-dihydro-1,4,2-dithiazines 3, were formed, depending upon the work-up procedure. Recently, the synthesis of 2 (R<sup>1</sup>=H, R<sup>2</sup>=allyl and phenyl) was briefly reported,<sup>5)</sup> but 3 has never yet been prepared. This paper will describe the synthesis, cleavage, and structural elucidation of a new heterocycle 3. The process is outlined below.

5) S. Hartig, J. Prak. Chem., 33, 216 (1966).



## Results

N-(2-Phenylethene-1-sulfonyl)-N'-alkylthioureas 2. A mixture of 1, potassium carbonate, and alkyl isothiocyanate in acetone was refluxed for 15—25 hr with stirring to yield the potassium salt of 2 as a normal product. This was filtered, dissolved in water, and acidified to give 2 (Table 1, Method A). The structure of 2 was confirmed by a study of its IR, NMR,

<sup>1)</sup> Presented in part at the 24th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1971.

<sup>2)</sup> S. Hirooka, Nippon Kagaku Zasshi, 83, 156 (1962).

<sup>3)</sup> B. M. Culbertson and S. Dietz, J. Chem. Soc., C, 1968, 90, 992.

<sup>4)</sup> E. D. Bergmann, D. Ginsburg, and R. Pappo, "Organic Reactions," Vol. 10, New York (1959), p. 241.

Table 1. R<sup>1</sup>C<sub>6</sub>H<sub>4</sub>CH<sub>B</sub>=CH<sub>A</sub>SO<sub>2</sub>NHCSNHR<sup>2</sup> 2

	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$						TABLE 1.	R'C6H4CHB=CHASO2NHCSNHR2 2	SO2NHCSN	HR <sup>2</sup> 2						
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Compd.		22	Yield	(%)		UV делнон		Calco				Found	(%) p	
H CH, CH, 95 94 197–138 267 (22700) 46.88 4.72 10.93 46.89 4.72 10.94 197 198 199 199 199 199 199 199 199 199 199	H CH <sub>4</sub> 95 94 137—138 267(23700) 46.88 4.72 10.93 H $\kappa_{\rm c}(H_4)$ 77 79 130—131 267(23700) 48.89 5.22 10.37 H $\kappa_{\rm c}(H_4)$ 77 79 130—131 267(23700) 48.89 5.22 10.37 H $\kappa_{\rm c}(H_4)$ 85 90 240—242 274(11300) 41.30 3.81 9.63 22.05 $\rho_{\rm c}(\Pi)$ CH <sub>4</sub> 97 110—111 267(23700) 48.89 5.22 10.37 $\rho_{\rm c}(\Pi)$ CH <sub>4</sub> 99 92 216—212 274(11300) 41.30 3.81 9.63 22.05 $\rho_{\rm c}(\Pi)$ CH <sub>4</sub> 99 93 216—213 277(23600) 48.89 5.22 10.37 $\rho_{\rm c}(H_4)$ CH <sub>4</sub> 94 100 249—242 277(23600) 48.89 5.22 10.37 $\rho_{\rm c}(H_4)$ CH <sub>4</sub> 94 100 249—242 277(23600) 48.89 5.22 10.37 $\rho_{\rm c}(H_4)$ CH <sub>4</sub> 94 100 249—242 277(23600) 48.89 5.22 10.37 $\rho_{\rm c}(H_4)$ CH <sub>4</sub> 94 100 249—242 277(23600) 48.89 5.22 10.37 $\rho_{\rm c}(H_4)$ CH <sub>4</sub> 87 104—101 277(23600) 48.89 5.22 10.37 $\rho_{\rm c}(H_4)$ CH <sub>4</sub> 87 22 100—211 218(23600) 48.89 5.22 10.37 $\rho_{\rm c}(H_4)$ CH <sub>4</sub> 87 82 210—211 218(23600) 48.89 5.22 10.37 $\rho_{\rm c}(H_4)$ CH <sub>4</sub> 87 82 210—212 218(21600) 41.30 3.81 9.63 22.05 $\rho_{\rm c}(H_4)$ CH <sub>4</sub> 81 92 220—222 225(21000) 41.30 3.81 9.63 22.05 $\rho_{\rm c}(H_4)$ CH <sub>4</sub> 81 92 220—222 225(21000) 41.30 3.81 9.63 22.05 $\rho_{\rm c}(H_4)$ CH <sub>4</sub> 81 92 220—222 225(21000) 41.30 3.81 9.63 22.05 $\rho_{\rm c}(H_4)$ CH <sub>4</sub> 98 92 220—222 228(24000) 35.28 3.71 8.96 19.38 $\rho_{\rm c}(H_4)$ CH <sub>4</sub> 61 94 82 210—212 228(24000) 35.28 3.71 8.96 19.38 $\rho_{\rm c}(H_4)$ CH <sub>4</sub> 64 88 216—212 228(24000) 35.28 3.71 8.96 19.38 $\rho_{\rm c}(H_4)$ CH <sub>4</sub> 64 88 216—212 228(24000) 35.28 3.71 8.96 19.37 23.69 $\rho_{\rm c}(H_4)$ CH <sub>4</sub> 64 88 216—212 228(24000) 35.27 9.96 210.37 23.69	1		4	A <sup>8</sup> )	Bp		$(\varepsilon_{ m max})$	Ö	H	Z	S	C	Н	Z	S
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	<b>2a</b>	H	$CH_3$	95	94	137—138	267 (23700)	46.88	4.72	10.93	And the second s	46.85	4.89	10.95	
H $n^{-}$ C, H $n^$	H $h$	<b>2</b> b	Н	$\mathrm{C_2H_5}$	29	87	86 —96	267 (22700)	48.89	5.22	10.37		48.84	5.29	10.26	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	<b>2c</b>	Н	$n\text{-}\mathrm{C}_4\mathrm{H}_9$	72	9/	110-1111	267 (22200)	52.34	80.9	9.39		52.51	90.9	9.30	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2 <b>d</b>	Н	$\langle H \rangle$	57	79	130—131		55.55	6.22	8.64		55.80	6.34	8.78	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	<b>2e</b>	p-CI	CH3	85	06	240242	274 (11300)	41.30	3.81	9.63	22.05	41.54	4.05	9,75	99.13
$m$ -Cl         CH <sub>4</sub> 94         92         233-238         41130         3.81         9.63         22.05         411.37         3.85 $\rho$ -Cl         CH <sub>4</sub> 99         99         246-247         276 (27500)         48.89         3.81         9.63         22.05         411.37         3.82 $\rho$ -CH <sub>4</sub> CH <sub>4</sub> 94         100         149-151         277 (25600)         48.89         5.22         10.37         48.71         5.27         10.37 $\rho$ -CH <sub>4</sub> CH <sub>4</sub> 100         149-151         277 (25600)         48.89         5.22         10.37         48.71         5.27         10.37         48.71         5.27         11.00         3.19         48.79         5.57         48.71         5.27         11.00         3.19         48.70         48.71         5.27         11.00         3.19         48.71         5.27         11.00         3.19         48.71         5.27         1         48.71         5.27         1         48.71         5.27         1         48.71         5.27         1         48.71         5.27         1         48.71         48.71         5.24         1         48.71         48.71         48.72	Fig. 10   CH <sub>3</sub>   94   92   233-235   41.30   3.81   9.63   22.05     PER   CH <sub>3</sub>   94   92   216-218   41.30   3.81   9.63   22.05     PER   CH <sub>3</sub>   94   100   149-151   277 (25600)   83.82   9.63   22.05     PCH <sub>3</sub>   CH <sub>4</sub>   94   100   149-151   277 (25600)   80.82   9.85   22.05     PCH <sub>4</sub>   CH <sub>4</sub>   94   100   149-151   273 (23200)   80.70   5.67   9.86   22.51     Ichhod A, b) Method B.	<b>2£</b>	p-Cl	$C_2H_5$	44	87	110—111	•	43.34	4.29	9.19	21.03	43.41	4.16	0.30	90 99
Fig. 1. CH <sub>3</sub> 90 93 216–218 41.30 3.81 9.63 22.05 41.05 3.22 P-CH <sub>4</sub> CH	Figure 3. (CH <sub>3</sub> ) 90 93 216–218 41.30 3.81 9.63 2.05 Pb. (CH <sub>3</sub> ) 6.64 6.89 6.247 276(2500) 50.70 5.67 9.86 22.51 tethod A, b) Method B. (C <sub>3</sub> H <sub>4</sub> ) 23 76 108–110 277(25600) 50.70 5.67 9.86 22.51 tethod A, b) Method B. (C <sub>4</sub> H <sub>4</sub> ) 24 100 149–151 277(25600) 50.70 5.67 9.86 22.51 tethod A, b) Method B. (C <sub>4</sub> H <sub>4</sub> ) 24 100 149–151 277(25600) 50.70 5.67 9.86 22.51 tethod A, b) Method B. (C <sub>4</sub> H <sub>4</sub> ) 24 100 149–151 277(25600) 50.70 5.67 9.86 22.51 tethod A, b) Method B. (C <sub>4</sub> H <sub>4</sub> ) 24 100 149–151 277(25600) 50.70 5.67 9.86 22.51 tethod A, b) Method B. (C <sub>4</sub> H <sub>4</sub> ) 24 100 149–151 277(25600) 46.88 4.72 10.93 24.98 H $^{\circ}$ $^{$	$^{2g}$	<i>m</i> -Cl	$CH_3$	94	92	233—235		41.30	3.81	9.63	22.05	41.37	3.85	62.6	20.03
Feb. CH, a 90 96 245–247 276 (27500) 85.82 8.31 8.36 19.13 35.90 3.19 p-CH, a CH, a 94 100 149–151 277 (25600) 48.89 5.22 10.37 49.71 5.22 1 p-CH, a CL, H,	Fig. 6. CH <sub>8</sub> B) 96 245-247 276 27500) 35.82 3.31 8.36 19.13 b.CH <sub>8</sub> CL <sub>8</sub> CH <sub>8</sub> CL <sub>8</sub> CH <sub>8</sub> B) 96 245-247 2762600) 48.89 5.22 10.37 c.LH <sub>8</sub> CL <sub>8</sub> H <sub>8</sub> B) 6.22 10.37 c.LH <sub>8</sub> CL <sub>8</sub> H <sub>8</sub> B) 6.22 10.37 c.LH <sub>8</sub> CL <sub>8</sub> H <sub>8</sub> B) 6.22 10.37 c.LH <sub>8</sub> CL <sub>8</sub> H <sub>8</sub> B) 6.22 10.37 c.LH <sub>8</sub> CL <sub>8</sub> H <sub>8</sub> B) 6.22 10.37 c.LH <sub>8</sub> CL <sub>8</sub> H <sub>8</sub> B) 6.22 10.37 c.LH <sub>8</sub> CL <sub>8</sub> H <sub>8</sub> B) 6.22 10.37 c.LH <sub>8</sub> CL <sub>8</sub> H <sub>8</sub> B) 6.22 10.37 c.LH <sub>8</sub> CL <sub>8</sub> B) 6.22 10.20 10.37 c.LH <sub>8</sub> CL <sub>8</sub> B) 6.22 10.20 10.37 c.LH <sub>8</sub> CL <sub>8</sub> B) 6.22 10.20 10.32 10.3	$^{2}\mathrm{h}$	ø-Cl	$CH_3$	06	93	216—218		41.30	3.81	9.63	22.05	41.05	3.92	9.72	22.16
Figure 1. Fig. 1. The Line 1. Table 1. Table 1. The Line 1. The L	Formal	<b>2i</b>	$p ext{-Br}$	$CH_3$	8	96	245—247	276(27500)	35.82	3.31	8.36	19.13	35.90	3.19	8.21	19.28
Further   C_{4}H_{4}   C_{4}H_{5}   C_{4}H_{5}   C_{4}H_{5}   C_{4}H_{5}   C_{4}H_{5}   C_{4}H_{5}   C_{4}H_{5}   C_{4}H_{5}   C_{5}H_{5}   C_{5}	Form	73	$p ext{-CH}_3$	$ m CH_3$	94	100	149—151	277 (25600)	48.89	5.22	10.37		48.71	5.23	10.30	
Child A, b) Method B.   TABLE 2.   S   NHR   S   TABLE 2.   R   C_H   C_H   S   S   S   S   S   S   S   S   S	TABLE 2.   NHR*   NHrod B.   Nethod B.   Nethod B.   Nethod B.   Nethod B.   Nethod B.   Nethod B.   TABLE 2.   $\frac{S}{C_h}$   $\frac{C_h}{C_h}$   $\frac{S}{C_h}$   $\frac{C_h}{C_h}$   $\frac{S}{C_h}$   $\frac{C_h}{C_h}$   $\frac{S}{C_h}$   $\frac{C_h}{C_h}$   $\frac{S}{C_h}$   $\frac{C_h}{C_h}$   $\frac{S}{C_h}$   $$	7k	$p ext{-CH}_3$	$C_2H_{\mathbf{s}}$	23	9/	108—110	273(23200)	50.70	2.67	98.6	22.51	50.72	5.57	99.6	21.92
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	a) N		) Method B.												
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$							A	VHR2							
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$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	R1 R2 $\frac{\text{R}^{1}\text{GH}}{\text{G}^{1}}$ $\frac{\text{K}^{1}\text{G}^{1}\text{G}}{\text{G}^{1}}$ $\frac{\text{R}^{1}\text{G}^{1}\text{H}}{\text{G}^{1}}$ $\frac{\text{C}^{1}\text{G}^{1}\text{G}}{\text{G}^{1}}$ $\frac{\text{H}^{2}}{\text{G}^{1}}$ $\frac{\text{G}^{1}\text{G}^{1}\text{G}}{\text{G}^{1}\text{max}}$ $\frac{\text{G}^{1}\text{G}^{1}\text{G}}{\text{G}^{1}\text{max}}$ $\frac{\text{G}^{1}\text{G}}{\text{G}^{1}\text{G}}$ $\frac{\text{G}^{1}\text{G}^{1}\text{G}}{\text{G}^{1}\text{max}}$ $\frac{\text{G}^{1}\text{G}}{\text{G}^{1}\text{G}}$ $\frac{\text{G}^{1}\text{G}^{1}\text{G}}{\text{G}^{1}\text{G}}$ $\frac{\text{G}^{1}\text{G}}{\text{G}^{1}\text{G}}$ $\frac{\text{G}^{1}\text{G}^{1}\text{G}}{\text{G}^{1}\text{G}}$ $\frac{\text{G}^{1}\text{G}}{\text{G}^{1}\text{G}}$						TABL		,Z-							
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$							R¹C,H4ĊH \	ΩH							
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	H CH <sub>3</sub> B7 B2 $(\epsilon_{max})$ C H N S S $(\epsilon_{max})$ C H N S S $(\epsilon_{max})$ H CH <sub>3</sub> B7 B2 $(\epsilon_{max})$ C $(\epsilon_{max})$ C H N S S $(\epsilon_{max})$ B7 B2 $(\epsilon_{max})$ B8 B8 $(\epsilon_{max})$ B1	Compd		20 20	Yield	(%)		1		Calco	1 (%)			Foun		
H         CH <sub>3</sub> 87         82 $210-211$ $218(23500)$ $46.88$ $4.72$ $10.93$ $24.98$ $46.75$ $4.67$ <	H         CH <sub>s</sub> 87         82 $210-211$ $218(23500)$ $46.88$ $4.72$ $10.93$ $24.98$ H         C <sub>2</sub> H <sub>5</sub> 61         94 $174-175$ $218(21600)$ $48.89$ $5.22$ $10.37$ H $n$ -C <sub>4</sub> H <sub>5</sub> 77         96 $150-151$ $218(19900)$ $55.34$ $6.08$ $9.39$ P-CI         CH <sub>3</sub> 81         92 $250-252$ $225(21200)$ $41.30$ $3.81$ $9.63$ $22.05$ P-CI         CH <sub>3</sub> 84         92 $250-252$ $225(21200)$ $41.30$ $3.81$ $9.63$ $22.05$ p-CI         CH <sub>3</sub> 84         92 $220-224$ $219(21800)$ $41.30$ $3.81$ $9.63$ $22.05$ p-CI         CH <sub>3</sub> 84         93 $222-224$ $219(21800)$ $41.30$ $3.81$ $9.63$ $22.05$ p-CI         Ch <sub>4</sub> 84         93 $222-224$ $219(21800)$ $41.30$ $3.81$ $6.63$ $6.63$ $6.63$			4	Ü	Ω <sup>ρ</sup>		$(\varepsilon_{ m max})$	U	H	z	SO	ט	н	z	SO
H $C_aH_a$ 61         94         174—175 $218(21600)$ 48.89         5.22         10.37         48.97         5.14         1           H $n$ - $C_4H_a$ 77         96         150—151 $218(19900)$ 52.34         6.08         9.39         52.36         5.29         5.36           H $n$ - $C_4H_a$ 77         96         150—151 $218(19900)$ 55.55         6.22         8.64         52.36         5.39         5.39 $\rho$ -Cl $CH_a$ 81         92         250—252         225(21200)         41.30         3.81         9.63         22.05         41.35         43.43         4.09         41.36         43.43         4.09 $\rho$ -Cl $C_aH_b$ 84         92         220—224         2219(21800)         41.30         3.81         9.63         22.05         41.34         3.96 $\rho$ -Cl $CH_b$ 84         93         222—224         219(21800)         41.30         3.81         9.63         22.05         41.48         3.84 $\rho$ -Cl $CH_b$ 84         93         222—224         219(24800)         43.34	H $G_2H_5$ 61         94 $174-175$ $218(21600)$ $48.89$ $5.22$ $10.37$ H $n_C d_+ H_5$ 77         96 $150-151$ $218(19900)$ $52.34$ $6.08$ $9.39$ H $n_C d_+ H_5$ 63         86 $201-202$ $218(19800)$ $55.55$ $6.22$ $8.64$ P-CI $C_2 H_5$ 67         92 $250-252$ $225(21200)$ $41.30$ $3.81$ $9.63$ $22.05$ P-CI $C_2 H_5$ 67         92 $201-202$ $225(21200)$ $41.30$ $3.81$ $9.63$ $22.05$ $\rho$ -CI $C_2 H_5$ 84         93 $224-236$ $220(25100)$ $41.30$ $3.81$ $9.63$ $22.05$ $\rho$ -CI $CH_5$ 84         93 $222-224$ $219(21800)$ $41.30$ $3.81$ $9.63$ $22.05$ $\rho$ -CI $CH_5$ 84         93 $222-224$ $219(21800)$ $41.30$ $3.81$ $9.63$ $21.03$	3 <b>a</b>	H	$CH_3$	87	82	210—211	218 (23500)	46.88	4.72	10.93	24.98	46.75	4.67	10.80	24.70
H $n$ -C <sub>4</sub> H <sub>6</sub> 77         96         150—151         218 (19900)         52.34         6.08         9.39         52.36         5.95           H $n$ -C <sub>4</sub> H <sub>6</sub> 63         86         201—202         218 (19800)         55.55         6.22         8.64         56.29         6.03 $\rho$ -Cl         CH <sub>3</sub> 81         92         250—252         225 (21200)         41.30         3.81         9.63         22.05         41.35         4.09 $\rho$ -Cl         Ch <sub>3</sub> 84         92         220—252         220 (25100)         41.30         3.81         9.63         22.05         41.34         3.91         4.09 $\rho$ -Cl         Ch <sub>3</sub> 84         93         222—224         219 (21800)         41.30         3.81         9.63         22.05         41.34         3.94 $\rho$ -Cl         Ch <sub>4</sub> 84         93         222—224         219 (21800)         41.30         3.81         9.63         22.05         41.34         3.94 $\rho$ -Cl         Ch <sub>4</sub> 89         222—224         219 (24800)         43.34         4.29         9.13         21.34         4.35 $\rho$ -Br	H $n$ -C <sub>4</sub> H <sub>9</sub> 77         96         150—151         218 (19900)         55.35         6.08         9.39           H $\frac{1}{1}$	3b	H	$\mathrm{C_2H_5}$	61	94	174—175	218 (21600)	48.89	5.22	10.37		48.97	5.14	10.29	
H         H	H         H         H         H         E         S         S         C         118 (19800)         55.55         6.22         8.64 $\frac{1}{2}$ $\rho$ -Cl         CL <sub>2</sub> H <sub>3</sub> 81         92         250—252         225 (21200)         41.30         3.81         9.63         22.05 $\rho$ -Cl         CL <sub>2</sub> H <sub>3</sub> 67         92         201—202         41.30         3.81         9.63         22.05 $\rho$ -Cl         CH <sub>3</sub> 84         93         222—224         219 (21800)         41.30         3.81         9.63         22.05 $\rho$ -Cl         CH <sub>3</sub> 84         93         222—224         219 (21800)         41.30         3.81         9.63         22.05 $\rho$ -Cl         CL <sub>2</sub> H <sub>5</sub> 71         90         150—151         219 (24800)         43.34         4.29         9.19         21.03 $\rho$ -Br         CL <sub>2</sub> H <sub>5</sub> 88         249—251         228 (20400)         37.82         3.75         8.02         18.36 $\rho$ -CH <sub>3</sub> $\rho$ -CH <sub>3</sub> 94         86         215—217         223 (27700)         48.89         5.22         10.37         9.86 $\rho$ -	3c	H	$n\text{-}\mathrm{C}_4\mathrm{H}_9$	11	96	150—151	218 (19900)	52.34	80.9	9.39		52.36	5.95	9.26	
$\boldsymbol{p}$ -ClCH38192 $250-252$ $225(21200)$ $41.30$ $3.81$ $9.63$ $22.05$ $41.35$ $4.05$ $\boldsymbol{p}$ -Cl $\boldsymbol{C}_{2}$ -H <sub>5</sub> 6792 $201-202$ $43.34$ $4.29$ $9.19$ $21.03$ $43.43$ $4.09$ $\boldsymbol{m}$ -Cl $\boldsymbol{C}_{2}$ -H <sub>5</sub> 9489 $234-236$ $220(25100)$ $41.30$ $3.81$ $9.63$ $22.05$ $41.34$ $3.96$ $\boldsymbol{o}$ -Cl $\boldsymbol{C}_{2}$ -H <sub>5</sub> 7190 $150-151$ $219(24800)$ $43.34$ $4.29$ $9.19$ $21.03$ $43.53$ $43.53$ $\boldsymbol{p}$ -Br $\boldsymbol{C}_{2}$ -H <sub>5</sub> 6888 $249-251$ $228(20400)$ $35.82$ $3.31$ $8.36$ $19.13$ $36.01$ $3.32$ $\boldsymbol{p}$ -Br $\boldsymbol{C}_{2}$ -H <sub>5</sub> $55$ 90 $230-232$ $228(19700)$ $37.82$ $37.8$ $37.89$ $37.89$ $\boldsymbol{p}$ -CH <sub>3</sub> $\boldsymbol{C}$ -H <sub>5</sub> $34$ $49$ $86$ $215-217$ $223(27700)$ $48.89$ $5.22$ $10.37$ $23.68$ $47.60$ $5.06$ $15$ $\boldsymbol{p}$ -CH <sub>3</sub> $\boldsymbol{Q}$ -H <sub>5</sub> $$	$\boldsymbol{\rho}$ -Cl         CH <sub>3</sub> 81         92         250—252         225 (21200)         41.30         3.81         9.63         22.05 $\boldsymbol{\rho}$ -Cl $G_2$ -H <sub>5</sub> 67         92         201—202         43.34         4.29         9.19         21.03 $\boldsymbol{\rho}$ -Cl $G_2$ -H <sub>5</sub> 84         92         234—236         220 (25100)         41.30         3.81         9.63         22.05 $\boldsymbol{\rho}$ -Cl $G_2$ -H <sub>5</sub> 71         90         150—151         219 (24800)         41.30         3.81         9.63         22.05 $\boldsymbol{\rho}$ -Cl $G_2$ -H <sub>5</sub> 71         90         150—151         219 (24800)         43.34         4.29         9.19         21.03 $\boldsymbol{\rho}$ -Br $G_2$ -H <sub>5</sub> 68         88         249—251         228 (20400)         35.82         3.75         8.02         18.36 $\boldsymbol{\rho}$ -Ch <sub>3</sub> $\boldsymbol{G}$ -H <sub>5</sub> 94         86         215—217         223 (27700)         48.89         5.22         10.37         23.68 $\boldsymbol{\rho}$ -Ch <sub>3</sub> $\boldsymbol{\rho}$ -Ch <sub>4</sub> 49         85         204—206         223 (28200)         50.70         5.67         9.86         18.36	3 <b>d</b>	Н	$\langle H \rangle$	63	98	201 - 202	218 (19800)	55.55	6.22	8.64		56.29	6.03	8.35	
$\boldsymbol{p}\text{-Cll}$ $\mathbf{C}_2\mathbf{H}_5$ $67$ $92$ $201-202$ $43.34$ $4.29$ $9.19$ $21.03$ $43.43$ $4.09$ $\boldsymbol{m}\text{-Cll}$ $\mathbf{CH}_3$ $\mathbf{GH}_3$ $94$ $89$ $234-236$ $220(25100)$ $41.30$ $3.81$ $9.63$ $22.05$ $41.34$ $3.96$ $\boldsymbol{o}\text{-Cll}$ $\mathbf{CH}_3$ $84$ $93$ $222-224$ $219(21800)$ $41.30$ $3.81$ $9.63$ $22.05$ $41.48$ $3.84$ $\boldsymbol{o}\text{-Cl}$ $\mathbf{CH}_3$ $68$ $88$ $249-251$ $228(20400)$ $35.82$ $3.31$ $8.36$ $19.13$ $36.01$ $3.32$ $\boldsymbol{p}\text{-Br}$ $\mathbf{C}_2\mathbf{H}_3$ $68$ $88$ $249-251$ $228(20400)$ $37.82$ $3.75$ $8.02$ $18.36$ $3.789$ $3.789$ $\boldsymbol{p}\text{-CH}_3$ $\mathbf{CH}_3$ $\mathbf{GH}_3$	$p$ -Cl $G_2$ Hs         67         92 $201-202$ 43.34         4.29         9.19         21.03 $m$ -Cl $CH_3$ 94         89 $234-236$ $220(25100)$ 41.30         3.81         9.63         22.05 $o$ -Cl $CH_3$ 84         93 $222-224$ $219(21800)$ 41.30         3.81         9.63         22.05 $o$ -Cl $CH_3$ 71         90         150-151 $219(24800)$ 41.30         3.81         9.63         22.05 $p$ -Br $CH_3$ 68         88 $249-251$ $228(20400)$ 35.82         3.31         8.36         19.13 $p$ -CH <sub>3</sub> $CH_3$ 94         86 $215-217$ $223(27700)$ 48.89         5.22         10.37         23.68 $\Delta$ -CH <sub>3</sub> $\Delta$ -CH <sub>3</sub> $\Delta$ -CH <sub>3</sub> 49         85 $204-206$ $223(28200)$ 50.70         5.67         9.86 $\Delta$ -CH <sub>3</sub>	Зе	<i>p</i> -CI	CH3	81	92	250—252	225(21200)	41.30	3.81	9.63	22.05	41.35	4.05	9.75	22.13
m-ClCH39489 $234-236$ $220(25100)$ $41.30$ $3.81$ $9.63$ $22.05$ $41.34$ $3.96$ $o$ -ClCH38493 $222-224$ $219(21800)$ $41.30$ $3.81$ $9.63$ $22.05$ $41.48$ $3.84$ $o$ -ClCgH37190 $150-151$ $219(24800)$ $43.34$ $4.29$ $9.19$ $21.03$ $43.53$ $43.53$ $p$ -BrCH36888 $249-251$ $228(20400)$ $35.82$ $3.31$ $8.36$ $19.13$ $36.01$ $3.32$ $p$ -CH3CH3GH386 $230-232$ $228(19700)$ $37.82$ $3.75$ $8.02$ $18.36$ $37.89$ $3.61$ $p$ -CH3CH3 $49$ 86 $215-217$ $223(27700)$ $48.89$ $5.22$ $10.37$ $23.68$ $47.60$ $5.06$ $11$ $p$ -CH3CgH34985 $204-206$ $223(28200)$ $50.70$ $5.67$ $9.86$ $50.85$ $5.75$	m-Cl         CH <sub>3</sub> 94         89         234—236         220 (25100)         41.30         3.81         9.63         22.05           o-Cl         CH <sub>3</sub> 84         93         222—224         219 (21800)         41.30         3.81         9.63         22.05           o-Cl         C <sub>2</sub> H <sub>5</sub> 71         90         150—151         219 (24800)         43.34         4.29         9.19         21.03           p-Br         CH <sub>3</sub> 68         88         249—251         228 (2400)         35.82         3.31         8.36         19.13           p-CH <sub>3</sub> Ch <sub>4</sub> 94         86         215—217         228 (19700)         37.82         3.75         8.02         18.36           p-CH <sub>3</sub> Ch <sub>4</sub> 86         215—217         223 (27700)         48.89         5.22         10.37         23.68           Method C,         b) Method D.         10.37         204—206         223 (28200)         50.70         5.67         9.86         3.68	3£	<i>p</i> -Cl	$\mathrm{C_2H_5}$	29	92	$201 - \!\!\!-\!\!\!\!-\!\!\!\!202$		43.34	4.29	9.19	21.03	43.43	4.09	9.19	21.10
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	o-Cl         CH <sub>s</sub> 84         93         222—224         219(21800)         41.30         3.81         9.63         22.05           o-Cl         C <sub>2</sub> H <sub>s</sub> 71         90         150—151         219(24800)         43.34         4.29         9.19         21.03           p-Br         CH <sub>s</sub> 68         88         249—251         228(20400)         35.82         3.31         8.36         19.13           p-Br         C <sub>2</sub> H <sub>s</sub> 55         90         230—232         228(19700)         37.82         3.75         8.02         18.36           p-CH <sub>s</sub> CH <sub>s</sub> 49         86         215—217         223(27700)         48.89         5.22         10.37         23.68           Method C, b) Method D.         Method D.         30.70         5.67         9.86         3.56		<i>m</i> -CI	$CH_3$	94	83	234—236	220(25100)	41.30	3.81	9.63	22.05	41.34	3.96	9.68	22.18
o-Cl $C_2H_5$ 7190150—151 $219(24800)$ $43.34$ $4.29$ 9.19 $21.03$ $43.53$ $4.32$ $\textbf{p}\text{-Br}$ $CH_3$ 6888 $249$ —251 $228(20400)$ 35.823.31 $8.36$ 19.1336.013.32 $\textbf{p}\text{-Br}$ $C_2H_5$ 5590 $230$ —232 $228(19700)$ 37.823.75 $8.02$ 18.3637.893.61 $\textbf{p}\text{-CH}_3$ $CH_3$ 9486 $215$ —217 $223(27700)$ 48.895.2210.3723.6847.605.061 $\textbf{a}$ $\textbf{p}\text{-CH}_3$ $C_2H_5$ 4985 $204$ —206 $223(28200)$ 50.705.679.8650.855.75	o-Cl         C <sub>2</sub> H <sub>5</sub> 71         90         150—151         219 (24800)         43.34         4.29         9.19         21.03           P-Br         CH <sub>3</sub> 68         88         249—251         228 (20400)         35.82         3.31         8.36         19.13           P-Br         Ch <sub>2</sub> H <sub>5</sub> 55         90         230—232         228 (19700)         37.82         3.75         8.02         18.36           P-CH <sub>3</sub> CH <sub>3</sub> 94         86         215—217         223 (27700)         48.89         5.22         10.37         23.68           Method C, b) Method D.         Method D.         Action of the control o	3 <b>p</b>	9-CI	$CH_s$	84	93	222—224	219(21800)	41.30	3.81	9.63	22.05	41.48	3.84	9.65	22.12
$p\text{-Br}$ CH <sub>3</sub> 6888249—251228 (20400)35.823.318.3619.1336.013.32 $p\text{-Br}$ $C_2H_5$ 5590230—232228 (19700)37.823.758.0218.3637.893.61 $p\text{-CH}_3$ CH <sub>3</sub> 9486215—217223 (27700)48.895.2210.3723.6847.605.061a $p\text{-CH}_3$ $C_2H_5$ 4985204—206223 (28200)50.705.679.8650.855.75	p-br         CH <sub>3</sub> 68         88         249—251         228 (20400)         35.82         3.31         8.36         19.13           p-Br         C <sub>2</sub> H <sub>5</sub> 55         90         230—232         228 (19700)         37.82         3.75         8.02         18.36           p-CH <sub>3</sub> CH <sub>3</sub> 94         86         215—217         223 (27700)         48.89         5.22         10.37         23.68           method C, b) Method D.         Method C, b) Method D.         85         204—206         223 (28200)         50.70         5.67         9.86	:5 :5		$C_2H_{\mathfrak{p}}$	71	6	150—151	219 (24800)	43.34	4.29	9.19	21.03	43.53	4.32	9.27	21.17
$p$ -br $C_{u}H_{s}$ 55         90         230—232         228(19700)         37.82         3.75         8.02         18.36         37.89         3.61 $p$ -CH <sub>s</sub> CH <sub>s</sub> 94         86         215—217         223(27700)         48.89         5.22         10.37         23.68         47.60         5.06         1 $p$ -CH <sub>s</sub> C <sub>2</sub> H <sub>s</sub> 49         85         204—206         223(28200)         50.70         5.67         9.86         50.85         5.75	$p\text{-Br}$ $C_2H_5$ $55$ $90$ $230-232$ $228(19700)$ $37.82$ $3.75$ $8.02$ $18.36$ $p\text{-CH}_3$ $CH_3$ $CH_3$ $48$	:F	p-Br	$CH_3$	89	88	249—251	228 (20400)	35.82	3.31	8.36	19.13	36.01	3.32	8.35	19.20
<i>p</i> -CH <sub>3</sub> CH <sub>3</sub> 94 86 215—217 223(27700) 48.89 5.22 10.37 23.68 47.60 5.06 1 <i>p</i> -CH <sub>3</sub> C₂H <sub>5</sub> 49 85 204—206 223(28200) 50.70 5.67 9.86 50.85 5.75	p-CH <sub>3</sub> CH <sub>3</sub> 94         86         215—217         223 (27700)         48.89         5.22         10.37         23.68           p-CH <sub>3</sub> C <sub>2</sub> H <sub>5</sub> 49         85         204—206         223 (28200)         50.70         5.67         9.86           Method C, b) Method D.         Action of the control of the c	¥ .	p-Br	$\mathrm{C}_{p}^{\mathrm{H}_{g}}$	22	06	230—232	228 (19700)	37.82	3.75	8.02	18.36	37.89	3.61	8.35	18.36
P-CH <sub>3</sub> C <sub>2</sub> H <sub>5</sub> 49 85 204—206 223(28200) 50.70 5.67 9.86 50.85 5.75	<i>P</i> -CH <sub>3</sub> C <sub>2</sub> H <sub>5</sub> 49 85 204—206 223 (28200) 50.70 5.67 9.86 Method C, b) Method D.	<u>ا</u> د	p-CH <sub>3</sub>	$\widetilde{\operatorname{CH}}_{3}$	96	98	- 1	223 (27700)	48.89	5.22	10.37	23.68	47.60	5.06	10.00	23.68
The second section is		arc	p-CH <sub>3</sub>	$C_2H_5$	49	82		223 (28200)	50.70	2.67	98.6		50.85	5.75	9.82	

and mass spectra and by the results of elemental analyses. The IR spectrum of 2a displayed bands at 3320  $(v_{\rm NH})$  and 1610  $(v_{\rm C=C})$  cm<sup>-1</sup>. The NMR spectrum of 2a exhibited an AB pattern centered at  $\delta$  7.28 and  $\delta$ 7.77  $(J_{\rm AB}{=}15.2~{\rm Hz})$  due to the vicinal olefinic protons,  $H_{\rm A}$  and  $H_{\rm B}$ . The large magnitude of this coupling proves that 2 has the *trans* rather than the cis configuration.

3 - Alkylamino - 5 - phenyl - 1,1 - dioxo-5,6 - dihydro-1,4,2 - dithiazines 3. The Base-Catalyzed Intramolecular Cycliza-When the potassium salt of 2 detion of 2. scribed above was dissolved in warm water (Table 2, Method C), or when 2 was dissolved in a dilute alkali (Table 2, Method D), a new heterocycle, 3, began to separate out after a few minutes. This Michaeltype reaction carried out at pH values below 12.55 gave 3 in a good yield, and the rate of cycloaddition increased with an increase in the base concentration. Only a one-fourth equivalent of the base was sufficient to effect the cycloaddition of the sulfonylthiourea. In the pH range from 12.55 to 13.40, a mixture of 2 and 3 was obtained. Under strongly basic conditions (pH>13.40), no cycloaddition occurred. The IR spectrum of 3a displayed a strong band at 1560-1535 cm<sup>-1</sup> due to the N=C bond, but no absorption due to the C=C group was observed in the region of 1610 cm.-1 In NMR pattern of 3a, ring protons, H<sub>A</sub>H<sub>C</sub>H<sub>R</sub> appeared as an ABX pattern consisting of three quartets of  $H_A$  centered at  $\delta 3.53$ ,  $H_C$   $\delta$  3.67 and  $H_B$   $\delta$ 5.00 ( $J_{AC}$ =14.0 Hz,  $J_{AB}$ =11.7 Hz, and  $J_{BC}$ =4.4 Hz) respectively (Fig. 1). The observed coupling con-

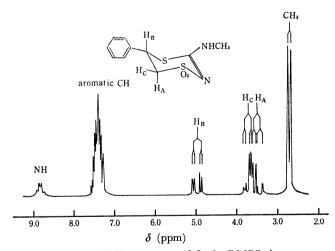


Fig. 1. NMR spectrum of 3a in DMSO-d<sub>6</sub>.

stants,  $J_{AB}$  and  $J_{BC}$ , may be compared with those for the axial-axial and axial-equatorial protons respectively. The peak at m/e 121.011 in the mass spectrum was in entire agreement with the fragment ion  $C_6H_5CS^+$ , derived from only the six-membered heterocycle, 3. The structures of 3b-3m were inferred because they were analogous with 3a in their preparations and spectral data. The Michael mechanism is assumed to be like Scheme 1.

Thermal Cyclization of 2. Thioureas, 2, were cyclized to 3 by heating; they were then divided into two groups. The changes in their IR spectra showed that the first group, 2a—2d, 2f, 2j, and 2k, underwent

Scheme 1.

a cyclization upon melting, while the second group, **2e** and **2g—2i**, underwent such a cyclization before melting. The cyclization temperatures of the latter, observed in their DTA curves, were as follows: **2e**, 141—146°C; **2g**, 131—135°C; **2h**, 140—145°C; **2i**, 157—160°C. These cycloadducts, when recrystallized, gave melting points identical with those of the products obtained by Methods C and D.

Base-Catalyzed Ring-Cleavage of 3. The 3 cycloadduct could be split into 2 when the reaction media were more basic than those used in effecting the cycloaddition (Table 1, Method B). Cleavage proceeded very fast in a solvent such as alkaline aqueous acetone, even at 0°C. Only cleaved 2 was obtained when the pH of the solution was above 13.30. A mixture of 2 and 3 was obtained in the pH range from 12.70 to 13.30. This ring-cleavage is the reverse of the Michael cycloaddition, and a mechanism in the direction the reverse of that in Scheme 1 is assumed.

## **Discussion**

We have been interested in 2 because the SO<sub>2</sub> group can conjugate with and activate a neighboring ethylenic double bond and stabilize the thiolate anion in basic media. As 2 has both donor and acceptor in one molecule, it should be possible to effect intramolecular Michael cycloaddition. It has indeed been found that 2 gives the intramolecular cycloadduct 3 in weakly basic media. Compounds with the general formulation —CH=CHSO<sub>2</sub>NHC(=S)— would give intramolecular Michael cycloadducts.

A Michael reversible system can be influenced by the basicity of the solution. Cleavage seems to require a base B:, strong enough to remove active  $\beta$ -hydrogen. A  $\beta$  sulfonyl group is known to accelerate the rate of the base-catalyzed elimination. Gleavage proceeded too rapidly to determine certain details of this reaction, but the higher rate of cleavage was clearly associated with the higher concentration of the base.

## Experimental

The melting points were determined on a Yanagimoto micro-melting-point measuring apparatus MP-S2 and are

<sup>6)</sup> E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, New York (1959), p. 499.

uncorrected. The IR and UV spectra were recorded on JASCO IRA-1 and Hitachi EPS-3T spectrometers respectively. The NMR spectra were determined with a Varian HA-100 spectremeter, with TMS as the internal standard and the mass spectra, with a JMS-01SG spectrometer.

N-(2-Phenylethene-1-sulfonyl)-N'-methylthiourea 2a. Method A: To 2-phenylethene-1-sulfonamide 0.0164 mol) in acetone (30 ml), we added methyl isothiocyanate  $(1.32~\mathrm{g},~0.0180~\mathrm{mol})$  and anhydrous potassium carbonate (1.32 g, 0.0220 mol), after which the reaction mixture was refluxed for 20 hr with stirring. The resulting potassium salt of 2a was collected on a filter and washed with acetone to remove the unchanged sulfonamide. This salt was dissolved in water (200 ml), and the solution was acidified with concentrated hydrochloric acid to give 4.0 g (95%) of 2a. Recrystallization from methanol then gave colorless crystals. IR (KBr): 3320 ( $\nu_{NH}$ ), 1610 ( $\nu_{C=C}$ ), 1570  $(\delta_{\rm NH})$ , 1495, 1435, 1380  $(v_{\rm SO_2})$ , 1150, and 1130  $(v_{\rm SO_2})$ , 1050, 960, 885, 740, and 690 cm<sup>-1</sup>. NMR (acetone- $d_6$ ):  $\delta$  3.08 (d,  $J_{\rm NHCH}=\!5.0~{\rm Hz},~3{\rm H},~{\rm CH_3}),~7.28$  (d,  $J_{\rm AB}\!=\!15.2$ Hz, 1H, H<sub>A</sub>), 7.77 (d,  $J_{AB}$ =15.2 Hz, 1H, H<sub>B</sub>), 7.47 $\pm$ 0.05 (m, 5H, phenyl), 8.40 (broad, 1H, SO<sub>2</sub>NH), 8.90 (broad, 1H, NH). Mass spectrum (75 eV) m/e (rel. intensity): 77 (56), 91 (24), 103 (41), 135 (41), 136 (100), 192 (29), 256  $(M^+, 1.8).$ 

Method B: To 3-methylamino-5-phenyl-1,1-dioxo-5,6-dihydro-1,4,2-dithiazine (0.51 g, 0.0020 mol) in acetone (30 ml), we added a  $1.0 \,\mathrm{N}$  NaOH solution (4.0 ml, 0.0040 mol) and then stirred the mixture for 1 hr at room temperature. The acetone was then evaporated under reduced

pressure, and the residual solution was acidified with concentrated hydrochloric acid to give 0.48 g (94%) of 2a.

3-Methylamino-5-phenyl-1,1-dioxo-5,6-dihydro-1,4,2-dithiazine Method C: When potassium salt of 2a obtained 3a. from 2-phenylethene-1-sulfonamide (2.20 g, 0.0120 mol) by Method A was dissolved in warm water (150 ml), 3a began to separate out after a few minutes. After the mixture had stood overnight, it was filtered to give 1.91 g (87%) of 3a. Recrystallization from methanol gave colorless crystals. IR (KBr): 3280 ( $\nu_{NH}$ ), 1560—1535 ( $\nu_{N=C}$ ), 1405, 1300  $(\nu_{SO_2})$ , 1125  $(\nu_{SO_2})$ , 960, 750, and 690 cm<sup>-1</sup>. NMR (DMSO $d_6$ ):  $\delta$  2.74 (d,  $J_{\text{NHCH}_3}$ =4.5 Hz, 3H, CH<sub>3</sub>), 3.53 (q,  $J_{\text{AC}}$ = 14.0 Hz,  $J_{\text{AB}}$ =11.7 Hz, 1H, H<sub>A</sub>), 3.67 (q,  $J_{\text{AC}}$ =14.0 Hz,  $J_{BC}$ =4.4 Hz, 1H, H<sub>C</sub>), 5.00 (q,  $J_{AB}$ =11.7 Hz,  $J_{BC}$ = 4.4 Hz, 1H,  $H_B$ ),  $7.41 \pm 0.1$  (m, 5H, phenyl), 8.70 (broad, 1H, NH). Mass spectrum (75 eV) m/e (rel. intensity): 77 (26), 78 (25), 91 (38), 104 (100), 119 (34), 121.011 (13), 135 (38), 136 (25), 177 (6), 191 (20), 256.032 (calculated molecular weight, 256.034, 21).

Method D: When 2a (0.77 g, 0.0030 mol) was dissolved in a warm 0.1 M  $K_2\text{CO}_3$  solution (30 ml, 0.0030 mol), 3a began to separate out in a few minutes. After the mixture had stood overnight, it was filtered to give 0.63 g (82%) of 3a.

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