Synthesis of Arylethylenesulfonamides and Intramolecular Rearrangement of *N*-(Arylethylenesulfonyl)thioureas

Kiyoshi HASEGAWA, Syuzi HIROOKA and Tadashi SASAKI*

Department of Industrial Chemistry, Faculty of Engineering, Toyama University, Takaoka-shi, Toyama 933

** Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chigusa-ku, Nagoya 464*

(Received December 13, 1974)

The reactions of *p*- and *p'*- substituted *N*-(2,2-diarylethylenesulfonyl)- (**8**), *N*-[2-phenyl-2-(α-naphthyl)ethylenesulfonyl]- (**9**), and *N*-(*p*-nitrostyrene-1-sulfonyl)-*N'*-alkylthioureas (**12**) with bases afforded new intramolecularly rearranged *N*-alkyl-*S*-(2,2-diarylvinyl)- (**13**), *N*-alkyl-*S*-[2-phenyl-2-(α-naphthyl)vinyl]- (**14**), and *N*-alkyl-*S*-(*p*-nitrostyryl)isothioureas (**15**), respectively. *p*- and *p'*-Substituted 2,2-diarylethylene-*N*-methylsulfonamides (**6**) were treated with carbon disulfide and alkyl halides in the presence of a base to give alkyl 2,2-diarylvinyl trithiocarbonates (**17**). The order of reactivity of the sulfonylthioureas and -amides indicates that the rearrangement is retarded by electron-releasing *p*-substituents on benzene rings (Cl>H>CH_3>OCH_3).

Waldan and Pütter reported that *N*-arylnitrostyrenesulfonamide undergoes intramolecular rearrangement on C-1 to afford a sulfur free compound, stilbene derivatives.[1] The reaction requires the presence of an electron-withdrawing nitro group in the *ortho* or *para* position. In continuation of our studies on α,β-unsaturated sulfonamides,[2a-d] we have recently proposed[3] a five-membered Sn mechanism for the formation of trithiocarbonates ($(C_6H_5)_2C{=}CHSC(=S)SR$ (**17**) from 2,2-diphenylethylenesulfonamide (**5a**) ($R^1{=}R^2{=}H$) in the presence of carbon disulfide, and concluded that this rearrangement on C-1 is characteristic of **5a**, in which C-2 has two phenyl groups. However, the effect of *p*- and *p'*-substituents on the formation of **17** was not investigated. We have now studied the base treatment of thioureas **8**, **9** and **12** which were prepared as model compounds to confirm the proposed mechanism. This paper describes the mechanism for a Smiles-type reaction of the thioureas and for the formation of **17** from **6**, carbon disulfide and alkyl halides, and also describes the effect of *p*-substituents on the yield of the rearranged products.

Results and Discussion

Syntheses of α,β-Unsaturated Sulfonamides and Thioureas. The convenient sulfochlorination method of styrene[4] gave generally low yields (<10%) when applied to *p*- and *p'*-substituted 1,1-diarylethylenes (**1**). Scheme 1 shows the synthetic pathways of sulfonamides and thioureas. Compound **1** and dioxane–sulfur trioxide gave 2,2-diarylethylenesulfonates (**3**) (Table 1), which were converted into 2,2-diarylethylenesulfonyl chlorides (**4**) (Table 2). Sulfonamides **5** and **6** were pre-

TABLE 1. SODIUM SULFONATES[a]

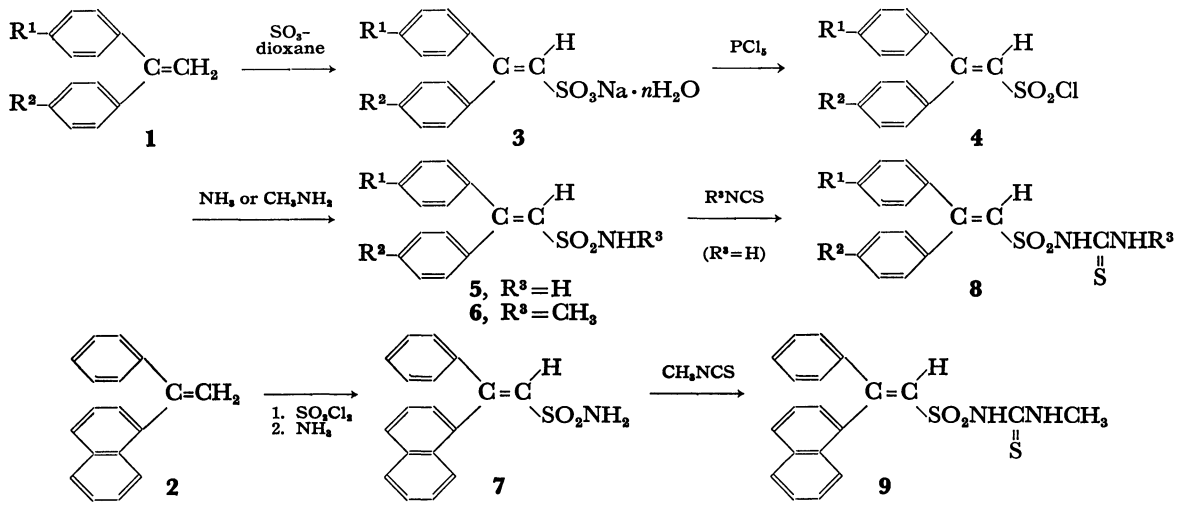
Compd.	R^1	R^2	*n*	Yield[b] (%)	Mp (°C)	Calcd (%)			Found (%)		
						C	H	S	C	H	S
3a	H	H	1	85	174—176	55.99	4.36	10.68	55.75	4.07	10.51
3b	H	Cl	1	64	177—179	50.23	3.61	9.58	50.00	3.87	9.81
3c	Cl	Cl	2	86	170—171	43.42	3.38	8.28	43.16	3.22	8.36
3d	H	CH_3	2	70	167—168	54.21	5.16	9.65	53.92	5.05	9.58
3e	CH_3	CH_3	2	78	140—142	55.48	5.53	9.26	55.42	5.32	9.37
3f	H	OCH_3	1	54	115—116	54.53	4.58	9.71	54.31	4.40	9.87
3g	OCH_3	OCH_3	1	56	122—124	53.32	4.76	8.90	53.42	4.77	8.89

a) They have water of crystallization (n=1—2). b) Sulfonates **3a-e** were slightly soluble in cold water. Sulfonates **3f** and **3g** were moderately soluble in cold water, and several crops of crystals were taken by evaporating the aqueous filtrate.

TABLE 2. SULFONYL CHLORIDES

Compd	R^1	R^2	Yield (%)	Mp (°C)	Recrystn solvent	Calcd (%)			Found (%)		
						C	H	S	C	H	S
4a	H	H	71	81— 82[a]	b	60.32	3.98	11.50	60.16	3.72	11.42
4b	H	Cl	56	94— 95	b	53.69	3.22	10.24	53.46	2.94	10.22
4c	Cl	Cl	49	89— 91	c	48.36	2.61	9.22	48.54	2.47	9.39
4d	H	CH_3	33	119—120	b	61.53	4.48	10.95	61.40	4.58	10.83
4e	CH_3	CH_3	10	56— 58	c	62.63	4.93	10.45	62.87	4.78	10.22
4f	H	OCH_3	17	88— 90	c	58.34	4.24	10.83	58.63	4.04	10.77
4g	OCH_3	OCH_3	42	109—111	d	56.71	4.46	9.46	56.46	4.68	9.46

a) Lit.[5] mp 65 °C. b) $CHCl_3$–petroleum ether. c) Benzene–petroleum ether. d) Ether–petroleum ether.



Scheme 1.

Table 3. Sulfonamides

Compd	R^1	R^2	R^3	Yield (%)	Mp (°C)	Calcd (%) C	H	N	S	Found (%) C	H	N	S
5b	H	Cl	H	94	116—117	57.24	4.12	4.77	10.91	56.98	4.02	4.98	10.98
5c	Cl	Cl	H	95	152—153	51.22	3.38	4.27	9.77	51.48	3.36	4.00	9.41
5d	H	CH_3	H	97	151—152	65.92	5.53	5.13	11.72	66.20	5.65	5.22	11.68
5e	CH_3	CH_3	H	95	146—147	66.88	5.96	4.88	11.14	67.04	5.93	4.61	11.15
5f	H	OCH_3	H	97	92— 94	62.28	5.23	4.84	11.06	62.25	5.10	4.84	11.12
5g	OCH_3	OCH_3	H	95	149—150	60.18	5.37	4.39	10.12	60.16	5.29	4.12	10.12
6a	H	H	CH_3	93	119—120	65.92	5.53	5.13	11.72	66.11	5.59	5.27	11.77
6b	H	Cl	CH_3	92	96— 98	58.53	4.58	4.55	10.42	58.77	4.62	4.65	10.30
6c	Cl	Cl	CH_3	93	132—134	52.64	3.83	4.09	9.37	52.84	3.69	4.35	9.56
6d	H	CH_3	CH_3	91	145—146	66.88	5.96	4.88	11.14	67.01	6.16	4.87	11.04
6e	CH_3	CH_3	CH_3	90	118—119	67.76	6.36	4.65	10.62	67.51	6.60	4.74	10.52
6f	H	OCH_3	CH_3	98	107—109	63.36	5.65	4.62	10.55	63.25	5.86	4.37	10.71
6g	OCH_3	OCH_3	CH_3	94	78— 79	61.25	5.75	4.20	9.40	61.46	5.48	3.95	9.17
7	1-Phenyl-1-(α-naphthyl)ethylene-sulfonamide			78— 80[a]		69.89	4.89	4.53	10.15	69.64	4.78	4.24	9.86

a) Overall yield from **2**.

Table 4. Thioureas

Compd	R^1	R^2	R^3	Yield (%)	Mp (°C)	Calcd (%) C	H	N	S	Found (%) C	H	N	S
8a	H	H	CH_3	95	158—159	57.83	4.85	8.43	19.26	57.97	4.77	8.37	19.33
8b	H	H	C_2H_5	72	142—144	58.95	5.24	8.09	18.48	58.73	5.21	7.95	18.26
8c	H	H	n-C_3H_7	77	154—156	59.99	5.59	7.77	17.76	59.80	5.47	7.70	17.68
8d	H	H	n-C_4H_9	67	151—153	60.95	5.92	7.48	17.09	61.00	5.82	7.77	16.96
8e	H	H	C_6H_5	89	142—143	63.95	4.60	7.10	16.23	63.85	4.78	7.03	16.33
8f	H	H	p-ClC_6H_4	95[a]	137—139	54.01	3.45	6.00	13.73	54.08	3.75	5.77	13.35
8g	H	H	p-$CH_3C_6H_4$	95[a]	190—191	59.17	4.29	6.27	14.33	58.89	4.37	6.28	14.09
8h	H	Cl	CH_3	58	136—138	52.38	4.12	7.64	17.48	52.20	3.98	7.68	17.30
8i	Cl	Cl	CH_3	49	133—134	47.88	3.52	6.98	15.98	48.17	3.51	6.80	15.91
8j	H	CH_3	CH_3	95	151—152	58.95	5.24	8.09	18.48	58.95	5.32	7.89	18.44
8k	CH_3	CH_3	CH_3	91	168—170	59.99	5.59	7.77	17.76	60.27	5.52	8.00	17.67
8l	H	OCH_3	CH_3	53	132—134	56.35	5.01	7.73	17.66	56.28	4.84	7.91	18.07
8m	OCH_3	OCH_3	CH_3	91	145—146	55.10	5.14	7.14	16.31	54.85	5.05	7.13	16.18
9	2-Phenyl-2-(α-naphthyl)-ethylenesulfonyl		CH_3	68	164—166	62.82	4.75	7.33	16.74	62.89	4.48	7.31	16.94
12	p-Nitrostyrene-1-sulfonyl		CH_3	18	234—236	39.87	3.68	13.95	21.25	40.12	3.55	13.73	21.01

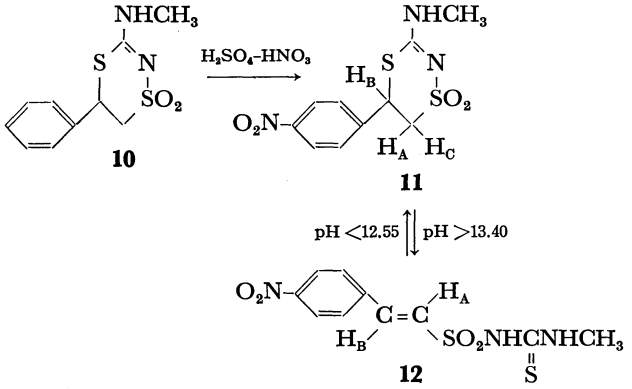
a) Purified as potassium salts.

Table 5. Isothioureas

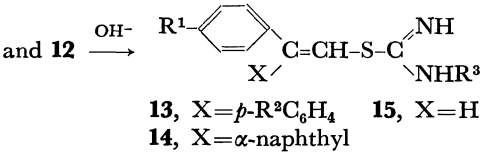
Compd	R^1	X[a]	R^3	Yield(%) Method A[b]	Yield(%) Method B[c]	Mp (°C)	Calcd (%) C	Calcd (%) H	Calcd (%) N	Calcd (%) S	Found (%) C	Found (%) H	Found (%) N	Found (%) S
13a	H	C_6H_5	CH_3	70	93	146—147	71.62	6.06	10.44	11.93	71.90	6.16	10.34	11.75
13b	H	C_6H_5	C_2H_5	56	92	164—166	72.32	6.43	9.92	11.33	72.26	6.47	9.90	11.20
13c	H	C_6H_5	n-C_3H_7	31[d]		141—143	72.95	6.80	9.45	10.80	72.84	6.76	9.21	10.83
13d	H	C_6H_5	C_6H_5	75	78	195—196	76.34	5.49	8.48	9.69	76.24	5.25	8.27	9.63
13e	H	ClC_6H_4	CH_3	89	97	64— 66	63.46	4.99	9.25	10.59	63.64	4.73	9.14	10.58
13f	Cl	ClC_6H_4	CH_3	92	98	217—218	56.98	4.18	8.31	9.51	56.88	4.08	8.22	9.25
13g	H	$H_3CC_6H_4$	CH_3	41	90	159—161	72.32	6.43	9.92	11.33	72.54	6.43	9.72	11.05
13h	CH_3	$H_3CC_6H_4$	CH_3	30	89	160—162	72.95	6.80	9.45	10.40	72.70	6.64	9.23	10.18
13i	H	$H_3COC_6H_4$	CH_3	27	81	130—132	68.44	6.08	9.39	10.73	68.25	6.21	9.20	10.37
13j	OCH_3	$H_3COC_6H_4$	CH_3	5	51	172—173	65.84	6.14	8.53	9.75	65.83	6.41	8.29	9.68
14	H	α-naphthyl	CH_3		80	82— 84	75.45	5.70	8.80		75.65	5.90	9.07	
15	NO_2	H	CH_3	79		181—182	50.63	4.67	17.72	13.49	50.73	4.52	17.75	13.69

a) X=*p*-$R^2C_6H_4$. b) 80 °C, 2 hr in DMF. c) 80 °C, 15 hr in DMF. d) Purified by chromatography on silicagel using $CHCl_3$ as the eluent.

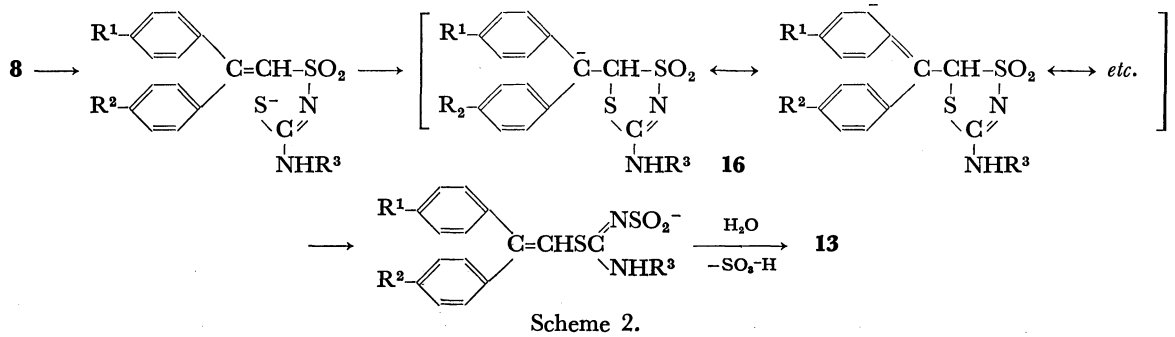
pared from them with aqueous ammonia or methylamine (Table 3). A 2-α-naphthyl derivative (**7**) was obtained by a procedure similar to that described by Culbortson and Dietz.[4] A mixture of **5**, potassium carbonate and isothiocyanates in acetone was refluxed to yield thioureas **8**. Similar treatment of **7** afforded **9** (Table 4). As a nitrated derivative, **12**, could not be formed from *p*-nitrostyrenesulfonamide and methyl isothiocyanate, it was prepared by nitration of 3-methylamino-5-phenyl-1,1-dioxo-5,6-dihydro-1,4,2-dithiazine[2a] (**10**) followed by hydrolytic cleavage of the ring C-S bond. Thiourea **12** was recyclized under weakly alkaline conditions and also by heating at 145 °C. The structures of **8**, **9**, **11** and **12** were determined on the basis of analytical and spectral data. The NMR spectrum of **11** shows that **11** consists of about a 3:2 mixture of 3-methylamino and 3-methylimino tautomers in DMSO-d_6.



A New Intramolecular Rearrangement of Thioureas to Isothioureas. Thioureas **8** and **9** were treated with ten molar equivalents of aqueous 5 M NaOH in DMF for 2 hr at 80 °C (Method A) or for 15 hr at 80 °C (Method B) to afford rearranged isothioureas **13** and **14** respectively (Table 5).



The rearrangement was carried out with variations of the *p*- and *p'*-substituents from electron-withdrawing to -releasing groups. All of the isothioureas were resistant to hydrolytic decomposition in aqueous 10 M NaOH even for 15 hr at 80 °C. The structures of **13** and **14** were determined on the basis of analytical and spectral data. The IR spectra of **13** and **14** displayed no SO_2 bands. The formation of isothioureas has a tendency to be favored by polar solvents. For example, **13a** was obtained by Method A (2 hr, 80 °C) in the following yields: ethanol 86%, DMSO 85%, no solvent 72%, DMF 70%, diglyme 31% and dioxane 26%. More concentrated aqueous NaOH than 2 M was necessary to effect rearrangement. The yield increased with concentration of base and with aqueous 10 M NaOH **13a** was obtained in 92% yield even at room temperature after 3 days. The results of Method A shown in Table 5 indicate that the rate of rearrangement is



Scheme 2.

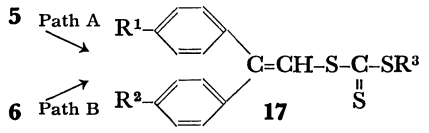
Table 6. 2,2-Diarylvinyl trithiocarbonates[a)]

Compd	R^1	R^2	R^3	Yield (%) path A	Yield (%) path B	Mp (°C)	Calcd (%) C	Calcd (%) H	Calcd (%) S	Found (%) C	Found (%) H	Found (%) S
17a	H	H	CH_3	55	54	110—111						
17b	H	H	C_2H_5	52	45	87— 88						
17c	H	H	n-C_3H_7	44	42	40— 41						
17d	H	H	n-C_4H_9	39	38	36— 37						
17e	H	Cl	CH_3	58	60	84— 85	57.04	3.89	26.55	57.28	3.96	26.84
17f	Cl	Cl	CH_3	66	74	70— 71	51.74	3.26	25.20	51.51	3.05	26.90
17g	H	CH_3	CH_3	46	50	75— 77	64.55	5.10	30.35	64.84	4.87	29.80
17h	CH_3	CH_3	CH_3	43	41	67— 68	65.44	5.49	29.06	65.65	5.25	28.86
17i	H	OCH_3	CH_3	39	28	76— 78	61.44	4.85	28.89	61.58	4.58	28.84
17j	OCH_3	OCH_3	CH_3	27	5	oil	59.66	5.01	26.50	59.76	4.86	26.62

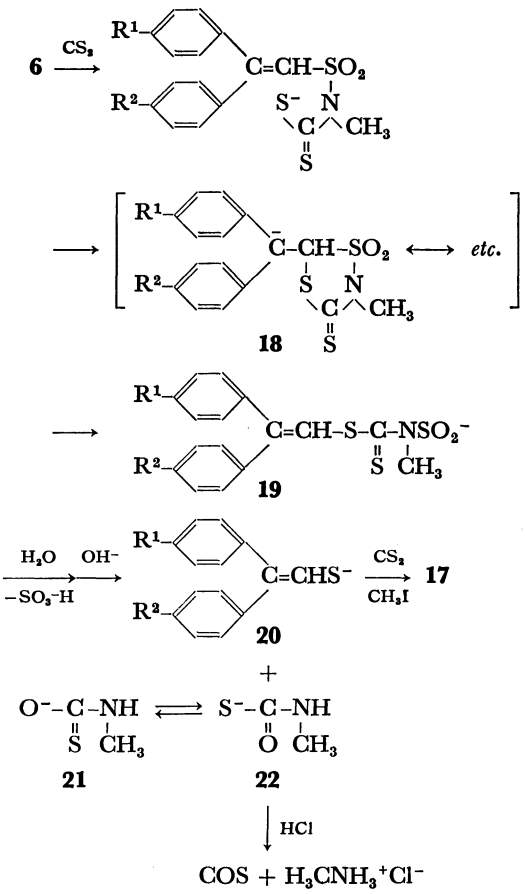
a) Purified by chromatography on silica gel using benzene–n-hexane (**17a**—**e** 1 : 1, **17f**—**h** 1 : 5, and **17i**—**j** 1 : 1 v/v) as the eluent.

increased by electron-withdrawing p,p'-substituents (Cl $>$H$>$$CH_3$$>$$OCH_3$). The probable interpretation may involve the formation of a five-membered cyclic intermediate such as **16** and subsequent removal of sulfite moiety (Scheme 2). An electron-withdrawing chlorine substituent may enhance the stabilization of **16** and electron-releasing methyl and methoxy substituents would have opposite effects. In this connection, **12**, a p-nitrated derivative of N-(2-phenylethene-1-sulfonyl)-N'-methylthiourea[2a)] underwent a rearrangement in aqueous 5 M NaOH under even more moderate conditions (60 °C, 10 min) than those used with **8** to afford N-methyl-S-(p-nitrostyryl)isothiourea (**15**) in 79% yield.

Reaction of Sulfonamides with Carbon Disulfide. In the same way as reported in the formation of trithiocarbonate **17** from **5a**[3)] methylsulfonamides **6** also gave **17** from two molar equivalents of carbon disulfide and alkyl halides in the presence of base (Table 6). The



yield from **5** (Path A) or **6** (Path B) was increased by electron-withdrawing p,p'-substituents (Cl$>$H$>$$CH_3$$>$$OCH_3$). The order is in accord with that obtained in the rearrangement of thioureas. The structures of **17a**—**d** were characterized by comparison of their IR spectra and melting points with those of authentic samples[3)] and **17e**—**j** by their analytical and spectral data. The proposed mechanism for the formation of **17** from **6** is shown in Scheme 3. The mechanism is similar to that[3)] described in the formation of **17** from **5a** except that base-catalyzed hydrolysis of dithiocarbamate (**19**) is followed by degradation to diphenylvinylthiol (**20**) and N-methylthiocarbamate (**21**). Acid-catalyzed decomposition[6)] of **21** or **22** gave carbonyl sulfide and methylammonium chloride. In addition to the resonance stabilization of **18** by two phenyl groups, the stabilization of **18** by the electron-withdrawing groups, R^1 and R^2, would provide an important driving force for the thiolate anion to attack on C-1. It is a novel case[7)]



Scheme 3.

that the rearrangement could occur under moderate conditions even when R^1 and R^2 are electron-releasing groups.

Experimental

All melting points were determined on a Yanagimoto micro-melting point measuring apparatus, MP-S2, and are uncorrected. The IR spectra were recorded on a JASCO IRA-1 spectrometer. The NMR spectra were determined with a JEOL JNM-MH-100 spectrometer, using tetramethylsilane as the internal standard, and the mass spectra were recorded at

75 eV on a JEOL-O1SG-2 spectrometer. Column chromatography was performed with Wakogel C-200.

Reagents. *p*-Substituted diphenylethylenes were prepared by dehydration of the corresponding carbinols obtained from *p*-substituted acetophenone or α-acetonaphtone and phenylmagnesium bromide: 1-*p*-Chlorophenyl-1-phenylethylene, bp 136—140 °C/3 mmHg (lit,[8] 134—136 °C/1.5 mmHg); 1-*p*-tolyl-1-phenylethylene, bp 126—129 °C/3 mmHg (lit,[9] 278—294 °C); 1-*p*-anisyl-1-phenylethylene, bp 140—150 °C/2 mmHg, mp 74—75 °C (lit,[10] bp 155—170 °C/2 mmHg, mp 75 °C); 1-phenyl-1-(α-naphthyl)ethylene, mp 58—59 °C (lit,[9] 60 °C). *p,p'*-Disubstituted diphenylethylenes were prepared by dehydration of the corresponding carbinols obtained from *p*-substituted phenylmagnesium bromide (2 mol) and ethyl acetate (1 mol): 1,1-Diphenylethylene, bp 127—132 °C/10 mmHg (lit,[11] 113 °C/2 mmHg); 1,1-bis(*p*-chlorophenyl)ethylene, bp 150—158 °C/3 mmHg, mp 84—85 °C (lit,[12] mp 84—85 °C); 1,1-bis(*p*-tolyl)ethylene, bp 132—136 °C/4 mmHg, mp 61—62 °C (lit,[10] mp 62.5—63.0 °C), 1,1-bis(*p*-anisyl)ethylene, mp 141—143 °C (lit,[10] 144—145 °C).

Sodium 2,2-Diphenylethylenesulfonate (3a). Diphenylethylene was sulfonated with dioxane–sulfur trioxide by a procedure similar to that used for the sulfonation of styrene.[4] The resulting brown solution was neutralized with aqueous NaOH to give **3a**. Recrystallization from water gave monohydrate of **3a** as colorless thin plates. IR (KBr): 3050 (=CH), 1600 (C=C), and 1200 (SO_2) cm^{-1}. NMR (DMSO-d_6) δ: 6.84 (s, 1, CH), 7.33 (s, 10, $2C_6H_5$).

2,2-Diphenylethylenesulfonyl Chloride (4a). Dry **4a** (28.20 g, 0.100 mol) was treated with PCl_5 (24.99 g, 0.120 mol) similar to the procedure of chlorination of sodium 2-phenylethylene-1-sulfonate[13] to give a yellow brown oil. Recrystallization from $CHCl_3$–petroleum ether gave 19.70 g (71%) of **4a**. IR (KBr): 3060 (=CH), 1600 (C=C), 1330 and 1160 (SO_2) cm^{-1}. NMR ($CDCl_3$) δ: 7.09 (s, a, CH), 7.28±0.06 (m, 10, $2C_6H_5$). MS *m/e*: 89, 102, 152, 165, 178, 179 (base peak), 214, 243 and 278 (M^+).

Crude **4c**, **4e**, and **4f—g** were chromatographed on silica gel using benzene–*n*-hexane (**4c** and **4e** 1 : 1, **4f—g** 5 : 1 v/v) as the eluene and recrystallized from the solvents shown in Table 2.

2,2-Diphenylethylene-N-*methylsulfonamide (6a).* To a stirred solution of **4a** (2.78 g, 0.100 mol) in benzene (10 ml) was added dropwise a 30% aqueous methylamine (4.14 g, 0.040 mol). After stirring was continued for 1 hr at 40—50 °C the mixture was cooled and resultant precipitates were filtered to give 2.54 g (93%) of **6a**. Recrystallization from benzene gave colorless crystals. IR (KBr): 3340 (NH), 3060 (=CH), 1600 (C=C), 1315, 1150, and 1120 (SO_2) cm^{-1}. NMR ($CDCl_3$) δ: 2.42 (d, J_{NH-CH_3}=5.0 Hz, 3, CH_3), 3.58 (broad, 1, NH), 6.64 (s, 1, CH), 7.20±0.06 (m, 10, $2C_6H_5$). MS *m/e*: 89, 102, 152, 165, 167, 178, 179 (base peak), 209 243 and 273 (M^+).

N-*(2,2-Diphenylethylenesulfonyl)*-N'-*methylthiourea (8a).* To a solution of **5a** (7.79 g, 0.030 mol) in acetone (20 ml) was added methyl isothiocyanate (2.63 g, 0.036 mol) and anhydrous K_2CO_3 (6.21 g, 0.045 mol), and the reaction mixture was refluxed for 10 hr with stirring. The resulting potassium salt of **8a** was filtered and washed with acetone to remove unreacted **6a**. The salt was dissolved in water (300 ml), and the solution was acidified with concd HCl to give 9.50 g (95%) of **8a**. Recrystallization from methanol gave colorless crystals. IR (KBr): 3320 (NH), 3060 (=CH), 1600 (C=C), 1570 (NH), 1380, 1180, and 1130 (SO_2) cm^{-1}. NMR (MDSO-d_6) δ: 3.00 (s, 3, CH_3), 3.40 (broad, 1, $N\underline{H}CH_3$), 7.12 (s, 1, CH), 7.32±0.10 (m, 10, $2C_6H_5$), 7.80 (broad, 1, $SO_2N\underline{H}$). MS *m/e*: 89, 102, 121, 134, 152, 165, 167, 178, 179, 195, 211, 212 (base peak), 243, 268, and 298. M^+ was not observed.

Thioureas, **8b**, **8c**, and **8d**, were obtained by evaporation of acetone from the filtrate and subsequent recrystallization of the residual oils from methanol.

*3-Methylamino-5-(*p-*nitrophenyl)-5,6-dihydro-1,4,2-dithiazine-1,1-dioxide (11).* To a stirred mixture of concd HNO_3 (*d*= 1.42, 40 ml) and concd H_2SO_4 (40 ml) was added 3-methylamino-5-phenyl-5,6-dihydro-1,4,2-dithiazine-1,1-dioxide (4.17 g, 0.0163 mol) portionwise at 0—5 °C. After stirring was continued for 3 hr at 5 °C, the solution was poured onto ice water (400 ml), and the solid was filtered to give 4.78 g (98%) of the crude product which was most likely contaminated with *ortho* and *meta* isomers. Repeated fractional recrystallization from methanol gave a *para* isomer (**11**) as pale-yellow crystals. IR (KBr): 3240 (NH), 1560 (N=C), 1520 (NO_2), 1340 (NO_2) and 1115 (SO_2) cm^{-1}. NMR (DMSO-d_6) δ: 2.78 (d, J_{NH-CH_3}= 4.5 Hz, 1.7H, $NHC\underline{H}_3$), 2.78 (s, 1.3H, $=NCH_3$), 3.57 (q, 1, H_A), 3.83 (q, 1, H_C), 5.25 (q, 1, H_B), J_{AB}=6.0 Hz, J_{AC}=13.5 Hz, J_{BC}=4.5 Hz, 7.60—8.50 (m, 4, C_6H_4), a NH proton was ambiguous. MS *m/e*: 57 (base peak), 91, 103, 120, 135, 149, 164, 166, 181, 191, 236, 255, and 301 (M^+).

N-*(*p-*Nitrostyrene-1-sulfonyl)*-N'-*methylthiourea (12).* When aqueous 1 M NaOH (21.0 ml, 0.0214 mol) was added to a stirred suspension of **11** (3.23 g, 0.0107 mol) in acetone (42 ml), a deep brown solution was formed. After stirring was continued for 10 min, acetone was removed *in vacuo* and the residual solution was acidified with concd HCl to give **12** (1.50 g) as brown crystals. Recrystallization from acetone gave 0.57 g (18%) of **12** as pale-yellow crystals. IR (KBr): 3330 (NH), 3040 (=CH), 1615 (C=C), 1560 (NH), 1520, 1490 and 1350 (NO_2), 1150 and 1130 (SO_2) cm^{-1}. NMR DMSO-d_6) δ: 2.74 (d, J_{NH-CH_3}=4.0 Hz, 3, CH_3), 7.40 (d, 1, H_A), 7.94 (d, 1, H_B), J_{AB}=15.0 Hz, 7.40—8.20 (m, 4, C_6H_4), two NH protons were ambiguous. Mass spectrum was identical with that of **11** because of ready cyclization of **12** to **11** on heating.

N-*Methyl*-S-*(2,2-diphenylvinyl)isothiourea (13a).* To a stirred solution of **8a** (0.40 g, 0.0012 mol) in DMF (6 ml) was added aqueous 5M NaOH (2.4 ml, 0.012 mol) and the mixture was stirred for 2 hr at 80 °C. The mixture was poured onto ice water (100 ml). The precipitates were filtered to give 0.224 g (70%) of **13a**. Recrystallization from methanol gave colorless crystals. IR (KBr): 3400, 3260 and 3180 (NH), 1605 (C=N), 1470, 1450, 1360, 1040, 770 and 695 cm^{-1}. NMR ($CDCl_3$) δ: 3.05 (s, 3, CH_3), 6.50—5.30 (broad, 2, 2NH), 6.74 (s, 1, CH), 7.24 (s, 10, $2C_6H_5$). MS *m/e*: 42, 44, 57, 77, 165, 178, 193, 212, 219, 234 (base peak) and 268 (M^+).

N-*Methyl*-S-*(*p-*nitrostyryl)isothiourea (15).* Similar to the synthesis of **13a**, **12** (0.36 g, 0.0012 mol) was treated with aqueous 5M NaOH (2.40 ml, 0.012 mol) in DMF (3 ml) for 10 min at 60 °C to give 0.22 g (79%) of **15**. Recrystallization from acetone gave yellow crystals. IR (KBr): 3400, 3260, and 3170 (NH), 1620 (C=N), 1510, 1470, 1370, and 1350 (NO_2), 1255, 1050, 940, 825, 800, 750, and 730 cm^{-1}. NMR ($CDCl_3$) δ: 3.30 (d, J_{NH-CH_3}=5.0 Hz, 3, CH_3), 6.60 (d, 1, H_A), 8.18 (d, 1, H_B), J_{AB}=15.0 Hz, 7.20—7.80 (broad, 1, NH), 8.50 (broad, 1, $N\underline{H}CH_3$), 7.28—8.10 (m, 4, C_6H_4). MS *m/e*: 42, 57, 76, 89, 102, 115, 131, 136, 178, 180, 203, and 237 (M^+).

*Methyl 2,2-bis(*p-*chlorophenyl)vinyl trithiocarbonate (17f).* *Path A*: A solution of **5c** (0.295 g, 0.00090 mol) in DMF (3 ml) was treated with aqueous 5M NaOH (0.54 ml, 0.0027 mol), carbon disulfide (0.21 g, 0.0027 mol), and then methyl iodide (0.16 g, 0.0011 mol) by the way described by us[3] to give yellow crystals. Chromatography on silica gel to remove **5c** gave 0.220 g (66%) of pure **17f** as yellow crystals.

Path B: By using the way described in Path A, 0.241 g

(74%) of **17f** was obtained from **6c** (0.30 g, 0.00088 mol), aqueous 5M NaOH (0.52 ml, 0.0026 mol), carbon disulfide (0.17 g, 0.0022 mol) and methyl iodide (0.16 g, 0.0011 mol). Materials which were contained in the filtrate of **17f** were examined. Sulfite anion, SO_3^{-2}, in the filtrate was oxidized with H_2O_2 and detected by $BaSO_4$ precipitation. Carbonyl sulfide was confirmed with lead paper. Methylammonium chloride was converted into a red rhodamine dye exhibiting yellow green fluorescence.[14]

The authors wish to thank Mr. S. Ikeda, Mr. H. Annaka, Mr. Y. Mizukami and Mr. T. Yamamoto for assistance in preparing some of the compounds.

References

1) E. Waldan and R. Pütter, *Angew. Chem.*, **84**, 822 (1972).
2) a) K. Hasegawa and S. Hirooka, This Bulletin, **45**, 525 (1972); b) K. Hasegawa and S. Hirooka, *ibid.*, **45**, 1567 (1972); c) K. Nakahashi, S. Hirooka, and K. Hasegawa, *ibid.*, **45**, 3217 (1972); d) K. Hasegawa, T. Sasaki, and S. Hirooka, *ibid.*, **46**, 696 (1973).
3) K. Hasegawa, T. Sasaki, and S. Hirooka, *ibid.*, **46**, 2894 (1973).
4) B. M. Culbortson and S. Dietz, *J. Chem. Soc., C*, **1968**, 992.
5) A. P. Terentév and R. A. Gracheva, *Zhur Obshchei Khim.*, **30**, 3663 (1960). *Chem. Abstr.*, **55**, 18659f (1961).
6) E. Müller, Houben-Weyl, "Methoden der Organishen Chemie," George Thieme Verlag, Stuttgart (1955). Vol. XI/2, p. 782 and 823.
7) W. E. Truce, E. M. Kreider, and W. W. Brand, "Organic Reactions," Vol. 18, Wiley, New York, N. Y., 1970, p. 103.
8) S. N. Ege and K. W. Sherk, *J. Amer. Chem. Soc.*, **75**, 354 (1953).
9) C. D. Hurd and C. N. Webb, *ibid.*, **49**, 549 (1927).
10) A. G. Evans, N. Jones, P. M. S. Jones, and J. H. Thomas, *J. Chem. Soc.*, **1956**, 2757.
11) C. F. H. Allen, "Organic Syntheses," Coll. Vol. I, (1956), p. 226.
12) W. L. Beneze and M. J. Allen, *J. Org. Chem.*, **22**, 352 (1957).
13) C. S. Rodestvedt Jr., and F. G. Bordwell, "Organic Syntheses," Coll. Vol. IV, (1963), p. 846.
14) F. Feigl, "Spot Tests in Organic Analysis," Elsevier, Maruzen Asian Edition, Tokyo, (1960), p. 275.