sults were found in the presence of potassium tert-butoxide in *tert*-butyl alcohol or if **3a** was stirred in dioxane–D_2O (30:1) at 82° for 24 hr.

Acknowledgment. Support of this work by PHS Grant CA-04474 of the National Cancer Institute is gratefully acknowledged.

Registry No.—1 (R = Ph; R^1 = H), 7654-06-0; **2b**, 51932-77-5; **3a**, 33070-60-9; **3b**, 51932-78-6; **3b** picrate, 51932-79-7; **7a**, 51932-80-0; **7b**, 51932-81-1; **10**, 51932-82-2; **14**, 33070-61-0; **15a**, 51932-83-3; **15b**, 51932-84-4; **15c**, 51932-85-5; **19**, 33070-62-1; **22**, 51932-86-6; **28**, 51932-87-7; benzoyl chloride, 98-88-4; acetic acid, 64-19-7.

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Formation of 5-Aryl-5,6-dihydro-4*H*-1,2,4-thiadiazine 1,1-Dioxides and *N*-*trans*-Styrylamidines by Base Treatment of *N*-(*trans*-Styrylsulfonyl) amidines[1]

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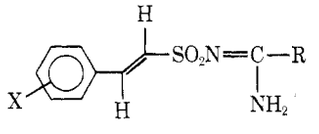
Treatment of *N*-(*trans*-styrylsulfonyl)amidines (**1**) with base affords 5-aryl-5,6-dihydro-4*H*-1,2,4-thiadiazine 1,1-dioxides (**2**) and/or *N*-(*trans*-styryl)amidines (**3**). Formation of **3** is favored by electron-withdrawing substituents in the styryl aromatic ring and by polar reaction solvents. Possible mechanisms for the formation of **2** and **3** are discussed. With electron-rich aromatic rings, intramolecular Michael addition occurs predominantly at the carbon atom β to the sulfonyl group to afford the expected product **2**. However, with electron-withdrawing substituents in the aromatic ring, we propose that addition occurs α to the sulfonyl group to afford an unstable thiadiazoline intermediate, which gives **3** by loss of SO_2. This rearrangement of **1** to **3** is analogous to a Smiles rearrangement in which intramolecular nucleophilic attack occurs on a vinylic rather than an aromatic carbon.

We recently reported the synthesis of 5-aryl-4*H*-1,2,4-thiadiazine 1,1-dioxides by base-catalyzed, intramolecular cyclization of *N*-(α-bromostyrylsulfonyl)amidines.[2] As an approach to the synthesis of 5-aryl-5,6-dihydro-4*H*-1,2,4-thiadiazine 1,1-dioxides (**2**), we treated *N*-(*trans*-styrylsulfonyl)amidines (**1**) with base and obtained dihydrothiadiazines **2** and/or *N*-(*trans*-styryl)amidines **3**. This paper examines some of the parameters which determine the types

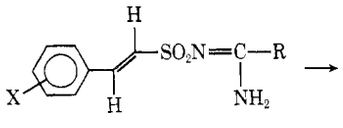
Table I
***N*-(*trans*-Styrylsulfonyl)amidines (1)[a]**



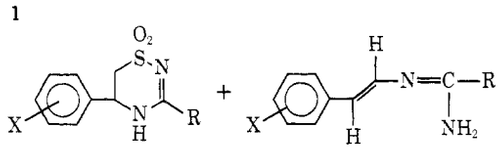
Compd	X	R	Mp, °C	Crystn solvent	Yield, %	Formula
1a	H	Me	134.5–137	*i*-PrOAc	76	$C_{10}H_{12}N_2O_2S$
1b	H	Ph	192.5–194.5	Me_2CO	90	$C_{15}H_{14}N_2O_2S$
1c	4-Cl	Me	166.5–169.5	EtOAc	93	$C_{10}H_{11}ClN_2O_2S$
1d	3,4-Cl_2	Me	197.5–198.5	Me_2CO–*i*-Pr_2O	83	$C_{10}H_{10}Cl_2N_2O_2S$
1e	3,4-Cl_2	Ph	147–150	MeOH	88	$C_{15}H_{12}Cl_2N_2O_2S$
1f	3,4-Cl_2	$PhCH_2$	159–161	*i*-PrOH	81	$C_{16}H_{14}Cl_2N_2O_2S$
1g	4-NO_2	Me	203–203.5	MeCN	92	$C_{10}H_{11}N_3O_4S$
1h	4-NO_2	Ph	171–173	*i*-PrOH	87	$C_{15}H_{13}N_3O_4S$
1i	2-NO_2	Me	175–178	Me_2CO–*i*-Pr_2O	85	$C_{10}H_{11}N_3O_4S$

[a] Satisfactory analytical data (±0.3% for C, H, N) were reported for compounds **1a–i**, **2a–f**, and **3a–j**: Ed.

Table II



1



2 3

	X	R	Solvent	2 yield, %	3 yield, %
a	H	Me	DMSO	60	3
b	H	Ph	DMSO	84	6.5
c	4-Cl	Me	DMSO	27	12
d	3,4-Cl_2	Me	DMSO	2	70
e	3,4-Cl_2	Ph	DMSO	3[a]	68[a,b]
f	3,4-Cl_2	$PhCH_2$	DMSO	3	41
f	3,4-Cl_2	$PhCH_2$	Me_2CO	31[c]	
g	4-NO_2	Me	DMSO		46
h	4-NO_2	Ph	Me_2CO		96
i	2-NO_2	Me	Me_2CO		88
j	2-NO_2	Ph	Me_2CO		78[d]

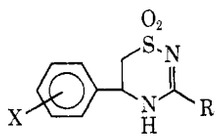
[a] Unreacted starting material was recovered (18%). [b] Compound **3e** was obtained in 49% yield after 30 hr reaction time. [c] Reaction time was 24 hr. [d] Overall yield from 2-nitrostyrylsulfonyl chloride. The intermediate **1j** was not isolated.

cm^{-1}, assigned to NH_2-deformation modes, and C=N absorption at 1520–1560 cm^{-1}, typical of the SO_2N=C- group.[3-6]

The products from base treatment of **1** are shown in Table II and their physical properties in Tables III and IV. The dihydrothiadiazines have similar infrared and nmr spectra to those reported recently.[3] The *N*-styrylamidine salts have typical amidinium absorptions[7,8] in their infrared spectra, with strong bands at ~1675 (C=N^+) and ~3000 cm^{-1} (NH). In the nmr spectra (DMSO-d_6) the NH protons appear as broad signals, close to δ 10.0 (1 H) and 12.0 (2 H), and they undergo exchange on addition of D_2O. The trans vinylic protons in these compounds appear as doublets ($J \simeq 14.0$ Hz) at about δ 6.8 and 8.0. In spectra of the *N*-styrylamidine free bases, these doublets are shifted upfield to about δ 6.2 and 7.4, respectively, consistent with the values reported by Advani, *et al.*[9]

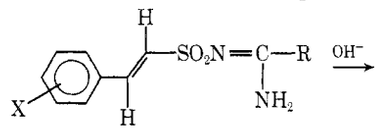
Treatment of the unsubstituted *N*-(styrylsulfonyl)amidines **1a** and **1b** with NaOH in DMSO for 64 hr at 25° gave the expected 5-phenyl-5,6-dihydro-4*H*-1,2,4-thiadiazine 1,1-dioxides **2a** and **2b** in high yields along with small amounts of the corresponding *N*-(*trans*-styryl)amidines **3a** and **3b.** The monochloro-*N*-(styrylsulfonyl)amidine **1c** afforded a relatively larger amount of styrylamidine **3c,** whereas the 3,4-dichloro derivatives **1d** and **1e** gave high yields of *N*-styrylamidines **3d** and **3e** with only traces of the corresponding dihydrothiadiazines **2d** and **2e.** Some unreacted starting material was recovered from these reactions even after 64 hr and lower yields of products were obtained after shorter reaction times. The phenylacetamidine

Table III
5-Aryl-5,6-dihydro-4*H*-1,2,4-thiadiazine 1,1-Dioxides (2)

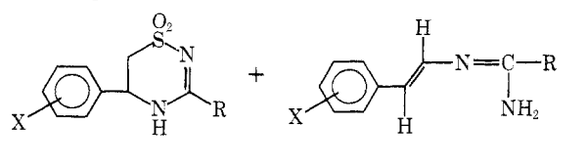


Compd	X	R	Mp, °C	Crystn solvent	Formula
2a	H	Me	276.5–278.5	MeCN	$C_{10}H_{12}N_2O_2S$
2b	H	Ph	235.5–236.5	MeCN	$C_{15}H_{14}N_2O_2S$
2c	4-Cl	Me	274.5–277.5	Me_2CO–*i*-Pr_2O	$C_{10}H_{11}ClN_2O_2S$
2d	3,4-Cl_2	Me	257–259.5	MeOH	$C_{10}H_{10}Cl_2N_2O_2S$
2e	3,4-Cl_2	Ph	300–301	MeOH	$C_{15}H_{12}Cl_2N_2O_2S$
2f	3,4-Cl_2	$PhCH_2$	282.5–284	MeOH	$C_{16}H_{14}Cl_2N_2O_2S$

of products formed by base treatment of **1** and the mechanisms of formation of these products.



1



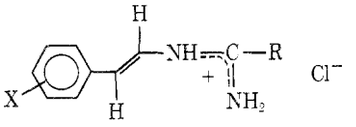
2 3

The *N*-(*trans*-styrylsulfonyl)amidines (**1,** Table I) were obtained by reaction of the appropriate amidine with a *trans*-styrylsulfonyl chloride.[2] The infrared spectra of these compounds show strong absorption at 1635–1655

1f also rearranged to a *N*-styrylamidine (**3f**) under these conditions, but afforded only the dihydrothiadiazine **2f** when the reaction was carried out in acetone. Treatment of *N*-(2- or 4-nitrostyrylsulfonyl)amidines **1g–j** with NaOH in DMSO or acetone caused rapid rearrangement (<1 hr) to *N*-styrylamidines **3g–j.** It is apparent, therefore, that this rearrangement is facilitated by electron-withdrawing aromatic substituents and by solvents of high polarity.

Likely mechanisms for the formation of dihydrothiadiazines (**2**) and *N*-styrylamidines (**3**) are shown in Scheme I. Base treatment of sulfonylamidine **1** affords an anion which may be drawn as the resonance structures **4a** and **4b.** The N anion in **4b** may attack the C atom either α or β to the sulfonyl group to give the carbanion **7** or **5,** respectively. With an unsubstituted aromatic ring, the carbanion **5** is apparently preferred to **7,** and a dihydrothiadiazine **2** is the major product. However the presence of electron-withdrawing substituents in the aromatic ring would stabilize **7**

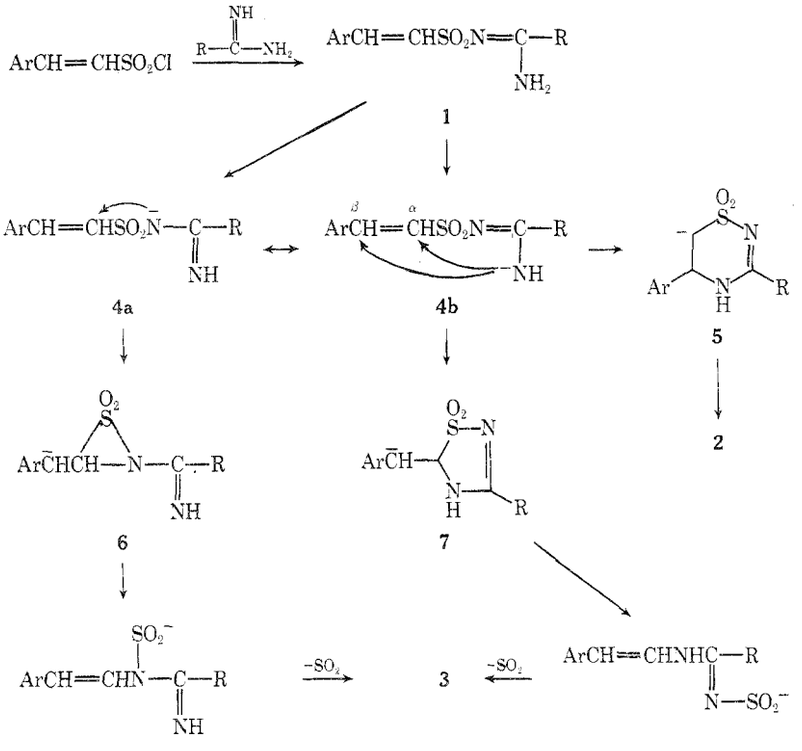
Table IV
***N*-(*trans*-Styryl)amidines (3)**



Compd	X	R	Mp,[a] °C	Crystn solvent	Formula
3a	H	Me	167–183	*i*-PrOH	$C_{10}H_{13}ClN_2$
3b	H	Ph	226.5–228	MeOH–*i*-Pr_2O	$C_{15}H_{15}ClN_2$
3c	4-Cl	Me	228–234.5	MeOH–*i*-Pr_2O	$C_{10}H_{12}Cl_2N_2$
3d	3,4-Cl_2	Me	215–224	MeOH–*i*-Pr_2O	$C_{10}H_{11}Cl_3N_2$
3e	3,4-Cl_2	Ph	243–248.5	EtOH–MeOH–*i*-Pr_2O	$C_{15}H_{13}Cl_3N_2$
3f	3,4-Cl_2	$PhCH_2$	216–219	*i*-PrOH	$C_{18}H_{20}Cl_2N_2O_4S$[b]
3g	4-NO_2	Me	247–247.5	MeOH	$C_{10}H_{12}ClN_3O_2$
3h	4-NO_2	Ph	255–257	MeCN	$C_{17}H_{19}N_3O_6S$[c]
3i	2-NO_2	Me	227–229	EtOH–*i*-Pr_2O	$C_{10}H_{12}ClN_3O_2$
3j	2-NO_2	Ph	219.5–221.5	MeOH–*i*-Pr_2O	$C_{15}H_{14}ClN_3O_2$

[a] The crude free bases of the following compounds were isolated as solids: **3c**, mp 134–136°; **3d**, mp 125–128°; **3g**, mp 142–143°; **3h**, mp 160–162°. [b] Analyses were obtained on the isethionate salt, mp 132.5–134.5° (MeCN). [c] Analyses were obtained on the isethionate salt, mp 204–206.5° (MeOH–*i*-Pr_2O).

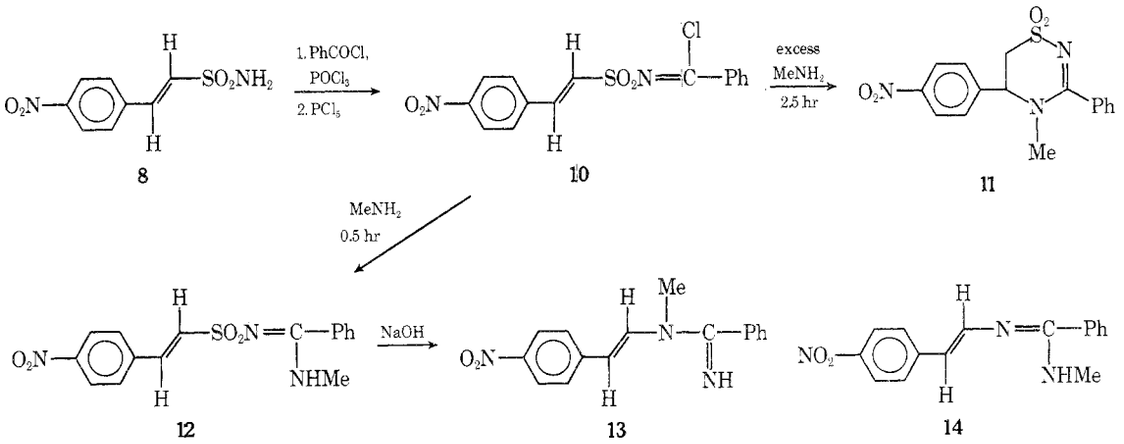
Scheme I



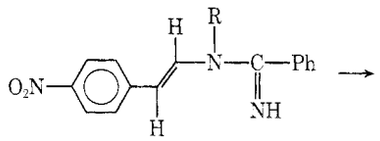
by delocalization of the negative charge and the intermediate **7** would be preferred over **5**. This five-membered heterocycle may then break down to afford a *N*-styrylamidine **3** by *β-elimination* of the SO_2 group followed by hydrolysis of the resulting *N*-sulfonyl intermediate. A somewhat analogous intramolecular attack in 4-nitrobenzenesulfonyl guanidines has been described.[10–12] Alternatively, *N*-styrylamidines **3** could form from **4a**, *via* a Ramberg–Bäcklund type of intramolecular reaction,[13] to afford a three-membered ring intermediate **6**, which could then undergo ring opening and elimination of SO_2.

In order to distinguish between these two routes to *N*-styrylamidines, we prepared *N*-methyl-*N'*-(4-nitrostyrylsulfonyl)benzamidine **12** as shown in Scheme II, and studied its rearrangement with base. The chloroimidate **10** was obtained by a method similar to that of Lawson and Tinkler,[14] but treatment of **10** with excess methylamine in acetone for 2.5 hr gave the dihydrothiadiazine **11** instead of the sulfonylamidine **12**. Apparently, under these conditions, the initially formed **12** underwent cyclization to **11**. This is the only instance of dihydrothiadiazine formation from nitro-substituted *N*-(styrylsulfonyl)amidines that we have observed. When we treated **10** with a limited amount of methylamine for a short time, we obtained the desired sulfonylamidine **12**, which was converted to *N*-methyl-*N*-(*trans*-4-nitrostyryl)benzamidine **13** by NaOH in acetone. This is the product expected from the route involving a five-membered ring intermediate.

Scheme II

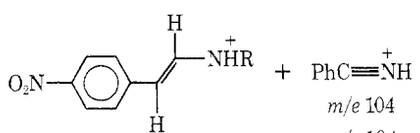


It is distinguishable by nmr and mass spectra from **14**, the product expected from the alternate three-membered intermediate. In the nmr spectrum of **13** in DMSO-d_6, no coupling of the *N*-methyl protons is observed, in contrast to the doublet observed for the *N*-methyl protons of **12**. The major fragments in the mass spectra of **13** and **3** appear to be due to the molecular ions, PhC≡NH$^+$, and 4-nitrostyrylamine fragments in agreement with the fragmentation pattern of *N*-phenylbenzamidines.[15] The



3, R = H, *m/e* 267

13, R = Me, *m/e* 281



m/e 164

m/e 178

m/e 104

m/e 104

styrylamine fragment with *m/e* 178 is consistent with that expected from **13** but not from **14**. The absence of a PhC≡N$^+$–Me fragment is also consistent with structure **13**.

This rearrangement of *N*-(*trans*-styrylsulfonyl)amidines is, therefore, analogous to a Smiles arrangement[10] in which the intramolecular nucleophilic attack occurs on a vinylic carbon rather than an aromatic carbon. The scope of the reaction may be similar to that of the Smiles rearrangement.[10]

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded on a Beckman IR-9 spectrophotometer. Nmr data were obtained with a Varian A-60A or XL-100 spectrometer with tetramethylsilane as an internal standard. Mass spectra were measured on a Varian MAT 311 spectrometer. Microanalytical and spectral data were supplied by the Physical Analytical Department of Mead Johnson & Co. Satisfactory analytical data (±0.4% for C, H, and N) were reported for all new compounds. The styrylsulfonyl chlorides used in this work were obtained by previously described methods.[2] Phenylacetamidine benzenesulfonate was prepared by the method of Oxley and Short.[16] *trans*-4-Nitrostyrylsulfonamide (**9**) was obtained by the method of Bordwell, *et al.*[17]

***N*-(*trans*-Styrylsulfonyl)acetamidine (1a).** A mixture of acetamidine hydrochloride (14.2 g, 0.15 mol) and 50% aqueous NaOH (12.0 g, 0.15 mol) in acetone (200 ml) was stirred vigorously for 10 min and then cooled to 10° in an ice bath. Finely powdered *trans*-styrylsulfonyl chloride (10.1 g, 0.05 mol) was then added, in portions, at such a rate as to maintain the reaction temperature at about 10°. The mixture was stirred for an additional 10 min and then concentrated under reduced pressure. Water (100 ml) was added to the residue and the mixture was acidified with 3 *N* HCl. Insoluble solid was collected by filtration, washed with water, air dried, and crystallized from *i*-PrOAc to afford 8.5 g (76%) of **1a** as white crystals: nmr ($CDCl_3$) δ 7.84 (broad s, 1, NH), 7.64 (d, 2, *J* = 15.5 Hz, =CH), 7.45 (m, 5, ArH), 6.92 (d, 2, J = 15.5 Hz, =CH), 6.73 (broad s, 1, NH), 2.16 (s, 3, CH_3); ir (KBr) 3435, 3335, 3250 (NH), 1645 (NH_2), 1550 (C=N), 1270, 1130 cm^{-1} (SO_2).

Other *N*-(styrylsulfonyl)amidines in Table I were prepared by similar procedures. Reaction of *trans*-2-nitrostyrylsulfonyl chloride with benzamidine, according to this procedure, failed to afford a solid product **1j**. The crude **1j** was extracted into $CHCl_3$ and converted to **3j** by treatment with NaOH in Me_2CO (method B below).

Base Treatment of *N*-(*trans*-Styrylsulfonyl)amidines. A. In DMSO. *N*-(*trans*-Styrylsulfonyl)benzamidine (**1b**) (4.3 g, 0.015 mol) was added in portions to a stirred mixture of 50% aqueous NaOH (1.2 g, 0.015 mol) in DMSO (25 ml). The mixture was stirred at 25° for 64 hr, poured into cold water (250 ml), and made strongly basic with 5% aqueous NaOH. It was extracted several times with ether and the extracts were washed with water and dried (K_2CO_3). Evaporation of the solvent gave a yellow oil that formed a salt with ethanolic HCl. The crude salt was triturated with acetone and crystallized to afford 0.25 g (6.5%) of ***N*-(*trans*-styryl)benzamidine hydrochloride (3b):** nmr (DMSO-d_6) δ 12.03 (broad s, 1, NH), 10.33 (broad, 2, NH_2), 8.25 (d, 1, *J* = 14.0 Hz, =CH), 8.0–7.1 (m, 10, ArH), 6.95 (d, 1, *J* = 14.0 Hz, =CH); ir (KBr) ~3050 (broad, NH), 1665 cm^{-1} (broad, C=N).

Acidification of the aqueous alkaline fraction with 3 *N* HCl precipitated a white solid, which was washed with water, air dried, and crystallized to afford 2.3 g (84%) of **5,6-dihydro-3,5-diphenyl-4*H*-1,2,4-thiadiazine 1,1-dioxide (2b):** nmr (DMSO-d_6) δ 9.67 (broad s, 1, NH), 7.93 and 7.55 (m, 10, ArH), 5.17 (dd, 1, *J* = 5.5, 11.5 Hz, CH), 3.47 (m, 2, CH_2); ir (KBr) 3310 (NH), 1550 (C=N), 1300 and 1130 cm^{-1} (SO_2).

Compounds **2a–e** in Table III and **3a–f** in Table IV were obtained in similar procedures.

B. In Acetone. A suspension of *N*-(*trans*-4-nitrostyrylsulfonyl)benzamidine (**1h**, 9.9 g, 0.03 mol) in acetone (100 ml) was stirred with 50% aqueous NaOH (8.0 g, 0.1 mol) in water (20 ml) for 1 hr. Evaporation of the solvent left an orange-red solid that was stirred with water (50 ml), filtered, washed thoroughly with water, and air dried. Trituration of the solid with 2-propanol afforded 7.7 g (96%) of *N*-(*trans*-4-nitrostyryl)benzamidine (**3h**): mp 160–162°; nmr (DMSO-d_6) δ 8.3–7.0 (m, 12, ArH, =CH, NH), 6.40 (d, 1, *J* = 14.0 Hz, =CH); ir (KBr) 3470, 3315, 3200 (NH), 1625, 1550 (C=N), 1505 and 1345 cm^{-1} (NO_2); mass spectrum *m/e* (rel intensity) 267 (30, M$^+$), 234 (60), 164 (35, M – PhC≡N), 104 (100, PhC≡NH$^+$). A portion of this solid, in hot acetonitrile, was acidified with ethanolic HCl. On cooling, the solution **3h** separated as yellow crystals: nmr (DMSO-d_6) δ 11.83 (broad s, 1, NH), 10.17 (broad s, 2, NH_2), 8.50 (d, 1, *J* = 14.0 Hz, =CH), 8.24 (d, 2, *J* = 9.0 Hz, ArH), 8.0–7.5 (m, 5, ArH), 7.70 (d, 2, *J* = 9.0 Hz, ArH), 6.97 (d, 1, *J* = 14.0 Hz, =CH); ir (KBr) 3020 (broad, NH), 1670 cm^{-1} (broad, C=N).

The *N*-styrylamidines **3i** and **3j** in Table IV were obtained in similar procedures. The free bases of these compounds were isolat-

ed as oils on evaporation of the reaction solvent. They were extracted into chloroform, washed with water, dried (K_2CO_3), and converted to hydrochloride salts. By a similar procedure, the dihydrothiadiazine **2f** (Table III) was obtained after a 24-hr reaction time by extraction of the crude product into ethyl acetate, evaporation of the solvent, and trituration of the residue with hot ethanol.

***N*-(*trans*-4-Nitrostyrylsulfonyl)benzamide (9).** A mixture of *trans*-4-nitrostyrylsulfonamide (18.2 g, 0.08 mol), benzoyl chloride (12.6 g, 0.09 mol), and $POCl_3$ (13.8 g, 0.09 mol) was heated on a steam bath for 1.5 hr. The mixture was then diluted with ethyl acetate (20 ml), cooled, and filtered to afford 19.0 g (76%) of yellow solid **9**: mp 192–195° (ethyl acetate–hexane); ir (KBr) 3290 (NH), 1685 cm^{-1} (C=O). *Anal.* Calcd for $C_{15}H_{12}N_2O_5S$: C, 54.21; H, 3.64; N, 8.43. Found: C, 53.86; H, 3.63; N, 8.28.

***N*-(*trans*-4-Nitrostyrylsulfonyl)benzimidoyl Chloride (10).** A suspension of **9** (14.9 g, 0.045 mol) in dry benzene (500 ml) was refluxed and stirred with PCl_5 (10.4 g, 0.05 mol) for 8 hr. The resulting solution was allowed to stand overnight at 25° and afforded 8.2 g of pale-yellow solid, mp 158–166°. Concentration of the filtrate to about 100 ml gave an additional 2.5 g of solid, mp 158–161°. Crystallization of the crude product from ethyl acetate gave analytically pure **10**, mp 168–175°. *Anal.* Calcd for $C_{15}H_{11}ClN_2O_4S$: C, 51.36; H, 3.16; N, 7.99. Found: C, 51.46; H, 3.09; N, 7.79.

5,6-Dihydro-4-methyl-5-(4-nitrophenyl)-3-phenyl-1,2,4-thiadiazine 1,1-Dioxide (11). Methylamine was bubbled into a solution of **10** (5.25 g, 0.015 mol) in acetone (100 ml) for 2.5 hr. The red solution was concentrated under reduced pressure, diluted with water (50 ml), and acidified with 3 *N* HCl. The mixture was stirred for several minutes and insoluble product was collected by filtration and air dried. After trituration of the solid with 2-propanol (30 ml) and then isopropyl ether, 3.2 g (61%) of **11** was obtained as a pink solid: mp 179.5–181° dec after crystallization from acetonitrile; nmr (DMSO-d_6) δ 8.15 (d, 2, J = 8.5 Hz, ArH), 7.66 (d, 2, J = 8.5 Hz, ArH), 7.50 (s, 2, =CH), 5.03 (dd, 1, J = 8.5, 6.0 Hz, CH), 3.40 (m, 2, CH_2), 3.02 (s, 3, NCH_3); ir (KBr) 1530 (broad, C=N) 1315 and 1165 cm^{-1} (SO_2). *Anal.* Calcd for $C_{16}H_{15}N_3O_4S$: C, 55.64; H, 4.38; N, 12.17. Found: C, 55.77; H, 4.32; N, 12.23.

***N*-Methyl-*N'*-(*trans*-4-nitrostyrylsulfonyl)benzamidine (12).** Methylamine was passed slowly into a solution of **10** (6.3 g, 0.018 mol) in dry acetone (50 ml) for 5 min at 25°. The mixture was stirred for another 25 min at 25° and then concentrated. Water (50 ml) and chloroform (150 ml) were added and the mixture was shaken vigorously and then filtered. Insoluble material was stirred and heated with chloroform (200 ml) and then cooled. Filtration of insoluble material gave 0.6 g of **12**. The chloroform filtrates were combined, washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. Trituration of the residue with methanol afforded an additional 3.5 g of **12**. A sample crystallized from acetonitrile to give analytically pure **12**: mp 155.5–157° dec; nmr (DMSO-d_6) δ 9.00 (broad s, 1, NH), 8.21 (d, 2, J = 9.0 Hz, ArH), 7.85 (d, 2, J = 9.0 Hz, ArH), 7.70–7.25 (m, 6, ArH and =CH), 7.12 (d, 1, J = 15.0 Hz, =CH), 2.92 (d, 3, J = 4.0 Hz, NCH_3); ir (KBr) 3235 (broad, NH), 1550 (broad, C=N), 1345 and 1120 cm^{-1} (SO_2). *Anal.* Calcd for $C_{16}H_{15}N_3O_4S$: C, 55.64; H, 4.38; N, 12.17. Found: C, 55.29; H, 4.24; N, 12.16.

***N*-Methyl-*N*-(*trans*-4-nitrostyryl)benzamidine Hydrochloride (13).** A mixture of **12** (3.45 g, 0.01 mol) and 10% aqueous NaOH (25 ml) in acetone (100 ml) was stirred at 25° for 30 min. The solvent was removed under reduced pressure and the residue was diluted with water and extracted into chloroform. The extract was washed with water, dried (K_2CO_3), and concentrated to a red oil, which formed a salt with ethanolic HCl. Trituration of the crude salt with acetone and crystallization from methanol–isopropyl ether afforded 2.4 g (75%) of **13** as a pale-yellow solid: mp 247.5–249.5° dec; nmr (DMSO-d_6) δ 10.70 (broad s, 2, NH_2), 8.22 (d, 2, J = 9.0 Hz, ArH), 8.0–7.6 (m, 8, ArH, =CH), 6.90 (d, 1, J = 14.0 Hz, =CH), 3.44 (s, 3, NCH_3); ir (KBr) 2940 (broad, NH), 1675 and 1650 cm^{-1} (C=N). *Anal.* Calcd for $C_{16}H_{16}ClN_3O_2$: C, 60.47, H, 5.08; N, 13.22. Found: C, 60.66; H, 5.03; N, 13.35.

A sample of **13** was converted to the free base by 10% aqueous NaOH in methanol. The solution was concentrated and the free base was extracted into chloroform, washed with water, and dried (K_2CO_3). Evaporation of the solvent gave the orange free base of **13**: mp 105–110°; nmr ($CDCl_3$) δ 8.01 (d, 2, J = 9.0 Hz, ArH), 7.54 (d, 1, J = 14.0 Hz, =CH), 7.6–7.3 (m, 6, ArH, NH), 7.14 (d, 2, J = 9 Hz, ArH), 5.77 (d, 1, J = 14.0 Hz, =CH), 3.32 (s, 3, NCH_3); ir (KBr) 3315 (NH), 1635, 1590 (C=N), 1505 and 1330 cm^{-1} (NO_2); mass spectrum *m/e* (rel intensity) 281 (22, M^+), 178 (35, M − PhC≡N), 159 (25), 104 (100, PhC≡NH^+).

Registry No.—**1a**, 52147-70-3; **1b**, 52147-71-4; **1c**, 52196-19-7; **1d**, 52147-72-5; **1e**, 52196-20-0; **1f**, 52147-73-6; **1g**, 52147-74-7; **1h**, 52147-75-8; **1i**, 52147-76-9; **2a**, 52148-03-5; **2b**, 52148-04-6; **2c**, 52148-05-7; **2d**, 52148-06-8; **2e**, 52148-07-9; **2f**, 52148-08-0; **3a**, 52147-77-0; **3b**, 52147-78-1; **3c**, 52147-79-2; **3c** (free base), 52147-80-5; **3d**, 52147-81-6; **3d** (free base), 52147-82-7; **3e**, 52147-83-8; **3f**, 52147-85-0; **3g**, 52194-04-4; **3g** (free base), 52147-86-1; **3h**, 52147-88-3; **3h** (free base), 52147-87-2; **3i**, 52147-89-4; **3j**, 52147-90-7; **8**, 52147-91-8; **9**, 52147-92-9; **10**, 52147-93-0; **11**, 52148-09-1; **12**, 52147-94-1; **13**, 52147-95-2; **13** (free base), 52147-96-3; ArCH=CH-SO_2Cl (Ar = Ph), 52147-97-4; ArCH=$CHSO_2Cl$ (Ar = 4-ClC_6H_4), 52147-98-5; ArCH=$CHSO_2Cl$ (Ar = 3,4-$Cl_2C_6H_3$), 52147-99-6; ArCH=$CHSO_2Cl$ (Ar = 4-$NO_2C_6H_4$), 52148-00-2; ArCH=$CHSO_2Cl$ (Ar = 2-$NO_2C_6H_4$), 52148-01-3; $RC(NH)NH_2$ (R = Me), 143-37-3; $RC(NH)NH_2$ (R = Ph), 618-39-3; $RC(NH)NH_2$ (R = $PhCH_2$), 5504-24-5.

References and Notes

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