Convenient Preparations of 3,5-Disubstituted 1,2,4-Thiadiazoles by Oxidative Dimerization of Thioamides

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3,5-Disubstituted 1,2,4-thiadiazoles **2** were prepared by reaction of thioamides **1** with DMSO in the presence of such an electrophilic reagent as 1-methyl-2-chloropyridinium iodide, benzoyl chloride, acetyl chloride, hydrochloric acid, or trimethylsilyl chloride in organic solvents at room temperature in high yields. Thiadiazoles **2** were also obtained by reaction of **1** with NBS at room temperature in high yields. Thioamide *S*-oxides reacted with electrophilic reagents at room temperature to give the corresponding thiadiazoles **2** in high yields.

Thiadiazoles are useful for bactericides,[1-3] fungicides,[1-4] herbicides,[5,6] antibiotics,[7-9] *etc.*, and a number of preparations for them have been reported. The preparation of 3,5-disubstituted 1,2,4-thiadiazoles can be roughly divided into three methods; intermolecular cyclization,[10,11] intermolecular cyclization of two different molecules,[12,13] and oxidative dimerization of the same molecules.[14-17] Some of the methods by the oxidative dimerization of thioamides, however, suffer disadvantages that substituents in 3,5-positions are limited mainly to aryl groups[14] and that by-products such as nitriles and isothiocyanates are formed.[5,18]

It is known well that the sulfur atom in thioamide easily reacts with electrophilic reagents and that resulting sulfonium salts[19-21] are very reactive with nucleophilic reagents to give various products. When an electrophilic reagent is constructed of a pair of a soft electrophile such as X^+ and a counter anion having a low nucleophilicity, the resulting sulfonium salt would eliminate HX immediately to form unstable thiazirine[17] or nitrile sulfide[22] equivalent, which is regarded as an oxidized form of thioamides and a precursor of thiadiazoles. On the basis of such a view, thioamide **1** was allowed to react with DMSO in the presence of an electrophilic reagent in organic solvent at room temperature to obtain thiadiazole **2** in high yields. In this paper, we report convenient preparations of 3,5-disubstituted 1,2,4-thiadiazoles by oxidative dimerization of thioamides using DMSO–electrophilic reagent systems and NBS. A preparation of thiadiazoles by reaction of thioamide *S*-oxides with electrophilic reagents is also described.

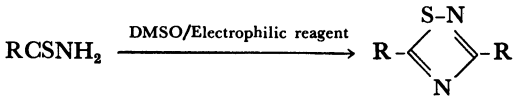
Results and Discussion

The conversion of thioamides **1** to 3,5-disubstituted 1,2,4-thiadiazoles **2** using DMSO–electrophilic reagent systems is shown in Table 1. These conversions do not occur in the absence of either DMSO or such electrophilic reagents as 1-methyl-2-chloropyridinium iodide **3** (Runs 1 and 2 in Table 1), and do not necessarily need one equivalent of **3** (Run 3 in Table 1). Moreover, the conversion to thiadiazole **2a** is successful in most organic solvents (Runs 3—7 in Table 1). The arenecarbothioamides **1a—g** could be converted to the corresponding thiadiazoles **2a—g** in high yields. The conversion of 2-(substituted phenyl)ethanethioamides **1h—j** to thiadiazoles **2h—j** was also achieved in moderate yield (Runs 18—20 in Table 1). When benzoyl chloride, acetyl chloride, 36% HCl, or trimethylsilyl chloride was used as electrophilic reagent thiadiazole **2a** was also obtained in high yield (Runs 21—24 in Table 1). However, thiobenzamide **1a** reacted with such sulfoxides as dibutyl sulfoxide and dibenzyl sufoxide in the presence of **3** at room temperature in CH_2Cl_2 giving thiadiazole **2a** in high yield (Runs 9 and 10 in Table 1). However, in the reaction with diphenyl sulfoxide having a low nucleophilicity, thiadiazole **2a** was obtained only in 9% yield at reflux for 6 h (Run 11 in Table 1). The corresponding sulfides were obtained in a series of these reactions. In the reaction of **3** with DMSO, 1-methyl-2(1*H*)-pyridineone was hardly obtained at room temperature, but it was quantitatively formed at 80 °C for 2 h along with iodine.

On the other hand, thiadiazoles **2** were obtained in high yields by the reaction of thioamide *S*-oxides **4** with an electrophilic reagent such as **3**, trimethylsilyl chloride, benzoyl chloride, acetic anhydride, or 36% HCl. It is interesting that the yields of 3,5-dibenzyl-1,2,4-thiadiazoles **2h—k** were enhanced. These results are shown in Table 2. No thiadiazole **2a** was obtained by stirring at room temperature for 24 h in CH_2Cl_2 in the absence of electrophilic reagent (Run 1 in Table 2), apparently implying that thiobenzamide *S*-oxide **4a** was activated by electrophilic reagent (Run 2 in Table 2). Consequently, the formation of thiadiazoles **2** may be as illustrated in Scheme 1.

As shown in Table 1, the reaction of thiobenzamide **1a** with DMSO gave quantitatively thiadiazole **2a** even with an addition of 0.03 equivalent of pyridinium salt **3** at 60 °C for 2.5 h. Thiobenzamide **1a** reacted also with 36% HCl in DMSO at room tem-

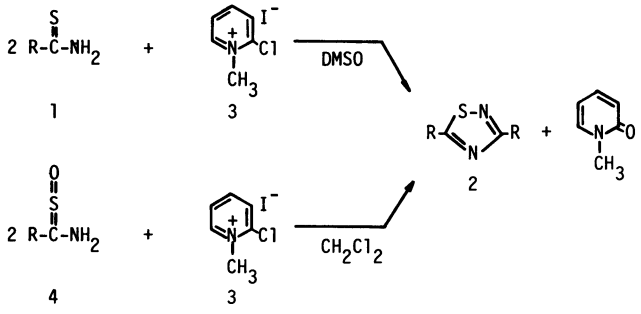
35 TABLE 1. CONVERSION TO 3,5-DISUBSTITUTED 1,2,4-THIADIAZOLES USING DMSO-ELECTROPHILIC REAGENTS[a]



1 2

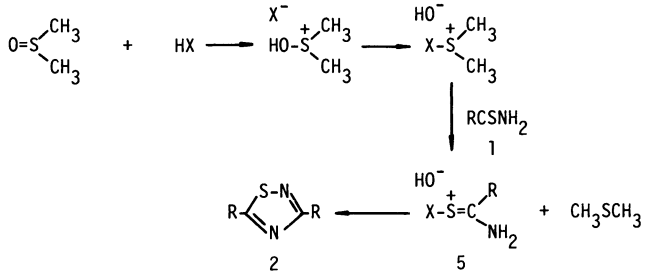
Run	Thioamide R		Solvent	DMSO equiv	Electrophilic reagent	equiv	Temp °C	Time h	Product	Yield %
1	C_6H_5	**1a**	DMSO	—	—		60	2	**2a**	0
2	C_6H_5	**1a**	CH_2Cl_2	0	Py salt[b]	1.0	Reflux	4	**2a**	0
3	C_6H_5	**1a**	DMSO	—	Py salt	0.03	60	2.5	**2a**	quant.
4	C_6H_5	**1a**	CH_2Cl_2	0.5	Py salt	0.5	r.t.	14	**2a**	48
5	C_6H_5	**1a**	CH_2Cl_2	1.0	Py salt	0.5	r.t.	4	**2a**	94
6	C_6H_5	**1a**	C_6H_6	1.0	Py salt	0.5	r.t.	4	**2a**	90
7	C_6H_5	**1a**	EtOH	1.0	Py salt	0.5	r.t.	4	**2a**	84
8[c]	C_6H_5	**1a**	CH_2Cl_2	1.1	Py salt	0.5	r.t.	13	**2a**	83
9	C_6H_5	**1a**	CH_2Cl_2	1.0[d]	Py salt	1.0	r.t.	18	**2a**	86
10	C_6H_5	**1a**	CH_2Cl_2	1.0[e]	Py salt	1.0	r.t.	18	**2a**	78[f]
11	C_6H_5	**1a**	CH_2Cl_2	1.0[g]	Py salt	1.0	Reflux	6	**2a**	9
12	4-$CH_3C_6H_4$	**1b**	DMSO	—	Py salt	0.5	40	1.5	**2b**	93
13	4-ClC_6H_4	**1c**	DMSO	—	Py salt	0.5	r.t.	6	**2c**	91
14	4-$CH_3OC_6H_4$	**1d**	DMSO	—	Py salt	0.5	35	24	**2d**	quant.
15	4-$(CH_3)_2NC_6H_4$	**1e**	CH_2Cl_2	1.0	Py salt	0.5	r.t.	7	**2e**	52
16	1-Naphthyl	**1f**	CH_2Cl_2	1.0	Py salt	0.5	r.t.	6	**2f**	52[h]
17	2-Naphthyl	**1g**	CH_2Cl_2	1.0	Py salt	1.0	r.t.	7	**2g**	79
18	$C_6H_5CH_2$	**1h**	CH_2Cl_2	1.0	Py salt	0.25	r.t.	5 d	**2h**	36
19	4-$CH_3C_6H_4CH_2$	**1i**	CH_2Cl_2	1.0	Py salt	0.25	r.t.	29	**2i**	48
20	4-$ClC_6H_4CH_2$	**1j**	CH_2Cl_2	1.0	Py salt	0.25	r.t.	4 d	**2j**	26
21	C_6H_5	**1a**	CH_2Cl_2	1.1	PhCOCl	0.5	r.t.	0.5	**2a**	99[i]
22	C_6H_5	**1a**	CH_2Cl_2	1.1	CH_3COCl	0.5	r.t.	0.5	**2a**	94
23	C_6H_5	**1a**	CH_2Cl_2	1.1	$(CH_3)_3SiCl$	(Excess)	r.t.	0.5	**2a**	65
24	C_6H_5	**1a**	DMSO	—	36% HCl	0.5	r.t.	8	**2a**	quant.
25	C_6H_5	**1a**	CH_2Cl_2	1.1	$(CH_3CO)_2O$	1.2	Reflux	2	**2a**	2[j]
26	C_6H_5	**1a**	CH_2Cl_2	1.1	CH_3I	1.2	r.t.	5 d	**2a**	0

a) Thioamide: 1 mmol; solvent: 2 ml. b) Py salt: 1-methyl-2-chloropyridinium iodide. c) 20 mmol of phenylacetylene was added. d) Dibutyl sulfoxide. e) Dibenzyl sulfoxide. f) Dibenzyl sulfide was obtained in 71% yield. g) Diphenyl sulfoxide. h) 1-Naphthonitrile was obtained in 44% yield. i) Benzoic acid was obtained in 93% yield. j) 89% of thiobenzamide **1a** was recovered.



1 3 2 4 3

Scheme 1.



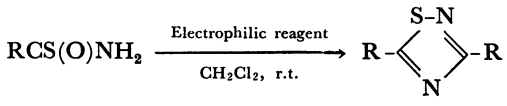
2 1 2 5

Scheme 2.

perature for 8 h giving quantitatively thiadiazole **2a** (Run 24 in Table 1), which suggests that both HCl and HI generated in the reaction of thiobenzamide **1a** with DMSO in the presence of **3** also participate in the formation of thiadiazole **2a**.[23-26] Therefore, the conversion to thiadiazoles **2** by the reaction of thioamides **1** with DMSO in the presence of electrophilic reagent may proceed as shown in Scheme 2.[27]

If thiadiazoles **2** are formed *via* sulfonium salt **5**, they must be obtained by the reaction of thioamides **1** with NBS. As had been expected, various thioamides **1** reacted with NBS at room temperature to give the cor-

Table 2. Conversion of thioamide *S*-oxides to 3,5-disubstituted 1,2,4-thiadiazoles using electrophilic reagents[a)]

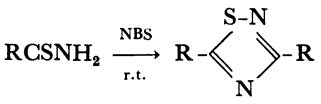


4 **2**

Run	Thioamide *S*-oxide/R		Electrophilic reagent/equiv		Time/h	Product	Yield/%
1	C_6H_5	**4a**	—		24	**2a**	0
2	C_6H_5	**4a**	Py salt	0.27	0.5	**2a**	97
3	4-$CH_3C_6H_4$	**4b**	Py salt	0.5	1	**2b**	70
4	4-$CH_3OC_6H_4$	**4d**	Py salt	0.5	0.5	**2d**	72
5	1-Naphthyl	**4f**	Py salt	0.5	24	**2f**	63
6	$C_6H_5CH_2$	**4h**	Py salt	0.5	1.25	**2h**	70
7	4-$CH_3C_6H_4CH_2$	**4i**	Py salt	0.5	24	**2i**	70
8	4-$ClC_6H_4CH_2$	**4j**	Py salt	0.5	24	**2j**	70
9	4-$CH_3OC_6H_4CH_2$	**4k**	Py salt	0.5	24	**2k**	64
10	C_6H_5	**4a**	$(CH_3)_3SiCl$	(Excess)	2	**2a**	69
11[b)]	4-ClC_6H_4	**4c**	36% HCl	0.5	9	**2c**	quant.
12	4-$ClC_6H_4CH_2$	**4j**	PhCOCl	1.3	10	**2j**	73
13	4-$ClC_6H_4CH_2$	**4j**	$(CH_3CO)_2O$	1.3	2.5	**2j**	68

a) Thioamide *S*-oxide: 1 mmol; CH_2Cl_2: 2 ml. b) 5 ml of EtOH was added.

Table 3. Conversion to 3,5-disubstituted 1,2,4-thiadiazoles using NBS[a)]



1 **2**

Run	Thioamide/R		Solvent	Time/h	Product	Yield/%
1[b)]	C_6H_5	**1a**	$CHCl_3$	13	**2a**	39[c)]
2	C_6H_5	**1a**	$CHCl_3$	21	**2a**	quant.
3	4-$CH_3C_6H_4$	**1b**	$CHCl_3$	20	**2b**	93
4	4-$CH_3OC_6H_4$	**1d**	$CHCl_3$	1	**2d**	83
5	1-Naphthyl	**1f**	CH_2Cl_2	0.5	**2f**	82
6	$C_6H_5CH_2$	**1h**	$CHCl_3$	26	**2h**	78
7	4-$CH_3C_6H_4CH_2$	**1i**	CH_2Cl_2	1	**2i**	79
8	4-$ClC_6H_4CH_2$	**1j**	$CHCl_3$	23	**2j**	72
9	4-$CH_3OC_6H_4CH_2$	**1k**	CH_2Cl_2	1	**2k**	86

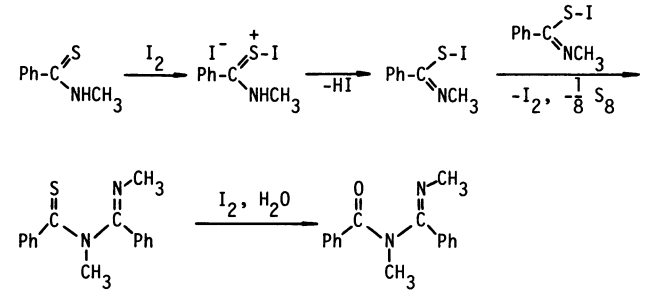
a) Thioamide: 1 mmol; NBS: 1.1 mmol; solvent: 2 ml. b) NBS: 0.5 mmol. c) 37% of thiobenzamide **1a** was recovered.

responding thiadiazoles **2** in high yields. These results are shown in Table 3.

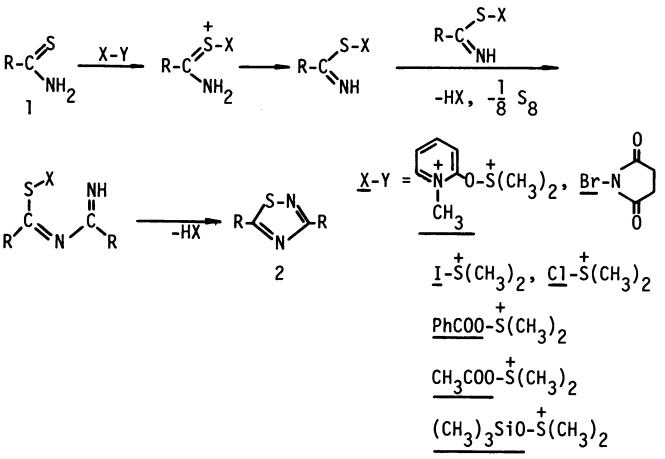
A few mechanisms have been reported for the formation of 3,5-disubstituted 1,2,4-thiadiazoles by the oxidative dimerization of thioamides. One of them[28)] comprises a route *via* dithiazoline, which is formed by the reaction of thioamide–bromine adduct with thioamide. Another mechanism[22)] resorts to the 1,3-dipolar adduct of nitrile sulfide, which is formed by way of photooxidation through extrusion of thioamide hydrogens under aerobic conditions. The conversion of thioamide into 3,5-disubstituted 1,2,4-thiadiazole *via* dithiazoline by bromine proceeds through the reaction of thioamide–bromine adduct with one more molecule of thioamide and accompanies loss of hydrogen sulfide. In a series of these reactions, however, the use of equimolar amounts of thioamide and NBS or DMSO–electrophilic reagent was needed for bringing the reaction to completion and no hydrogen sulfide but elemental sulfur was obtained in all reaction systems (Runs 4 and 5 in Table 1, and Runs 1 and 2 in Table 3). Consequently, the mechanism *via* dithiazoline is unlikely. On the other hand, the mechanism *via* thiazirine[17)] or nitrile sulfide[22)] also is considered infeasible for the following reason. Benzonitrile *N*-sulfide is known to undergo 1,3-dipolar cycloaddition with such a dipolarophile as dimethyl acetylenedicarboxylate,[29)] phenylacetylene,[22)] or benzonitrile[22)] to give dimethyl 3-phenylisothiazole-4,5-dicarboxylate, 3,4-diphenylisothiazole, or 3,5-diphenyl-1,2,4-thiadiazole, respectively. Thiobenzamide **1a** reacted with DMSO–pyridinium salt **3** in the presence of phenylacetylene in CH_2Cl_2 at room temperature for 13 h to give 3,5-diphenyl-1,2,4-thiadiazole **2a** and 1-methyl-2(1*H*)-pyridinethione in 83 and 18% yields, respectively, and no adduct with phenylacetylene was obtained. (Run 8 in Table 1). A solution of *p*-(methyl)thiobenzamide **1c** (1 mmol), *p*-methoxybenzonitrile (3 mmol), DMSO (1 mmol), and **3** (0.5 mmol) in CH_2Cl_2 (2 ml) was stirred at room temperature for 8 h to give only 3,5-di-*p*-tolyl-1,2,4-thiadiazole **2c** in 88% yield, and *p*-methoxybenzonitrile was quantitatively recovered. Both of these results suggest that the mechanism through thiazirine or nitrile sulfide is unlikely.

N-(methyl)thiobenzamide reacted with iodine in the presence of Et_3N in CH_2Cl_2 at room temperature for 1 d to give N^1-benzoyl-N^1,N^2-dimethylbenzamidine in

41% yield along with a trace amount of N^1-thiobenzoyl-N^1,N^2-dimethylbenzamidine and elemental sulfur



Scheme 3.



Scheme 4.

in 70% yield. N^1-thiobenzoyl-N^1,N^2-dimethylbenzamidine reacts with H_2O in the presence of iodine to give N^1-benzoyl-N^1,N^2-dimethylbenzamidine quantitatively. The pathway for this sequence would be given in Scheme 3.

It is apparent that the sulfonium intermediate **5** (X=I, Br, Cl, CH_3COO, PhCOO, $(CH_3)_3SiO$, or 1-methyl-2-pyridiniooxy) is present in a series of these reactions as judged from the reaction of thioamide *S*-oxides **4** with electrophilic reagents and of thioamides **1** with NBS. Therefore, conversion of thioamides **1** to 3,5-disubstituted 1,2,4-thiadiazoles **2** using DMSO-electrophilic reagents or NBS would proceed as shown in Scheme 4.

Experimental

General. The thioamides[30] and thioamide *S*-oxides[31] were prepared according to the literatures. The other reagents were commercial reagent grade materials and were purified by recrystallization or by distillation prior to use. IR spectra were recorded with a Hitachi 295 infrared spectrophotometer. ^{1}H NMR spectra were recorded with a Hitachi R-22 (90 MHz) spectrometer in carbon tetrachloride or deuteriochloroform solution containing tetramethylsilane as an internal standard. Mass spectra were recorded with a Hitachi RMU-6M spectrometer, with a direct inlet system, operating at 20 eV. For column chromatography Wakogel C-300 was used.

Preparation of 3,5-Diphenyl-1,2,4-thiadiazole **2a** *by DMSO-1-Methyl-2-chloropyridinium Iodide* **3**. A solution of

TABLE 4. PHYSICAL AND ANALYTICAL DATA OF THIADIAZOLES

Product	Mp θ_m/°C	^{1}H NMR spectra δ, $CDCl_3$	MS (20 eV) m/z (M^+)	Found (Calcd)/%			
				C	H	N	S
2a	91—91.5(EtOH) (lit,[32] 89—90)	7.41—7.79(6H, m), 7.91—8.03(2H, m), 8.31—8.41(2H, m)	238				
2b	130.5—131(EtOH) (lit,[33] 135—137)	2.40(6H, s), 7.21(2H, s), 7.30(2H, s), 7.89(2H, d, J=9 Hz), 8.24(2H, d, J=9 Hz)	266				
2c	161.5—162(EtOH-$CHCl_3$) (lit,[32] 161—162)	7.42(2H, d, J=9 Hz), 7.44(2H, d, J=9 Hz), 7.92(2H, d, J=9 Hz), 8.26(2H, d, J=9 Hz)	306				
2d	139—139.5(EtOH-$CHCl_3$) (lit,[32] 139—140)	3.85(6H, s), 6.96(4H, d, J=9 Hz), 7.93(2H, d, J=9 Hz), 8.30(2H, d, J=9 Hz)	298				
2e	223(EtOH-$CHCl_3$) (lit,[14] 223)	3.04(12H, s), 6.46, 6.81(4H, m) 7.88(2H, d, J=9 Hz), 8.24(2H, d, J=9 Hz)	324				
2f	99—100(MeOH-$CHCl_3$)	7.40—7.80(6H, m), 7.80—8.10(5H, m) 8.40—8.60(1H, m), 8.80—9.00(1H, m), 9.10—9.30(1H, m)	338	77.88 (78.08)	4.05 (4.17)	8.11 (8.28)	9.43 (9.47)
2g	180—180.5(EtOH-$CHCl_3$)	7.24—7.60(4H, m), 7.79—8.13(7H, m), 8.39—8.54(2H, m), 8.91(1H, s)	153 (B.p.)	77.55 (78.08)	3.94 (4.17)	7.89 (8.28)	9.62 (9.47)
2h	Oil(lit,[32] 39)	4.28(2H, s), 4.31(2H, s), 7.31(10H, s)	266				
2i	59(EtOH)	2.29(3H, s), 2.39(3H, s), 4.23(2H, s) 4.26(2H, s), 7.03—7.26(8H, m)	294	72.72 (73.43)	6.14 (6.16)	9.26 (9.52)	11.08 (10.89)
2j	60—62(EtOH)	3.75(3H, s), 3.78(3H, s), 4.20(2H, s), 4.24(2H, s), 6.79—6.93(4H, m), 7.17—7.28(4H, m)	326	65.23 (66.23)	5.49 (5.56)	8.19 (8.58)	10.15 (9.82)
2k	87(EtOH-$CHCl_3$)	4.23(2H, s), 4.28(2H, s), 7.28(8H, s)	334	56.86 (57.32)	3.50 (3.61)	8.11 (8.36)	9.55 (9.56)

thiobenzamide **1a** 137 mg (1 mmol), DMSO 78 mg (1 mmol), and **3** 128 mg (0.5 mmol) in CH_2Cl_2 (2 ml) was stirred at room temperature for 4 h, and the reaction mixture was filtered. After removal of CH_2Cl_2, the residue was purified by silica-gel column chromatography using $CHCl_3$ as an eluent to afford thiadiazole **2a** in 94% yield. The preparation of 3,5-disubstituted 1,2,4-thiadiazoles **2** by DMSO–**3** also was carried out in a similar manner as above. The physical properties and elemental analyses of thiadiazoles **2** are shown in Table 4.

Preparation of 3,5-Disubstituted 1,2,4-Thiadiazoles 2 by DMSO–Electrophilic Reagents (Benzoyl Chloride, Acetyl Chloride, 36% HCl, Trimethylsilyl Chloride, Acetic Anhydride, and Methyl Iodide). A typical procedure is described below for the preparation of 3,5-diphenyl-1,2,4-thiadiazole **2a** by DMSO–benzoyl chloride. A solution of thiobenzamide **1a** 137 mg (1 mmol), DMSO 86 mg (1.1 mmol), and benzoyl chloride 78 mg (0.5 mmol) in CH_2Cl_2 (2 ml) was stirred at room temperature for 30 min, and the reaction mixture was filtered. After removal of CH_2Cl_2, the residue was purified by silica-gel column chromatography using $CHCl_3$ as an eluent to afford thiadiazole **2a** and benzoic acid in 100 and 93% yields, respectively.

Preparation of 3,5-Disubstituted 1,2,4-Thiadiazoles 2 by NBS. A typical procedure is described below for the preparation of 3,5-bis(*p*-methoxybenzyl)-1,2,4-thiadiazole **2k**. A solution of (*p*-methoxyphenyl)thioacetamide **1k** 181 mg (1 mmol) and NBS 196 mg (1.1 mmol) in CH_2Cl_2 (2 ml) was stirred at room temperature for 1 h. To this reaction mixture was added 2 ml of 10% NaOH and an extraction with $CHCl_3$ was applied. After removal of $CHCl_3$, the residue was purified by silica-gel column chromatography using $CHCl_3$ as an eluent to give thiadiazole **2k** in 88% yield.

Conversion of Thioamide S-Oxides 6 to 3,5-Disubstituted 1,2,4-Thiadiazoles 2 by Electrophilic Reagents (Pyridinium Salt 3, Benzoyl Chloride, Trimethylsilyl Chloride, Acetic Anhydride, and 36% HCl). A typical procedure is described below for the preparation of 3,5-bis(*p*-chlorophenyl)-1,2,4-thiadiazole **2c** by the reaction of *p*-(chloro)thiobenzamide *S*-oxide **4c** with 36% HCl. A solution of **4c** 188 mg (1 mmol) and 36% HCl 51 mg (0.5 mmol) in EtOH (5 ml) was stirred at room temperature for 9 d, and a large amount of water was added to the reaction mixture to precipitate white crystals. The crude crystals were collected and purified by silica-gel column chromatography using $CHCl_3$ as an eluent to afford thiadiazole **2c** quantitatively.

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