# Syntheses of Arylsulfonyl-1,3,4-thiadiazoles [1]



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Reaction of sodium arylsulfinate with 2-aryl-5-chloro-1,3,4-thiadiazole gave 2-aryl-5-arylsulfonyl-1,3,4-thiadiazole (**3**) in good yield. Starting from readily available 2-amino-5-benzylmercapto-1,3,4-thiadiazole compound **7** was obtained in three steps in moderate yield. Reaction of compound **7** with sodium arylsulfinate afforded 2,5-diarylsulfonyl-1,3,4-thiadiazole (**11**). Oxidation of compound **10** with hydrogen peroxide in acetic acid gave 2-arylsulfonyl-5-benzylsulfonyl-1,3,4-thiadiazole (**12**), in high yield.

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It has been shown that substituted 1,3,4-thiadiazole-2-sulfides and sulfones have antimicrobial, amebicide, parasiticide and antifungal activities [2-4]. We would like to report the syntheses of the title compounds as possible effective drugs against tropical diseases [5].

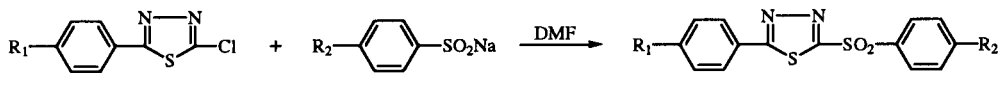
The syntheses of the title compounds were accomplished as shown in Scheme 1. Nucleophilic substitution reaction of 1,3,4-thiadiazole derivatives with strong electron withdrawing substitution in the 2-position is a valuable procedure for preparing 2,5-disubstituted 1,3,4-thiadiazoles [6]. A halogen atom in 1,3,4-thiadiazole derivatives can be readily displaced by nucleophiles [7-8]. The reaction of 2-aryl-5-chloro-1,3,4-thiadiazole **1** [7], with various nucleophiles such as methoxide [9], phenoxide, thiophenoxide, amine and azide [7] had already been described, but to date no nucleophilic substitution with sodium arylsulfinates **2** has been reported. However, 3-substituted-5-chloro-1,2,4-thiadiazoles react with sodium phenylsulfinate readily in refluxing ethanol [10]. The reaction of 2-aryl-5-chloro-1,3,4-thiadiazoles **1** with sodium arylsulfinates **2** in refluxing ethanol did not give

Table 1

| Compound | MP°C [a] | Yield | Formula | C% Calcd. | C% Found | H% Calcd. | H% Found | N% Calcd. | N% Found |
|---|---|---|---|---|---|---|---|---|---|
| **3a** | 161-163 [b] | 64 | $C_{14}H_{10}N_2O_2S_2$ | 55.63 | 55.83 | 3.31 | 3.48 | 9.27 | 9.07 |
| **3b** | 135-137 | 69 | $C_{15}H_{12}N_2O_2S_2$ | 56.96 | 56.71 | 3.80 | 3.52 | 8.86 | 8.98 |
| **3c** | 145-147 | 60 | $C_{14}H_9ClN_2O_2S_2$ | 49.93 | 49.99 | 2.67 | 2.81 | 8.32 | 8.11 |
| **3d** | 179-181 | 64 | $C_{15}H_{12}N_2O_3S_2$ | 54.22 | 53.95 | 3.61 | 3.41 | 8.43 | 8.35 |
| **3e** | 238-240 | 65 | $C_{14}H_9ClN_2O_2S_2$ | 49.93 | 50.12 | 2.67 | 2.80 | 8.32 | 8.51 |
| **3f** | 244-246 | 61 | $C_{14}H_9N_3O_4S_2$ | 48.41 | 48.11 | 2.59 | 2.68 | 12.10 | 11.75 |
| **5a** | 299-301 | 60 | $C_{10}H_9N_3O_3S_2$ | 42.40 | 42.11 | 3.18 | 3.20 | 14.84 | 14.70 |
| **5b** | 298-300 | 64 | $C_{11}H_{11}N_3O_3S_2$ | 44.44 | 44.61 | 3.70 | 3.70 | 14.14 | 14.31 |
| **6a** | 172-174 | 90 | $C_8H_7N_3O_2S_2$ | 39.83 | 39.60 | 2.90 | 3.12 | 17.43 | 17.23 |
| **6b** | 213-215 | 91 | $C_9H_9N_3O_2S_2$ | 42.35 | 42.00 | 3.53 | 3.75 | 16.47 | 16.18 |
| **7a** | 97-99 | [c] | $C_8H_5ClN_2O_2S_2$ | 36.85 | 36.99 | 1.92 | 1.61 | 10.75 | 10.54 |
| **7b** | 101-103 | [d] | $C_9H_7ClN_2O_2S_2$ | 39.34 | 39.07 | 2.55 | 2.81 | 10.20 | 9.95 |
| **7c** | 100-102 | 48 [e] | $C_8H_4Cl_2N_2O_2S_2$ | 32.54 | 32.18 | 1.36 | 1.30 | 9.49 | 9.18 |
| **7d** | 65-67 | 55 [e] | $C_9H_7ClN_2O_3S_2$ | 34.18 | 34.00 | 2.41 | 2.58 | 9.64 | 10.01 |
| **9** | oil | 76 | $C_9H_7ClN_2S_2$ | 44.54 | 44.85 | 2.89 | 2.61 | 11.55 | 11.78 |
| **10a** | 86-88 | 55 | $C_{15}H_{12}N_2O_2S_3$ | 51.72 | 52.02 | 3.45 | 3.45 | 8.05 | 8.31 |
| **10b** | 84-86 | 66 | $C_{16}H_{14}N_2O_2S_3$ | 53.04 | 52.80 | 3.87 | 3.96 | 7.73 | 7.61 |
| **10c** | 89-91 | 54 | $C_{15}H_{11}ClN_2O_2S_3$ | 47.06 | 47.31 | 2.88 | 2.98 | 7.32 | 6.99 |
| **10d** | 79-81 | 62 | $C_{16}H_{14}N_2O_3S_3$ | 50.79 | 50.60 | 3.70 | 3.62 | 7.41 | 7.71 |
| **11a** | 181-183 | 65 | $C_{14}H_{10}N_2O_4S_3$ | 45.90 | 46.20 | 2.73 | 2.52 | 7.65 | 7.64 |
| **11b** | 205-207 | 68 | $C_{16}H_{14}N_2O_4S_3$ | 48.73 | 48.81 | 3.55 | 3.41 | 7.11 | 7.11 |
| **11c** | 230-232 | 60 | $C_{14}H_8Cl_2N_2O_4S_3$ | 38.62 | 38.60 | 1.84 | 1.92 | 6.44 | 6.51 |
| **11d** | 188-190 | 66 | $C_{16}H_{14}N_2O_6S_3$ | 45.07 | 46.81 | 3.29 | 3.12 | 6.57 | 6.66 |
| **11e** | 168-170 | 63 | $C_{15}H_{12}N_2O_4S_3$ | 47.37 | 47.68 | 3.16 | 3.00 | 7.37 | 7.05 |
| **11f** | 201-203 | 60 | $C_{15}H_{11}ClN_2O_4S_3$ | 43.43 | 43.75 | 2.65 | 2.60 | 6.76 | 6.71 |
| **11g** | 201-203 | 60 | $C_{15}H_{11}ClN_2O_5S_3$ | 41.81 | 41.85 | 2.56 | 2.79 | 6.50 | 6.33 |
| **12a** | 192-194 | 53 | $C_{15}H_{12}N_2O_4S_3$ | 47.37 | 47.09 | 3.16 | 2.94 | 7.37 | 7.06 |
| **12b** | 184-186 | 62 | $C_{16}H_{14}N_2O_4S_3$ | 48.73 | 49.00 | 3.55 | 3.58 | 7.11 | 7.37 |
| **12c** | 172-174 | 55 | $C_{15}H_{11}ClN_2O_4S_3$ | 43.43 | 43.42 | 2.65 | 2.80 | 6.76 | 6.55 |
| **12d** | 166-168 | 52 | $C_{16}H_{14}N_2O_5S_3$ | 46.83 | 46.61 | 3.41 | 3.39 | 6.83 | 7.17 |
| **13** | 128-130 | 75 | $C_9H_7ClN_2O_2S_3$ | 39.34 | 39.98 | 2.55 | 2.23 | 10.20 | 10.51 |

[a] All compounds were crystallized from ethanol. [b] Ref 13, mp 161.5-162.5. [c] Method A: 23% yield, Method B: 55% yield. [d] Method A: 26% yield, Method B: 66% yield. [e] This compound was prepared by Method B.

Scheme 1



**1a-d**

**a**, $R_1 = H$
**b**, $R_1 = OCH_3$
**c**, $R_1 = Cl$
**d**, $R_1 = NO_2$

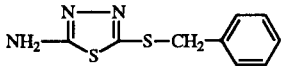
**2a-c**

**a**, $R_2 = H$
**b**, $R_2 = CH_3$
**c**, $R_2 = Cl$

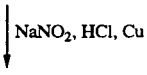
**3a-f**

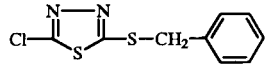
**a**, $R_1 = H$, $R_2 = H$
**b**, $R_1 = H$, $R_2 = CH_3$
**c**, $R_1 = H$, $R_2 = Cl$
**d**, $R_1 = OCH_3$, $R_2 = H$
**e**, $R_1 = Cl$, $R_2 = H$
**f**, $R_1 = NO_2$, $R_2 = H$

Method B:

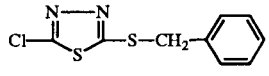


**8**

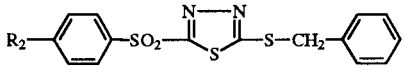




**13**

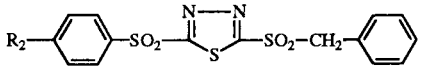


**9**



**10a-d**

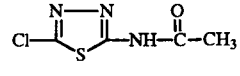
**a**, $R_2 = H$
**b**, $R_2 = CH_3$
**c**, $R_2 = Cl$
**d**, $R_2 = OCH_3$



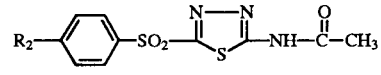
**12a-d**

**a**, $R_2 = H$
**b**, $R_2 = CH_3$
**c**, $R_1 = Cl$
**d**, $R_2 = OCH_3$

Method A:

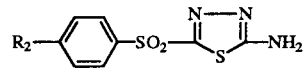


**4**



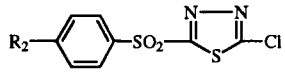
**5a-b**

**a**, $R_2 = H$
**b**, $R_2 = CH_3$



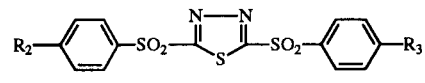
**6a-b**

**a**, $R_2 = H$
**b**, $R_2 = CH_3$



**7a-d**

**a**, $R_2 = H$
**b**, $R_2 = CH_3$
**c**, $R_2 = Cl$
**d**, $R_2 = OCH_3$



**11a-g**

**a**, $R_2 = H$, $R_3 = H$
**b**, $R_2 = CH_3$, $R_3 = CH_3$
**c**, $R_2 = Cl$, $R_3 = Cl$
**d**, $R_2 = OCH_3$, $R_3 = OCH_3$
**e**, $R_2 = H$, $R_3 = CH_3$
**f**, $R_2 = CH_3$, $R_3 = Cl$
**g**, $R_2 = OCH_3$, $R_3 = Cl$

the desired compounds **3**. However reaction in dimethylformamide at reflux temperature gave 2-aryl-5-arylsulfonyl-1,3,4-thiadiazoles **3** in good yield (Scheme 1).

The synthesis of the intermediate 2-arylsulfonyl-5-chloro-1,3,4-thiadiazoles **7** was tried according to method A (Scheme 1).

The reaction of 2-acetamido-5-chloro-1,3,4-thiadaizole **4** [11] with sodium arylsulfinates gave 2-acetamido-5-arylsulfonyl-1,3,4-thiadiazoles **5** in good yield. Hydrolysis of compounds **5** followed by diazotation of compounds **6** in the presence of copper powder afforded 2-arylsulfonyl-5-chloro-1,3,4-thiadiazoles **7** in low yield. The latter compounds could be prepared in good yield starting from 2-amino-5-benzylmercato-1,3,4-thiadiazole **8** [12]. Diazotation of compound **8** in the presence of copper powder afforded 2-benzylmercapto-5-chloro-1,3,4-thiadiazole **9**. Reaction of compound **9** with sodium arylsulfinate in refluxing DMF gave 2-arylsulfonyl-5-benzylmercapto-1,3,4-thiadiazoles **10**. Oxidative chlorination of **10** gave the desired compounds **7** in good yield.

Reaction of sodium arylsulfinate with compound **7** in refluxing ethanol yielded 2,5-diarylsulfonyl-1,3,4-thiadiazoles **11**. Oxidation of compounds **10** with hydrogen peroxide in acetic acid afforded 2-arylsulfonyl-5-benzylsulfonyl-1,3,4-thiadiazoles **12**. Under similar conditions oxidation of compound **9** gave 2-benzylsulfonyl-5-chloro-1,3,4-thiadiazole (**13**).

The physical constants of the compounds prepared are summarized in Table 1.

## EXPERIMENTAL

Melting points were taken on a Kofler hot stage apparatus and are uncorrected. The ir spectra were obtained using a Perkin-Elmer Model 267 spectrograph (potassium bromide disks). The $^1$H nmr spectra were recorded on a Bruker AC-80 spectrometer and chemical shifts ($\delta$) are in ppm relative to internal tetramethylsilane. The mass spectra were run on a Finigan TSQ-70 spectrometer at 70 ev.

Syntheses of 2-Aryl-5-arylsulfonyl-1,3,4-thiadiazoles **3a-f**.

General Procedure.

A stirring mixture of compounds **1** (0.01 mole) [7] and compounds **2** (0.01 mole) in DMF (30 ml) was refluxed for 2-3 hours. The solvent was removed under reduced pressure. To the residue water was added (30 ml). The precipitate was filtered and crystallized from ethanol.

2-(4-Methylphenylsulfonyl)-5-phenyl-1,3,4-thiadiazole (**3b**).

This compound was prepared according to the general procedure in 69% yield; mp 135-137°; ir (potassium bromide): $\nu$ 1342 and 1159 cm$^{-1}$ ($SO_2$); $^1$H nmr (deuteriochloroform): 8.04 (d, 2H, $J_{AB}$ = 8.0 Hz, aromatic), 7.90 (m, 2H, Ph), 7.53 (m, 3H, Ph), 7.40 (d, 2H, $J_{AB}$ = 8.0 Hz, aromatic) and 2.46 ppm (s, 3H, $CH_3$); ms: m/z (%) 348 ($M^+$, 35), 330 (7), 167 (7), 160 (18), 149 (59), 91 (100), 77 (14).

*Anal.* Calcd. for $C_{15}H_{12}N_2O_2S_2$: C, 56.96; H, 3.80; N, 8.86. Found: C, 56.71; H, 3.52; N, 8.98.

2-Acetamido-5-phenylsulfonyl-1,3,4-thiadiazole (**5a**).

A stirring mixture of compound **4** [11] (1.77 g, 0.01 mole) and sodium phenylsulfinate (**2a**) (1.64 g, 0.01 mole) in DMF (30 ml) was refluxed for 5 hours. The solvent was removed under reduced pressure and water was added (50 ml) to the residue. The precipitate was filtered and crystallized from ethanol to give 1.7 g (60%) of **5a**, mp 299-301°; ir (potassium bromide): $\nu$ 3140 (NH), 1700 (C=O), 1349 and 1150 cm$^{-1}$ ($SO_2$); $^1$H nmr (deuteriochloroform): 8.10 (m, 2H, $C_6H_5$), 7.62 (m, 3H, $C_6H_5$) and 2.41 ppm (s, 3H, $CH_3$).

*Anal.* Calcd. for $C_{10}H_9N_3O_3S_2$: C, 42.40; H, 3.18; N, 14.84. Found: C, 42.11; H, 3.20; N, 14.70.

2-Amino-5-phenylsulfonyl-1,3,4-thiadiazole (**6a**).

A stirring mixture of **5a** (2.83 g, 0.01 mole) in ethanol (30 ml) and concentrated hydrochloric acid (6 ml) was refluxed for 5 hours. The solvent was removed under reduced pressure and water was added (30 ml) to the residue. The precipitate was filtered and washed with water. The product crystallized from ethanol to give 2.17 g (90%) of **6a**, mp 172-174 ° .

*Anal.* Calcd. for $C_8H_7N_3O_2S_2$: C, 39.83; H, 2.90; N, 17.43. Found: C, 39.60; H, 3.12; N, 17.23.

2-Amino-5-(4-methylphenylsulfonyl)-1,3,4-thiadiazole (**6b**).

This compound was prepared similar to **6a** in 91% yield, mp 213-215°; ir (potassium bromide): $\nu$ 3430, 3335 ($NH_2$), 1333 and 1165 cm$^{-1}$ ($SO_2$); $^1$H nmr (deuteriochloroform): 7.92 (d, 2H, $J_{AB}$ = 8.0 Hz, $C_6H_4$), 7.45 (d, 2H, $J_{AB}$ = 8.0 Hz, $C_6H_4$) and 2.49 ppm (s, 3H, $CH_3$); ms: m/z (%) 255 ($M^+$, 10), 191 (40), 155 (6), 150 (20), 149 (100), 91 (65), 74 (11), 65 (51).

2-Chloro-5-phenylsulfonyl-1,3,4-thiadiazole (**7a**).

Method A.

To a stirring solution of concentrated hydrochloric acid (35 ml) and water (10 ml), containing copper powder (0.5 g), at -5°, a mixture of compound **10a** (2.41 g, 0.01 mole) and sodium nitrite (2.76 g, 0.04 mole) was added in small portions. The reaction mixture was allowed to reach room temperature and was stirred for an additional 1 hour, then heated at 60° for 15 minutes. The cooled reaction mixture was extracted with chloroform (3 x 50 ml). The organic layer was washed with water and dried (sodium sulfate). The solvent was removed under reduced pressure to give a solid that was purified by flash chromatography on silica gel eluting with 5% chloroform/hexan to give 0.6 g (23%) of **7a**, mp 97-99°.

2-Chloro-5-(4-methylphenylsulfonyl)-1,3,4-thiadiazole (**7b**).

This compound was prepared similar to **7a** in 26% yield, mp 101-103°; ir (potassium bromide): $\nu$ 1340, 1160 cm$^{-1}$ ($SO_2$); $^1$H nmr (deuteriochloroform): 7.99 (d, 2H, $J_{AB}$ = 8.0 Hz, $C_6H_4$) 7.41 (d, 2H, $J_{AB}$ = 8.0, $C_6H_4$ ) and 2.47 ppm (s, 3H, $CH_3$).

Syntheses of 2-arylsulfonyl-5-chloro-1,3,4-thiadiazoles **7a-d**.

General Procedure (Method B).

A stirring mixture of compound **10** (0.01 mole) in anhydrous dioxan (50 ml) was treated with chlorine for 20 minutes at 5°.

The solvent was removed under reduced pressure to give a solid that was purified by flash chromatography on silica gel eluting with 5% chloroform/hexane to give **7**. The product crystallized from ethanol.

2-Chloro-5-(4-chlorophenylsulfonyl)-1,3,4-thiadiazole (**7c**).

This compound was prepared according to the general procedure in 48% yield, mp 100-102°; ir (potassium bromide): ν 1342, 1160 $cm^{-1}$ ($SO_2$); $^1H$ nmr (deuteriochloroform): 7.05 (d, 2H, $J_{AB}$ = 8.0 Hz, aromatic) and 7.58 ppm (d, 2H, $J_{AB}$ = 8.0 Hz, aromatic).

Syntheses of 2,5-Diarylsulfonyl-1,3,4-thiadiazoles **11a-g**.

General Procedure.

A stirring mixture of compound **7** (0.01 mole) and sodium arylsulfinate **2** (0.01 mole) in ethanol (30 ml) was refluxed for 0.5 hour. The solvent was removed under reduced pressure and water (30 ml) was added. The precipitate was filtered and crystallized from ethanol to give **11**.

2,5-Bis(phenylsulfonyl)-1,3,4-thiadiazole (**11a**).

This compound was prepared according to the general procedure in 65% yield, mp 181-183°; ir (potassium bromide): ν 1352, 1160 $cm^{-1}$ ($SO_2$); $^1H$ nmr (deuteriochloroform): 8.13 (m, 2H, $C_6H_5$) and 7.67 ppm (m, 3H, $C_6H_5$).

2-(4-Chlorophenylsulfonyl)-5-(4-methylphenylsulfonyl)-1,3,4-thiadiazole (**11f**).

This compound was prepared according to the general procedure in 60% yield, mp 201-203°; ir (potassium bromide): ν 1356, 1158 $cm^{-1}$ ($SO_2$); $^1H$ nmr (deuteriochloroform): 8.05 (d, 2H, $ClC_6H_4$, $J_{AB}$ = 8.7 Hz), 7.98 (d, 2H, $CH_3C_6H_4$, $J_{AB}$ = 8.0 Hz), 7.58 (d, 2H, $ClC_6H_4$, $J_{AB}$ = 8.7 Hz), 7.40 (d, 2H, $CH_3C_6H_4$, $J_{AB}$ = 8.0 Hz) and 2.46 ppm (s, 3H, $CH_3$).

*Anal.* Calcd. for $C_{15}H_{11}ClN_2O_4S_3$: C, 43.43; H, 2.65; N, 6.76. Found: C, 43.75; H, 2.60; N, 6.71.

2-Benzylmercapto-5-chloro-1,3,4-thiadiazole (**9**).

This compound was prepared similar to **5**. It was purified by flash chromatography on silica gel eluting with 5% chloroform/hexane to provide 76% of **9** as a colorless oil; $^1H$ nmr (deuteriochloroform): 7.37 (m, 5H, $C_6H_5$) and 4.55 ppm (s, 2H, $CH_2$); ms: m/z (%) 243 ($M^+$, 32), 162 (18), 148 (29), 133 (11), 126 (24), 119 (19), 105 (39), 92 (23), 91 (100), 86 (11), 83 (19), 77 (15), 65 (12).

Syntheses of 2-Arylsulfonyl-5-benzylmercapto-1,3,4-thiadiazoles **10a-d**.

General Procedure.

A stirring mixture of compound **9** (0.01 mole) and sodium arylsulfinate **2** (0.01 mole) in DMF (30 ml) was refluxed for 1 hour. The solvent was removed under reduced pressure and water (50 ml) was added. The crude material was filtered and crystallized from a large volume of ethanol.

2-Phenylsulfonyl-5-benzylmercapto-1,3,4-thiadiazole (**10a**).

This compound was prepared as explained above in 55% yield, mp 86-88°; ir (potassium bromide): ν 1340 and 1168 $cm^{-1}$ ($SO_2$); $^1H$ nmr (deuteriochloroform): 8.10 (m, 2H, $C_6H_5SO_2$), 7.60 (m, 3H, $C_6H_5SO_2$), 7.34 (m, 5H, $C_6H_5$) and 4.55 ppm (s, 2H, $CH_2$); ms: m/z (%) 348 ($M^+$, 35) 330 (7), 160 (18), 149 (59), 91 (100) and 77 (14).

*Anal.* Calcd. for $C_{15}H_{12}N_2O_2S_3$: C, 51.72; H, 3.45; N, 8.05. Found: C, 52.02; H, 3.45; N, 8.31.

Syntheses of 2-Arylsulfonyl-5-benzylsulfonyl-1,3,4-thiadiazoles **12a-d**.

General Procedure.

To a stirring mixture of compound **10** in glacial acetic acid (15 ml) was added 30% hydrogen peroxide solution (15 ml) and the mixture was heated on a steam bath for 30 minutes. After cooling, water (45 ml) was added, and the precipitate was filtered and crystallized from ethanol to give **12**.

2-(4-Methylphenylsulfonyl)-5-benzylsulfonyl-1,3,4-thiadiazole (**12b**).

This compound was prepared according to the general procedure in 62% yield, mp 184-186; ir (potassium bromide): ν 1342, 1333, 1167 and 1150 $cm^{-1}$ ($SO_2$); $^1H$ nmr (deuteriochloroform): 8.03 (d, 2H, $CH_3C_6H_4$, $J_{AB}$ = 8.0 Hz), 7.40 (d, 2H, $CH_3C_6H_4$, $J_{AB}$ = 8.0 Hz), 7.26 (m, 5H, $C_6H_5$), 4.76 (s, 2H, $CH_2$) and 2.46 ppm (s, 3H, $CH_3$); ms: m/z (%) 394 ($M^+$, 6), 330 (96), 182 (17), 175 (85), 149 (90), 139 (44), 105 (80), 91 (100), 65 (77).

2-Benzylsulfonyl-5-chloro-1,3,4-thiadiazole (**13**).

This compound was prepared similar to **10** from **9** in 75% yield, mp 128-130°; ir (potassium bromide): ν 1340 and 1157 $cm^{-1}$ ($SO_2$); $^1H$ nmr (deuteriochloroform): 7.26 (m, 5H, $C_6H_5$) and 4.76 ppm (s, 2H, $CH_2$); ms: m/z (%) 274 ($M^+$, 15), 212 (13), 210 (39), 91 (100), 65 (45).

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