Reactions of Tetrasulfur Tetranitride with Aryl Dibromomethyl Ketones: One-pot Synthesis of 3-Aroylformamido-4-aryl-1,2,5-thiadiazoles and their Reactions

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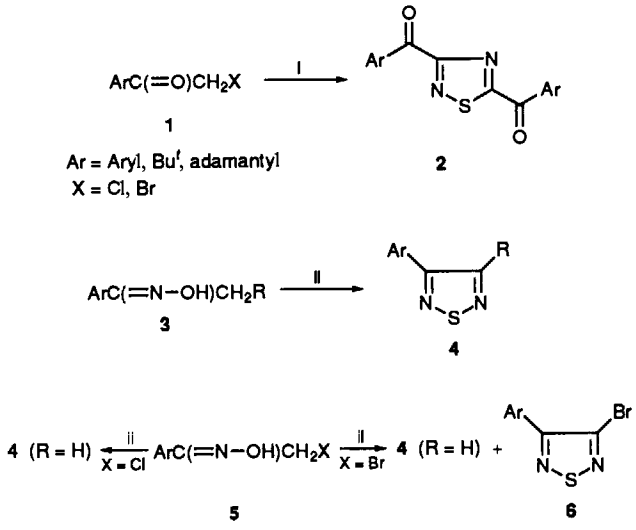
Heating of dibromomethyl aryl ketones with tetrasulfur tetranitride (S_4N_4) at 115 °C without a solvent gave 3-aroylformamido-4-aryl-1,2-5-thiadiazoles **8** as major products (12–71%) and 3,5-diaroyl-1,2,4-thiadiazoles **2** as minor products in certain cases. The structures of compounds **8** were determined based on the X-ray analysis of 3-benzoylformamido-4-phenyl-1,2,5-thiadiazole **8a** and comparison with an authentic sample of comound **8a**, as well as all the spectroscopic and analytical data of compounds **8**. Oxidation of compounds **8** with *m*-chloroperbenzoic acid in chloroform at room temperature gave compounds **2** (0–66%), whereas reduction of compounds **8** with sodium boranuide in a mixture of chloroform–ethanol at room temperature gave 3-amino-4-aryl-1,2,5-thiadiazoles **10** (71–93%). Treatment of 3-(3-nitrobenzoylformamido)-4-(3-nitrophenyl)-1,2,5-thiadiazole **8d** with either sodium hydroxide in aqueous *p*-dioxane at reflux or sodium hydride in chloroform at room temperature gave 3-amino-4-(3-nitrophenyl)-1,2,5-thiadiazole **10d** in 56 and 80% yield, respectively.

Previously we have shown that the reactions of tetrasulfur tetranitride (S_4N_4) with monohalogenomethyl aryl ketones or the corresponding alkyl ketones **1** without α-hydrogens in the alkyl groups in chlorobenzene at 110–115 °C gave 3,5-diaroyl- and 3,5-diacyl-1,2,4-thiadiazoles **2**, respectively as major products.[1] Since only minute amounts of 1,2,4-thiadiazole were reported to be formed in the reactions of dibenzyl ketone with S_4N_4,[2] it was believed that the halogen atom at the α-position of the ketones **1** played an important role in the formation of the 1,2,4-thiadiazoles. On the other hand, 3-aryl- or 3-alkyl-4-aryl-1,2,5-thiadiazoles 4 were formed by the reactions of alkyl aryl ketoximes **3** having at least two hydrogens α to the oxime functionality with S_4N_4 in *p*-dioxane at reflux.[3] This result was in contrast with those obtained from the reactions of diaryl ketoximes with S_4N_4 in toluene at reflux from which the corresponding diarylimino sulfides, diaryl ketones, and/or arylamide, arylimine, and aminosulfenamide were isolated.[4]

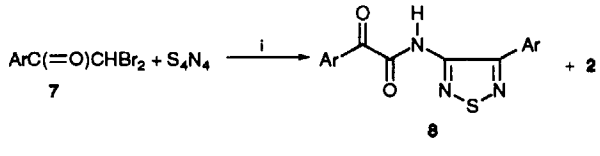
The synergism between a halogen atom and an oxime functionality was also observed in the reactions of aryl monohalogenomethyl ketoximes **5** with S_4N_4 in *p*-dioxane at reflux.[5] From the reactions of compounds **5** (X = Cl) were obtained 1,2,5-thiadiazoles 4 (R = H) in excellent yields except for the reactions of *p*-anisyl chloromethyl ketoxime **5** (Ar = *p*-$MeOC_6H_4$, X = Cl), whereas those of compounds **5** (X = Br) under the same conditions as in the reactions of the chloro analogues afforded compounds 4 (R = H) and 3-aryl-4-bromo-1,2,5-thiadiazoles **6**. Interestingly, the total yields of the two products, **4** and **6**, obtained from the reactions of compounds **5** (X = Br) were comparable to those of the single products **4** (R = H) obtained from the corresponding oxime **5** (X = Cl), which stimulated us to investigate further the effects of the halogen atoms in the reactions of aryl dibromomethyl ketones **7** with S_4N_4. Our results are described herein.



Scheme 1 *Reagents and conditions:* i, S_4N_4, C_6H_5Cl, 110–115 °C; ii, S_4N_4, *p*-dioxane, heat

Results and Discussion

Reactions of Dibromides **7** *with* S_4N_4.—Compounds **7** were prepared according to the literature methods.[6,7] A mixture of the appropriate amount of both a compound **7** and S_4N_4 was slowly heated to 115 °C, during which time the compound **7** melted and S_4N_4 was dissolved in it concomitant with initiation of the reaction. The colour of the solution turned gradually from orangish yellow to dark. Heating was continued until no spot corresponding to S_4N_4 was observed on TLC [silica gel; R_f of S_4N_4 0.75 (benzene)]. Chromatography of the reaction mixture gave the corresponding 3-aroylformamido-4-aryl-1,2,5-thiadiazole **8** as a major product and compound **2** as a minor product depending on starting compound **7**, in addition to unchanged substrate **7** and a complex mixture. Attempts were made to reduce the amount of unchanged starting material **7** by increasing the concentration of S_4N_4. However, yields of compounds **8** decreased drastically and separation of the reaction mixture by chromatography was troublesome due to



Conditions for reaction of dibromo ketones **7** with S_4N_4 to prepare glyoxylamides **8**. i, 115 °C.

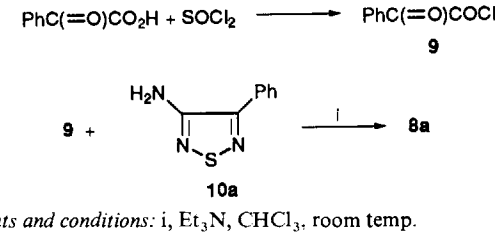
Table 1 Synthesis of 3-aroylformamido-4-aryl-1,2,5-thiadiazoles **8**

Entry (substrate)	Ar	Time (*t*/h)	Product	Yield (%)[a]	By-product	Yield (%)[a]
7a	Ph	5	**8a**	13		
7b	4-ClC_6H_4	10	**8b**	12	**2a**	2
7c	4-BrC_6H_4	10	**8c**	28	**2b**	11
7d	3-$O_2NC_6H_4$	10	**8d**	48	**2c**	12
7e	4-$O_2NC_6H_4$	10	**8e**	69	**2d**	10
7f	4-NCC_6H_4	10	**8f**	59		
7g	2-Naphthyl	5	**8g**	52		
7h	2-Thienyl	6	**8h**	15		
7i	3-$Br_2CHCOC_6H_4$	10	**8i**	71		

[a] Isolated yield based on the amount of compound **7** consumed.

the presence of much tarry material. The yields of products **8** are summarized in Table 1.

Structural Identification of Products **8**.—^{1}H NMR spectra of the compounds **8** showed a singlet due to NH between δ_H 9.73 and 11.98. All aryl protons appeared as a multiplet in the region δ_H 6.67–9.25 except for those of **8h**, which exhibited a double doublet at δ_H 7.94 with J = 4.9 and 1.2 Hz and at δ_H 8.57 with J = 4.0 and 1.2 Hz. A multiplet at δ_H 7.13–7.31 was assigned to the four protons at C-4 and C-5 of two thienyl groups. IR spectroscopy of compounds **8** exhibited a band in the range ν_{max} 3240–3350 cm^{-1}, indicating the presence of an NH band. Compounds **8a**, **8d**, **8g** and **8i** showed two strong bands, at ν_{max} 1675–1678 and 1694–1698 cm^{-1}, which indicated the presence of two different carbonyl groups, whereas compounds **8b**, **8c**, **8e**, **8f** and **8h** showed the corresponding bands at ν_{max} 1640–1669 and 1672–1718 cm^{-1}. ^{13}C NMR (50.3 MHz; $CDCl_3$) spectroscopy of compound **8d** exhibited sixteen peaks consisting of a weak peak at δ_C 185.39, indicating the presence of a carbonyl carbon of the benzoyl group, together with other peaks at δ_C 122.07, 124.30, 124.40, 128.68, 130.51, 130.68, 132.96, 133.55, 133.92, 135.76, 147.70, 147.91, 149.00, 153.03 and 162.32. Mass spectroscopy of each compound **8** showed a corresponding molecular-ion peak and elemental analysis of each compound **8** was in good agreement with the corresponding structure. In spite of their reasonable spectroscopic and analytical data being available, a difficulty in assigning the correct structures of compounds **8** was encountered. In particular, it was cumbersome to rationalize the formation of the products obtained from the subsequent chemical reactions of compounds **8** (*vide infra*). The structural ambiguity was finally solved by X-ray crystallography. X-Ray analysis of compound **8a** showed clearly the presence of two adjacent carbonyl groups bonded to the phenyl group and the nitrogen atom, respectively, as shown in Fig. 1. The structure of compound **8a** was also confirmed by comparison with that of



Reagents and conditions: i, Et_3N, $CHCl_3$, room temp.

an authentic sample which was prepared by the reaction of benzoylformyl chloride **9** with 3-amino-4-phenyl-1,2,5-thiadiazole **10a** (*vide infra*). Selected bond lengths for compound **8a** are given in Table 2.

Oxidation of Compounds **8** *with* m-*Chloroperbenzoic Acid* (*MCPBA*).—Before the X-ray analysis of compound **8a**,

Table 2 Selected bond lengths (Å) for compound **8a**[a]

S(1)–N(1)	1.635	C(9)–N(3)	1.401
S(1)–N(2)	1.611	C(8)–N(3)	1.355
N(1)–C(10)	1.313	C(8)–O(1)	1.221
N(2)–C(9)	1.330	C(7)–C(8)	1.510
C(9)–C(10)	1.467	C(7)–O(2)	1.216

[a] Crystallographic numbering scheme, see Fig. 1.

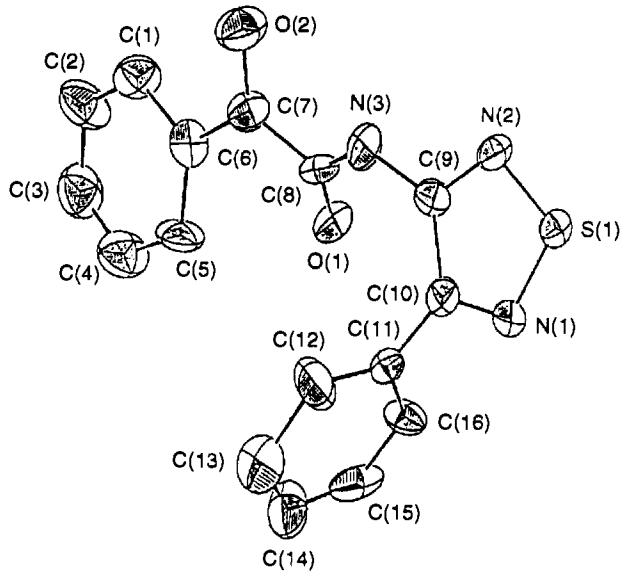
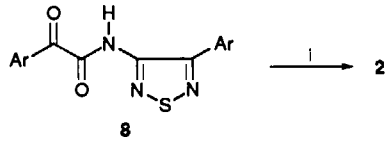


Fig. 1 ORTEP view of compound **8a**

oxidation of compounds **8** with MCPBA was carried out in order to obtain information about the structure of compounds **8**. Reaction of a compound **8** (1 mol equiv.) with MCPBA (5 mol equiv.) in chloroform for 7 h at room temperature gave compounds **2** as the only identifiable products in moderate yields. The structural identification of products **2b**–**2e** was made based on the structure of the parent **2a**, which was the only previously known compound among the 1,2,4-thiadiazoles **2**



Reagents and conditions: i, MCPBA, $CHCl_3$, room temp.

prepared. The yields of products **2** and the reaction times are summarized in Table 3.

It has been known for some time that 3,5-disubstituted 1,2,5-thiadiazoles are oxidized to form the corresponding 1,2,5-thiadiazole 1-oxides by either MCPBA[8,9] or dinitrogen tetraoxide.[9] However, the formation of compounds **2** from the oxidation of the glyoxylamides **8** by MCPBA suggests that the initial oxidation might not occur in the same way. Further study is necessary in order to elucidate the mechanism of the formation compounds **2** from substrates **8**.

Reduction of Compounds **8** *by Sodium Boranuide* ($NaBH_4$).—To a solution of a glyoxylamide **8** (1 mol equiv.) in a mixture of chloroform and ethanol (1 : 1) was added sodium boranuide (2 mol equiv.), and the mixture was stirred at room temperature for 1 h. TLC (silica gel) showed no spot corresponding to substrate **8**, and a new spot with higher R_f-value than that of compound **8** was observed. The new spot, identified as that of the corresponding 3-amino-4-aryl-1,2,5-thiadiazole **10**, was

Table 3 Formation of 3,5-diaroyl-1,2,4-thiadiazoles **2**

Compound	Ar	Time (*t*/h)	Yield (%)[a]	
8a	Ph	7	**2e**[c]	39
8b	4-ClC_6H_4	48	*b*	
8c	4-BrC_6H_4	48	*b*	
8d	3-$O_2NC_6H_4$	7	**2c**	59
8e	4-$O_2NC_6H_4$	7	**2d**	63
8f	4-NCC_6H_4	7	**2f**	66
8g	2-Naphthyl	7	**2g**	43
8h	2-Thienyl	7	*b*	

[a] Isolated yield. [b] Only compounds **8b**, **8c** and **8h** were recovered, in 77, 82 and 43% yield, respectively. [c] Known compound.[1]

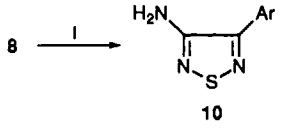
Table 4 Synthesis of 3-amino-4-aryl-1,2,5-thiadiazoles **10**

Compound	Ar	Yield (%)[a]
10a	Ph	78[b]
10b	4-ClC_6H_4	92
10c	4-BrC_6H_4	91[b]
10d	3-$O_2NC_6H_4$	89
10e	4-$O_2NC_6H_4$	93
10f	4-NCC_6H_4	86
10g	2-Naphthyl	84
10h	2-Thienyl	71[b]

[a] Isolated yield. [b] Known compounds.

separated by chromatography as the only identifiable product. The yields of products **10** are summarized in Table 4.

Only a few 3-amino-4-aryl-1,2,5-thiadiazoles, such as 3-amino-4-phenyl- **10a**,[10] 3-amino-4-(4-bromophenyl)- **10c**,[10] 3-



10

Reagents and conditions: i, $NaBH_4$, $CHCl_3$–EtOH, room temp.

amino-4-(2-thienyl)- **10h**,[11] and 3-amino-4-(*p*-tolyl)-1,2,5-thiadiazole,[10] have previously been reported. They were obtained from the reactions of substituted acetylenes with S_4N_4 in refluxing toluene in 3–9% yield. Consequently, treatment of glyoxylamides **8** with $NaBH_4$ would be a good synthetic method for compounds **10**.

Treatment of Compound **8d** *with Acids and Bases.*—In order to study the stability of compounds **8** under both acidic and basic conditions, compound **8d** (0.313 mmol) was chosen as a model, and was treated with conc. hydrochloric acid (2 cm^3) in *p*-dioxane (30 cm^3) at room temperature for 24 h. Essentially no change was observed on TLC. However, 3-amino-4-(3-nitrophenyl)-1,2,5-thiadiazole **10d** was obtained in 71% yield after refluxing of the mixture for 6 h. In the meantime, attempted analysis of compound **8d** with sodium hydroxide in a mixture of water and *p*-dioxane (1 : 5) at room temperature for 24 h gave only a 6% yield of compound **10d**, with 72% recovery of substrate **8d**. However, complete hydrolysis of compound **8d** occurred after 6 h reflux under the same conditions, to give an isolated yield of compound **10d**, after chromatography, of 56%. In addition, treatment of compound **8d** with sodium hydride in chloroform for 1 h at room temperature, followed by chromatography, gave compound **10d** in 80% yield. Similar treatment of compound **8d** with sodium hydride under the same conditions as in the foregoing reaction, followed by addition of methyl iodide, did not give any methylated products and only compound **10d** was isolated, in 80% yield. In conclusion, compound **8d** undergoes hydrolysis to give compound **10d** by treatment with either hydrochloric acid in *p*-dioxane or sodium hydroxide in aqueous *p*-dioxane at reflux, and the hydrolysis takes place rapidly even at room temperature by treatment with sodium hydride in chloroform.

Experimental

All m.p.s were determined on a Fisher-Johns melting point apparatus and are uncorrected. IR spectra were obtained on a Perkin-Elmer Model 283 spectrophotometer for samples as KBr pellets or thin films. ^1H NMR spectra were determined on either a Bruker 80 MHz or a Varian EM 360 A 60 MHz spectrometer using tetramethylsilane as internal standard. *J* Values are given in Hz. ^{13}C NMR spectra were recorded on a Varian VXR-200S spectrometer operating at 50.3 MHz. Mass spectra were obtained by electron impact at 70 eV on a Varian MAT 711 spectrometer. Elemental analyses were determined by Korea Basic Science Center. Column chromatography was performed on silica gel (Merck, 70–230 or 240–400 mesh, ASTM). Light petroleum refers to the fraction with distillation range 30–70 °C. Neutrality was determined using Hydrion pH test paper.

Tetrasulfur tetranitride was prepared by the reaction of sulfur monochloride with ammonia gas at room temperature.[12] MCPBA (50–60%) was obtained from Aldrich. Aryl dibromomethyl ketones, **7a–d** and **7g**, were prepared by the literature methods, and compounds **7e**, **f**, **h**, i were prepared by a method analogous to that in the literature:[13] 2,2-dibromo-1-phenylethanone **7a**, m.p. 36–37 °C (lit.,[13] 36 °C); 2,2-dibromo-1-(4-chlorophenyl)ethanone **7b**, m.p. 92–93 °C (lit.,[13] 93–94 °C); 2,2-dibromo-1-(4-bromophenyl)ethanone **7c**, m.p. 91–92 °C (lit.,[13] 93–94 °C); 2,2-dibromo-1-(3-nitrophenyl)ethanone **7d**, m.p. 54–55 °C (lit.,[13] 55–56 °C); *2,2-dibromo-1-(4-nitrophenyl)ethanone* **7e**, m.p. 54–55 °C (from EtOH) (Found: C, 29.7; H, 1.6; N, 4.3; Br, 49.4. $C_8H_5Br_2NO_3$ requires C, 29.75; H, 1.6; N, 4.3; Br, 49.5%); ν_{max}(KBr)/cm^{-1} 1696, 1601, 1528, 1510, 1344, 1322, 1267, 994, 866, 854 and 786; δ_H(80 MHz; $CDCl_3$) 6.62 (1 H, s, CH) and 8.30 (4 H, s, ArH); 4-(*2,2-dibromoacetyl)benzonitrile* **7f**, m.p. 98–99 °C (from EtOH) (Found: C, 35.5; H, 1.6; N, 4.6; Br, 52.7. $C_9H_5Br_2NO$ requires C, 35.7; H, 1.7; N, 4.6; Br, 52.75%); ν_{max}(film)/cm^{-1} 2224, 1690, 1408, 1293, 1270, 995, 864 and 755; δ_H(80 MHz; $CDCl_3$) 7.55 (1 H, s, CH) and 8.02 (4 H, dd, *J* 7.2 and 26.7, ArH); 2,2-dibromo-1-(2-naphthyl)ethanone **7g**, m.p. 99–100 °C (lit.,[13] 101–102 °C); *2,2-dibromo-1-(2-thienyl)ethanone* **7h**, oily liquid (Found: C, 25.3; H, 1.35; Br, 56.1. $C_6H_4Br_2OS$ requires C, 25.4; H, 1.4; Br, 56.3%); ν_{max}(film)/cm^{-1} 1661, 1507 and 1405; δ_H(80 MHz; $CDCl_3$) 6.44 (1 H, s, CH), 7.04–7.19 (1 H, m, ArH) and 7.62–7.98 (2 H, m, ArH); *1,3-bis(dibromoacetyl)benzene* **7i**, oily liquid (Found: C, 25.0; H, 1.2; Br, 66.7. $C_{10}H_6Br_4O_2$ requires C, 25.1; H, 1.3; Br, 66.9%); ν_{max}(film)/cm^{-1} 1693, 1593, 1281, 1179, 907, 731 and 628; δ_H(80 MHz; $CDCl_3$) 7.59 (2 H, s, CH), 7.69 (1 H, t, *J* 8.0, ArH), 8.32 (2 H, d, *J* 8.0, ArH) and 8.75 (1 H, s, ArH).

General Procedure for the Reactions of Aryl Dibromomethyl Ketones with S_4N_4.—A mixture of an aryl dibromomethyl ketone (6–11 mmol) and S_4N_4 (0.3–0.5 mol equiv.) was slowly heated to 115 °C. Heating was continued until no spot corresponding to S_4N_4 was observed on TLC [R_f 0.75 (benzene)]. The reaction mixture was cooled to room temperature. Hot ethyl acetate (20 cm^3) was added and the mixture was filtered. The filtrate was concentrated under reduced pressure and the residue was chromatographed on silica gel (70–230 mesh, 2 × 12 cm). Elution with hexane (100 cm^3) gave sulfur, and a series of solvents were then used to elute the other products (see below).

3-Benzoylformamido-4-phenyl-1,2,5-thiadiazole **8a**. In accord-

ance with the above general procedure, a mixture of compound **7a** (2363 mg, 8.50 mmol) and S_4N_4 (509 mg, 2.76 mmol) was heated for 5 h. Chromatography of the reaction mixture with a mixture of hexane–benzene (1:1) as eluent gave unchanged compound **7a** (1.829 mg, 77% recovery). Elution next with chloroform gave the *title compound* **8a** (37 mg, 13%) as a solid, m.p. 137–138.5 °C (from CCl_4) (Found: C, 62.1; H, 3.5; N, 13.45; S, 10.5. $C_{16}H_{11}N_3O_2S$ requires C, 62.1; H, 3.6; N, 13.6; S, 10.4%); ν_{max}(KBr)/cm^{-1} 3240, 1694, 1675, 1592, 1528, 1500, 1461, 1446, 1425, 1268, 1170, 885, 859, 780, 752 and 702; δ_H(80 MHz; $CDCl_3$) 7.39–8.49 (10 H, m, Ph) and 9.81 (1 H, s, NH); *m/z* 309 (1.8%, M^+), 204 (15.1), 121 (29.7), 119 (72.5), 117 (100), 105 (80.7) and 77 (28.6).

3-(4-*Chlorobenzoylformamido*)-4-(4-*chlorophenyl*)-1,2,5-*thiadiazole* **8b**. In accordance with the above general procedure, a mixture of substrate **7b** (2291 mg, 7.33 mmol) and S_4N_4 (523 mg, 2.84 mmol) was heated for 10 h. Chromatography of the reaction mixture with a mixture of hexane–benzene (3:1) as eluent gave unchanged compound **7b** (1.657 mg, 72% recovery) and 2-bromo-1-(4-chlorophenyl)ethanone (100 mg, 0.428 mmol). Elution with benzene then gave 3,5-bis(4-chlorobenzoyl)-1,2,4-thiadiazole **2a** (6 mg, 2%), m.p. 200–202 °C (lit.,[1] 200–202 °C). Elution next with a mixture of hexane–ethyl acetate (3:1) gave the *title compound* **8b** (47 mg, 12%) as a yellowish grey solid, m.p. 149–151 °C (from CCl_4) (Found: C, 50.8; H, 2.35; N, 11.3; S, 8.6. $C_{16}H_9Cl_2N_3O_2S$ requires C, 50.8; H, 2.4; N, 11.1; S, 8.5%); ν_{max}(KBr)/cm^{-1} 3350, 1715, 1651, 1581, 1416, 1402, 1400, 1294, 1278, 1260, 1145, 1093, 1011, 820, 786 and 559; δ_H[60 MHz; $(CD_3)_2SO$–$CDCl_3$] 7.52–8.36 (8 H, m, ArH) and 11.85 (1 H, s, NH); *m/z* 378 (0.2%, M^+), 240 (5.7), 238 (15.6), 141 (30.8), 139 (100) and 111 (26.7).

3-(4-*Bromobenzoylformamido*)-4-(4-*bromophenyl*)-1,2,5-*thiadiazole* **8c**. In accordance with the above general procedure, a mixture of substrate **7c** (4002 mg, 11.22 mmol) and S_4N_4 (1009 mg, 5.48 mmol) was heated for 10 h. Chromatography of the reaction mixture with a mixture of hexane–benzene (1:1) as eluent gave unchanged compound **7c** (3477 mg, 87% recovery) and 2-bromo-1-(4-bromophenyl)ethanone (22 mg, 5%). Elution with benzene then gave 3,5-bis(4-bromobenzoyl)-1,2,4-thiadiazole **2b** (40 mg, 11%), m.p. 119–120 °C (lit.,[1] 120–121 °C). Elution next with chloroform gave the *title compound* **8c** (105 mg, 28%) as a solid, m.p. 167–169 °C (from CCl_4) (Found: C, 41.1; H, 1.9; N, 9.1; S, 7.0. $C_{16}H_9Br_2N_3O_2S$ requires C, 41.1; H, 1.9; N, 9.0; S, 6.9%); ν_{max}(film)/cm^{-1} 3342, 1711, 1657, 1580, 1521, 1502, 1396, 1292, 1280, 1147, 1072, 1010, 821, 790, 781 and 560; δ_H[60 MHz; $(CD_3)_2SO$–$CDCl_3$] 7.73–8.40 (8 H, m, ArH) and 10.6 (1 H, s, NH); *m/z* 469 (6.7%, $M^+ + 2$), 467 (14.1, M^+), 465 (6.5), 183 (100) and 155 (32.9).

3-(3-*Nitrobenzoylformamido*)-4-(3-*nitrophenyl*)-1,2,5-*thiadiazole* **8d**. In accordance with the above general procedure, a mixture of substrate **7d** (2059 mg, 6.38 mmol) and S_4N_4 (503 mg, 2.73 mmol) was heated for 10 h. Chromatograhy of the reaction mixture with a mixture of hexane–benzene (1:1) as eluent gave unchanged compound **7d** (1128 mg, 55% recovery). Elution with chloroform gave 3,5-*bis*(3-*nitrobenzoyl*)-1,2,4-*thiadiazole* **2c** (71 mg, 12%), m.p. 116–117 °C (from CCl_4) (Found: C, 50.2; H, 2.2; N, 14.4; S, 8.6. $C_{16}H_8N_4O_6S$ requires C, 50.0; H, 2.1; N, 14.6; S, 8.3%); ν_{max}(film)/cm^{-1} 3083, 1675, 1660, 1609, 1528, 1349, 1266, 1090, 904, 849, 720, 697 and 678; δ_H(60 MHz; $CDCl_3$) 7.92–9.81 (8 H, m, ArH); *m/z* 384 (3.9%, M^+), 150 (100), 104 (39.4) and 76 (43.1). Elution next with a mixture of hexane–ethyl acetate (3:2) gave the *title compound* **8d** (276 mg, 48%) as a yellow solid, m.p. 179.5–181 °C (from CCl_4–$CHCl_3$) (Found: C, 48.0; H, 2.1; N, 17.7; S, 8.2. $C_{16}H_9N_5O_6S$ requires C, 48.1; H, 2.3; N, 17.5; S, 8.0%); ν_{max}(KBr)/cm^{-1} 3319, 1691, 1677, 1610, 1532, 1350, 1260, 1179, 1100, 915, 785 and 734; δ_H[200 MHz; $(CD_3)_2SO$] 7.63–8.79 (8 H, m, ArH) and 11.98 (1 H, s, NH); δ_C[$(CD_3)_2SO$] 185.39, 162.32, 153.03, 149.00, 147.91, 147.70, 135.76, 133.92, 133.55, 132.96, 130.68, 130.51, 128.68, 124.40, 124.30 and 122.07; *m/z* 399 (0.2%, M^+), 249 (0.5), 150 (100), 134 (9.9), 104 (28.8) and 76 (22.5).

3-(4-*Nitrobenzoylformamido*)-4-(4-*nitrophenyl*)-1,2,5-*thiadiazole* **8e**. In accordance with the above general procedure, a mixture of compound **7e** (2025 mg, 6.27 mmol) and S_4N_4 (501 mg, 2.72 mmol) was heated for 10 h. Chromatography of the reaction mixture with a mixture of hexane–benzene (1:4) as eluent gave unchanged compound **7e** (1113 mg, 55% recovery). Elution with chloroform gave 3,5-*bis*(4-*nitrobenzoyl*)-1,2,4-*thiadiazole* **2d** (53 mg, 10%), m.p. 119–121 °C (from CCl_4) (Found: C, 50.1; H, 2.1; N, 14.7; S, 8.5. $C_{16}H_8N_4O_6S$ requires C, 50.0; H, 2.1; N, 14.6; S, 8.3%); ν_{max}(KBr)/cm^{-1} 1672, 1655, 1599, 1346, 1315, 1278, 1194, 1119, 1002, 872, 850, 826 and 719; δ_H(60 MHz; $CDCl_3$) 8.60 (2 H, d, *J* 8.4, ArH) 8.69 (4 H, s, ArH) and 9.03 (2 H, d, *J* 8.4, ArH); *m/z* 384 (0.2%, M^+), 150 (100), 104 (26) and 76 (19.6). Elution with a mixture of hexane–ethyl acetate (1:1) gave the *title compound* **8e** (393 mg, 69%) as a yellow solid, m.p. 182–184 °C (from CCl_4–acetone) (Found: C, 48.25; H, 2.3; N, 17.4; S, 8.2. $C_{16}H_9N_5O_6S$ requires C, 48.1; H, 2.3; N, 17.5; S, 8.0%); ν_{max}(film)/cm^{-1} 3346, 1718, 1668, 1592, 1528, 1509, 1349, 1314, 1263, 1150, 874, 855, 781, 739 and 558; δ_H[80 MHz; $CDCl_3$–$(CD_3)_2SO$] 8.06 (2 H, d, *J* 8.8, ArH) 8.31 (4 H, s, ArH), 8.33 (2 H, d, *J* 8.8, ArH) and 11.64 (1 H, s, NH); *m/z* 399 (2.4%, M^+), 249 (7.0), 248 (9.2), 232 (12.2), 222 (17.3), 150 (100), 104 (35.6), 134 (6.4), 120 (16.2) and 76 (27.2).

3-(4-*Cyanobenzoylformamido*)-4-(4-*cyanophenyl*)-1,2,5-*thiadiazole* **8f**. In accordance with the above general procedure, a mixture of compound **7f** (2042 mg, 6.74 mmol) and S_4N_4 (507 mg, 2.75 mmol) was heated for 10 h. Chromatography of the reaction mixture with benzene as eluent gave unchanged **7f** (846 mg, 41% recovery). Elution next with a mixture of hexane–ethyl acetate (1:1) gave the *title compound* **8f** (422 mg, 59%) as an orangish solid, m.p. 222–224 °C (from CCl_4–acetone) (Found: C, 60.2; H, 2.4; N, 19.5; S, 9.1. $C_{18}H_9N_5O_2S$ requires C, 60.2; H, 2.5; N, 19.5; S, 8.9%); ν_{max}(KBr)/cm^{-1} 3345, 2230, 1718, 1669, 1530, 1510, 1494, 1406, 1264, 1154, 864, 854, 834, 745 and 571; δ_H(80 MHz; $CDCl_3$) 7.80 (2 H, d, *J* 8.0, ArH), 7.84 (2 H, d, *J* 8.8, ArH), 8.01 (2 H, d, *J* 8.0, ArH), 8.24 (2 H, d, *J* 8.8, ArH) and 11.62 (1 H, s, NH); *m/z* 359 (2.9%, M^+), 229 (11.3), 130 (100) and 102 (41.5).

4-(2-*Naphthyl*)-3-(2-*naphthylcarbonylformamido*)-1,2,5-*thiadiazole* **8g**. In accordance with the above general procedure, a mixture of substrate **7g** (2044 mg, 6.23 mmol) and S_4N_4 (506 mg, 2.75 mmol) was heated for 5 h. Chromatography of the reaction mixture with a mixture of hexane–benzene (1:1) as eluent gave unchanged compound **7g** (1837 mg, 90%). Elution with a mixture of hexane–ethyl acetate (1:1) gave the *title compound* **8g** (67 mg, 52%) as a pale brown solid, m.p. 89–90 °C (from light petroleum–CCl_4) (Found: C, 70.5; H, 3.6; N, 10.4; S, 8.0. $C_{24}H_{15}N_3O_2S$ requires C, 70.4; H, 3.7; N, 10.3; S, 7.8%); ν_{max}(KBr)/cm^{-1} 3240, 1694, 1677, 1621, 1530, 1501, 1480, 1280, 1121, 833, 816, 798 and 740; δ_H(80 MHz; $CDCl_3$) 7.49–8.27 (13 H, m, ArH), 9.25 (1 H, s, ArH) and 9.98 (1 H, s, NH); *m/z* 409 (6.8%, M^+), 155 (100) and 127 (57.8).

4-(2-*Thienyl*)-3-(2-*thienylcarbonylformamido*)-1,2,5-*thiadiazole* **8h**. In accordance with the above general procedure, a mixture of substrate **7h** (2018 mg, 7.11 mmol) and S_4N_4 (501 mg, 2.72 mmol) was heated for 6 h. Chromatography of the reaction mixture with a mixture of hexane–benzene (1:1) as eluent gave unchanged compound **7h** (1432 mg, 71% recovery). Elution with methylene dichloride gave the *title compound* **8h** (48 mg, 15%) as a pale brown solid, m.p. 48–51 °C (from hexane–CCl_4) (Found: C, 45.0; H, 2.4; N, 13.0; S, 30.1. $C_{12}H_7N_3O_2S_3$ requires C, 44.9; H, 2.2; N, 13.1; S, 29.9%); ν_{max}(film)/cm^{-1} 3330, 1706, 1640, 1530, 1497, 1441, 1406, 1355, 1265, 1219, 1158, 1050, 990, 860, 800, 754 and 735; δ_H(80 MHz;

$CDCl_3$) 7.13–7.31 (4 H, m, thienyl ArH), 7.94 (1 H, dd, *J* 4.9 and 1.2, thienyl ArH), 8.57 (1 H, dd, *J* 4.0 and 1.2, thienyl ArH) and 9.89 (1 H, s, NH); *m/z* 321 (2.5%, M^+), 210 (9.0), 111 (100) and 83 (9.6).

3-[3-(*Dibromoacetyl*)*benzoylformamido*]-4-[3-(*dibromoacetyl*)*phenyl*]-1,2,5-*thiadiazole* **8i**. In accordance with the above general procedure, a mixture of substrate **7i** (2088 mg, 4.37 mmol) and S_4N_4 (511 mg, 2.77 mmol) was heated for 10 h. Chromatography of the reaction mixture with benzene as eluent gave unchanged compound **7i** (1554 mg, 74% recovery). Elution with a mixture of hexane–ethyl acetate (1 : 1) gave the *title compound* **8i** (282 mg, 71%) as a pale yellow solid, m.p. 142–145 °C (from CCl_4) (Found: C, 34.05; H, 1.6; N, 5.9; S, 4.5. $C_{20}H_{11}Br_4N_3O_4S$ requires C, 34.0; H, 1.1; N, 5.95; S, 4.5%); ν_{max}(KBr)/cm^{-1} 3250, 1698, 1678, 1594, 1530, 1289, 1245, 1161, 687 and 631; δ_H(80 MHz; $CDCl_3$) 6.67 (1 H, s, CH), 6.68 (1 H, s, CH), 7.55–7.82 (2 H, m, ArH), 7.99–8.65 (5 H, m, ArH), 9.08 (1 H, m, ArH) and 9.73 (1 H, s, NH).

General Procedure for the Reaction of Compounds **8** *with MCPBA*.—A solution of a mixture of compound **8** and MCPBA in chloroform (20 cm^3) was stirred at room temperature for 7 h and was then poured into an excess of 5% aq. sodium carbonate. The mixture was extracted with chloroform (30 cm^3 × 3). The combined organic layer was washed with water three times and dried on anhydrous magnesium sulfate. After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel (230–400 mesh, 2 × 12 cm).

3,5-*Dibenzoyl*-1,2,4-*thiadiazole* **2e**. In accordance with the above general procedure, the residue obtained from a stirred solution of a mixture of compound **8a** (159 mg, 0.514 mmol) and MCPBA (463 mg) was chromatographed. Elution with a mixture of hexane–benzene (1 : 3) gave the title compound **2e** (59 mg, 39%), m.p. 67 °C (lit.,[1] 65–66 °C).

3,5-*Bis*(3-*nitrobenzoyl*)-1,2,4-*thiadiazole* **2c**. In accordance with the above general procedure, the residue obtained from a stirred solution of a mixture of compound **8d** (153 mg, 0.383 mmol) and MCPBA (328 mg) was chromatographed. Elution with a mixture of hexane–ethyl acetate (3 : 1) gave the title compound **2c** (87 mg, 59%).

3,5-*Bis*(4-*nitrobenzoyl*)-1,2,4-*thiadiazole* **2d**. In accordance with the above general procedure, the residue obtained from a stirred solution of a mixture of compound **8e** (143 mg, 0.358 mmol) and MCPBA (317 mg) was chromatographed. Elution with a mixture of hexane–ethyl acetate (1 : 1) gave the title compound **2d** (86 mg, 63%).

3,5-*Bis*(4-*cyanobenzoyl*)-1,2,4-*thiadiazole* **2f**. In accordance with the above general procedure, the residue obtained from a stirred solution of a mixture of compound **8f** (148 mg, 0.412 mmol) and MCPBA (355 mg) was chromatographed. Elution with a mixture of hexane–ethyl acetate (1 : 1) gave the *title compound* **2f** (93 mg, 66%), m.p. 159–161 °C (from CCl_4) (Found: C, 62.6; H, 2.5; N, 16.3; S, 9.5. $C_{18}H_8N_4O_2S$ requires C, 62.8; H, 2.3; N, 16.3; S, 9.3%); ν_{max}(KBr)/cm^{-1} 2231, 1681, 1645, 1604, 1408, 1324, 1289, 1216, 1007, 905, 872 and 764; δ_H(80 MHz; $CDCl_3$) 7.86 (2 H, d, *J* 8.8, ArH), 7.88 (2 H, d, *J* 8.8, ArH), 8.41 (2 H, d, *J* 8.8, ArH) and 8.73 (2 H, d, *J* 8.8, ArH); *m/z* 344 (3.5%, M^+), 130 (51.5), 102 (27.6) and 40 (100).

3,5-*Di*(2-*naphthoyl*)-1,2,4-*thiadiazole* **2g**. In accordance with the above general procedure, the residue obtained from a stirred solution of a mixture of compound **8g** (137 mg, 0.335 mmol) and MCPBA (338 mg) was chromatographed. Elution with benzene gave the *title compound* **2g** (57 mg, 43%), m.p. 118–120 °C (from CCl_4) (Found: C, 73.1; H, 2.15; N, 7.3; S, 8.3. $C_{24}H_{14}N_2O_2S$ requires C, 73.1; H, 2.0; N, 7.1; S, 8.1%); ν_{max}(film)/cm^{-1} 1658, 1645, 1615, 1589, 1462, 1390, 1348, 1270, 1170, 1120, 1095, 1001, 820 and 754; δ_H(80 MHz; $CDCl_3$) 7.34–8.02 (10 H, m, ArH), 8.25–8.50 (2 H, m, ArH), 8.92 (1 H, m, ArH) and 9.45 (1 H, m, ArH); *m/z* 394 (7.6%, M^+), 155 (100) and 127 (89.7).

Reaction of Compound **8b** *with MCPBA*.—In accordance with the above general procedure, the residue obtained from a stirred solution of a mixture of compound **8b** (257 mg, 0.679 mmol) and MCPBA (584 mg) was chromatographed. Elution with chloroform gave unchanged substrate **8b** (197 mg, 77% recovery). No 3,5-bis(4-chlorobenzoyl)-1,2,4-thiadiazole was isolated.

Reaction of Compound **8c** *with MCPBA*.—In accordance with the above general procedure, the residue obtained from a stirred solution of a mixture of compound **8c** (235 mg, 0.503 mmol) and MCPBA (433 mg) was chromatographed. Elution with chloroform gave unchanged substrate **8c** (193 mg, 82% recovery). No 3,5-bis(4-bromobenzoyl)-1,2,4-thiadiazole was isolated.

Reaction of Compound **8h** *with MCPBA*.—In accordance with the above general procedure, the residue obtained from a stirred solution of a mixture of compound **8h** (202 mg, 0.629 mmol) and MCPBA (533 mg) was chromatographed. Elution with benzene gave unchanged substrate **8h** (86 mg, 43% recovery). No 3,5-bis(2-thienylcarbonyl)-1,2,4-thiadiazole was isolated.

General Procedure for the Reaction of Compounds **8** *with Sodium Boranuide*.—A mixture of a compound **8** (1 mol equiv.) and $NaBH_4$ (2 mol equiv.) in a solution of a mixture of chloroform–ethanol (1 : 1; 20 cm^3) was stirred at room temperature for 1 h. The mixture was poured into water (100 cm^3) and extracted with ethyl acetate (30 cm^3 × 3). The combined extracts were dried on anhydrous magnesium sulfate. After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel (230–400 mesh, 1 × 12 cm).

3-*Amino*-4-*phenyl*-1,2,5-*thiadiazole* **10a**. In accordance with the above general procedure, the residue obtained from a stirred solution of a mixture of compound **8a** (98 mg, 0.317 mmol) and $NaBH_4$ (26 mg, 0.687 mmol) was chromatographed. Elution with chloroform gave the title compound **10a** (44 mg, 78%), m.p. 99–100 °C (lit.,[11] 100–102 °C).

3-*Amino*-4-(4-*chlorophenyl*)-1,2,5-*thiadiazole* **10b**. In accordance with the above general procedure, the residue obtained from a stirred solution of a mixture of compound **8b** (201 mg, 0.531 mmol) and $NaBH_4$ (40 mg, 1.06 mmol) was chromatograhed. Elution with chloroform gave the *title compound* **10b** (104 mg, 92%), m.p. 126–128 °C (from CCl_4) (Found: C, 45.9; H, 2.9; N, 20.0; S, 15.35. $C_8H_6ClN_3S$ requires C, 45.4; H, 2.9; N, 19.85; S, 15.15%); ν_{max}(KBr)/cm^{-1} 3418, 3300, 3200, 1621, 1516, 1496, 1440, 1094, 1019, 865 and 835; δ_H(80 MHz; $CDCl_3$) 4.81 (2 H, s, NH_2), 7.46 (2 H, d, *J* 8.3, ArH) and 7.73 (2 H, d, *J* 8.3, ArH); *m/z* 213 (31.8%, M^+ + 2), 211 (90.2, M^+), 171 (18.9), 169 (53.8), 139 (12.5), 137 (33.6), 102 (18.9) and 74 (100).

3-*Amino*-4-(4-*bromophenyl*)-1,2,5-*thiadiazole* **10c**. In accordance with the above general procedure, the residue obtained from a stirred solution of a mixture of compound **8c** (153 mg, 0.328 mmol) and $NaBH_4$ (25 mg, 0.661 mmol) was chromatographed. Elution with chloroform gave the title compound **10c** (76 mg, 91%), m.p. 131–133 °C (lit.,[11] 134–135 °C).

3-*Amino*-4-(3-*nitrophenyl*)-1,2,5-*thiadiazole* **10d**. In accordance with the above general procedure, the residue obtained from a stirred solution of a mixture of compound **8d** (154 mg, 0.386 mmol) and $NaBH_4$ (29 mg, 0.767 mmol) was chromatographed. Elution with chloroform gave the *title*

compound **10d** (76 mg, 89%), m.p. 114–116 °C (from CCl_4) (Found: C, 43.4; H, 2.9; N, 25.4; S, 14.6. $C_8H_6N_4O_2S$ requires C, 43.2; H, 2.7; N, 25.2; S, 14.4%); ν_{max}(KBr)/cm^{-1} 3420, 3305, 1630, 1524, 1441, 1352, 869 and 789; δ_H(80 MHz; $CDCl_3$) 4.85 (2 H, s, NH_2), 7.59–7.79 (1 H, m, ArH), 8.10–8.36 (2 H, m, ArH) and 8.65–8.71 (1 H, m, ArH); *m/z* 222 (100%, M^+), 180 (19.5), 175 (54.6), 174 (46.8), 148 (1.3), 122 (10.7) and 74 (97.9).

3-*Amino*-4-(4-*nitrophenyl*)-1,2,5-*thiadiazole* **10e**. In accordance with the above general procedure, the residue obtained from a stirred solution of a mixture of compound **8e** (143 mg, 0.358 mmol) and $NaBH_4$ (27 mg, 0.714 mmol) was chromatographed. Elution with chloroform gave the *title compound* **10e** (74 mg, 93%), m.p. 204–206 °C (from CH_2Cl_2–CCl_4) (Found: C, 43.2; H, 2.8; N, 25.4; S, 14.6. $C_8H_6N_4O_2S$ requires C, 43.2; H, 2.7; N, 25.2; S, 14.4%); ν_{max}(KBr)/cm^{-1} 3480, 3421, 3306, 1632, 1599, 1350, 859 and 831; δ_H(80 MHz; $CDCl_3$) 5.96 (2 H, s, NH_2), 7.97 (2 H, d, *J* 9.6, ArH) and 8.24 (2 H, d, *J* 9.6, ArH); *m/z* 222 (45%, M^+), 180 (15.5), 150 (14), 148 (1.8), 130 (23.5), 122 (11.4) and 74 (100).

3-*Amino*-4-(4-*cyanophenyl*)-1,2,5-*thiadiazole* **10f**. In accordance with the above general procedure, the residue obtained from a stirred solution of a mixture of compound **8f** (116 mg, 0.323 mmol) and $NaBH_4$ (26 mg, 0.687 mmol) was chromatographed. Elution with chloroform gave the *title compound* **10f** (56 mg, 86%), m.p. 155–157 °C (from CCl_4) (Found: C, 53.6; H, 3.0; N, 27.9; S, 16.0. $C_9H_6N_4S$ requires C, 53.45; H, 3.0; N, 27.7; S, 15.85%); ν_{max}(film)/cm^{-1} 3470, 3348, 3230, 2248, 1645, 1610, 1532, 1448, 1410, 1332, 1312, 1270, 878 and 840; δ_H(80 MHz; $CDCl_3$) 4.82 (2 H, s, NH_2), 7.77 (2 H, d, *J* 8.0, ArH) and 7.95 (2 H, d, *J* 8.0, ArH); *m/z* 202 (98.0%, M^+), 160 (30.0), 128 (20.6), 102 (16.7) and 74 (100).

3-*Amino*-4-(2-*naphthyl*)-1,2,5-*thiadiazole* **10g**. In accordance with the above general procedure, the residue obtained from a stirred solution of a mixture of compound **8g** (163 mg, 0.398 mmol) and $NaBH_4$ (30 mg, 0.793 mmol) was chromatographed. Elution with chloroform gave the *title compound* **10g** (76 mg, 84%), m.p. 92–94 °C (from hexane–CCl_4) (Found: C, 63.5; H, 4.0; N, 18.7; S, 14.3. $C_{12}H_9N_3S$ requires C, 63.4; H, 4.0; N, 18.5; S, 14.1%); ν_{max}(KBr)/cm^{-1} 3440, 3282, 1624, 1514, 1506, 1492, 904, and 825; δ_H(80 MHz; $CDCl_3$) 4.67 (2 H, s, NH_2) and 7.48–8.24 (7 H, m, ArH); *m/z* 227 (100%, M^+), 185 (22.1), 153 (38.3), 127 (13.8) and 126 (14.6).

3-*Amino*-4-(2-*thienyl*)-1,2,5-*thiadiazole* **10h**. In accordance with the above general procedure, the residue obtained from a stirred solution of a mixture of compound **8h** (151 mg, 0.470 mmol) and $NaBH_4$ (36 mg, 0.952 mmol) was chromatographed. Elution with chloroform gave the title compound **10h** (61 mg, 71%), m.p. 116–117 °C (lit.,[12] 117–118 °C).

Treatment of Compound **8d** *with Conc. Hydrochloric Acid.*—(a) *At room temperature.* A mixture of compound **8d** (125 mg, 0.313 mmol) and conc. hydrochloric acid (2 cm^3) in *p*-dioxane (30 cm^3) was stirred for 24 h. The mixture was poured into water (150 cm^3), and neutralized with 5% aq. sodium carbonate. The aqueous solution was extracted with ethyl acetate (30 cm^3 × 3). The extracts were washed with water and dried over magnesium sulfate. Removal of the solvent, followed by chromatography of the residue on silica gel (230–400 mesh) with a mixture of hexane–ethyl acetate (3:1) as eluent, gave unchanged starting material **8d** (118 mg, 94% recovery).

(b) *At reflux.* A mixture of compound **8d** (138 mg, 0.346 mmol) and conc. hydrochloric acid (2 cm^3) in *p*-dioxane (30 cm^3) was stirred for 6 h. The reaction mixture was cooled to room temperature and worked up as described in (a). Chromatography (silica gel, 230–400 mesh, 1 × 12 cm) of the residue with chloroform as eluent gave compound **10d** (55 mg, 71%).

Treatment of Compound **8d** *with Sodium Hydroxide.*—(a) *At room temperature.* A mixture of compound **8d** (126 mg, 0.316 mmol) and sodium hydroxide (pellet, 31 mg) in a mixture of *p*-dioxane–water (5:1; 30 cm^3) was stirred at room temperature for 24 h. The reaction mixture was poured into water (150 cm^3), and was neutralized with 10% aq. hydrochloric acid. The aqueous solution was extracted with ethyl acetate (30 cm^3 × 3). The extracts were washed with water and dried over magnesium sulfate. Removal of the solvent, followed by chromatography (silica gel, 230–400 mesh, 1 × 12 cm) of the residue with chloroform as eluent, gave compound **10d** (4 mg, 6%). Elution next with a mixture of hexane–ethyl acetate (3:1) gave starting material **8d** (91 mg, 72% recovery).

(b) *At reflux.* A mixture of compound **8d** (142 mg, 0.356 mmol) and sodium hydroxide (pellet, 33 mg) in a mixture of *p*-dioxane–water (5:1; 30 cm^3) was refluxed for 6 h. The reaction mixture was worked up as described in (a). Chromatography using chloroform as eluent gave **10d** (44 mg, 56%) as the only identifiable product.

Treatment of Compound **8d** *with Sodium Hydride.*—To a mixture of compound **8d** (137 mg, 0.343 mmol) and sodium hydride (13 mg, 41.7 mmol) was added chloroform (30 cm^3), and the mixture was stirred for 1 h. TLC [silica gel; hexane–ethyl acetate (3:1)] showed a single spot, of which the R_f-value {0.45 [hexane–ethyl acetate (3:1)]} was higher than that (0.34) of starting material **8d**. The mixture was extracted with ethyl acetate (30 cm^3 × 3) and the extracts were dried over magnesium sulfate. Evaporation of the solvent gave a residue, which was chromatographed on silica gel (230–400 mesh, 1 × 12 cm). Elution with chloroform gave compound **10d** (61 mg, 80%).

X-Ray Structure Determination of Compound **8a**.—*Crystal data:* $C_{16}H_{11}N_3O_2S$, M = 309.3, monoclinic, space group $P2_1c$, a = 4.827(1), b = 19.465(2), c = 15.476(2) Å, V = 1451.5(3) Å^3, Z = 4, D_X = 1.42 g cm^{-3}, μ(Mo-Kα) = 2.7 cm^{-1}. Data were measured on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo-Kα radiation using $\omega/2\theta$ scans for 1690 reflections with 735 reflections having $F_o > 3\sigma(F_o)$. Crystals were grown from hexane. Positional parameters and their estimated standard deviations, and bond distances and angles, have been deposited at the Cambridge Crystallographic Data Centre.*

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* See Instructions for Authors, in the January issue.

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