

REACTIONS OF MONOHALOMETHYL ARYL KETOXIMES WITH  
TETRASULFUR TETRANITRIDE: MUCH IMPROVED SYNTHESIS OF  
3-ARYL-1,2,5-THIADIAZOLES

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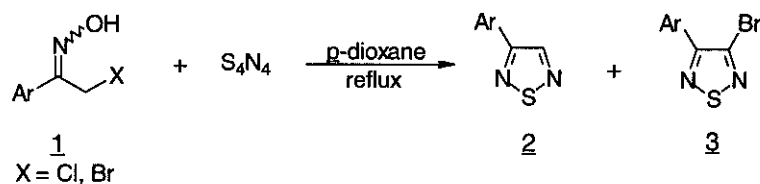
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**Abstract** - Reactions of chloromethyl aryl ketoximes (**1**, X = Cl) with tetrasulfur tetranitride in *p*-dioxane at reflux for 4 h afforded 3-aryl-1,2,5-thiadiazoles (**2**) in 37-92% yields, whereas those of bromo analogs under the same conditions gave **2** and 3-aryl-4-bromo-1,2,5-thiadiazoles (**3**) in 48-81% and 17-31% yields, respectively. However, the compounds (**3**) were not formed in the presence of pyridine.  $\alpha$ -Nitrosostyrene and its ring-substituted derivatives (**4**) are proposed as intermediates for the formations of **2**.

In the previous papers we have shown that the reactions of monobromomethyl aryl ketones and the corresponding alkyl ketones without  $\alpha$ -hydrogens on the alkyl group with tetrasulfur tetranitride ( $S_4N_4$ ) in chloroform at reflux gave 3,5-diaroyl- or 3,5-diacyl-1,2,4-thiadiazoles as major products.<sup>1</sup> On the other hand, the analogous reactions of alkyl aryl ketoximes having at least two  $\alpha$ -hydrogens on the alkyl group in *p*-dioxane at reflux afforded 3-substituted or 3,4-disubstituted 1,2,5-thiadiazoles.<sup>2</sup> The yields of the known products among the 1,2,5-thiadiazoles prepared were slightly improved in comparison with those reported.<sup>3</sup>

In order to understand the effects of possible synergism between the  $\alpha$ -halogen atom and the oxime functionality in alkyl aryl ketones, the reactions of monohalomethyl aryl ketoximes (**1**) with  $S_4N_4$  were investigated. The results are described herein.

A mixture of **1** (X = Cl, 4 mmol) and  $S_4N_4$  (4 mmol) in *p*-dioxane (20 ml) was refluxed for 4 h until  $S_4N_4$  had disappeared completely. During which time, the solution became cloudy and much white solids deposited. The reaction mixture was cooled to room temperature and filtered to remove the white solids, which showed no  $^1H$  Nmr signals. Concentration of the filtrate, followed by chromatography on silica gel [230-400 mesh, hexane/benzene (3:1)] gave 3-aryl-1,2,5-thiadiazoles (**2**) in good yields except for the reaction with *p*-anisyl chloromethyl ketoxime (**1e**). The results are summarized in Table 1.

Table 1. Synthesis of 3-Aryl-1,2,5-thiadiazoles (2) and 3-Aryl-4-bromo-1,2,5-thiadiazoles (3).

<u>1</u>	Ar	X	yield,* %	
			<u>2</u>	<u>3</u>
<u>a</u>	C <sub>6</sub> H <sub>5</sub>	Cl	<u>a</u> 87 (85)	
<u>b</u>	p-MeC <sub>6</sub> H <sub>4</sub>	Cl	<u>b</u> 80 (85)	
<u>c</u>	p-ClC <sub>6</sub> H <sub>4</sub>	Cl	<u>c</u> 88 (83)	
<u>d</u>	p-BrC <sub>6</sub> H <sub>4</sub>	Cl	<u>d</u> 92 (82)	
<u>e</u>	p-MeOC <sub>6</sub> H <sub>4</sub>	Cl	<u>e</u> 37 (57)	
<u>f</u>	C <sub>6</sub> H <sub>5</sub>	Br	<u>a</u> 61 (29)	<u>a</u> 29
<u>g</u>	p-MeC <sub>6</sub> H <sub>4</sub>	Br	<u>b</u> 48 (32)	<u>b</u> 31
<u>h</u>	p-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	Br	<u>f</u> 81 (26)	<u>c</u> 17

\* Isolated yield. Numbers in the parenthesis represent the yields in the presence of pyridine (1.1 equiv).

The Table shows that introduction of a chlorine atom to the methyl group of aryl methyl ketoximes causes the increase of the yields of 3-aryl-1,2,5-thiadiazoles (2a-2d) strikingly in comparison with those obtained from other reactions previously studied under various conditions.<sup>3</sup> In fact, no such high yields of organic products have been obtained in the reactions of S<sub>4</sub>N<sub>4</sub>. The low yield (37%) of 2e is not unexpected in view of the results in which the reaction of o-methoxyacetophenone oxime with S<sub>4</sub>N<sub>4</sub> did not give the corresponding 1,2,5-thiadiazoles at all in spite of the formations of the corresponding 1,2,5-thiadiazoles from the ketoximes with other substituents such as o-amino-, p-amino-, o-hydroxy-, and m-hydroxy groups<sup>2</sup> as well as other relevant results.<sup>4</sup>

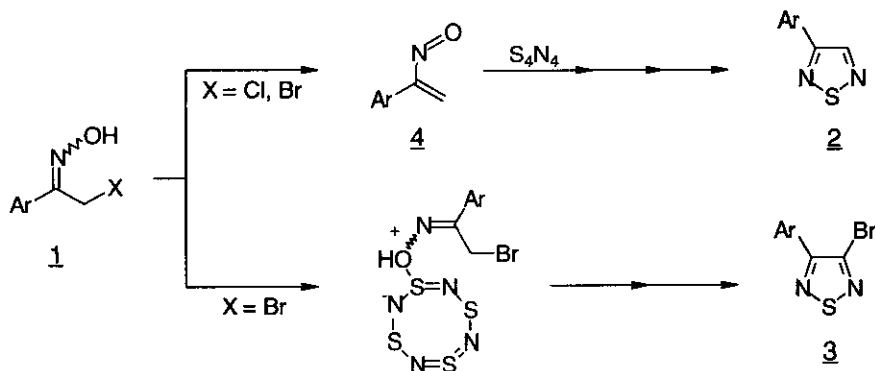
In the meantime, the analogous reactions of monobromomethyl ketoximes (1f-1h) under the same conditions as in the reactions of the monochloro analogs (1a-1e) afforded reduced yields of 2 (from 87% to 61% for 2a; from 80% to 48% for 2b) along with 3-aryl-4-bromo-1,2,5-thiadiazoles (3a-3c). The bromo-1,2,5-thiadiazoles, to our knowledge, have never been previously reported in the literature. Although the yields of 2a and 2b decreased somewhat in the reactions of monobromomethyl ketoximes (1f-1g), the total yields of two products, i.e. 2a and 3a (90%); 2b and 3b (79%), were comparable with the yields of 87% for 2a obtained from 1a and 80% for 2b obtained from 1b. The formations of 2 from chloromethyl ketoximes (1, X = Cl) but the

formations of **2** and **3** from bromomethyl ketoximes (**1**, X = Br) together with the comparable total yields in both reactions suggest that two competitive reactions play an important role in these reactions.

Since the bromine atom is known to be generally a better leaving group than the chlorine atom without regard to S<sub>N</sub>1 or S<sub>N</sub>2 reaction,<sup>5</sup> the isolations of **3** only from the reactions of bromo ketoximes (**1**, X = Br) imply the involvement of intermediates generated from **1** prior to the direct reactions between **1** and S<sub>4</sub>N<sub>4</sub>.

$\alpha$ -Nitrosostyrene and its ring-substituted derivatives (**4**) were reported to be readily formed by treatments of either  $\alpha$ -chloro or  $\alpha$ -bromo ketoximes with heterogeneous bases such as sodium carbonate and potassium carbonate in aprotic solvent<sup>6</sup> and their synthetic applications have been extensively studied.<sup>7</sup> With the expectation of the possible involvement of **4** as intermediates in mind, a mixture of **1g** (4 mmol), S<sub>4</sub>N<sub>4</sub> (4 mmol), and sodium carbonate (1.1 equiv) in *p*-dioxane (20 ml) was heated at reflux for 4 h. From the reaction mixture were obtained **2b** and **3b** in 61% and 16% yields, respectively, and the total yield (77%) of two products was close to the total yield (79%) of **2b** and **3b** obtained in the absence of sodium carbonate. Thus the increased yield of **2b** from 48% to 61% at the expense of the yield of **3b** from 31% to 16% by employing sodium carbonate as a heterogeneous base is conceived to support the assumption that 1-nitroso-1-(*p*-tolyl)ethylene **4** (Ar = *p*-MeC<sub>6</sub>H<sub>4</sub>) is generated more readily in these conditions than in the absence of sodium carbonate to react with S<sub>4</sub>N<sub>4</sub> to give **2b**.

Therefore, two pathways are tentatively proposed for the formations of **2** and **3**: the formation of **4** as an intermediate, followed by the reaction with S<sub>4</sub>N<sub>4</sub> to give **2** and a nucleophilic attack of a hydroxy group of **1** to an electron-deficient sulfur atom of S<sub>4</sub>N<sub>4</sub>, followed by a series of rearrangement to lead to **3** as proposed in the literature.<sup>8</sup>



The same reaction was repeated in the presence of a homogeneous base such as pyridine (3 equiv) under the same reaction conditions. Neither **2b** nor **3b** was detected and only an intractable mixture was obtained. The

result seems to be similar to the reported result<sup>6</sup> in which no adducts derived from the cyclization reactions of **4** were obtained in the presence of a homogeneous base. However, by employing 1 equiv of pyridine was isolated **2b** in 32% yield along with the foregoing white solids. No **3b** was detected under the conditions. Similarly no halogeno-1,2,5-thiadiazoles were detected either in the reactions of chloro- (**1a-1e**) or bromomethyl aryl ketoximes (**1f-1h**) in the presence of pyridine (1.1 equiv) as shown in Table 1.

At this moment it is rather difficult to explain the reason why the yields of **2a-2d** are not much affected in the cases of  $\alpha$ -chloromethyl aryl ketoximes (**1a-1d**) but those of **2a**, **2b**, and **2f** decrease drastically in the cases of  $\alpha$ -bromomethyl aryl ketoximes (**1f-1h**) in the presence of pyridine.

## EXPERIMENTAL

Tetrasulfur tetranitride ( $S_4N_4$ ) was prepared by the reaction of sulfur monochloride with ammonia gas at room temperature.<sup>10</sup>  $\alpha$ -Monohalomethyl aryl ketones were converted to the corresponding oximes according to the known procedures.<sup>11</sup> *p*-Dioxane was purchased from Duck San Inc. and distilled prior to use. Petroleum ether (bp 30-60°C) was purchased from Duck San Inc. IR spectra were obtained on a Perkin-Elmer Model 283 spectrometer. <sup>1</sup>H Nmr spectra were determined on a Bruker 80 MHz spectrometer using tetramethylsilane as an internal standard. Mass spectra were obtained by electron impact at 70 eV on a Varian MAT 711. Elemental analyses were determined by Korea Basic Science Center. Melting points were measured on a Fisher-Johns melting point apparatus and are uncorrected. Column chromatography was performed on a silica gel (Merck 230-400 mesh, ASTM).

**General Procedure for the Reaction of  $\alpha$ -Monohalomethyl Aryl Ketoximes with  $S_4N_4$ .** (i) A mixture of  $\alpha$ -monohalomethyl aryl ketoxime (4 mmol) and  $S_4N_4$  (4 mmol) in *p*-dioxane (20 ml) was refluxed for 4 h and then cooled to room temperature. Filtration of the white solid formed, followed by evaporation of the solvent gave a residue, which was chromatographed on silicagel (2  $\times$  12 cm). Sulfur was removed first by elution with petroleum ether (100 ml) and then appropriate solvents were used for the elution of other products. (ii) The reactions performed in the presence of pyridine were worked up in the same manner as described in (i).

**3-Phenyl-1,2,5-thiadiazole (**2a**):** (i) Chromatography of the reaction mixture obtained from the reaction of  $\alpha$ -chloromethyl phenyl ketoxime (**1a**) (683 mg, 4.03 mmol) with  $S_4N_4$  (747 mg, 4.05 mmol) using carbon tetrachloride (200 ml) gave **2a** (567 mg, 3.50 mmol, 87%): mp 42-43°C (from Et<sub>2</sub>O) (lit.,<sup>12</sup> 42-44°C). (ii)

Chromatography of the reaction mixture obtained from the reaction of **1a** (681 mg, 4.02 mmol) with  $S_4N_4$  (741 mg, 4.02 mmol) in the presence of pyridine (0.35 ml) using a mixture of *n*-hexane and carbon tetrachloride (4:1, 150 ml) gave unreacted  $S_4N_4$  (42 mg, 0.228 mmol, 6%). Elution next with a mixture of *n*-hexane and benzene (3:1, 200 ml) gave **2a** (552 mg, 3.40 mmol, 85%). (iii) Chromatography of the reaction mixture obtained from the reaction of  $\alpha$ -bromomethyl phenyl ketoxime **1f** (643 mg, 3.00 mmol) with  $S_4N_4$  (553 mg, 3.00 mmol) using a mixture of *n*-hexane and carbon tetrachloride (4:1, 80 ml) gave 3-bromo-4-phenyl-1,2,5-thiadiazole (**3a**) (209 mg, 0.867 mmol, 29%): mp 56-57°C (from *n*-hexane): Ir (film) ( $\nu$ ,  $cm^{-1}$ ) 1440, 1352, 1143, 963, 832, 818, 773, 716, 698;  $^1H$  nmr ( $CDCl_3$ ,  $\delta$ , ppm) 7.40-7.58 (3 H, m, ArH), 7.81-8.03 (2 H, m, ArH); ms ( $m/z$ ) 242 ( $M^+ + 2$ , 50.3), 240 ( $M^+$ , 46.6), 135 (100,  $M^+ - BrCN$ ), 103 (12.9,  $M^+ - BrCNS$ ). Anal. Calcd for  $C_8H_5N_2BrS$ : C, 39.85; H, 2.09; N, 11.62; S, 13.30. Found: C, 39.76; H, 2.13; N, 11.60; S, 13.33. Elution next with carbon tetrachloride (200 ml) gave **2a** (298 mg, 1.84 mmol, 61%). (iv) Chromatography of the reaction mixture obtained from the reaction of **1f** (644 mg, 3.01 mmol) with  $S_4N_4$  (554 mg, 3.01 mmol), in the presence of pyridine (0.26 ml) using a mixture of *n*-hexane and carbon tetrachloride (4:1, 100 ml) gave **2a** (142 mg, 0.875 mmol, 29%). Elution next with carbon tetrachloride (200 ml) gave unreacted  $S_4N_4$  (92 mg, 0.499 mmol, 17%).

**3-(*p*-Tolyl)-1,2,5-thiadiazole (2b):** (i) Chromatography of the reaction mixture obtained from the reaction of  $\alpha$ -chloromethyl *p*-tolyl ketoxime (**1b**) (736 mg, 4.01 mmol) with  $S_4N_4$  (752 mg, 4.08 mmol) using a mixture of *n*-hexane and benzene (3:1, 200 ml) gave **2b** (564 mg, 3.20 mmol, 80%): mp 56-57°C (from *n*-hexane) (lit.,<sup>12</sup> 56-57°C). (ii) Chromatography of the reaction mixture obtained from the reaction of **1b** (712 mg, 3.88 mmol) with  $S_4N_4$  (724 mg, 3.93 mmol) in the presence of pyridine (0.35 ml) using a mixture of *n*-hexane and carbon tetrachloride (4:1, 150 ml) gave unreacted  $S_4N_4$  (48 mg, 0.260 mmol, 7%). Elution next with a mixture of *n*-hexane and benzene (3:1, 200 ml) gave **2b** (583 mg, 3.31 mmol, 85%). (iii) Chromatography of the reaction mixture obtained from the reaction of  $\alpha$ -bromomethyl *p*-tolyl ketoxime (**1g**) (690 mg, 3.03 mmol) with  $S_4N_4$  (556 mg, 3.02 mmol) using a mixture of *n*-hexane and carbon tetrachloride (4:1, 100 ml) gave 3-bromo-4-(*p*-tolyl)-1,2,5-thiadiazole (**3b**) (242 mg, 0.949 mmol, 31%): mp 25°C (from MeOH): Ir (film) ( $\nu$ ,  $cm^{-1}$ ) 1615, 1451, 1349, 1160, 1141, 982, 963, 820, 735;  $^1H$  nmr ( $CDCl_3$ ,  $\delta$ , ppm) 2.42 (3 H, s, Me), 7.29 (2 H, d,  $J = 8.0$  Hz, ArH), 7.82 (2H, d,  $J = 8.0$  Hz, ArH); ms ( $m/z$ ) 256 ( $M^+ + 2$ , 44), 254 ( $M^+$ , 57.2), 149 (100,  $M^+ - BrCN$ ), 117 (19.3,  $M^+ - BrCNS$ ). Anal. Calcd for  $C_9H_7N_2BrS$ : C, 42.37; H, 2.77; N, 10.98; S, 12.57. Found: C, 42.29; H, 2.71; N, 10.92; S, 12.60. Elution next with carbon tetrachloride (200 ml) gave **2b** (255 mg, 1.45 mmol, 48%). (iv) Chromatography of the reaction

mixture obtained from the reaction of **1g** (690 mg, 3.03 mmol) with  $S_4N_4$  (558 mg, 3.03 mmol) in the presence of pyridine (0.26 ml) using a mixture of *n*-hexane and carbon tetrachloride (3:1, 100 ml) gave **2b** (170 mg, 0.965 mmol, 32%). Elution next with carbon tetrachloride (150 ml) gave unreacted  $S_4N_4$  (123 mg, 0.668 mmol, 22%).

**3-(p-Chlorophenyl)-1,2,5-thiadiazole (2c)**: (i) Chromatography of the reaction mixture obtained from the reaction of  $\alpha$ -chloromethyl *p*-chlorophenyl ketoxime **1c** (820 mg, 4.02 mmol) with  $S_4N_4$  (742 mg, 4.03 mmol) using a mixture of *n*-hexane and benzene (3:1, 200 ml) gave **2c** (697 mg, 3.54 mmol, 88%): mp 101-102°C (from *n*-hexane) (lit.,<sup>12</sup> 101-102°C). (ii) Chromatography of the reaction mixture obtained from the reaction of **1c** (821 mg, 4.02 mmol) with  $S_4N_4$  (741 mg, 4.02 mmol) in the presence of pyridine (0.35 ml) using a mixture of *n*-hexane and carbon tetrachloride (4:1, 150 ml) gave unreacted  $S_4N_4$  (87 mg, 0.472 mmol, 12%). Elution next with a mixture of *n*-hexane and benzene (2:1, 200 ml) gave **2c** (657 mg, 3.34 mmol, 83%).

**3-(p-Bromophenyl)-1,2,5-thiadiazole (2d)**: (i) Chromatography of the reaction mixture obtained from the reaction of  $\alpha$ -chloromethyl *p*-bromophenyl ketoxime (**1d**) (995 mg, 4.00 mmol) with  $S_4N_4$  (742 mg, 4.03 mmol) using a mixture of *n*-hexane and benzene (1:1, 200 ml) gave **2d** (891 mg, 3.70 mmol, 92%): mp 119-120°C (from  $CCl_4$ ) (lit.,<sup>12</sup> 120-121°C). (ii) Chromatography of the reaction mixture obtained from the reaction of **1d** (1,011 mg, 4.07 mmol) with  $S_4N_4$  (748 mg, 4.06 mmol) in the presence of pyridine (0.35 ml) using a mixture of *n*-hexane and carbon tetrachloride (4:1, 100 ml) gave unreacted  $S_4N_4$  (94 mg, 0.510 mmol, 13%). Elution next with a mixture of *n*-hexane and benzene (1:1, 200 ml) gave **2d** (802 mg, 3.33 mmol, 82%).

**3-(p-Methoxyphenyl)-1,2,5-thiadiazole (2e)**: (i) Chromatography of the reaction mixture obtained from the reaction of  $\alpha$ -chloromethyl *p*-methoxyphenyl ketoxime (**1e**) (799 mg, 4.00 mmol) with  $S_4N_4$  (746 mg, 4.05 mmol) using a mixture of *n*-hexane and carbon tetrachloride (4:1, 100 ml) gave unchanged  $S_4N_4$  (72 mg, 0.391 mmol, 10%). Elution next with a mixture of *n*-hexane and benzene (2:1, 150 ml) gave **2e** (284 mg, 1.48 mmol, 37%): mp 71-72°C (from *n*-hexane): Ir (film) ( $\nu$ ,  $cm^{-1}$ ) 1620, 1528, 1477, 1348, 1310, 1289, 1255, 1227, 1183, 1028, 933, 898, 840, 790, 740;  $^1H$  nmr ( $CDCl_3$ ,  $\delta$ , ppm) 3.86 (3 H, s, MeO), 7.00 (2 H, d,  $J = 9.0$  Hz, ArH), 7.93 (2 H, d,  $J = 9.0$  Hz, ArH), 8.82 (1 H, s, HC=N); ms ( $m/z$ ) 192 ( $M^+$ , 100), 165 ( $M^+ - HCN$ ), 133 ( $M^+ - HCNS$ ). Anal. Calcd for  $C_9H_8N_2OS$ : C, 56.23; H, 4.19; N, 14.57; S, 16.68. Found: C, 56.27; H, 4.20; N, 14.61; S, 16.70. (ii) Chromatography of the reaction mixture obtained from the reaction of **1e** (807 mg, 4.04 mmol) with  $S_4N_4$  (748 mg, 4.06 mmol) in the presence of pyridine (0.35

ml) using a mixture of *n*-hexane and carbon tetrachloride (4:1, 200 ml) gave unreacted S<sub>4</sub>N<sub>4</sub> (150 mg, 0.814 mmol, 20%). Elution next with a mixture of *n*-hexane and benzene (3:1, 150 ml) gave **2e** (444 mg, 2.31 mmol, 57%).

**3-(*p*-Nitrophenyl)-1,2,5-thiadiazole (2f)** (i) Chromatography of the reaction mixture obtained from the reaction of  $\alpha$ -bromomethyl *p*-nitrophenyl ketoxime (**1h**) (778 mg, 3.00 mmol) with S<sub>4</sub>N<sub>4</sub> (553 mg, 3.00 mmol) using a mixture of *n*-hexane and carbon tetrachloride (3:1, 100 ml) gave 3-bromo-4-(*p*-nitrophenyl)-1,2,5-thiadiazole (**3c**) (145 mg, 0.507 mmol, 17%): mp 101-102°C (from *n*-hexane): Ir (KBr) ( $\nu$ , cm<sup>-1</sup>) 1611, 1525, 1355, 1156, 979, 871, 840, 726; <sup>1</sup>H Nmr (CDCl<sub>3</sub>,  $\delta$ , ppm) 8.16 (2 H, d, J = 9.6 Hz, ArH), 8.38 (2 H, d, J = 9.6 Hz, ArH); ms (m/z) 287 (M<sup>+</sup> + 2), 96.4), 285 (M<sup>+</sup>, 100), 257 (36.4), 255 (36.9). Anal. Calcd for C<sub>8</sub>H<sub>4</sub>N<sub>3</sub>O<sub>2</sub>BrS: C, 33.58; H, 1.41; N, 14.69; S, 11.21. Found: C, 33.55; H, 1.45; N, 14.70; S, 11.27. Elution next with benzene (200 ml) gave **2f** (505 mg, 2.44 mmol, 81%): mp 172°C (from CCl<sub>4</sub>): Ir (KBr) ( $\nu$ , cm<sup>-1</sup>) 1601, 1510, 1330, 1110, 1084, 930, 890, 859, 791, 758, 695; <sup>1</sup>H nmr (CDCl<sub>3</sub>,  $\delta$ , ppm) 8.17 (2 H, d, J = 9.6 Hz, ArH), 8.38 (2 H, d, J = 9.6 Hz, ArH), 9.00 (1 H, s, HC=N); ms (m/z) 207 (M<sup>+</sup>, 100), 180 (6.8, M<sup>+</sup> - HCN), 177 (36, M<sup>+</sup> - NO), 134 (45.4), 122 (17.2). Anal. Calcd for C<sub>8</sub>H<sub>3</sub>N<sub>3</sub>O<sub>2</sub>S: C, 46.37; H, 2.43; N, 20.28; S, 15.47. Found: C, 46.40; H, 2.40; N, 20.31; S, 15.44. (ii) Chromatography of the reaction mixture obtained from the reaction of **1h** (781 mg, 3.02 mmol) with S<sub>4</sub>N<sub>4</sub> (561 mg, 3.04 mmol) in the presence of pyridine (0.26 ml) using a mixture of *n*-hexane and carbon tetrachloride (4:1, 200 ml) gave unreacted S<sub>4</sub>N<sub>4</sub> (57 mg, 0.309 mmol, 10%). Elution next with carbon tetrachloride (200 ml) gave **2f** (161 mg, 0.777 mmol, 26%).

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