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# A STEPWISE SYNTHESIS OF BI-1,2,5-THIADIAZOLE COMPOUNDS USING $S_4N_4 \cdot SbCl_5$ COMPLEX

**Kil-Joong Kim* and Kyongtae Kim**

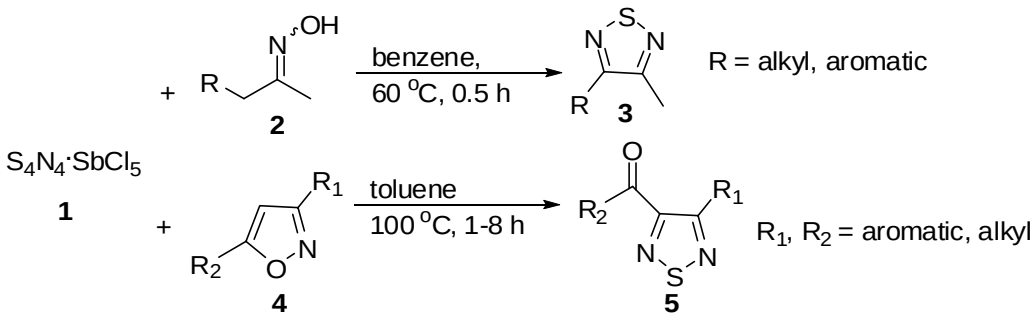
School of Chemistry & Molecular Engineering, Seoul National University, Seoul 151-742, Korea. * Current address: Department of Chemistry, Texas A&M University, College Station, TX 77843-3255, USA. E-mail: kiljoong@mail.chem.tamu.edu

**Abstract** – Bi-1,2,5-thiadiazole compounds (**7**) were synthesized step by step by reaction of 1-(4-substituted-3-1,2,5-thiadiazolyl)alkanone oximes (**6**) with tetrasulfur tetranitride antimony pentachloride complex ($S_4N_4 \cdot SbCl_5$, **1**) in toluene at 100 °C for 0.5 h in 28 - 80% yields.

## INTRODUCTION

The thiadiazole compounds have been broadly applied in the areas of electronics, nonlinear optics, sensors or corrosion protection as well as pharmaceutical, agricultural and polymer chemistry.[1] In particular, diheterocyclic compounds such as bi-1,2,5-thiadiazole have attracted much attention of both physical and organic chemists since they appear as structural subunits in many natural products and in conducting polymer like polypyrroles and polythiophenes.[2] They are known to be useful as packing materials, fiber, electrical insulators and membranes for reverse osmosis. However, only a few methods have been reported on the synthesis of bi-1,2,5-thiadiazole, which has limited substituents at the 1,2,5-thiadiazole ring and is not readily available.[3,4]

We have interested in exploiting the potential synthetic utility of $S_4N_4 \cdot SbCl_5$ complex (**1**) in view of the synthesis of various heterocyclic compounds. More interestingly, $S_4N_4 \cdot SbCl_5$ showed a very different reactivity from free $S_4N_4$. In our previous works, it gave a corresponding chloro compounds from the reaction with α-bromomethyl and α-bromoethyl ketones.[5] And 3-alkyl-4-methyl-1,2,5-thiadiazoles (**3**) were obtained regiospecifically upon reaction with alkyl methyl ketoximes (**2**, Scheme 1).[6] Furthermore, from the reaction with 3,5-disubstituted isoxazoles (**4**) were isolated 4-substituted 3-acyl- and 3-aroyl-1,2,5-thiadiazoles (**5**) in fair to moderate yields (Scheme 1).[7]

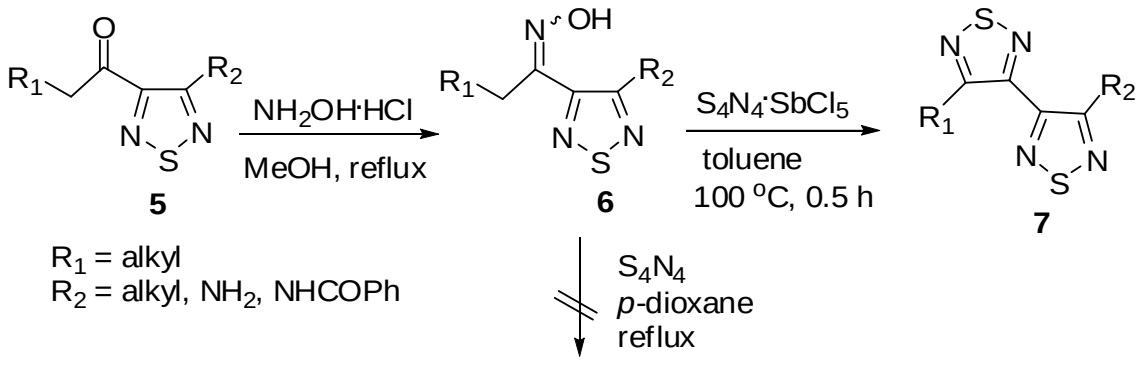



Scheme 1

Based on these results, we expected that making bi-1,2,5-thiadiazole compound (**7**) stepwisely via the 1-(4-substituted-3-1,2,5-thiadiazolyl)alkanone oximes (**6**) should be possible. The results are described herein.

## RESULTS AND DISCUSSION

Some alkanones **5** with at least two protons at the α-position were selected and prepared by the procedure of the previous report.[7] Alkanone **5** did not react with $S_4N_4{\cdot}SbCl_5$ in refluxing tolune at all. They were converted to the corresponding oximes **6** according to the literature method[8] except **6f** was prepared by oximation of 1-(4-acetamido-3-1,2,5-thiadiazolyl)ethanone with hydroxylamine hydrochloride accompanied by hydrolysis of acetamido substituent. The reactions with $S_4N_4{\cdot}SbCl_5$ (**1**) were monitored by disappearance of the spot corresponding to oxime **6** on TLC (silica gel, $R_f$ = 0.05, $CCl_4$ : $CHCl_3$ = 1 : 1). When oximes **6** were treated with a slight excess amount of $S_4N_4{\cdot}SbCl_5$ in toluene at 100 °C for 0.5 h, it gave 4,4′-disubstituted-3,3′-bi-1,2,5-thiadiazoles (**7**) in 28-80% yields (Scheme 2). The results of oximes (**6**) and bi-1,2,5-thiadiazoles (**7**) were listed in Tables 1.




Scheme 2

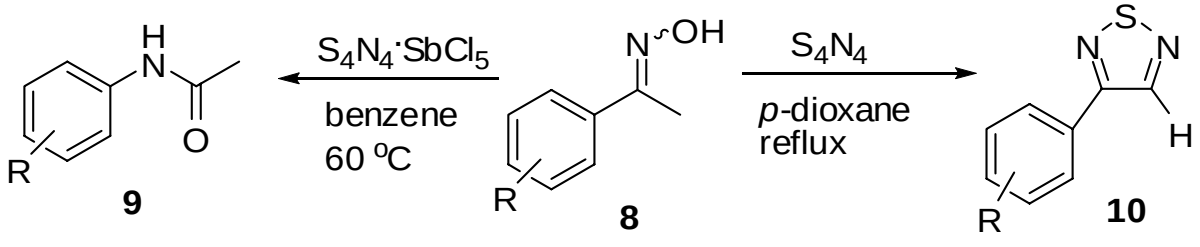
Table 1. Reaction conditions and yields of oximes (**6**) and bi-1,2,5-thiadiazoles (**7**)

| Entry | $R_1$ | $R_2$ | Yield[a] (%) | Conditions[b] (mmol) | | Yield[a] (%) |
|---|---|---|---|---|---|---|
| | | | **6** | **6** | **1** | **7** |
| a | H | $CH_3$ | 72 | 0.67 | 0.67 | 73 |
| b | $CH_3$ | $CH_3$ | 52 | 0.52 | 0.62 | 48 |
| c | $C_2H_5$ | $CH_3$ | 56 | 0.49 | 0.62 | 28 |
| d | $PhCH_2$ | $CH_3$ | 74 | 0.69 | 0.72 | 37 |
| e | 4-$BrC_6H_4CH_2$- | $CH_3$ | 69 | 0.28 | 0.31 | 30 |
| f | H | $NH_2$ | 41[c] | 0.39 | 0.62 | 44 |
| g | H | PhCONH- | 52 | 0.27 | 0.31 | 80 |
| h | H | $PhCO_2CH_2$- | 73 | 0.27 | 0.31 | 61 |

[a] Isolated yields. [b] All reactions were carried out in toluene at 100 °C for 0.5 h. [c] **6f** was obtained from hydrolysis of 4-acetamido group.

Bi-1,2,5-thiadiazole (**7**) were all pale yellow solids except for oily **7d** and **7i**. The structures of compounds **7** were determined based on the spectroscopic and mass spectral data and elemental analyses. Table 1 shows that the yields of bi-1,2,5-thiadiazole depend on a steric hindrance of the substituent $R_1$ (**7a**, **7b**, and **7c**). In spite of the same $R_1$ substituent as **6a**, **6g**, and **6h**, the reaction of **6f** with **1** gave **7f** in a relatively low yield **(**44**%)**, which might be explained by the presence of extra-nucleophilic amino group that could participate in other impurity producing reaction. However, no other product was isolated from this reaction.

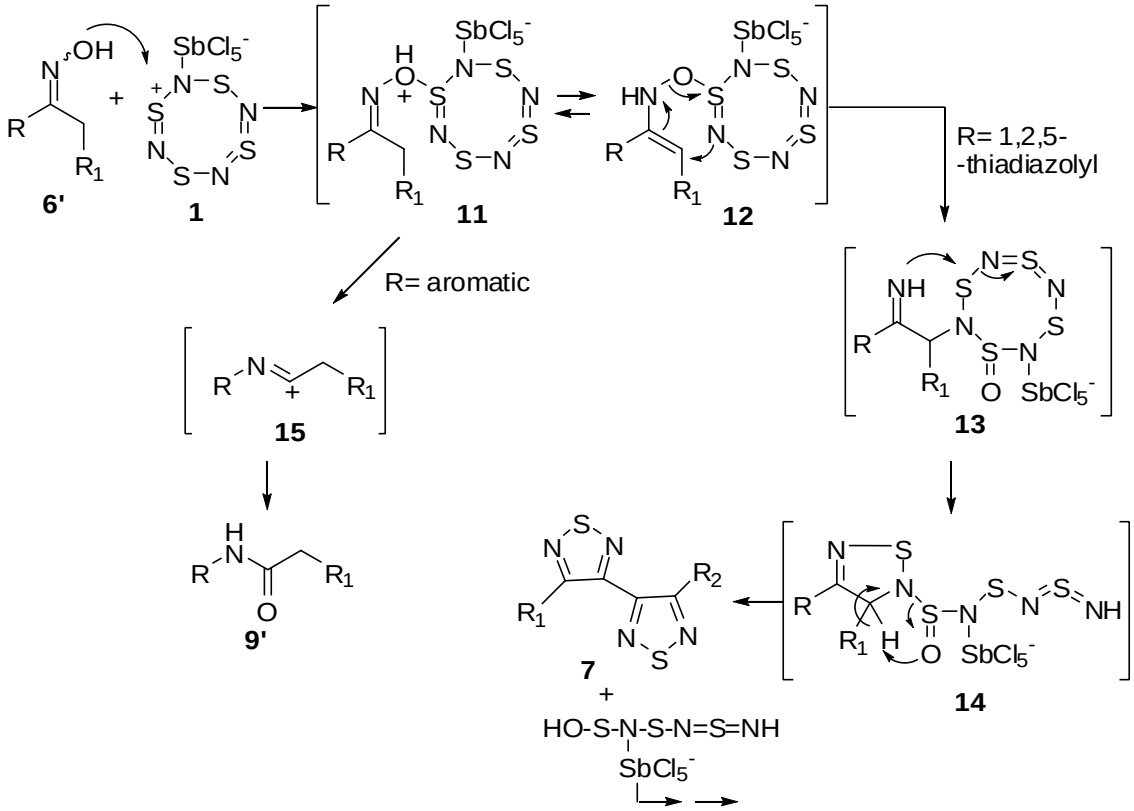
To our surprise, the synthesis of 1,2,5-thiadiazole was complete in a very short time (0.5 h). According to our results, the short reacion time has been a distinguishing feature in the reaction of $S_4N_4{\cdot}SbCl_5$ unlike free $S_4N_4$. When oxime **6** was treated with free $S_4N_4$ in refluxing *p*-dioxane for 4 h, only trace amounts of sulfur, quantitative oxime and $S_4N_4$ (57%) were recovered (Scheme 2). It was very interesting to compare this result with the previous report that 1-arylethanone oximes (**8**) reacted with free $S_4N_4$ in refluxing *p*-dioxane to give 3-aryl-1,2,5-thiadiazoles (**10**) in moderate yields (Scheme 3).[9]




Scheme 3

On the contrary, 1-arylethanone oxime (**8**) reacted with $S_4N_4{\cdot}SbCl_5$ in toluene at 60 °C to give a *N*-arylethanamide (**9**) by a Beckmann type of rearrangement (Scheme 3).[6] This difference can be explained by a more electron-withdrawing property of 1,2,5-thiadiazole than benzene ring and a decreased nucleophilicity of hydroxyl group. The pronounced acidity of 3-hydroxy-1,2,5-thiadiazole ($pK_a$ 5.10) and 3-carboxylic acid ($pK_a$ 2.47) reflect the magnitude of the electron-withdrawing effect on substituent compared with phenol ($pK_a$ 10.0) and benzoic acid ($pK_a$ 4.20).[1] Consequently, more electrophilic $S_4N_4{\cdot}SbCl_5$ than free $S_4N_4$ may be required to drive the reaction with less nucleophilic oximes **6**.

The mechanism for the formation of 1,2,5-thiadiazole from oxime **2** with **1** was demonstrated in the previous work.[6] The mechanism for **7** was thought to follow the same route and shown in scheme 4 including the formation of *N*-arylalkanamide (**9′**).




Scheme 4

The formation of bi-1,2,5-thiadiazole (**7**) can be explained by a nucleophilic attack of oxime **6′** to the electron deficient sulfur of **1** to give an intermediate **11**. Deprotonation, followed by tautomerization would yield exclusively a more stablized enamine type of an intermediate **12**, which presumably undergoes an rearrangement to give an intermediate **13**. The intramolecular nucleophilic attack of an imino nitrogen of **13** to sulfur concomitant with an S-N bond cleavage would lead to a new intermediate **14**, which undergoes aromatization to give **7**. Aromatization leading to **7** may be a driving force for a bond cleavage

between sulfinyl and the ring nitrogen of **14**. The more electron-withdrawing effect of 1,2,5-thiadiazole leads the unstable intermediate **11** to the more stabilized one **12**. On the contrary, benzene ring with more electron density might drive a different reaction route to give a *N*-arylalkanamide **9′** via imminium ion **15** by a Beckmann type of rearrangement.

A synthesis of bi-1,2,5-thidiazole one by one is a very unique result. This method, if another alkanone oxime is substituted at the bi-1,2,5-thiadiazole, may lead to a synthesis of a ter-1,2,5-thiadiazole or more ring-containing compound (not shown). So far bi-1,2,5-thiadiazoles have been formed at a time using trithiazyl trichloride ($N_3S_3Cl_3$) and $S_4N_4$ as a source of sulfur and nitrogen atom. It might be due to the difficulty of controlling the order of incoporating heteroatom because conjugated groups such as (*E*,*E*)-1,4-diphenylbuta-1,3-diene, (*E*,*E*)-1,4-diphenylbuta-1,3-diyne and *N*-alkyl-2,5-diphenylpyrrole,[3] or benzene ring such as 2,4,6-bromoresorcinol and 2,4,6-tribromophenol[10] should be used as a skeleton of 1,2,5-thiadiazole ring. In case of $N_3S_3Cl_3$, only a few examples with inert substituents such as phenyl and pyridyl at the 3 and 3′ positions of the bi-1,2,5-thiadiazole were reported,[3, 11] where bi-1,2,5-thiadiazole was obtained as one of several products. $S_4N_4$ needed many vigorous reaction steps to make a bi-1,2,5-thiadiazole. First, it should be treated first with 2,4,6-bromoresorcinol and 2,4,6-tribromophenol to give a 4-bromobenzo[1,2-c;3,4-c′]bis[1,2,5]thiadiazole, which was used for the synthesis of 4,4′-di(carboxylic)-3,3′-bi-1,2,5-thiadiazole and 4,4′-di(hydroxymethyl)-3,3′-bi-1,2,5-thiadiazole after oxidation to 4-hydroxybenzo[1,2-c;3,4-c′]bis[1,2,5]thiadiazole followed by cleavage of central benzene ring.[4, 10] It was an indirect route for bi-1,2,5-thiadiazole and needed vigorous conditions such as $H_2SO_4/CrO_3^{2-}$ in water or $NaBH_4$/TEA to cleave the benzene ring and limited the substituent to carboxylic acid and hydroxymethyl.

In conclusion, we have achieved a new stepwise synthetic method for a bi-1,2,5-thiadiazole compound, which is a very short route and readily available. Moreover, it can be used for a further elongation of 1,2,5-thiadiazole ring.

## EXPERIMENTAL

**General.** IR spectra were obtained on a Shimadzu 470 spectrophotometer, in which s, m and w in the parentheses mean strong, medium and weak band, respectively. $^1$H and $^{13}$C NMR spectra were measured on a Bruker AC 80 or 300 spectrometer using tetramethylsilane as an internal standard. MS spectra were obtained by electron impact at 70 eV using a VG 12-250 mass spectrometer. Elemental analyses were determined by the 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 70-230 or 240-400 mesh, ASTM). Tetrasulfur tetranitride ($S_4N_4$) and tetrasulfur tetranitride antimony pentachloride complex ($S_4N_4{\cdot}SbCl_5$) were prepared by the literature procedures.[12] A treatment of $S_4N_4$

requires special caution because of its explosive property. Toluene and benzene were purchased from Sigma-Aldrich (Milwaukee, WI, USA) and used as a solvent without further purification.

**1. General procedure for the synthesis of 1-(4-substituted-3-1,2,5-thiadiazolyl)alkanone oximes (6)**

Compounds **6** were prepared according to literature method from the reaction of compounds **5** and excess amount of $H_2NOH.HCl$ in refluxing methanol.[8]

**1.1 1-(3-Methyl-4-1,2,5-thiadizolyl)ethanone oxime (6a)**. White solid; mp 128-130 °C (*n*-hexane + $CCl_4$); $\delta_H$ (80 MHz, $CDCl_3$) 2.42 (s, 3 H), 2.73 (s, 3 H), 8.00 (s, 1 H); $\nu_{max}$ (KBr/$cm^{-1}$) 3216 (s), 1459 (w), 1417 (w), 1360 (w), 1075 (w), 1014 (s), 995 (m), 928 (m), 838 (s), 742 (w) and 707 (m). *Anal*. Calcd for $C_5H_7N_3OS$: C, 38.20 ; H, 4.49 ; N, 26.73 ; S, 20.40. Found: C, 38.23 ; H, 4.42 ; N, 26.70 ; S, 20.38.

**1.2 1-(3-Methyl-4-1,2,5-thiadiazolyl)propan-1-one oxime (6b)**. White solid; mp 84-85 °C (*n*-hexane); $\delta_H$ (80 MHz, $CDCl_3$) 1.19 (t, *J* = 8 Hz, 3 H), 2.70 (s, 3 H), 2.98 (q, *J* = 8 Hz, 2 H), 7.74 (s, 1 H); $\nu_{max}$ (KBr/$cm^{-1}$) 3232 (s), 1446 (m), 1027 (w), 969 (m), 921 (m), 838 (s) and 758 (w). *Anal*. Calcd for $C_6H_9N_3OS$: C, 42.09 ; H, 5.30 ; N, 24.54 ; S, 18.73. Found : C, 42.02 ; H, 5.34 ; N, 24.48 ; S, 18. 78.

**1.3 1-(3-Methyl-4-1,2,5-thiadiazolyl)butan-1-one oxime (6c)**. White solid; mp 54 °C (*n*-hexane); $\delta_H$ (80 MHz, $CDCl_3$) 0.96 (t, *J* = 6 Hz, 3 H), 1.43-1.87 (m, 2 H), 2.70 (s, 3 H), 2.96 (t, *J* = 6 Hz, 2 H), 7.89 (s, 1 H); $\nu_{max}$ (neat/$cm^{-1}$) 3280 (s), 2944 (m), 1452 (w), 1417 (m), 1084 (m), 1036 (m), 1020 (w), 950 (s), 841 (w), 784 (w), 726 (m) and 624 (w). *Anal*. Calcd for $C_7H_{11}N_3OS$ : C, 45.39 ; H, 5.99 ; N, 22.68 ; S, 17.31. Found : C, 45.35 ; H, 6.01 ; N, 22.72 ; S, 17. 34.

**1.4 1-(3-Methyl-4-1,2,5-thiadiazolyl)-3-phenylpropan-1-one oxime (6d)**. White solid; mp 101-102 °C (*n*-hexane); $\delta_H$ (80 MHz, $CDCl_3$) 2.64 (s, 3 H), 2.88 (t, *J* = 6 Hz, 2 H), 3.31 (t, *J* = 6 Hz, 2 H), 7.21 (s, 5 H), 7.89 (s, 1 H); $\nu_{max}$ (neat/$cm^{-1}$) 3296 (s), 1446 (w), 1417 (w), 1004 (w), 940 (m), 832 (s), 748 (w) and 694 (w). *Anal*. Calcd for $C_{12}H_{13}N_3OS$ : C, 58.28 ; H, 5.30 ; N, 16.99 ; S, 12.97. Found : C, 58.23 ; H, 5.33 ; N, 16. 95 ; S, 13.01.

**1.5 1-(3-Methyl-4-1,2,5-thiadiazolyl)-3-(4-bromophenyl)propan-1-one oxime (6e)**. Yellow solid; mp 140-141 °C ($CCl_4$); $\delta_H$ (80 MHz, $CDCl_3$) 2.67 (s, 3 H), 2.77-3.41 (m, 4 H), 7.23 (dd, *J* = 15, 10 Hz, 4 H), 7.70 (s, 1 H); $\nu_{max}$ (KBr/$cm^{-1}$) 3200 (m), 1475 (w), 1411 (m), 1270 (w), 1149 (w), 1062 (w), 1043 (w), 1001 (s), 940 (s), 860 (w), 832 (s) and 803 (w). *Anal*. Calcd for $C_{12}H_{12}N_3OBrS$ : C, 44.18 ; H, 3.71 ; N, 12.88 ; S, 9.83. Found : C, 44.20 ; H, 3.68 ; N, 12.95 ; S, 9.85.

**1.6 1-(3-Amino-4-1,2,5-thiadiazolyl)ethanone oxime (6f)**. White solid; mp 171-172 °C ($CHCl_3$); $\delta_H$ (80 MHz, DMSO) 2.36 (s, 3 H), 6.39 (s, 2 H, $NH_2$), 10.96 (s, 1 H, OH); $\nu_{max}$ (KBr/$cm^{-1}$) 3328 (w), 3216 (w), 3120 (w), 1584 (w), 1452 (m), 1424 (w), 1353 (w), 1017 (s), 944 (w), 838 (m), 713 (s), 601 (m) and 496 (s); MS (m/z) 158 ($M^+$, 100), 141 (46.23), 127 (6.83), 113 (11.61), 100 (4.46), 86 (7.69), 74 (35.94) and 67 (24.62). *Anal*. Calcd for $C_4H_6N_4OS$ : C, 30.37 ; H, 3.82 ; N, 35.42 ; S, 20.27. Found : C, 30.31 ; H, 3.85 ; N, 35.48 ; S, 20.23.

**1.7 1-(3-Benzamido-4-1,2,5-thiadiazolyl)ethanone oxime (6g)**. Yellow solid; mp 157-159 °C (EtOH); $\delta_H$ (80 MHz, DMSO) 2.43 (s, 3 H), 7.45-8.25 (m, 5 H), 11.97 (br, 2 H, OH and NH); $\nu_{max}$ (KBr/$cm^{-1}$) 3552 (w), 3456 (w), 3200 (m), 3040 (w), 2864 (w), 1680 (s), 1552 (s), 1494 (s), 1267 (m), 1227 (m), 1033 (s), 832 (w), 790 (w) and 694 (s). *Anal*. Calcd for $C_{11}H_{10}N_4O_2S$ : C, 50.37 ; H, 3.84 ; N, 21.36 ; S, 12.23. Found : C, 50.32 ; H, 3.88 ; N, 21.40 ; S, 12.28.

**1.8 1-(3-Benzoyloxymethy-4-1,2,5-thiadiazolyl)ethanone oxime (6h)**. Pale yellow solid; mp 136-138 °C ($CCl_4$); $\delta_H$ (80 MHz, $CDCl_3$) 2.41 (s, 3 H), 5.39 (s, 2 H), 7.27-7.72 (m, 3 H, ArH), 7.94-8.20 (m, 2 H), 8.29 (s, 1 H); $\nu_{max}$ (KBr/$cm^{-1}$) 3168 (m), 1705 (s), 1424 (w), 1270 (s), 1110 (w), 1065 (w), 1017 (w), 992 (w), 904 (w), 851 (w), 774 (w) and 700 (s). *Anal*. Calcd for $C_{12}H_{11}N_3O_3S$ : C, 51.98 ; H, 4.00 ; N, 15.15 ; S, 11.56. Found : C, 52.02 ; H, 4.03 ; N, 15.10 ; S, 11.60.

**2 General Procedure for the synthesis of 4,4′-Disubstituted 3,3′-bi-1,2,5-thiadiazoles (7):** To a solution of oxime **6** (0.267-0.687 mmol) in toluene (20 mL) was added complex **1** (0.310-0.724 mmol), which was stirred at 100 °C for 0.5 h. The color of the solution immediately turned dark. The reaction mixture was cooled to rt when a spot corresponding to oxime **6** ($R_f$ = 0.05, $CCl_4$ ; $CHCl_3$ = 1 : 1) had disappeared on TLC. The reaction mixture was filtered to remove the insoluble solids. After removal of toluene *in vacuo*, the residue was chromatographed on a silica gel column (70-230 mesh, 1.5 × 10 cm). Elution with *n*-hexane (50 mL) gave a trace amount of sulfur. Elution next with a mixture of $CCl_4$ and $CHCl_3$ (2 : 1) gave unreacted $S_4N_4$ (less than 10 mg). Elution with $CH_2Cl_2$ (50 mL) gave bi-1,2,5-thiadiazole compound **7,** which was recrystallized in an appropriate solvent. Compounds **7** except for oily **7d** and **7i** were all pale yellow solids.

**2.1 4-Methyl-3,3′-bi-1,2,5-thiadiazole (7a)**. Mp 87-89 °C (*n*-hexane); $\delta_H$ (80 MHz, $CDCl_3$) 2.99 (s, 3 H), 9.21 (s, 1 H); $\delta_C$ (300 MHz, $CDCl_3$) 17.74, 150.99, 151.86, 155.24, 160.48; $\nu_{max}$ (KBr/$cm^{-1}$) 1424 (w), 1369 (w), 1318 (w), 1276 (w), 1056 (w), 924 (w), 832 (m), 780 (w), 732 (w), 512 (s); MS (m/z) 184 ($M^+$,

100), 157 (17.25), 143 (21.78), 116 (16.18), 73 (29.52). *Anal*. Calcd for $C_5H_4N_4S_2$: C, 32.60; H, 2.19; N, 30.41; S, 34.80. Found: C, 32.56; H, 2.18; N, 30.45; S, 34.75.

**2.2 4,4′-Dimethyl-3,3′-bi-1,2,5-thiadiazole (7b)**. Mp 86-88 °C (*n*-hexane); $\delta_H$ (80 MHz, $CDCl_3$) 2.90 (s, 6 H); $\nu_{max}$ (KBr/$cm^{-1}$) 1408 (w), 1372 (w), 979 (w), 828 (s), 518 (s); MS (m/z) 198 ($M^+$, 100), 181 (11.85), 165 (5.25), 157 (39.98), 126 (8.43), 116 (23.00), 73 (50.97). *Anal*. Calcd for $C_6H_6N_4S_2$: C, 36.35; H, 3.05; N, 28.26; S, 32.34. Found: C, 36.30; H, 3.08; N, 28.25; S, 32.39.

**2.3 4-Ethyl-4′-methyl-3,3′-bi-1,2,5-thiadiazole (7c)**. Mp 51-52 °C (*n*-hexane); $\delta_H$ (80 MHz, $CDCl_3$) 1.38 (t, $J$ = 8 Hz, 3 H), 2.89 (s, 3 H), 3.33 (q, $J$ = 8 Hz, 2 H); $\nu_{max}$ (KBr/$cm^{-1}$) 2976 (w), 1449 (m), 1408 (m), 1369 (m), 1251 (m), 1014 (w), 998 (w), 960 (m), 828 (s), 518 (s); MS (m/z) 212 ($M^+$, 100), 197 (95.91), 179 (26. 99), 172 (18. 28), 166 (13.83), 157 (15.04), 138 (18.30), 126 (15.33), 116 (23.91), 87 (19.94), 73 (28.42). *Anal*. Calcd for $C_7H_8N_4S_2$: C, 39.61; H, 3.80; N, 26.39; S, 30.20. Found: C, 39.63; H, 3.77; N, 26.35; S, 30.25.

**2.4 4-Benzyl-4′-methyl-3,3′-bi-1,2,5-thiadiazole (7d)**. Oil; $\delta_H$ (80 MHz, $CDCl_3$) 2.79 (s, 3 H), 4.68 (s, 2 H), 7.22 (s, 5 H); $\nu_{max}$ (KBr/$cm^{-1}$) 3024 (w), 2912 (w), 1593 (w), 1484 (w), 1443 (m), 1420 (m), 1370 (w), 992 (m), 931 (w), 832 (s), 745 (m), 713 (m), 691 (m), 518 (m); MS (m/z) 274 ($M^+$, 100), 259 (7.53), 241 (11.76), 232 (23.42), 200 (5.94), 148 (6.23), 116 (29.00), 91 (16.22), 77 (3.55), 65 (7.28). *Anal*. Calcd for $C_{12}H_{10}N_4S_2$: C, 52.53; H, 3.67; N, 20.42; S, 23.37. Found: C, 52.50; H, 3.70; N, 20.39; S, 23.34.

**2.5 4-(4-Bromophenyl)-4′-methyl-3,3′-bi-1,2,5-thiadiazole (7e)**. Mp 76-78 °C (*n*-hexane); $\delta_H$ (80 MHz, $CDCl_3$) 2.86 (s, 3 H), 4.64 (s, 2 H), 7.38 (dd, $J$ = 11, 9 Hz, 4 H), 9.17 (s, 1H); $\nu_{max}$ (KBr/$cm^{-1}$) 1478 (m), 1420 (m), 1372 (w), 1331 (w), 1270 (w), 1065 (m), 1004 (m), 992 (m), 931 (w), 825 (s), 800 (w), 777 (w). *Anal*. Calcd for $C_{12}H_9N_4S_2Br$: C, 40.80; H, 2.57; N, 15.86; S, 18.15. Found: C, 40.78; H, 2.60; N, 15.88; S, 18.14.

**2.6 4-Amino-3,3′-bi-1,2,5-thiadiazole (7f)**. Mp 134-136 °C (*n*-hexane); $\delta_H$ (300 MHz, $CDCl_3$) 6.19 (s, 2 H, $NH_2$), 9.24 (s, 1 H); $\nu_{max}$ (KBr/$cm^{-1}$) 3392 (w), 3296 (w), 3200 (w), 1616 (s), 1529 (w), 1491 (w), 1433 (w), 1347 (w), 1302 (w), 937 (w), 848 (m), 816 (m), 784 (w), 505 (s); MS (m/z) 369 (2M-1, 11.18), 185 ($M^+$, 100), 158 (5.70), 143 (5.95), 126 (1.51), 112 (8.23), 74 (47.81). *Anal*. Calcd for $C_5H_3N_5S_2$: C, 30.45; H, 1.53; N, 35.51; S, 32.51. Found: C, 30.50; H, 1.50; N, 35.50; S, 32.55.

**2.7 4-Benzamido-3,3′-bi-1,2,5-thiadiazole (7g)**. Mp 161-162 °C ($CHCl_3$); $\delta_H$ (80 MHz, $CDCl_3$) 7.45-7.72 (m, 3 H, ArH), 7.94-8.21 (m, 2 H, ArH), 9.32 (s, 1H), 11.43 (s, 1 H, NH); $\nu_{max}$ (KBr/$cm^{-1}$) 3328 (w), 1686 (s), 1552 (w), 1510 (s), 1276 (w), 1238 (w), 1059 (w), 1024 (w), 956 (w), 912 (w), 825 (w), 784 (w), 697 (s); MS (m/z) 289 ($M^+$, 19.01), 207 (21.36), 105 (100), 77 (35.97). *Anal*. Calcd for $C_{11}H_7N_5OS_2$: C, 45.66; H, 2.44; N, 24.21; S, 22.16. Found: C, 45.71; H, 2.45; N, 24.18; S, 22.14.

**2.8 4-Benzoyloxymethyl-3,3′-bi-1,2,5-thiadiazole (7h)**. Mp 137-138 °C (*n*-hexane); $\delta_H$ (80 MHz, $CDCl_3$) 6.05 (s, 2 H), 7.33-7.63 (m, 3 H, ArH), 7.95-8.21 (m, 2 H, ArH), 9.25 (s, 1 H); $\nu_{max}$ (KBr/$cm^{-1}$) 1718 (s), 1598 (w), 1440 (w), 1267 (s), 1116 (m), 1062 (w), 1020 (w), 940 (w), 883 (w), 829 (w), 784 (w), 707 (s), 512 (w). *Anal*. Calcd for $C_{12}H_8N_4O_2S_2$: C, 47.36; H, 2.65; N, 18.41; S, 21.07. Found: C, 47.38; H, 2.63; N, 18.37; S, 21.10.

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