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Synthesis and characterization of 5-heteroarylsulfanyl-4-aryl-1,2,3-selena/thiadiazoles

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Abstract. Synthesis and spectral characterization of 2-methyl-5-[(4-aryl-1,2,3-selenadiazol-5-yl)sulfanyl]-1,3,4-thiadiazoles, 5-[4-aryl-1,2,3-selenadiazol-5-yl]sulfanyl-1-phenyl-1*H*-1,2,3,4-tetraazoles, 4-aryl-5-[(5-methyl-1,3,4-thiadiazol-2-yl)sulfanyl]-1,2,3-thiadiazole and 5-[4-aryl-1,2,3-thiadiazol-5-yl]sulfanyl-1-phenyl-1*H*-1,2,3,4-tetraazole have been reported.

Keywords. 1,2,3-Selenadiazoles; 1,2,3-thiadiazoles; 5-methyl-1,3,4-thiadiazole; 1-phenyl-1*H*-tetrazole; diheteroaryl sulfide.

1. Introduction

1,3,4-Thiadiazole derivatives have potent pharmacological activities like antibacterial,[1] antifungal,[2] antinflammatory,[3] herbicidal,[4] inhibitory activity,[5] analgesic activity,[6] antihistaminic and anticholinergic,[7] plant-growth regulating activity etc.[8] Compounds with a 1,2,3-thiadiazole moiety have been found to exhibit various pharmacological properties like antifungal,[9] pesticidal[10] and antibacterial activities. 4,5-*Bis*(p-methoxyphenyl)-1,2,3-thiadiazole possesses platelet aggregation inhibitory activity in humans[11] and some 1,2,3-thiadiazole derivatives are useful for the therapeutic and prophylactic treatment of viral, bacterial, fungal, and parasitic infections in humans and animals.[12]

Pentamethylene tetrazole is used as a stimulant for the central nervous system and to counteract the effects of over dosage of barbiturates.[13] Anti-inflammatory activity is shown by both substituted and unsubstituted tetrazoles.[14] A range of cephalosporin derivatives containing substituted tetrazole rings has been prepared and found to display antibacterial activity. An active antilipemic tetrazole molecule has progressed to clinical tests.[15] A large number of substituted chromone derivatives with tetrazole groups located at C-2 and C-3 have been prepared as potential antiallergic agents.

Compounds containing 1,2,3-selenadiazole moieties are well-known for their pharmacological properties like antifungal[16] and antibacterial activities.[17] Antibacterial activities of selenadiazoles fused with cycloheptindoles,[18] pyridines[19] and 5,7-diphenyl(4-alkyl)trihydropyran[20] have also been investigated. 1,2,3-Selenadiazoles bearing benzene-sulfonamides at 4-position have been tested for their antibacterial activity and most of them showed strong activity against *Bacillus cereus* and moderate activity against *Escherichia choli*.[21,22] 1,2,3-Selenadiazoles have been effectively utilized in the synthesis of semiconductor nanoparticles or nanopowder.[23]

2. Experimental

2.1 *Materials, methods and instruments*

Melting points were determined in open capillaries and are uncorrected. NMR spectra were recorded on a Bruker 300 MHz instrument in DMSO-d_6/$CDCl_3$ using TMS as internal standard. Chemical shifts are given in parts per million (δ-scale) and coupling constants are given in Hertz. NMR spectra are provided in the Supporting Information section. Microanalyses were carried out on a Perkin-Elmer instrument. Column chromatography was carried out in silica gel (60–120 mesh) using pet ether-ethyl acetate as eluent.

2.2 *The precursors for the semicarbazones* **4a–c**

2.2a *1-Phenyl-2-[(1-phenyl-1H-1,2,3,4-tetraazol-5-yl)sulfanyl]-1-ethanone*: 94% yield, m.p. 112°C, time 10 min. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.10 (s, 2H,

*For correspondence

-CH_2), 7.55–7.67 (m, 8H, -Ar-H), 8.05 (d, J = 7.5 Hz, 2H, -Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 42.6, 123.7, 128.5, 128.9, 129.9, 130.3, 133.4, 134.3, 134.8, 153.5, 192.1. Anal. Calcd. for $C_{15}H_{12}N_4OS$: C 60.79 H 4.08 N 18.91. Found: C 60.91 H 4.16 N 19.02.

2.2b *1-(4-Nitrophenyl)-2-[(1-phenyl-1H-1,2,3,4-tetraazol-5-yl)sulfanyl]-1-ethanone*: 93% yield, m.p. 173–174°C, time 10 min. ^{1}H NMR (300 MHz, DMSO-d_6): δ 5.19 (s, 2H, -CH_2), 7.67–8.38 (m, 10H, -Ar-H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 41.8, 124.0*, 130.0, 130.6, 133.5, 140.1, 150.2, 153.4, 192.4. Anal. Calcd. for $C_{15}H_{11}N_5O_3S$: C 52.78 H 3.25 N 20.52. Found: C 52.84 H 3.34 N 20.67.

2.2c *1-(4-Chlorophenyl)-2-[(1-phenyl-1H-1,2,3,4-tetraazol-5-yl)sulfanyl]-1-ethanone*: 94% yield, m.p. 178°C, time 10 min. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.04 (s, 2H, -CH_2), 7.50 (d, J = 8.4 Hz, 2H, -Ar-H), 7.56–7.63 (m, 5H, -Ar-H), 8.00 (d, J = 8.7 Hz, 2H, -Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 42.3, 123.8, 129.4, 129.9, 130.0, 130.3, 133.2, 133.4, 140.9, 153.3, 191.0. Anal. Calcd. for $C_{15}H_{11}ClN_4OS$: C 54.46 H 3.35 N 16.94. Found: C 54.58 H 3.43 N 17.02, are new and have been prepared by the methods adopted for the other ketones.

2.3 *General procedure for the preparation of semicarbazones* **2a–f** and **4a–c**

To a warm ethanolic solution of 2-(5-methyl-1,3,4-thiadiazolesulfanyl)-1-aryl-1-ethanone/1-aryl-2-[(1-phenyl-1H-1,2,3,4-tetraazol-5-yl)sulfanyl]-1-ethanone (0.005 mol), aqueous solution of semicarbazide hydrochloride (0.035 mol) and sodium acetate (0.035 mol) was added carefully avoiding turbidity formation. The reaction mixture was refluxed for 1.5–2 h, poured onto crushed ice and filtered. Semicarbazones **2** were crystallized from ethanol and semicarbazones **4,** obtained as viscous liquid, have not been characterized due to their poor solubility in NMR solvents and used as such for next stage.

2.3a *2-[(5-Methyl-1,3,4-thiadiazol-2-yl)sulfanyl]-1-phenylethylidene-1-hydrazine carboxamide* **(2a)**: 90% yield, m.p. 115–116°C, time 1.5 h. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.71 (s, 3H, -CH_3), 4.57 (s, 2H, -CH_2), 5.02–6.30 (bs, 2H, NH_2), 7.26–7.68 (m, 5H, -ArH), 10.21 (s, 1H, -NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.7, 27.3, 127.3, 128.6, 129.5, 135.8, 142.7, 157.7, 164.4, 165.0. Anal. Calcd. for $C_{12}H_{13}N_5OS_2$: C 46.89 H 4.26 N 22.78. Found: C 46.98 H 4.36 N 22.86.

2.3b *1-(4-Methylphenyl)-2-[(5-methyl-1,3,4-thiadiazol-2-yl)sulfanyl]ethylidene-1-hydrazine carboxamide* **(2b)**: 90% yield, m.p. 125-126°C, time 1.5 h. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.39 (s, 3H, -CH_3), 2.74 (s, 3H, -CH_3), 4.56 (s, 2H, -CH_2), 5.02–6.30 (bs, 2H, -NH_2), 7.22 (d, J = 8.1 Hz, 2H, -ArH), 7.57 (d, J = 8.1 Hz, 2H, -ArH), 10.13 (s, 1H, -NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.7, 21.3, 27.1, 125.9, 129.4, 133.0, 139.8, 143.0, 157.7, 164.4, 165.9. Anal. Calcd. for $C_{13}H_{15}N_5OS_2$: C 48.58 H 4.70 N 21.79. Found: C 48.64 H 4.83 N 21.92.

2.3c *1-(4-Methoxyphenyl)-2-[(5-methyl-1,3,4-thiadiazol-2-yl)sulfanyl]ethylidene-1-hydrazinecarboxamide* **(2c)**: 91% yield, m.p. 120–121°C, time 1.5 h. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.73 (s, 3H, -CH_3), 3.85 (s, 3H, -OCH_3), 4.55 (s, 2H, -CH_2), 5.10–6.40 (bs, 2H, NH_2), 6.92 (d, J = 8.7 Hz, 2H, -ArH), 7.64 (d, J = 8.7 Hz, 2H, -ArH), 10.05 (s, 1H, -NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.7, 27.2, 55.3, 114.0, 127.5, 128.3, 142.7, 157.7, 160.8, 164.4, 165.9. Anal. Calcd. for $C_{13}H_{15}N_5O_2S_2$: C 46.27 H 4.48 N 20.76. Found: C 46.38 H 4.54 N 20.87.

2.3d *1-(4-Chlorophenyl)-2-[(5-methyl-1,3,4-thiadiazol-2-yl)sulfanyl]ethylidene-1-hydrazinecarboxamide* **(2d)**: 94% yiled, m.p. 148–149°C, time 1.5 h. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.72 (s, 3H,-CH_3), 4.57 (s, 2H, -CH_2), 5.12–6.40 (bs, 2H, -NH_2), 7.36 (d, J = 8.4 Hz, 2H, -ArH), 7.62 (d, J = 8.4 Hz, 2H, -ArH), 10.29 (s, 1H, -NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.7, 27.3, 127.3, 128.8, 134.4, 135.4, 141.7, 157.7, 165.0, 166.1. Anal. Calcd. for $C_{12}H_{12}ClN_5OS_2$: C 42.16 H 3.54 N 20.49. Found: C 42.24 H 3.62 N 20.56.

2.3e *2-[(5-Methyl-1,3,4-thiadiazol-2-yl)sulfanyl]-1-(4-nitrophenyl)ethylidene]-1-hydrazine carboxamide* **(2e)**: 97% yield, m.p. 110–111°C, time 1.5 h. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.74 (s, 3H, -CH_3), 4.62 (s, 2H, -CH_2), 5.12–6.40 (bs, 2H, -NH_2), 7.87 (d, J = 9.0 Hz, 2H, -Ar-H), 8.27 (d, J = 9.0 Hz, 2H, -Ar-H); 10.55 (s, 1H, -NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.8, 27.4, 123.9, 126.7, 129.8, 130.1, 142.1, 157.9, 159.7, 160.3. Anal. Calcd. for $C_{12}H_{12}N_6O_3S_2$: C 40.90 H 3.43 N 23.85. Found: C 40.98 H 3.52 N 23.94.

2.3f *2-[(5-Methyl-1,3,4-thiadiazol-2-yl)sulfanyl]-1-(2-naphthyl)ethylidene]-1-hydrazine carboxamide* **(2f)**: 93% yield, m.p. 132–133°C, time 2 h. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.72 (s, 3H, -CH_3), 4.69 (s, 2H, -CH_2), 5.12–6.40 (bs, 2H, -NH_2), 7.52–8.08 (m, 6H, -Ar-H), 10.26 (s, 2H, -ArH, -NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.6, 27.1, 123.2, 125.7, 126.6, 127.8, 128.4, 128.7, 129.7, 132.3, 131.1, 133.6, 142.7, 164.3, 165.4, 166.0. Anal. Calcd. for $C_{16}H_{15}N_5OS_2$: C 53.76 H 4.23 N 19.59. Found: C 53.87 H 4.32 N 19.67.

2.4 *General procedure for the preparation of 1,2,3-selenadiazole derivatives* **3a–f** and **5a–b**

A solution of (0.001 mol) of the appropriate semicarbazones **2** or **4** was dissolved in dry THF by gentle warming and (0.005 mol) of powdered selenium dioxide was added by portion. The reaction mixture was heated to reflux on a water bath for an hour. The selenium deposited on cooling was removed by filtration and the filtrate was poured into crushed ice and extracted with chloroform. The product was obtained upon purification by column chromatography using silica gel (60–120 mesh).

2.4a *2-Methyl-5-[(4-phenyl-1,2,3-selenadiazol-5-yl)sulfanyl]-1,3,4-thiadiazole* **(3a)**: 74% yield, m.p. 130–131°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.82 (s, 3H, -CH_3), 7.60 (m, 3H, -Ar-H), 7.84 (d, J = 7.5 Hz, 2H, -Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.0, 129.1, 129.2, 129.3, 131.7, 142.1, 158.4, 159.2, 167.9. Anal. Calcd. for $C_{11}H_8N_4S_2Se$: C 38.94 H 2.38 N 16.51. Found: C 39.05 H 2.48 N 16.65.

2.4b *2-Methyl-5-[4-(4-methylphenyl)-1,2,3-selenadiazol-5-yl]sulfanyl-1,3,4-thiadiazole* **(3b)**: 70% yield, m.p. 131–132°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.45 (s, 3H, -CH_3), 2.81 (s, 3H, -CH_3), 7.36 (d, J = 8.0 Hz, 2H, -Ar-H), 7.72 (d, J = 8.0 Hz, 2H, -Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.0, 21.4, 128.8, 129.1, 129.6, 139.4, 141.2, 158.5, 159.7, 167.8. Anal. Calcd. for $C_{12}H_{10}N_4S_2Se$: C 40.79 H 2.85 N 15.86. Found: C 40.86 H 2.92 N 15.92.

2.4c *2-[4-(4-Methoxyphenyl)-1,2,3-selenadiazol-5-yl]sulfanyl-5-methyl-1,3,4-thiadiazole* **(3c)**: 72% yield, m.p. 135–136°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.69 (s, 3H, -CH_3), 3.77 (s, 3H, -OCH_3), 6.96 (d, J = 8.9 Hz, 2H, -Ar-H), 7.66 (d, J = 8.9 Hz, 2H, -Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.0, 55.4, 114.3, 124.1, 130.6, 140.6, 158.3, 159.8, 160.3, 167.8. Anal. Calcd. for $C_{12}H_{10}N_4OS_2Se$: C 39.02 H 2.73 N 15.17. Found: C 39.11 H 2.82 N 15.25.

2.4d *2-[4-(4-Chlorophenyl)-1,2,3-selenadiazol-5-yl]sulfanyl-5-methyl-1,3,4-thiadiazole* **(3d)**: 69% yield, m.p. 145–146°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.86 (s, 3H, -CH_3), 7.56 (d, J = 8.3 Hz, 2H, -Ar-H), 7.83 (d, J = 8.3 Hz, 2H, -Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.1, 129.2, 129.4, 131.2, 141.8, 158.6, 159.3, 163.0, 167.8. Anal. Calcd. for $C_{11}H_7ClN_4S_2Se$: C 35.35 H 1.89 N 14.99. Found: C 35.46 H 1.96 N 15.09.

2.4e *2-Methyl-5-[4-(4-nitrophenyl)-1,2,3-selenadiazol-5-yl]sulfanyl-1,3,4-thiadiazole* **(3e)**: 79% yield, m.p. 125–126°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.86 (s, 3H, -CH_3), 8.12 (d, J = 8.9 Hz, 2H, -Ar-H), 8.43 (d, J = 8.9 Hz, 2H, -Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.0, 129.0, 129.2, 129.3, 131.7, 141.7, 158.3, 159.6, 167.9. Anal. Calcd. for $C_{11}H_7N_5O_2S_2Se$: C 34.38 H 1.84 N 18.22. Found: C 34.46 H 1.91 N 18.33.

2.4f *2-Methyl-5-[4-(2-naphthyl)-1,2,3-selenadiazol-5-yl]sulfanyl-1,3,4-thiadiazole* **(3f)**: 76% yield, m.p. 140–141°C, time 1 h. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.82 (s, 3H, -CH_3), 7.52–8.31 (m, 9H, -Ar-H), 8.59 (s, 1H, -Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.0, 126.5, 126.7, 127.1, 127.8, 128.4, 128.8, 129.2, 130.7, 133.1, 133.4, 142.0, 158.3, 159.6, 167.9. Anal. Calcd. for $C_{15}H_{10}N_4S_2Se$: C 46.27 H 2.59 N 14.39. Found: C 46.34 H 2.65 N 14.45.

2.4g *5-[4-Phenyl-1,2,3-selenadiazol-5-yl]sulfanyl-1-phenyl-1H-1,2,3,4-tetraazole* **(5a)**: 65% yield, m.p. 152–153°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32–7.70 (m, 10H, -Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 123.9, 129.0, 129.2, 129.5, 129.8, 130.2, 131.1, 132.7, 140.3, 150.2, 159.4. Anal. Calcd. for $C_{15}H_{10}N_6SSe$: C 46.76 H 2.62 N 21.81. Found: C 46.87 H 2.78 N 21.94.

2.4h *5-[4-(4-Nitrophenyl)-1,2,3-selenadiazol-5-yl] sulfanyl-1-phenyl-1H-1,2,3,4-tetraazole* **(5b)**: 57% yield, m.p. 155–156°C, time 1 h. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.52–7.56 (m, 5H, -Ar-H), 7.92 (d, J = 8.6 Hz, 2H, -Ar-H), 8.26 (d, J = 8.6 Hz, 2H, -Ar-H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 124.7, 125.4, 130.7, 130.9, 131.8, 132.2, 135.3, 146.4, 148.1, 159.8, 170.3.

Anal. Calcd. for $C_{15}H_9N_7O_2SSe$: C 41.87 H 2.11 N 22.79. Found: C 41.99 H 2.18 N 22.84.

2.5 *General procedure for the preparation of 1,2,3-thiadiazole derivatives,* **3g** and **5c**

Appropriate semicarbazone of 0.01 mol was added by portion to 10 ml of thionyl chloride while cooling to −5°C with a freezing mixture. The reaction mixture was allowed to stir for about 2 h. The excess of thionyl chloride was decomposed using aqueous solution of sodium carbonate and extracted with chloroform. The product was obtained on purification by column chromatography using silica gel (60–120 mesh).

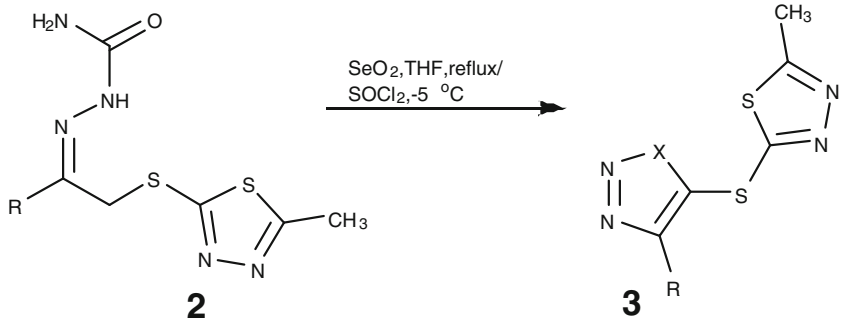
2.5a *4-(4-Chlorophenyl)-5-[(5-methyl-1,3,4-thiadiazol-2-yl)sulfanyl]-1,2,3-thiadiazole* **(3g)**: 65% yield, viscous oil, time 1 h. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.82 (s, 3H, -CH_3), 7.54 (d, J = 8.4 Hz, 2H, -Ar-H), 7.89 (d, J = 8.4 Hz, 2H, -Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.9, 128.5, 129.3*, 130.2, 136.0, 138.6, 159.5, 168.1 (*One carbon merged with other). Anal. Calcd. for $C_{11}H_7ClN_4S_3$: C 40.42 H 2.16 N 17.14. Found: C 40.53 H 2.24 N 17.23.

2.5b *5-[4-(4-Chlorophenyl)-1,2,3-thiadiazol-5-yl] sulfanyl-1-phenyl-1H-1,2,3,4-tetraazole* **(5c)**: 69% yield, m.p. 92–93°C, time 2 h. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44–7.63 (m, 7H, -Ar-H), 7.34 (d, J = 8.7 Hz, 2H, -Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 124.0, 127.9, 129.3, 129.6, 130.2, 131.1, 132.6, 135.2, 136.1, 149.8, 159.8. Anal. Calcd. for $C_{15}H_9ClN_6S_2$: C 48.32 H 2.43 N 22.54. Found: C 48.41 H 2.48 N 22.64.

3. Results and discussion

Heterocyclic compounds like 1,2,3- and 1,3,4-thiadiazoles, tetarazole and 1,2,3-selenadiazole may assume more importance, if we link any two of these heterocyclic nuclei by a sulfur atom. The work described in this article deals with the synthesis of such type of compounds. Selenadiazole nuclei[24–27] can be generated from semicarbozones with α-methylene hydrogen by the reaction with selenium dioxide. Accordingly, appropriate semicarbazones have been synthesized to generate new selenadiazole ring. The semicarbazones **2/4** planned for this synthetic sequence can be obtained from the ketone **1**.[28,29] The ketone **1** in turn can be prepared from appropriately substituted phenacyl bromide and 2-mercapto-5-methyl-1,3,4-thiadiazole/1-phenyl-1H- tetrazole-5-thiol in presence of triethylamine. The substituted phenacyl bromides have been prepared by the reaction of the corresponding acetophenone with bromine in dry ether.

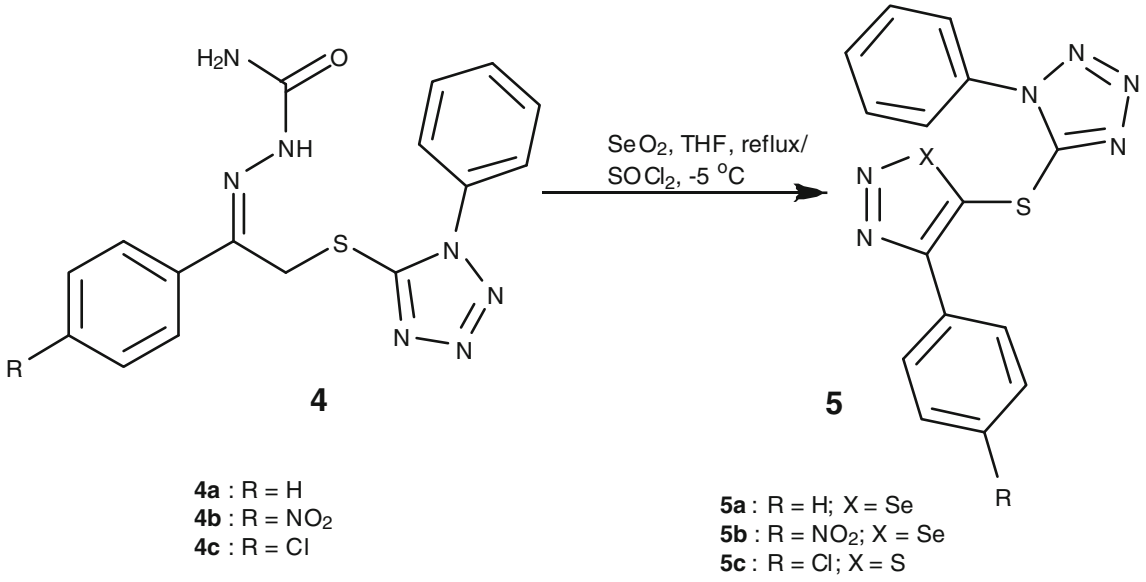
The semicarbazones **2/4** with α-methylene hydrogens when treated with selenium dioxide undergoes oxidative cyclization to give 1,2,3-selenadiazole. The reaction is very much facile in acetic acid, tetrahydrofuran or ethanol. In the present case, we employed tetrahydrofuran as the solvent of choice. The semicarbazone and selenium dioxide was taken in tetrahydrofuran and heated on a water bath, the ratio of semicarbazone and selenium dioxide taken being 1:5. Upon heating for one hour, the reaction goes for completion



2a : R=Phenyl
2b : R=4-Methylphenyl
2c : R=4-Methoxyphenyl
2d : R=4-Chlorophenyl
2e : R=4-Nitrophenyl
2f : R=2-Naphthyl

3a : R=Phenyl;X=Se
3b : R=4-Methylphenyl;X=Se
3c : R=4-Methoxyphenyl;X=Se
3d : R=4-Chlorophenyl;X=Se
3e : R=4-Nitrophenyl;X=Se
3f : R=2-Naphthyl;X=Se
3g : R=4-Chlorophenyl;X=S

Scheme 1. Synthesis of 1,2,3-selena/thiadiazoles derivatives, **3**.



Scheme 2. Synthesis of 1,2,3-selena/thiadiazoles derivatives, **5**.

giving good yield of resultant selenadiazole **3a–f** and **5a–b.** (schemes 1 and 2).

The structure of the synthesized selenadiazole has been confirmed by ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR spectrum of **3c** has four signals, two doublets and two singlets at 7.66, 6.96, 3.77 and 2.69 ppm respectively. The former two signals account for two hydrogens each, while the latter two signals account for three hydrogens each. In the ^{13}C NMR spectrum, the signal for the methyl carbon appears at 16.0 ppm, the signal for methoxy carbon appears at 55.4 ppm and the methine carbons of the anisyl ring appear at 114.3 and 130.6 ppm. The quaternary carbons appear at 124.1, 140.6, 158.3, 159.8, 160.3 and 167.8 ppm. The HMBC spectrum helps to assign the different quaternary carbons. The methyl hydrogens at 2.69 ppm has HMBC contour with carbon at 167.8 ppm confirming this carbon to be the 5^{th} carbon of the thiadiazole ring. The methoxy hydrogens at 3.77 ppm gives HMBC contour with the carbon at 160.3 ppm helping to assign this carbon as the carbon *ipso* to methoxy. This carbon has HMBC contour with the hydrogens at 7.66 ppm also. These hydrogen are the hydrogens *meta* to methoxy. These hydrogens give HMBC contour with carbon 159.8 ppm and hence this carbon should be the carbon adjacent to nitrogen in the selenadiazole ring. The carbon *para* to methoxy can be easily assigned from the fact that the doublet at 6.96 ppm gives a contour with the quaternary carbon at 124.1 ppm. The remaining two quaternary carbons are to be assigned between the carbons *ipso* to the sulfide ring.

After successfully generating selenadiazole rings attached to the 2-mercapto-5-methyl-1,3,4-thiadiazole/1-phenyl-1*H*- tetrazole-5-thiol, we plan to prepare representative thiadiazole ring connected to tetrazole/thiadiazole with sulfur atom, as semicarbazones can also be subjected to cyclisation with thionyl chloride to give thiadiazole. The semicarbazones **2d** and **4c** were then treated with excess thionyl chloride at low temperature to give considerable yield of final products **3g** and **5c**. Compounds **3g** and **5c** have been identified as the thiadiazole by ^{1}H and ^{13}C NMR spectra.

4. Conclusion

The synthesis of compounds in which two five-membered heterocyclic compounds — each of them having at least three heteroatoms — are connected by a sulfur atom has been described.

Supplementary information

The NMR spectra of the synthesized compounds are provided in the supporting information and can be found at www.ias.ac.in/chemsci.

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