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BENZO-1,4-OXATHIINS AND BENZO-1,4-DITHIINS FROM 4,5-DISUBSTITUTED 1,2,3-THIADIAZOLES

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Abstract – 4-Aryl(or heteroaryl)-5-heterosubstituted 1,2,3-thiadiazoles on heating in the presence of sodium hydride undergo ring opening with nitrogen elimination followed by recyclization to form the corresponding 1,4-benzoxathiins and 1,4-benzodithiins.

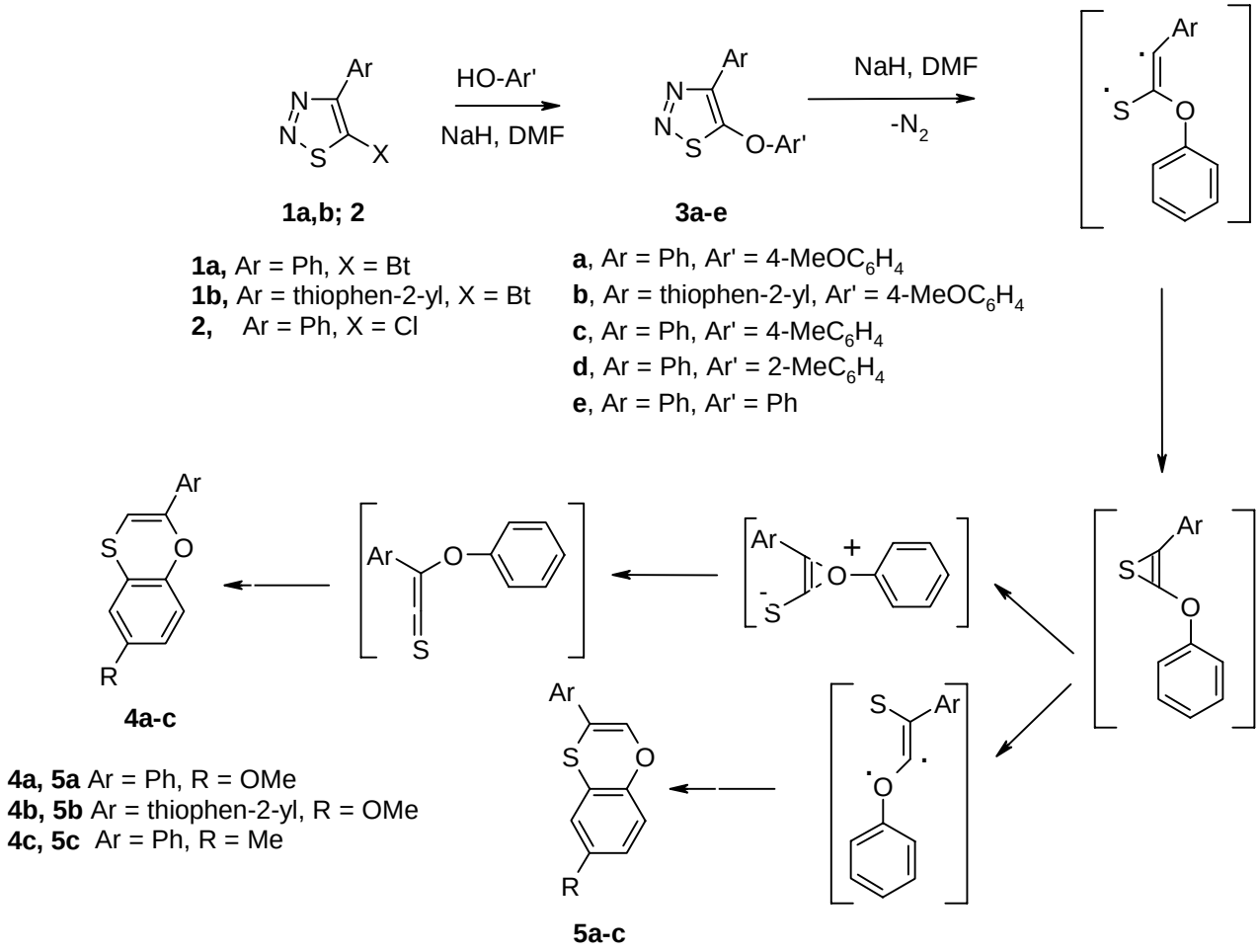
Six-membered heterocycles including S and O atoms are frequently bioactive.[1b-c] Known routes to 1,4-benzodithiines include reactions of phenyllithium with carbon disulfide,[2] cyclization of 1,8-diketones with 1,2-benzenedithiols[3] and cycloadditions of bromoacetone and chloro- or bromo acetophenone with benzene-1,2-dithiols.[4b] 2,3-Dihydro-1,4-benzodithiin and 2,3-dihydro-1,4-benzoxathiin have been prepared in good yields by a one-pot procedure from reaction of cyclohexanone derivatives with ethane-1,2-dithiol or 2-mercaptoethanol.[5a,b] In the oxathiin series, sulfur dichloride added to vinylic ethers to form 2,6-dichloro-1,4-oxathiins, which were dehydrohalogenated to the fully unsaturated 1,4-oxathiin and 3,5-dimethyl-1,4-oxathiin.[6] A benzo-1,4-oxathiin has recently been prepared by intramolecular ring closure of an alkenylselenonium salt.[7a,b]

RESULTS AND DISCUSSION

We now report a new approach to 1,4-benzoxathiins (**4a-c)** and 1,4-benzodithiins (**7,8,11)**: namely 4-aryl- and 4-heteroaryl-5-aryloxy-1,2,3-thiadiazoles (**3a-c)** in the presence of sodium hydride eliminate nitrogen to give 1,4-benzoxathiins (**4)**. 4-Aryl-5-arylthio-1,2,3-thiadiazoles (**6a-j)** similarly afford the corresponding 1,4-benzodithiins (**7,8,11)**.

4-Phenyl- and 4-heteroaryl-5-aryloxy-1,2,3-thiadiazoles (**3a-e)** (Scheme 1) and 4-phenyl- and 4-heteroaryl-5-arylthio-1,2,3-thiadiazoles (**6a-j)** (Scheme 2) were prepared from 1-(4-aryl-1,2,3-thiadiazol-5-yl)-1*H*-1,2,3-benzotriazoles (**1a,b)** according to the earlier reported procedures[8a,b] or from 4-phenyl-5-chloro-1,2,3-thiadiazole (**2)**. Phenols or thiophenols were dissolved in DMF and sodium hydride was added followed (after hydrogen evolution ceased) by **1a,b** or **2** all at 20 ^{o}C.

Transformations of 5-aryloxy-1,2,3-thiadiazoles (3). Heating DMF solutions of thiadiazoles (**3a-c)** briefly to 100 ^{o}C, in the presence of excess sodium hydride, cleave the 1,2,3-thiadiazole ring with nitrogen elimination[9] and causes subsequent intramolecular rearrangement of the intermediates to give 1,4-benzoxathiins (**4a-c)** (Scheme 1, Table 1). Similar treatment of **3d-e** did not give any isolable product, but 1,4-benzoxathiins were probably formed, as indicated by NMR spectral signals in the reaction mixture for the benzoxathiin ring protons.



Scheme 1

Benzoxathiins (**4a-c)** are crystalline compounds. Structures of **4a-c** are supported by their ^{1}H and ^{13}C NMR spectra: they show a characteristic signal for the proton of the benzoxathiin ring at 6.5 ppm in the ^{1}H NMR spectra. The structure of compound (**4a)** was unambiguously determined by single crystal X-Ray crystallography. Figure 1 shows a perspective view with selected bond distances and angles. The oxathiin ring exists in a boat conformation with S1 and O4 lying 0.499(2) and 0.409(2) Å, respectively, out of the plane defined by C2, C3, C4A and C8A. These features are similar to those found in the crystal structure of a structurally related compound.[10] In the solid state, the phenyl substituent in **4a** is twisted 13.2(2)° with respect to the plane defined by C2, C3 and O4 (Figure 1). There are no unusually short intermolecular contacts.

We believe that the formation of 1,4-benzoxathiins (**4a-c)** is accompanied by small quantities of the structural isomers (**5a-c)**. The crude products displayed two signals for each of the MeO and Me groups, two signals for the benzoxathiin ring protons in the proton spectra for **4a,5a** and **4c,5c,** and two signals for the MeO groups in the carbon spectra of **4a,5a** and **4b,5b**. For each compound the two signals were always in a ratio of ~10:1. Recrystallization of these mixtures gave the pure compounds (**4a-c)**.

A possible mechanism for the rearrangement **3→4, 5** (Scheme 1) involves elimination of nitrogen and formation of a biradical, followed by isomerization of the biradical with migration of the sulfur atom (minor isomers (5)) or *via* thiirene or oxonium anion with migration of the aryloxo group (major isomers **4**). The final step is the cyclization of a thioketene intermediate.

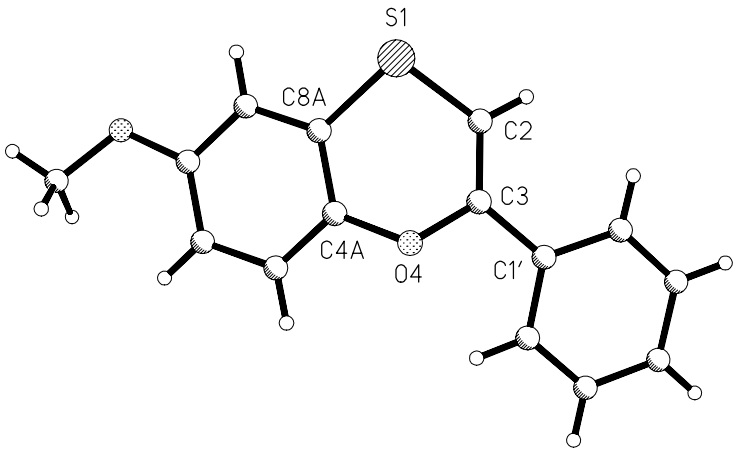
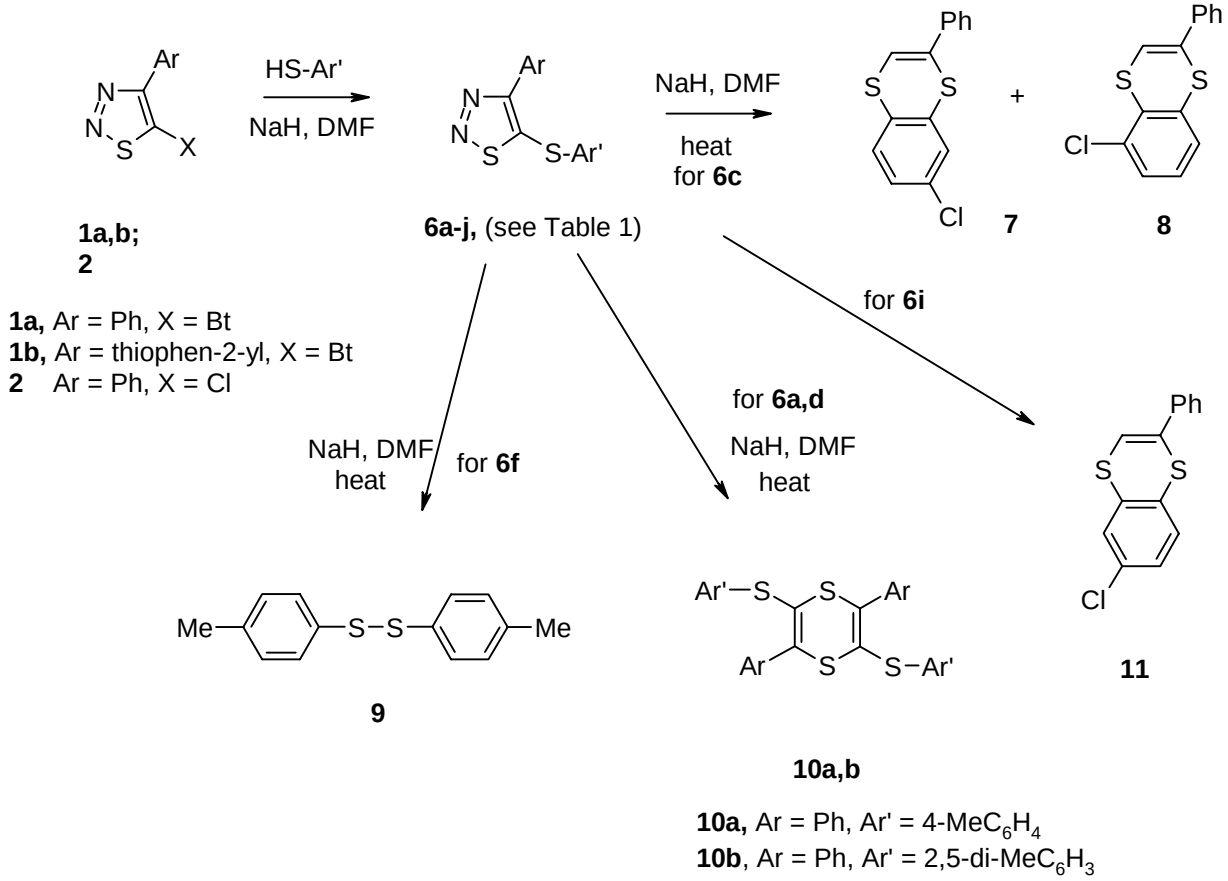


Figure 1. Perspective view of the X-Ray crystal structure of **4a**.
Selected bond lengths (Å) and angles(°): S1-C2 1.747(2), S1-C8A 1.762(2), C2-C3 1.323(3), C3-O4 1.390(2), O4-C4A 1.392(2), C4A-C8A 1.388(2), C3-C1' 1.479(3); C2-S1-C8A 97.9(1), S1-C2-C3 122.8(2), C2-C3-O4 120.6(2), C3-O4-C4A 116.9(1), C2-C3-C1' 126.7(2).

Table 1. Preparation of 4-aryl-5-aryloxy-1,2,3-thiadiazoles (**3)** and 4-aryl-5-arylthio-1,2,3-thiadiazoles (**6)** and their rearrangement products.

Starting material	1,2,3-Thiadiazoles (**3)** and (**6)**				Rearrangement Product	
N°	N°	Yield	Ar	Ar′	N°	Yield (%)
2	**3a**	89	Ph	4-$MeOC_6H_4$	**4a**	42
1b	**3b**	43	Thiophen-2-yl	4-$MeOC_6H_4$	**4b**	11
2	**3c**	80	Ph	4-MeC_6H_4	**4c**	60
1a	**3d**	50	Ph	2-MeC_6H_4	**-**	-
2	**3e**	64	Ph	Ph	**-**	-
2	**6a**	68	Ph	4-MeC_6H_4	**10a**	25
1a	**6b**	57	Ph	3-$MeOC_6H_4$	**-**	-
2	**6c**	51	Ph	3-ClC_6H_4	**7,8**	20
2	**6d**	88	Ph	2,5-di-MeC_6H_3	**10b**	47
1a	**6e**	50	Ph	2-Me-5-*t*-BuC_6H_3	**-**	-
1b	**6f**	73	Thiophen-2-yl	4-MeC_6H_4	**9**	35
1b	**6g**	71	Thiophen-2-yl	3-$MeOC_6H_4$	**-**	-
1b	**6h**	52	Thiophen-2-yl	3-Me-5-*t*-BuC_6H_3	**-**	-
2	**6i**	66	Ph	4-ClC_6H_4	**11**	66
2	**6j**	42	Ph	Ph	-	-

Transformations of 5-arylthio-1,2,3-thiadiazoles (6a-j). 1,2,3-Thiadiazoles (**6a,b,d,j)** did not react when stirred at 20 ^{0}C for several days in DMF in the presence of NaH (Scheme 2, Table 1). However, heating with NaH/DMF at 120 ^{0}C rearranged 5-(3-chlorophenylthio)-1,2,3-thiadiazole (**6c)** into a mixture of dithiins (**7,8)** (total yield is 20%). Under similar conditions (100-120 ^{0}C) **6a,d** were converted into the corresponding 2,5-bis(arylthio)-3,6-diphenyl-1,4-dithiins (**10a,b)**. The well-known formation of symmetrical 1,4-dithiines of type (**10)** from two molecules of a 1,2,3-thiadiazole is considered to occur *via* dimerization of a biradical intermediate.[9,11a,b]



Scheme 2

Only one isomer of dithiin (**11)** was obtained for thiadiazole (**6i). T**hiadiazole (**6j**) gave no rearrangement product, only started material being recovered from the reaction mixture, while analogous reaction of **6f** gave only the disulfide (**9**).

In conclusion, a novel transformation of 4,5-disubstituted 1,2,3-thiadiazoles leading to 1,4-benzoxathiins and 1,4-benzodithiins was elucidated.

EXPERIMENTAL

Compounds (**1a,b),** (**3b,e)** and **(6a,b,f-h)** were synthesized according to published procedures.[8a,b]

General methods. Melting points were determined on a hot stage apparatus and are uncorrected. NMR spectra were recorded on a Varian Gemini-300 spectrometer at 300 MHz for ^{1}H and 75 MHz for ^{13}C in chloroform-*d*. Chemical shift values are reported as δ ppm downfield from TMS as the internal standard for ^{1}H and a solvent as the internal standard for ^{13}C.

5-(4-Methoxyphenoxy)-4-phenyl-1,2,3-thiadiazole (3a). Obtained from **2**, by a similar procedure to that used for **3d**. Compound **(3a)** (89%) was recrystallized from EtOAc/Hex (1/1) as white microcrystals, mp

116–118 °C (lit.,[8a] mp 117–118 °C, from ether); ^{1}H NMR δ 3.84 (s, 3H), 6.94–7.53 (m, 7H), 8.18 (d, *J* = 7.4 Hz, 2H). ^{13}C NMR δ 55.9, 115.6, 120.3, 127.2, 128.8, 129.0, 130.5, 132.4, 145.5, 153.8, 158.4.

4-Phenyl-5-(4-methylphenoxy)-1,2,3-thiadiazole (3c). Obtained from **2** (80%) by a procedure similar to that for **3d**. Compound **(3c)** formed white crystals, mp 109-110 °C, from EtOAc; ^{1}H NMR δ 2.38 (s, 3H), 7.20 (dd, *J* = 15.3 Hz, *J* = 8.1 Hz, 4H), 7.40-7.49 (m, 3H), 8.18 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR δ 20.9, 118.4, 126.9, 128.5, 128.7, 130.2, 131.0, 136.9, 145.7, 157.5, 172.7. Anal. Calcd for $C_{15}H_{12}N_2OS$: C 67.14; H 4.52; N 10.44. Found: C 67.24; H 4.80; N 10.17.

5-(2-Methylphenoxy)-4-phenyl-1,2,3-thiadiazole (3d). Sodium hydride (0.14 g, 5.8 mmol, 60% suspension in mineral oil) was added to 2-methylphenol (0.55 g, 5.1 mmol) in DMF (10 mL) with stirring. After 20 min 1-(4-phenyl-1,2,3-thiadiazol-5-yl)-1*H*-1,2,3-benzotriazole **(1a)** (1.4 g, 5 mmol) was added. The reaction mixture was heated at 100 °C for 5 min, after 2 h EtOAc (45 mL) was added and reaction mixture was washed with water. The organic layer was dried over $MgSO_4$, the solvent was evaporated, the residue was purified by column chromatography (Ether/Hexane, 1/4), and the product was further recrystallized from ether. White crystals, yield 0.7 g (50%), mp 78–79 °C; ^{1}H NMR δ 2.30 (s, 3H), 7.20–7.44 (m, 5H), 7.51 (t, *J* = 7.7 Hz, 2H), 8.23 (d, *J* = 7.1 Hz, 2H). ^{13}C NMR δ 15.8, 118.8, 126.8, 127.3, 128.2, 128.5, 128.8, 129.0, 130.3, 132.4, 145.1, 158.2, 172.9. Anal. Calcd for $C_{15}H_{12}N_2OS$: C, 67.14; H, 4.51; N, 10.44. Found: C, 67.49; H, 4.51; N, 10.36.

4-Phenyl-5-phenoxy-1,2,3-thiadiazole (3e). Compound (**3e)** was obtained from **2**, the procedure is similar to **3d**, yield 64%, mp and NMR spectrum spectra corresponded to[8a].

6-Methoxy-2-phenyl-1,4-benzoxathiin (4a). Sodium hydride (0.08 g, 3.3 mmol, 60% suspension in mineral oil) was added to 4-phenyl-5-(4-methoxyphenoxy)-1,2,3-thiadiazole (**3a)** (0.4 g, 1.4 mmol) in DMF (25 mL). The reaction mixture was heated for 2 min at 100 °C and stirred overnight at rt. EtOAc (20 mL) was then added and the reaction mixture was washed with water. The organic layer was dried over $MgSO_4$, the solvent was evaporated, the residue was purified by column chromatography (Ether/Hex, 1/4) and recrystallized from EtOAc. White crystals, yield 0.15 g (42%), mp 83–86 °C; ^{1}H NMR δ 3.74 (s, 3H), 5.78 (s, 1H), 6.54 (d, *J* = 2.9 Hz, 3H), 6.61 (d, *J* = 2.9 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 1H), 7.25–7.39 (m, 3H), 7.54–7.59 (m, 2H). ^{13}C NMR δ 55.7, 93.3, 111.5, 113.0, 118.0, 124.2, 126.7, 128.4, 128.5, 133.4, 145.6, 150.4, 156.5. Anal. Calcd for $C_{15}H_{12}O_2S$: C, 70.29; H, 4.72. Found: C, 70.26; H, 4.79.

6-Methoxy-2-(thiophen-2-yl)-1,4-benzoxathiine (**4b)**. Sodium hydride (0.2 g, 4 mmol, 60% suspension in mineral oil) was added to 4-methoxyphenol (0.43 g, 3.5 mmol) in DMF (10 mL) with stirring. After 20 min 1-(4-thiophen-2-yl-1,2,3-thiadiazol-5-yl)-1*H*-1,2,3-benzotriazole (**1b)** (1 g, 3.5 mmol) was added. The reaction mixture was stirred overnight at rt. $CHCl_3$ (25 mL) was added and the reaction mixture was washed with water. The organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography (Ether/Hex, 1/1). After isolation of 5-(4-methoxyphenoxy)-4-(thiophen-2-yl)-1,2,3-thiadiazole (**3b),** the 6-methoxy-2-(thiophen-2-yl)-1,4-benzoxathiine (**4b)** was obtained. White crystals, yield (11%), mp 81-83 °C, from ether; ^{1}H NMR δ 3.78 (s, 3H), 5.89 (s, 1H), 6.65 (dd, *J* = 8.7 Hz, *J* = 2.7 Hz; 1H), 6.79 (d, *J* = 2.6 Hz; 1H), 6.97–7.06 (m, 3H), 7.13–7.15 (m, 1H). ^{13}C NMR δ 55.9, 93.2, 107.2, 110.8, 111.5, 122.5, 124.7, 126.8, 138.1, 148.2, 149.9, 156.3. Anal. Calcd for $C_{13}H_{10}O_2S_2$: C, 59.52; H, 3.84. Found: C, 59.12; H, 3.59.

6-Methyl-2-phenyl-1,4-benzoxathiine (4c). The compound (**4c)** was obtained from **3c**, by a procedure similar to **4a**. White crystals, yield (60%), mp 68-69 °C, from ether; ^{1}H NMR δ 2.24 (s, 3H), 5.80 (s, 1H), 6.81-6.90 (m, 3H), 7.31-7.38 (m, 3H), 7.58 (d, *J* = 6.5 Hz, 2H). ^{13}C NMR δ 20.2, 94.0, 117.2, 118.9, 124.2, 126.8, 128.3, 128.4, 128.5, 133.4, 134.5, 149.6, 150.0. Anal. Calcd for $C_{15}H_{12}OS$: C 74.97; H 5.03. Found: C 74.78; H 5.11.

5-[(3-Chlorophenyl)thio]-4-phenyl-1,2,3-thiadiazole (6c). Sodium hydride (0.29 g, 12 mmol, 60% suspension in mineral oil) was added to 3-chlorothiophenol (1.45 g, 10 mmol) in DMF (15 mL) with stirring. After 20 min, 4-phenyl-5-chloro-1,2,3-thiadiazole (**2)** (1.4 g, 10 mmol) was added. The reaction mixture was stirred for 3 h at rt and heated at 100 °C for 2 h. EtOAc (45 mL) was added and the reaction mixture was washed with water. The organic layer was dried over $MgSO_4$, the solvent was evaporated

and the residue was purified by column chromatography (EtOAc/Hex, 5/95). Colorless oil, yield 1.55 g (51%); ^{1}H NMR δ 7.38–7.55 (m, 7H), 7.97 (d, *J* = 7.1 Hz, 2H). ^{13}C NMR δ 128.5, 128.8, 129.3, 130.1, 130.4, 130.4, 131.2, 132.1, 134.7, 135.7, 147.9, 157.6. Anal. Calcd for $C_{14}H_9N_2ClS_2$: C, 55.16; H, 2.98; N, 9.19. Found: C, 55.52; H, 2.93; N, 9.74.

5-[(2,5-Dimethylphenyl)thio]-4-phenyl-1,2,3-thiadiazole (6d). The compound **(6d)** was obtained from **2,** by a procedure similar to **6c**; the reaction mixture was stirred at rt for 1h. The product was recrystallized from EtOAc/Hexane (1/1). Yield 88%. White crystals, mp 77–78 ^{o}C; ^{1}H NMR δ 2.30 (s, 3H); 2.40 (s, 3H), 7.22–7.26 (m, 2H), 7.43–7.58 (m, 2H), 7.52–7.57 (m, 2H), 8.02 (d, J = 7.7 Hz, 2H). ^{13}C NMR δ 19.9, 20.7, 128.2, 128.8, 128.9, 131.0, 131.6, 131.7, 132.0, 135.3, 137.7, 138.1, 151.9, 155.3. Anal. Calcd for $C_{16}H_{14}N_2S_2$: C, 64.40; H 4.73; N, 9.39. Found: C, 64.41; H, 4.97; N, 9.40.

5-{[5-(*t*-Butyl)-2-methylphenyl]thio}-4-phenyl-1,2,3-thiadiazole (6e). The compound **(6e)** was obtained from **1a,** by a procedure similar to **6c**; the reaction mixture was heated at 100 ^{o}C for 5 min and stirred for 3 h in rt. The product was recrystallized from EtOAc/Hexane (1/1). Yield 50%. White crystals, mp 98 ^{o}C; ^{1}H NMR δ 1.30 (s, 9H), 2.42 (s, 3H), 7.28–7.57 (m, 5H), 7.64 (d, *J* = 2.2 Hz, 1H), 8.03-8.05 (m, 2H). ^{13}C NMR δ 19.9, 31.1, 34.5, 128.1, 128.2, 128.7, 128.8, 131.0, 131.4, 131.7, 132.0, 138.2, 151.3, 152.4, 155.1. Anal. Calcd for $C_{19}H_{20}N_2S_2$: C, 67.02; H, 5.92; N, 8.23. Found: C, 66.93; H, 6.16; N, 8.21.

5-[(4-Chlorophenyl)thio]-4-phenyl-1,2,3-thiadiazole (6i). Compound (**6i)** was obtained from **2**, by a procedure similar to **6c**. Yield 67%, mp 87-88 °C; ^{1}H NMR δ 7.38–7.55 (m, 7H), 7.96 (d, *J* = 7.0 Hz, 2H). ^{13}C NMR δ 128.4, 128.8, 129.2, 130.5, 131.3, 134.2, 136.6, 142.0, 149.3, 156.9.

4-Phenyl-5-[(phenyl)thio]-1,2,3-thiadiazole (6j). The compound (**6j)** was obtained from **2** by a procedure similar to **6c**. White crystals, yield 42%, mp 38–40 ^{o}C; ^{1}H NMR δ 7.42–7.60 (m, 8H), 7.99 (d, *J* = 8 Hz, 2H). ^{13}C NMR δ 128.4, 128.7, 129.0, 130.3, 130.7, 132.9, 133.1, 133.5, 150.7, 156.3. Anal. Calcd for: $C_{14}H_{10}N_2S_2$. C 62.19; H 3.73; N 10.36. Found: C 62.87; H 3.80; N 10.65.

7-Chloro-2-phenyl-1,4-benzodithiin and 5-chloro-2-phenyl-1,4-benzodithiins (7,8). The compounds **(7,8)** were obtained from **6c,** by a procedure similar to **4a**; the reaction mixture was heated at 100 °C for 2 h. The products were purified by column chromatography (EtOAc/Hexane, 95/5) and a mixture of isomeric products was obtained. White crystals, yield 20% (mixture of isomers), mp 65–67 ^{o}C, from EtOAc/Hexane (1/1); ^{1}H NMR (for mixture of isomers) δ 6.54 (s, 1H), 6.59 (s, 1H), 7.03–7.40 (6H, m). ^{13}C NMR δ 115.7, 118.8, 119.6, 125.6, 126.0, 126.3, 126.3, 126.7, 127.0, 128.6, 128.6,136.2. Anal. Calcd for $C_{14}H_9ClS_2$: C, 60.74; H, 3.28. Found: C, 60.53; H, 3.03.

Bis(4-methylphenyl) disulfide (9). The compound **(9)** was formed from **6f,** by a procedure similar to **4a**; the reaction mixture was heated at 100 ^{0}C for 1 h. White crystals, yield 35%, mp 79 °C, from ether; ^{1}H NMR δ 2.31 (s, 6H), 7.10 (d, *J* = 7.9 Hz, 4H), 7.38 (d, *J* = 8.2 Hz, 4H). ^{13}C NMR δ 14.4, 128.4, 129.5, 129.8, 132.6, 135.8. Calcd for $C_{14}H_{14}S_2$: 246; GCMS found 246.

2,5-Bis[(4-methylphenyl)thio]-3,6-diphenyl-1,4-dithiin (10a). The compound **(10a)** was formed from **6a,** by a procedure similar to **4a**; the reaction mixture was heated at 100 °C for 20 min and stirred overnight at rt. Yellow crystals, yield 25%, mp 145-150 °C, from EtOAc/Hexane (1/1); ^{1}H NMR δ 2.25 (s, 3H), 2.31 (s, 3H), 7.02 (d, *J* = 7.8 Hz, 2H), 7.08–7.28 (m, 9H), 7.31–7.36 (m, 3H), 7.47–7.56 (m, 4H). ^{13}C NMR δ 20.9, 21.0, 110.8, 117.0, 127.0, 127.2, 127.4, 128.4, 128.5, 128.8, 129.1, 129.2, 129.8, 130.0, 131.1, 131.3, 131.8, 135.8, 137.2, 139.4, 140.1, 145.8. Anal. Calcd for $C_{30}H_{24}S_4$: C, 70.27; H, 4.72. Found: C, 70.36; H, 4.66.

2,5-Bis[(3,6-dimethylphenyl)thio]-3,6-diphenyl-1,4-dithiin (10b). The compound **(10b)** was obtained from **6d,** by a procedure similar to **4a**; the reaction mixture was heated at 100 °C for 10 min and stirred overnight at rt. Yield 47%, white crystals, mp 150-152 °C, from ether; ^{1}H NMR δ 2.21 (s, 3H), 2.22 (s, 3H), 2.36 (s, 3H), 6.80–7.57 (m, 16H). ^{13}C NMR δ 19.4, 19.6, 21.2, 126.5, 127.0, 127.3, 127.4, 127.5, 127.9, 128.3, 128.4, 128.5, 128.8, 128.9, 129.1, 129.2, 130.1, 130.3, 130.4, 131.3, 133.4, 133.9, 135.9, 136.5, 139.4. Anal. Calcd for $C_{32}H_{28}S_4$: C, 71.07; H, 5.22. Found: C, 71.05; H, 5.22.

6-Chloro-2-phenyl-1,4-benzodithiin (11). The compound **(11)** was obtained from **6I**, by a procedure similar to **4a**; the reaction mixture was heated at 70 ° for 3 h, column chromatography (EtOAc/Hexane,

95/5). Yield 66%, white crystals, mp 70–73 °C, from EtOAc/Hexane (1/1); ^{1}H NMR δ 6.55 (s, 1H), 7.08–7.38 (m, 8H). ^{13}C NMR δ 115.5, 120.8, 121.5, 122.2, 125.7, 126.1, 126.3, 127.0, 128.6, 131.9, 134.9, 136.2. Anal. Calcd for $C_{14}H_9ClS_2$: C, 60.75; H, 3.28. Found: C, 60.20; H, 3.13.

X-Ray crystallography.

Data were collected with a Siemens SMART CCD area detector, using graphite monochromatized MoKα radiation (λ = 0.71073 Å). The structure was solved by direct methods using SHELXS[12] and refined on F^2, using all data, by full-matrix least-squares procedures using SHELXL.[13] Hydrogen atoms were included in calculated positions, with isotropic displacement parameters 1.2 times the isotropic equivalent of their carrier carbons.

Crystal data for 4a: $C_{15}H_{12}O_2S$, MW 256.31, monoclinic, $P2_1/n$, a = 12.019(6), b = 5.437(2), c = 19.914(9) Å, β = 105.942(9) °, V = 1251.2(9) Å ^{3}, Z = 4, T = 22 °C, F(000) = 536, μ (MoKα) = 0.248 mm^{-1}, D_{calcd} = 1.361 g.cm^{-3}, $2\theta_{max}$ 53° (CCD area detector, 98% completeness), wR(F^2) = 0.1031 (all 2507 data), R = 0.0417 (2214 data with I > 2σI).

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