Synthesis and Structure of Substituted 5-Phenoxy-1,2,4-dithiazole-3-ones

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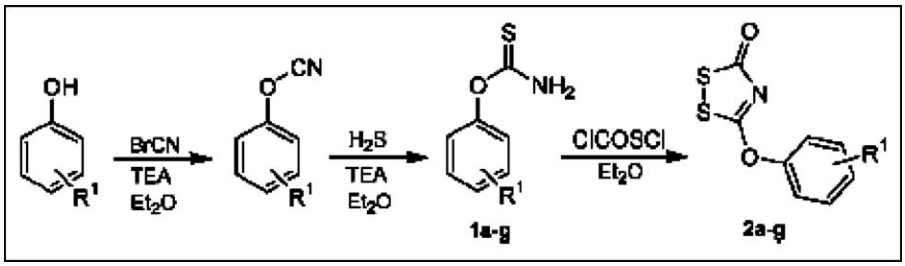

Seven new substituted 5-phenoxy-1,2,4-dithiazole-3-ones were prepared in modest yield (53–76%) from corresponding *O*-phenyl thiocarbamates and chlorocarbonylsulfenyl chloride in dry ether at −10 °C. All of the compounds were characterized by NMR and elemental analysis and some of them by X-ray diffraction. Preliminary kinetic measurements showed that the parent 5-phenoxy-1,2,4-dithiazole-3-one is a very efficient sulfurizing agent toward triphenyl phosphite.

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INTRODUCTION

1,2,4-Dithiazoles and related compounds belong among the group of less common heterocyclic compounds, although they possess various valuable properties. Their synthesis, structure, chemistry, and applications up until 2005 have been extensively reviewed in a series [1]. One of their most significant properties is their ability to serve as an efficient sulfurizing agent during the synthesis of oligonucleotide phosphorothioate analogues [2]. In particular, 5-ethoxy-1,2,4-dithiazole-3-one (EDITH) and 5-amino-1,2,4-dithiazole-3-thione (xanthane hydride) appear to be advantageous alternatives to existing sulfurizing reagents [2c,3]. In our previous papers [4], we dealt with the by-products and mechanism of the sulfurization of phosphines and phosphites using xanthane hydride and its *N*-methyl analogue. We found that these reagents are really efficient toward P(III) compounds (in terms of the bimolecular rate constants that vary from 0.5 to 3.87 × 10^3 L mol^{-1} s^{-1} for phosphites and from 2.6 × 10^2 to 5.9 × 10^5 L mol^{-1} s^{-1} for phospines). It is well known that the substituent(s) in the heterocyclic ring often strongly affect(s) its reactivity via polar effects. In this work, we decided to prepare substituted 5-phenoxy-1,2,4-dithiazole-3-ones, **2a–g**, whose sulfurizing efficiency might be similar or even better.

RESULTS AND DISCUSSION

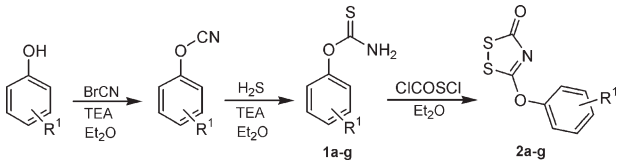
In the literature dealing with the synthesis of various 1,2,4-dithiazole-3-ones, several synthetic approaches starting from compounds having a >N—(C=S)— group can be found. Chlorocarbonylsulfenyl chloride [5], which is the most frequently used reagent for such synthesis, smoothly converts aliphatic and aromatic thioamides to 5-alkyl- or 5-aryl-1,2,4-dithiazole-3-ones [6]. The situation is more complex for thiocarbamates and thioureas. For example, *O*-ethylthiocarbamate gives 5-ethoxy-1,2,4-dithiazole-3-one (EDITH) and 3,5-diethoxy-1,2,4-thiadiazole [7] with the relative amounts depending very much on the solvent, whereas *N*-monosubstituted-*O*-alkylthiocarbamates are cyclized to 4-substituted 1,2,4-dithiazolidine-3,5-diones [8]. Also, *N*,*N*′-disubstituted thioureas afford [9] either 5-imino-1,2,4-dithiazole-3-ones or 2,4-disubstituted-1,2,4-thiadiazole-5-ones depending on the solvent, temperature, and the presence of a base.

Sulfurization of thioacylisocyanates [10] and desulfurization of 1,2,4-dithiazole-3-thiones [11] also give desired 1,2,4-dithiazole-3-ones.

In our case, we chose the reaction of substituted *O*-phenyl thiocarbamates (**1a–g**) with chlorocarbonylsulfenyl chloride in dry ether at −10°C likewise in ref. 7. Starting *O*-phenyl thiocarbamates (**1a–g**) were prepared according to combined procedure described elsewhere [12]. In the first step, substituted phenol was treated with cyanogen bromide, and the resulting substituted phenyl cyanate was transformed to **1a–g** without isolation (see Scheme 1 and the Experimental part).

The prepared 5-phenoxy-1,2,4-dithiazole-3-ones (**2a–g**) were characterized by ^{1}H, ^{13}C-NMR, and elemental

Scheme 1



analysis, and two of them were also characterized by X-ray diffraction (Figs. 1 and 2).

The X-ray study of **2b** and **2d** showed that the 1,2,4-dithiazole ring is essentially planar (torsion angles C1—S1—S2—C2 and S1—C1—N1—C2 are less than 0.2(3)°) which supports the idea of its aromatic character. In contrast to EDITH [7], where the ethoxy group is coplanar with the 1,2,4-dithiazole ring, the plane of the benzene rings in **2b** and **2d** are strongly deviated from the plane of the parent heterocycle (dihedral angles are –103.6(3) and 105.5(3), respectively). Some bond lengths and angles (Table 1) were found to be similar to other 1,2,4-dithiazole-3-ones, 3-thiones and five-membered cyclic disulfides with aromatic character [13]. The substitution of the benzene ring had almost no influence upon the bond lengths and angles (see Table 1).

Compound **2a** was preliminarily tested for sulfurization efficiency toward triphenyl phosphite which was the least reactive P(III) compound used in a previous study [4b]. The observed rate constant $k_{obs} = 100\ s^{-1}$ measured under pseudo-first order conditions in a 0.05*M* triphenyl phosphite solution (in THF) showed that **2a** is more than two orders of magnitude more reactive than xanthane hydride. A detailed study of the reactivity of the prepared compounds including the mechanism will, therefore, be the subject of a thorough kinetic study to be published in a more specialized journal.

EXPERIMENTAL

Starting *O*-phenyl thiocarbamates **1a–g** were prepared and purified by a modified method [12] (see below). All starting chemicals were purchased from commercial suppliers and used as received. Before use, the solvents were dried and distilled. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker Avance 3 - 400 MHz instrument in $CDCl_3$ solution. Chemical shifts δ were referenced to tetramethylsilane δ(TMS) = 0 ppm (^{1}H) or to the solvent residual peak δ($CDCl_3$) = 77.0 (^{13}C). The coupling constants *J* were quoted in Hz. The ^{13}C-NMR spectra were measured in a standard way and by means of the APT (Attached Proton Test) pulse sequence to distinguish CH, CH_3 and CH_2, C_{quart}. All NMR experiments were performed with the aid of the manufacturer's software. The elemental analyses were performed on an apparatus of Fisons Instruments, the EA 1108 CHN.

X-ray crystallography of 2b and 2d. The colorless single crystals of **2b** and **2d** suitable for X-ray determination were grown by slow vapor diffusion of hexane into a saturated ethyl acetate solution. The X-ray data for **2b** and **2d** were obtained at 150 K using an Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo K_α radiation (λ = 0.71073 Å), a graphite monochromator, and the φ and χ scan modes. Data reductions were performed with the DENZO-SMN [14]. The absorption was corrected by integration methods [15]. Structures were solved by direct methods (Sir92) [16] and refined by full matrix least-squares based on F^2 (SHELXL97) [17]. The hydrogen atoms were mostly localized on a difference Fourier map: however, to ensure uniformity of the treatment of the crystals, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom) or of 1.5 U_{eq} for the methyl moiety with C—H = 0.96 Å and 0.93 Å for the methyl and hydrogen atoms, respectively, in the aromatic ring.

$R_{int} = \Sigma F_o^2 - F_{o,mean}^2|/\Sigma F_o^2$, GOF = $[\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$ for all data, $R(F) = \Sigma|\ |F_o| - |F_c||/\Sigma|F_o|$ for observed data, $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{1/2}$ for all data.

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 769082 and 769083 for **2b** and **2d**, respectively. Copies of this information may be obtained free of charge

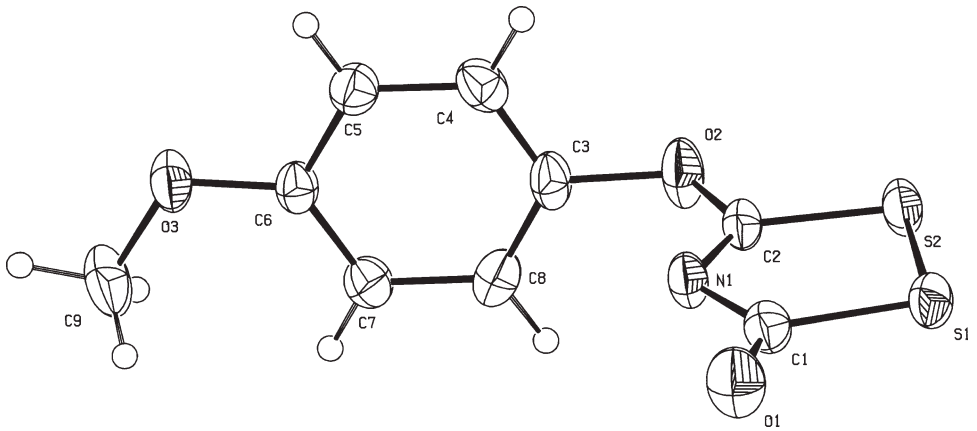


Figure 1. ORTEP view of compound 2b (thermal ellipsoids at 40% probability).

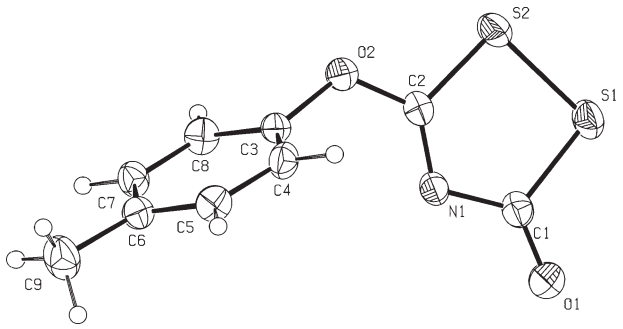


Figure 2. ORTEP view of compound 2d (thermal ellipsoids at 40% probability).

from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk). In the structure of **2d**, the Flack parameter has a meaningless standard uncertainty [18].

Compound 2b. $C_9H_7NO_3S_2$; monoclinic, space group $P\ 2_1/c$, $a = 8.1622(12)$, $b = 11.5321(11)$, $c = 11.0238(6)$ (Å), $\alpha = 90°$, $\beta = 102.63(2)°$, $\gamma = 90°$, $Z = 4$, $V = 1012.5(2)$ Å^3, Dc $= 1.583$ g cm^{-3}. Intensity data collected with 2.56–27.49°; 8105 independent reflections measured; 1798 observed [$I > 2s(I)$]. Final R index = 0.0377 (observed reflections), Rw = 0.0757 (all reflections), $S = 1.126$. CCDC 769082.

Compound 2d. $C_9H_7NO_2S_2$; orthorhombic, space group $P2_12_12_1$, $a = 7.0232(3)$, $b = 7.6181(3)$, $c = 18.5249(8)$ (Å), $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $Z = 4$, $V = 991.15(7)$ Å^3, Dc $= 1.510$ g cm^{-3}. Intensity data collected with 2.89–27.49°; 9857 independent reflections measured; 1868 observed [$I > 2s(I)$]. Final R index = 0.0382 (observed reflections), Rw = 0.0745 (all reflections), $S = 1.102$. CCDC 769083.

***O*-Phenyl thiocarbamates 1a–g; general procedure.** A solution of 0.04 mol of phenol and 0.04 mol of triethylamine in 50 mL of dry Et_2O was added dropwise to a solution of 0.04 mol cyanogen bromide in 50 mL of dry Et_2O over 20 min under stirring at –5°C, and the stirring was continued for 1.5 h. Triethylamonium-chloride was filtered off and H_2S was bubbled through the filtrate for 3 h at room temperature in the presence of catalytic amount of triethylamine. The solvent was then evaporated and the residue was recrystallized from $CHCl_3$-hexane mixture.

***O*-Phenyl thiocarbamate (1a).** Yield: 4.2 g (69%); m.p. 136–137°C (ref. 19 gives 134°C); ^{1}H-NMR (400 MHz): δ = 7.40 (m, 2H, ArH-3,5), 7.28 (m, 1H, ArH-4), 7.10 (m, 2H, ArH-2,6), 7.01 and 6.54 (2 × bs, 2H, NH_2); ^{13}C-NMR (100 MHz): δ = 191.8 (C=S), 153.3 (C—O), 129.3 (C-3,5), 126.4 (C-4), 122.4 (C-2,6).

***O*-4-Methoxyphenyl thiocarbamate (1b).** Yield: 5.4 g (73%); m.p. 146–147°C (ref. 20 gives 145–147°C), ^{1}H-NMR (400 MHz): δ = 7.03 (AA′XX′, 2H), 6.89 (AA′XX′, 2H), 6.64 and 6.44 (2 × bs, 2H, NH_2), 3.81 (s, 3H, CH_3); ^{13}C-NMR δ 192.4 (C=S), 157.6 (C—O), 147.0 (C—O), 123.1 (C-2,6), 114.2 (C-3,5), 55.5 (OCH_3).

***O*-3-Methoxyphenyl thiocarbamate (1c).** Yield: 4.0 g (54%); m.p. 129–132 °C, ^{1}H-NMR (400 MHz): δ = 7.28 (t, J 8.0 Hz, 1H, ArH-5), 6.85 (dd, J 8.4 and 1.6 Hz, 1H, ArH-4), 6.71 (dd, J 8.0 and 1.6 Hz, 1H, ArH-6), 6.69 (t, J 2.0 Hz, 1H, ArH-2) 6.70 and 6.47 (2 × bs, 2H, NH_2), 3.81 (s, 3H, CH_3); ^{13}C-NMR (100 MHz) δ = 191.7 (C=S), 160.3 (C—O), 154.2 (C—O), 129.6, 114.6, 112.2, 108.5, 55.4 (OCH_3). Anal. Calcd. for $C_8H_9NO_2S$: C 52.44; H 4.95; N 7.64; S 17.50. Found: C 52.71; H 5.01; N 7.23; S 17.17.

***O*-4-Methylphenyl thiocarbamate (1d).** Yield: 4.0 g (60%); m.p. 151–152°C (ref. 21 gives 153 °C); ^{1}H-NMR (400 MHz): δ = 9.19 and 8.98 (2 × bs, 2H, NH_2), 7.16 (AA′XX′, 2H), 6.92 (AA′XX′, 2H), 2.29 (s, 3H, CH_3); ^{13}C-NMR (100 MHz): δ = 190.7 (C=S), 151.6 (C—O), 134.8 (C-4), 129.6 (C-3,5), 122.6 (C-2,6), 20.5 (CH_3).

***O*-4-Chlorophenyl thiocarbamate (1e).** Yield 4.7 g (63%); m.p. 155–157°C (ref. 22 gives 165–166°C), ^{1}H-NMR (400 MHz): δ = 8.25 (AA′XX′, 2H), 7.39 (AA′XX′, 2H), 7.48 and 7.21 (2 × bs, 2H, NH_2); ^{13}C-NMR (100 MHz): δ = 191.4 (C=S), 151.7 (C—O), 131.9 (C—Cl), 129.4 (C-3,5), 123.9 (C-2,6).

***O*-3-Chlorophenyl thiocarbamate (1f).** Yield: 5.8 g (77%); m.p. 110–113°C (ref. 23 gives 122°C), ^{1}H-NMR (400 MHz): δ = 7.39 (t, J 8.0 Hz, 1H, ArH-5), 7.28 (m, 1H, ArH), 7.14 (t, J 2.0 Hz, 1H, ArH-2), 7.02 (m, 1H, ArH), 6.80 and 6.49 (2 × bs, 2H, NH_2); ^{13}C-NMR (100 MHz): δ = 191.2 (C=S), 153.6 (C—O), 134.5 (C—Cl), 129.9, 126.7, 123.2, 121.0.

***O*-3-Trifluoromethylphenyl thiocarbamate (1g).** Yield 4.6 g (52%); m.p. 108–110°C, ^{1}H-NMR (400 MHz): δ = 7.55 (m, 2H, ArH), 7.38 (m, 1H, ArH), 7.31 (m, 1H, ArH), 6.8 and 6.54 (2 × bs, 2H, NH_2); ^{13}C-NMR (100 MHz): δ = 191.1 (C=S), 153.2 (C—O), 131.8 (q, J 32 Hz, C-3), 129.8 (C-5), 126.3 (C-6), 123.4 (q, J 272 Hz, CF_3), 123.2 (q, J 3.7 Hz, C-4), 119.9 (q, J 3.8 Hz, C-2). Anal. Calcd. for $C_8H_6F_3NO_2S$: C 40.51; H 2.55; N 5.90; S 13.52. Found: C 40.28; H 2.25; N 6.00; S 13.43.

5-Phenoxy-1,2,4-dithiazole-3-ones 2a–g; general procedure. A solution of corresponding *O*-phenyl thiocarbamate **1a–g** (5 mmol) in dry Et_2O (50 mL) was added dropwise over 30 min into a stirred and externally chilled (–10°C) solution of chlorocarbonylsulfenyl chloride (0.66 g, 5 mmol) in dry Et_2O

Table 1

Selected bond lengths, bond angles, and torsion angles for **2b** and **2d**.

	2b	**2d**	EDITH [7]
	Bond lengths (Å)		
C1—N1	1.380(3)	1.372(3)	1.36(2)
C2—N1	1.278(3)	1.276(4)	1.26(2)
C1—S1	1.800(2)	1.810(2)	1.81(2)
C2—S2	1.733(2)	1.734(3)	1.76(2)
S1—S2	2.0454(14)	2.0386(10)	2.053(6)
C1—O1	1.202(3)	1.201(3)	1.23(2)
C2—O2	1.330(3)	1.332(3)	1.31(2)
	Bond angles (°)		
N1—C1—S1	114.79(16)	114.98(17)	116(1)
C1—S1—S2	94.78(8)	94.41(8)	93.3(5)
C2—S2—S1	91.50(9)	91.78(10)	91.9(5)
N1—C2—S2	124.00(18)	123.90(18)	123(1)
C1—N1—C2	114.93(19)	114.9(2)	–
	Torsion (dihedral) angles (°)		
C1—S1—S2—C2	−0.02(12)	−0.21(11)	–
N1—C1—S1—S2	0.11(17)	0.28(17)	–4(2)
C1—N1—C2—S2	0.2(3)	0.0(3)	–5(3)
S1—S2—C2—O2	−179.77(16)	−179.54(16)	175(1)
S2—S1—C1—O1	179.9(2)	−179.66(19)	180(2)
C5—C6—O3—C9	−178.4(2)	–	–
S2—C2/C3—C4	−103.6(3)	−105.5(3)	–

(50 mL). Then reaction mixture was stirred at −10°C for 2 h. Solvent was evaporated at reduced pressure, and the residue was recrystallized from ethyl acetate.

5-Phenoxy-1,2,4-dithiazole-3-one (2a). Yield: 0.56 g (53%); m.p. 73°C; ^{1}H-NMR (400 MHz): δ = 7.45 (m, 2H, Ar-H 3,5), 7.36 (m, 1H Ar-H4), 7.27 (m, 2H, Ar-H 2,6); ^{13}C-NMR (100 MHz): δ = 188.2 (C=O), 179.2 (C=N), 153.5 (C—O), 130.2 (C-3,5), 127.9 (C-4), 120.6 (C-2,6). Anal. Calcd. for $C_8H_5NO_2S_2$: C, 45.48; H, 2.39; N, 6.63; S, 30.36. Found: C, 45.28; H, 2.72; N, 7.00; S, 30.07.

5-(4-Methoxyphenoxy)-1,2,4-dithiazole-3-one (2b). Yield: 0.78 g (64%); m.p. 84°C; ^{1}H-NMR (400 MHz): δ = 7.21 (AA′XX′, 2H), 6.94 (AA′XX′, 2H), 3.83 (s, 3H, OCH_3); ^{13}C-NMR (100 MHz): δ = 189.0 (C=O), 179.3 (C=N), 158.9 (C—O), 146.8 (C—O), 121.9, 115.0, 55.7 (OCH_3). Anal. Calcd. for $C_9H_7NO_3S_2$: C, 44.80; H, 2.92; N, 5.80; S, 26.58. Found: 44.91; H, 2.84; N, 6.11; S, 26.64.

5-(3-Methoxyphenoxy)-1,2,4-dithiazole-3-one (2c). Yield: 0.78 g (64%); m.p. 102°C; ^{1}H-NMR (400 MHz): δ = 7.36 (t, ^3J 8.4 Hz, 1H, ArH-5), 6.92 (m, 1H, ArH), 6.86 (m, 1H, ArH), 6.82 (t, ^3J 2.2 Hz, 1H, ArH-2), 3.83 (s, 3H, OCH_3); ^{13}C-NMR δ = 188.1 (C=O), 179.3 (C=N), 160.8 (C—O), 154.1 (C—O), 130.5, 113.7, 112.6, 106.7, 55.6 (OCH_3). Anal. Calcd. for $C_9H_7NO_3S_2$: C, 44.80; H, 2.92; N, 5.80; S, 26.58. Found: 45.02; H, 3.15; N, 6.13; S, 26.84.

5-(4-Methylphenoxy)-1,2,4-dithiazole-3-one (2d). Yield: 0.84 g (74%); m.p. 78°C; ^{1}H-NMR (400 MHz): δ = 7.25 (AA′XX′, 2H), 7.16 (AA′XX′, 2H), 2.39 (s, 3H, CH_3); ^{13}C-NMR (100 MHz): δ = 188.6 (C=O), 179.4 (C=N), 151.3 (C—O), 138.2 (C-4), 130.7 (C-3,5), 120,5 (C-2,6), 21.0 (CH_3). Anal. Calcd. for $C_9H_7NO_2S_2$: C, 47.98; H, 3.13; N, 6.22; S, 28.47. Found: C, 47.67; H, 3.38; N, 6.34; S, 28.17.

5-(4-Chlorophenoxy)-1,2,4-dithiazole-3-one (2e). Yield: 0.89 g (72%); m.p. 94°C; ^{1}H-NMR (400 MHz): δ = 7.42 (AA′XX′, 2H), 7.25 (AA′XX′, 2H); ^{13}C-NMR (100 MHz): δ = 187.6 (C=O), 178.9 (C=N), 152.1 (C—O), 133.3 (C—Cl), 130.2 (C-3,5), 121,9 (C-2,6). Anal. Calcd. for $C_8H_4ClNO_2S_2$: C, 39.11; H, 1.64; Cl, 14.43; N, 5.70; S, 26.10. Found: C, 39.20; H, 1.83; Cl, 14.58; N, 6.08; S, 25.82.

5-(3-Chlorophenoxy)-1,2,4-dithiazole-3-one (2f). Yield: 0.94 g (76%); m.p. 77°C; ^{1}H-NMR (400 MHz): δ = 7.40 (t, ^3J 8.4 Hz, 1H, ArH-5), 7.35 (m, 1H, ArH), 7.32 (m, 1H, ArH), 7.02 (m, 1H, ArH); ^{13}C-NMR δ = 187.4 (C=O), 178.9 (C=N), 153.9 (C—O), 135.4 (C—Cl), 130.8, 128.0, 121.2, 118.9. Anal. Calcd. for $C_8H_4ClNO_2S_2$: C, 39.11; H, 1.64; Cl, 14.43; N, 5.70; S, 26.10. Found: C, 39.22; H, 1.92; Cl, 14.53; N, 6.00; S, 26.01.

5-(3-Trifluoromethylphenoxy)-1,2,4-dithiazole-3-one (2g). Yield 0.80 g (57%); m.p. 105°C, ^{1}H-NMR (400 MHz): δ = 7.63 (m, 1H, ArH), 7.60 (m, 1H, ArH), 7.56 (m, 1H, ArH), 7.52 (m, 1H, ArH); ^{13}C-NMR (100 MHz): δ = 187.3 (C=O), 178.8 (C=N), 153.8 (C—O), 132.8 (q, *J* 12.1 Hz, *C*-3), 130.8, 124.5 (q, *J* 3.7 Hz), 124.1, 122.1 (q, *J* 266 Hz, CF_3), 117.9 (q, *J* 3.7 Hz). Anal. Calcd. for $C_9H_4F_3NO_2S_2$: C, 38.71; H, 1.44; Cl, 20.41; N, 5.02; S, 22.96. Found: C, 38.80; H, 1.63; N, 5.39; S, 22.62.

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