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**Abstract:** Reaction of 3,4,4,5-tetrachloro-4*H*-1,2,6-thiadiazine with 2-mercaptoethan-1-ol (1 equiv.) gave 6,10-dichloro-1-oxa-4,8-dithia-7,9-diazaspiro[4.5]deca-6,9-diene in 12% yield. The compound was fully characterized.

Keywords: heterocycle; 1,2,6-thiadiazine; spirocycle; oxathiolane

## 1. Introduction

1,2,6-Thiadiazines are sulfur–nitrogen heterocycles that have wide applications [1]. Non-S-oxidized 4*H*-1,2,6-thiadiazines are rare but find uses in both the materials [2–4] and the biological sectors [5–11]. Their chemistry and applications have recently been reviewed [12]. Our interest in thiadiazines is currently focused on 3,4,4,5-tetrachloro-4*H*-1,2,6-thiadiazine (1), an unusual thiadiazine scaffold, which can be prepared either from dichloromalononitrile and SCl<sub>2</sub> [13] or from *N*-2,2-trichloro-2-cyanoacetimidoyl chloride and elemental sulfur [14]. Thiadiazine 1 can be readily transformed to aromatic 1,2,6-thiadiazines, such as 2-(3,5-dichloro-4*H*-1,2,6-thiadiazin-4-ylidene)malononitrile (2) [15], *N*-aryl-3,5-dichloro-4*H*-1,2,6-thiadiazin-4-imines 3 [16], 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one (4) [15], and 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-thione (5) [17]. Moreover, C4-saturated analogues, such as 4,4-diamino- [18], 4,4-dialkoxy-, and 4,4-bis(alkylthio)-3,5-dichloro-4*H*-1,2,6-thiadiazine 1 [17] (Scheme 1).

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Scheme 1. Selected transformations of tetrachlorothiadiazine 1.

As a continuation of our study on the conversion of tetrachlorothiadiazine **1** to 4,4ketals and thioketals, we investigated the formation of oxathiolanes. We intended to study the use of oxathiolanes as protected versions of thiadiazin-4-ones [19].

## 2. Results and Discussion

The reaction of tetrachlorothiadiazine 1 with 2-mercaptoethan-1-ol (1 equiv.) in DCM at *ca*. 20  $^{\circ}$ C led to a slow but complete consumption of the starting thiadiazine and the



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). isolation of the desired compound **9** in a low 12% yield (Scheme 2), while no other products were observed using TLC.



Scheme 2. Synthesis of 6,10-dichloro-1-oxa-4,8-dithia-7,9-diazaspiro[4.5]deca-6,9-diene (9).

Product **9** was isolated as colorless plates, mp 75–77 °C (from *n*-pentane/–40 °C). UVvis spectroscopy supported an intact thiadiazine ring ( $\lambda_{max}$  301 nm, log  $\varepsilon$  2.62). Mass spectrometry revealed a molecular ion (MH<sup>+</sup>) peak of *m*/*z* 243 (90%) along with a MH<sup>+</sup>+2 isotope peak at 245 (57%) and a MH<sup>+</sup>+4 isotope peak at 247 (17%) that supported the presence of two chlorines. The <sup>13</sup>C NMR spectroscopy showed the presence of two CH<sub>2</sub> resonances and two quaternary carbon resonances (see Supplementary Materials for the NMR spectra), while a correct elemental analysis (CHN) was obtained for the molecular formula C<sub>5</sub>H<sub>4</sub>Cl<sub>2</sub>N<sub>2</sub>OS<sub>2</sub>.

As product **9** is the only example of a C4 oxathiolane-substituted thiadiazine, we looked at the literature to comment on its NMR data. We were interested in comparing the C4 signals of O,O, O,S, and S,S ketals, as this *sp*<sup>3</sup> ring carbon of the thiadiazine was a potentially useful spectroscopic NMR 'handle'. Initially, we looked at a comparison between the ketal, oxathiolane, and thioketal derivatives of acetone **10**, **11**, and **12**, respectively (Figure 1). This showed that the quaternary carbon resonance shifts from 109 [20], to 92 [21] and 62 ppm [22] when oxygen is systematically replaced by sulfur. This up-field shift was also observed with our ketals and thioketals; the two ketals **7a** and **7b** showed a quaternary resonance at 96 and 92 ppm, while, for compound **9**, a reduction of 10 ppm units was observed, and, for thioketals **8a** and **8b**, a further reduction by 17 and 21 ppm, respectively, was observed [17]. Moreover, regarding compound **9**, the C3/4 resonances are in good agreement with compounds **7** and **8**, and the CH<sub>2</sub> resonances agree with compound **11**, thereby strengthening the structural determination of compound **9**.



**Figure 1.** Comparison of <sup>13</sup>C NMR data to literature compounds, numbers in ppm rounded to the closer integer.

Despite the multifunctional nature of oxathiolane **9**, further investigation of its chemistry was made difficult by the low yield of its preparation.

## 3. Materials and Methods

The reaction mixture was monitored by TLC using commercial glass-backed thinlayer chromatography (TLC) plates (Merck Kieselgel 60 F<sub>254</sub>). The plates were observed under UV light at 254 and 365 nm. The technique of dry flash chromatography was used throughout for all non-TLC scale chromatographic separations using Merck Silica Gel 60 (less than 0.063 mm) [23]. The melting point was determined using a PolyTherm-A, Wagner & Munz Kofler-Hotstage Microscope apparatus (Wagner & Munz, Munich, Germany). The solvent used for recrystallization is indicated after the melting point. The UV-vis spectrum was obtained using a Perkin-Elmer Lambda-25 UV-vis spectrophotometer (Perkin-Elmer, Waltham, MA, USA), and inflections are identified by the abbreviation "inf". The IR spectrum was recorded on a Shimadzu FTIR-NIR Prestige-21 spectrometer (Shimadzu, Kyoto, Japan) with a Pike Miracle Ge ATR accessory (Pike Miracle, Madison, WI, USA) and the strong, medium, and weak peaks are represented by s, m, and w, respectively. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance 500 machine [at 500 and 125 MHz, respectively, (Bruker, Billerica, MA, USA)]. Deuterated solvents were used for homonuclear lock, and the signals are referenced to the deuterated solvent peaks. Attached proton test (APT) NMR studies were used for the assignment of the  $^{13}$ C peaks as CH<sub>3</sub>, CH<sub>2</sub>, CH, and Cq (quaternary). The APCI+ mass spectrum was recorded on a Model 1260 Infinity II Quadrupole MSD, Agilent Technologies. 3,4,4,5-Tetrachloro-4H-1,2,6-thiadiazine (1) [13] was prepared according to the literature procedure.

6,10-Dichloro-1-oxa-4,8-dithia-7,9-diazaspiro[4.5]deca-6,9-diene (9)

2-Mercaptoethan-1-ol (70 µL, 1.00 mmol) was added to a stirred suspension of tetrachlorothiadiazine (9) (238 mg, 1.00 mmol) in DCM (5 mL), and the reaction mixture was stirred at *ca*. 20 °C until consumption of the starting material (TLC, 3 days). The mixture was then adsorbed onto silica and chromatographed (*n*-hexane/DCM 80:20) to give the *title compound* 9 (28 mg, 12%) as colorless plates, mp 75–77 °C (from *n*-pentane/–40 °C); R<sub>f</sub> 0.32 (*n*-hexane/DCM 80:20); (found: C, 24.79; H, 1.48; N, 11.36. C<sub>5</sub>H<sub>4</sub>Cl<sub>2</sub>N<sub>2</sub>OS<sub>2</sub> requires C, 24.70; H, 1.66; N, 11.52%);  $\lambda_{max}$ (DCM)/nm 244 (log  $\varepsilon$  2.85), 266 (2.88), 301 (2.62);  $v_{max}/cm^{-1}$ 2953 w, 2889 w and 2845 w (alkyl C-H), 1601 m, 1582 m, 1558 w, 1539 w, 1464 w, 1423 w, 1263 m, 1209 w, 1140 s, 1111 m, 1101 s, 1018 w, 999 m, 939 m, 893 s, 864 m, 799 m, 779 m;  $\delta_{H}$ (500 MHz; CDCl<sub>3</sub>) 4.65 (2H, t, *J* 5.8, OCH<sub>2</sub>), 3.45 (2H, t, *J* 5.8, SCH<sub>2</sub>);  $\delta_{C}$ (125.7 MHz; CDCl<sub>3</sub>) 141.1 (Cq), 82.0 (Cq), 76.7 (CH<sub>2</sub>), 36.6 (CH<sub>2</sub>); *m/z* (APCI+) 247 (MH<sup>+</sup>+4, 17%), 245 (MH<sup>+</sup>+2, 57%), 243 (MH<sup>+</sup>, 90), 209 (M<sup>+</sup>-Cl+2, 19), 207 (M<sup>+</sup>-Cl, 48), 195 (100).

**Supplementary Materials:** The following are available online, mol file, <sup>1</sup>H and <sup>13</sup>C NMR spectra of compound 9.

**Author Contributions:** A.S.K. and P.A.K. conceived the experiments; A.S.K. designed the experiments; A.S.K. wrote the paper; A.S.K. and P.A.K. edited the manuscript. All authors have read and agreed to the published version of the manuscript.

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