

Short Note

4,4-Dichloro-1,3-dithietane-2-one

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Abstract: The title compound, 4,4-dichloro-1,3-dithietane-2-one, was encountered when opening a commercial capped amber bottle labeled “thiophosgene” that had been stored in a cold room (4 °C) for decades without any special precautions. Treating it as an unknown, the structure was established by single crystal X-ray analysis, and confirmed by ¹³C NMR, FTIR, melting behavior, and elemental analysis; its behavior under several mass spectrometric conditions was also examined. The dithietane appears to be a spontaneously formed cyclodimer of thiophosgene in which exactly one (not zero, not both) of the dichloromethylene moieties has been hydrolyzed to a carbonyl function. The relative long-term stability of the hydrolyzed dimer, along with a pathway back to thiophosgene, suggests that it might serve as a storage vehicle for toxic thiophosgene. Furthermore, as noted elsewhere, the title compound reacts with nucleophiles under mild aqueous conditions, suggesting that it may be a useful probe in chemical biology.

Keywords: 4,4-dichloro-1,3-dithietane-2-one; thiophosgene; long-term storage of thiophosgene; thiophosgene dimer; partially hydrolyzed thiophosgene dimer; X-ray structural analysis; chemical biology



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1. Introduction

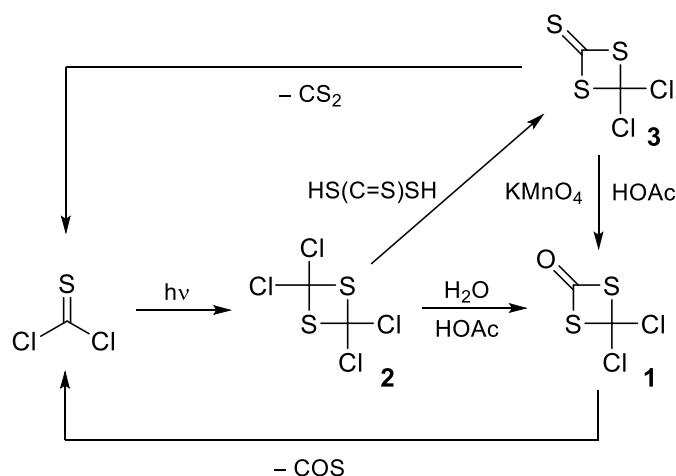
The corresponding author and his coworkers have had several occasions to work with thiophosgene (thiocarbonyl dichloride, CCl₂S) during the course of a half-century research career [1–4]. First reported in the mid-19th century [5], thiophosgene is a pungent red liquid (bp 73–76 °C) [6] that is generally prepared through the action of various reducing agents on trichloromethane sulfonyl chloride (also known as perchloromethylmercaptan, CCl₄S), which in turn is the product from chlorination of carbon disulfide [6–8].

Thiophosgene reacts readily with a variety of nucleophiles to form alkyl and aryl isothiocyanates, thiochloroformates, thioureas, thiocarbonates, thiocarbamates, and trithiocarbonates, as has been well reviewed [8,9]. These reagents and intermediates have been used for syntheses of a range of heterocyclic compounds [8,9] and can also provide stereospecific access to alkenes (Corey-Winter synthesis) [10,11].

Our own work used thiophosgene that was obtained from Aldrich (now Millipore-Sigma), a company based in Milwaukee, WI, USA. Once the needed amounts of thiophosgene were removed for whatever reactions were of interest, the amber glass bottle [originally holding 25 g of material] was recapped and returned to general storage in a cold room (4 °C) where it remained for several decades without any special precautions.

In 2015, one of the coauthors retrieved the bottle, hoping to use thiophosgene for their work, and was surprised to note that what had once been a red liquid had since, *without any experimental intervention*, quantitatively transformed into colorless transparent blocks of varying sizes with a melting point of 66–68 °C [*no decomposition*]. Elemental analysis consistent with $C_2Cl_2OS_2$, FTIR, ^1H (lack of signals) and ^{13}C NMR (two signals with diagnostic chemical shifts), and (most significantly) single crystal X-ray diffraction, as reported herein, all converged on the conclusion that the long-term storage derivative was 4,4-dichloro-1,3-dithietane-2-one (**1**).

It was only after we were confident in the structure that we conducted extensive literature searches. The specific molecule reported herein (i.e., **1** in Scheme 1) has been reported previously, including methodology for its *intentional* preparation [12–16], a number of experiments for its characterization [13–15,17], and finally its X-ray crystal structure [14,15,18] which, for technical reasons, is superseded by the present work. Thus, 20 h of photochemical irradiation (analytical quartz lamp) applied to neat thiophosgene gives rise to thiophosgene dimer **2**, which separates out as a solid upon cooling to –30 °C [13]. (Dimer **2** was almost surely observed much earlier by Rathke [7], who used only sunlight.) The isolated and recrystallized dimer **2** is then hydrolyzed under acidic conditions [HOAc–H₂O (3:1), ~60 °C, 0.5 h] to produce pure **1** in modest yield [13–16]. Alternatively, the title compound **1** can be obtained more indirectly, in a mediocre overall yield, by first creating the corresponding thiocarbonyl species **3** by the vigorous reaction of dimer **2** with neat trithiocarbonic acid [HS(C=S)SH], which is followed by oxidation/desulfurization of the thione function to the corresponding carbonyl by treatment of **3** with potassium permanganate in glacial acetic acid [14,15].



Scheme 1. Synthetic routes for the *intentional* formation of 4,4-dichloro-1,3-dithietane-2-one (**1**), as well as for the related compounds 2,2,4,4-tetrachloro-1,3-dithietane (**2**) and 2,2-dichloro-1,3-dithia-4-cyclobutanethione (**3**), starting from thiophosgene (left side). The scheme also discloses reported routes for decomposition of **1** or **3**. See text for further discussion and for references. The as-yet-unprecedented forward reaction of thiophosgene plus carbonyl sulfide (COS) *might* be another way to account for **1**.

2. Results and Discussion

2.1. X-Ray Structure

Preliminary work on the structure of **1** has been reported previously [14,15,18], enough to determine the space group and guess the arrangements of atoms, but not at the level of detail shown in the present paper (Table 1, Figure 1). The earlier unit cells of **1**, as well as that of **3**, match what is found here for **1** by transformation of the cell setting from $P2_1/c$ to $P2_1/n$ (i.e., to $a = 5.892(6)$, $b = 10.443(12)$, $c = 9.580(12)$, $\beta = 94.5(2)$ [18], or by swapping the a

and *c* axes in space group $P2_1/n$ [15]). Compounds **1** and **3** are isostructural, with the main difference being the slightly smaller unit cell metrics of **1** due to the presence of oxygen (C=O) in **1** versus the presence of sulfur (C=S) in **3**.

Table 1. Crystal structure and refinement data for 4,4-dichloro-1,3-dithietane-2-one (**1**).

Empirical formula	C ₂ Cl ₂ OS ₂
Formula weight	175.04
Temperature	100.0(5) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 5.8312(5)$ Å, $\alpha = 90^\circ$ $b = 10.3605(9)$ Å, $\beta = 94.4572(17)^\circ$ $c = 9.3858(8)$ Å, $\gamma = 90^\circ$
Volume	565.32(8) Å ³
Z	4
Density (calculated)	2.057 g/cm ³
Absorption coefficient	1.752 mm ^{−1}
<i>F</i> (000)	344
Crystal color, morphology	colorless, block
Crystal size	0.45 × 0.40 × 0.30 mm ³
Theta range for data collection	2.933 to 38.651°
Index ranges	−10 ≤ <i>h</i> ≤ 10, −18 ≤ <i>k</i> ≤ 18, −16 ≤ <i>l</i> ≤ 16
Reflections collected	41,413
Independent reflections	3169 [<i>R</i> (int) = 0.0216]
Observed reflections	3058
Completeness to $\theta = 37.785^\circ$	99.7%
Absorption correction	Multi-scan
Max. and min. transmission	0.7476 and 0.5909
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	3169/0/64
Goodness-of-fit on <i>F</i> ²	1.183
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0216, <i>wR</i> 2 = 0.0549
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0226, <i>wR</i> 2 = 0.0554
Largest diff. peak and hole	0.507 and −0.400 e [−] /Å ³

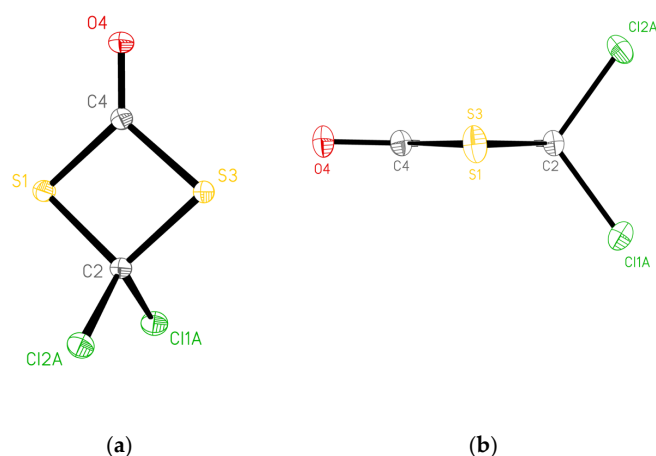


Figure 1. (a) Anisotropic displacement ellipsoid plot of 4,4-dichloro-1,3-dithietane-2-one (**1**) drawn at the 50% probability level. Note that the crystallographic numbering scheme differs from the IUPAC numbering scheme. (b) On-edge view, showing how in a plane defined by the ring atoms (S1, C2, S3, C4), the oxygen atom of **1** is only 0.032 Å out of plane.

The asymmetric unit of **1** contains one molecule in a general position, with the positions of other molecules dictated by the symmetry of the space group. The S₂C₂ core is undistorted, with an RMS deviation from planarity of 0.007 Å. Bond lengths and angles of **1** have been compiled (Table 2) and compared to those of the tetrachloro dimer **2** [18,19], as well as to averages from several non-cyclic (“linear”) RCH₂–S–(C=O)–S–CH₂R structures [20–23]. The cyclic core clearly constrains the S–C–S angles, which are all less than 100°, compared with those of the non-cyclic structures, which are 110.9°.

Table 2. Comparison of bond lengths [Å] and angles [°] in 4,4-dichloro-1,3-dithietane-2-one (**1**) with those of its putative direct precursor, 2,2,4,4-tetrachloro-1,3-dithietane (**2**), and with averages of non-cyclic RCH₂–S–(C=O)–S–CH₂R structures.

	1	2 ^a	Non-Cyclic
S1–C2	1.8420(7)	1.801(6)	
S1–C4	1.7825(7)		1.76
S3–C2	1.8229(7)	1.807(6)	
S3–C4	1.7764(7)		
C2–Cl1A	1.7745(7)	1.760(6)	
C2–Cl2A	1.7748(7)	1.778(6)	
S1–C2–S3	96.62(3)	96.1(6)	
S1–C4–S3	99.86(3)		110.9
C2–S1–C4	81.65(3)	83.9(5) ^b	
C2–S3–C4	81.85(3)		
Cl1A–C2–Cl2A	108.92(4)	107.1(4)	

^a Molecule is on a crystallographic inversion center with only (CCl₂–S) linkers (see Scheme 1). ^b Here “C4” is the symmetry equivalent of C2.

2.2. Additional Characterization of the Long-Term Storage Product

The material recovered in 2015 was submitted, with no additional manipulations or solvent washings, for elemental analysis. The observed results were in complete agreement with theory for C₂Cl₂OS₂. The melting point, in our hands, agreed with the literature values. Moreover, we found no evidence for decomposition of **1** upon melting. The melted material was allowed to resolidify, and found to remelt with the same mp (some material possibly lost through sublimation).

Further evidence supporting the structure of compound **1** came from IR and NMR spectroscopy. The IR showed major peaks at 1768 and 1708 cm^{−1}, consistent with a carbonyl that is part of a strained ring, and essentially identical to literature values [15]. “Fingerprint” peaks in the IR also matched the literature [15,17]. Furthermore, compound **1** was readily dissolved in CDCl₃ with TMS as a reference standard, and the ¹H NMR showed no other peaks, as might be expected for a compound without protons. The ¹³C NMR showed two peaks, one at δ 165.1 assigned to the carbonyl and the other at δ 70.4 assigned to the dichloromethylene moiety. These compare well with other carbonyl or CCl₂ resonances, and are within 0.2 ppm of the literature values for **1** [24].

In our hands, several state-of-the-art mass spectrometric methods in routine use at the University of Minnesota failed to produce molecular ions from **1**, but GC/MS was dominated by a signal corresponding to monoisotopic thiophosgene (*m/z*: obs. 113.9094, theor. 113.9098), as well as a base peak assigned to CClS⁺ (*m/z*: obs. 78.9407, theor. 78.94092); for both CCl₂S⁺ and CClS⁺, the expected satellites due to the ³⁷Cl isotope were also seen. These results suggested that under the analysis conditions, a cycloreversion had occurred, with concomitant formation of carbonyl sulfide (COS) (*m/z*: obs. 59.9666, theor. 59.9670). Our inability to detect a molecular ion for **1** stood in contrast to a 1970 report [15] of a relatively weak signal at *m/z* 174. We therefore arranged for additional analysis using instrumentation at the University of Wisconsin-Milwaukee. We concluded that molecules

of **1** survive the GC/MS, but overwhelmingly fragment to CCl_2S^+ and CClS^+ , consistent with the earlier results. However, in this latter study, careful examination of the region between m/z 150 and 180 revealed that the sought-after $\text{C}_2\text{Cl}_2\text{OS}_2^+$ molecular ion could indeed be observed with peaks (<1% of base) at m/z 174, 176, and 178 in the ratios expected for two chlorine atoms.

2.3. Mechanistic Possibilities to Account for the Long-Term Storage Product

It has been definitively established here that the title dithietane **1** is formed under the conditions described, although there is no way to accurately reconstruct either the timeline or the yield of this transformation. It is quite remarkable that the product obtained was exquisitely pure by multiple quantitative criteria, such as elemental analysis, ^{13}C NMR, and melting point determination. The aforementioned techniques would have revealed even small amounts of contaminating thiophosgene, or other potential products such as **2** or **3** (see Scheme 1). Furthermore, there is no evidence that **1**, once recognized and appreciated in 2015, was in any way labile under our subsequent ambient storage conditions (amber bottle, ambient light, 25 °C from 2015–2025).

To account for **1**, it seems plausible to us that thiophosgene had undergone head-to-tail cyclodimerization to **2** (a known compound, as already discussed), and that the carbonyl group in **1** had been installed by subsequent hydrolysis of one, but not both, of the dichloromethylene moieties in **2**. An alternative hypothesis would involve initial hydrolysis of thiophosgene to produce low levels of hydrogen chloride (HCl) plus carbonyl sulfide (COS), the latter of which might have undergone an acid-catalyzed [2 + 2] cycloaddition with thiophosgene to produce **1** under the closed conditions of the capped amber bottle. In either scenario, the source of water for the relevant hydrolysis step is undoubtedly moist air leaking into the bottle upon storage, or trapped within the bottle whenever it was capped.

An open question is whether or not cycloadditions leading either to **1** directly, or to **2** as a precursor to **1**, are photochemical in nature. If the answer is affirmative, the next question is how much light can get through amber bottles. Based on a report by Taylor and Poole [25], amber bottles (2 mm thick) show some low levels of light transmittance in the cyan to green region of the visible spectrum (~5 to 40% transmittance). Given the long-term storage conditions, a photochemical process cannot be excluded.

2.4. Potential Applications and Future Directions

The observations reported herein raise several mechanistic and practical questions that might warrant further investigation. Obviously, whoever was to carry out follow-up studies is unlikely to have the luxury of waiting multiple decades for the described circumstances to recur. Fortunately, the literature methods to create **1** intentionally (Scheme 1 and accompanying discussion) appear to be robust and accessible on a laboratory scale, as long as appropriate safety precautions are taken.

Even the older literature suggests that **1** will react with oxygen, sulfur, and nitrogen nucleophiles, with overall addition of two equivalents of the nucleophilic reagent [12,14,15]. We are particularly encouraged by the report of Rakitzis and Malliopoulou [16] that **1** deactivates Cathepsin D. It seems reasonable that a nucleophilic amino acid residue opens **1**, and this could be followed by thioacyl substitution with another residue leading to conformational changes and denaturation. Whether and how cross-linking occurs, as the authors indicate, is less clear. Nevertheless, such results suggest that **1** could be a useful probe for chemical biology applications such as protein modification.

In our hands, **1** is very stable, including the fact that when it is melted, the molten state resolidifies and then has the identical melting point. Wortmann et al. [14] report that **1** reverts to thiophosgene, slowly at 25 °C and more rapidly upon heating, with simultaneous

production of COS (Scheme 1, bottom), which is at variance with our observations [for that matter, **3** behaves similarly with the co-product being CS₂ (Scheme 1, top)]. Nevertheless, this discrepancy can surely be reconciled with further careful work, and suggests that **1** could be a safe, solid thiophosgene equivalent, in a manner analogous to the uses of trichloromethyl chloroformate (diphosgene; a liquid) [26] or bis(trichloromethyl)carbonate (triphosgene; a solid) as phosgene equivalents [26–28].

3. Materials and Methods

3.1. General

Melting data was recorded from a Stanford Research Systems, Inc. digital melting point apparatus (SRS DigiMelt) (Stanford Research Systems, Inc., Sunnyvale, CA, USA) set at a 2 °C per min ramp rate. Infrared spectral data was obtained on a Perkin Elmer Spectrum Two FTIR Spectrometer (Perkin Elmer, Inc., Shelton, CT, USA) with a UATR Two accessory. NMR data were acquired with CDCl₃ as solvent at 25 °C on a Bruker spectrometer (Bruker Corporation, Billerica, MA, USA) with a 5 mm probe, operating at an ¹H frequency of 400 MHz and a ¹³C frequency of 101 MHz. Elemental analysis was done by Atlantic Microlab, Inc., Norcross, GA, USA.

Two mass spectrometric experiments were conducted at the University of Minnesota. In the first, the mass spectral data was collected on an Agilent 7200 GC/QTOF-MS using a 30 m × 0.25 mm DB-5 column. The sample was dissolved in methanol and 1 µL was injected. The front inlet temperature was 250 °C with a 1:10 split. The GC temperature program started at 80 °C (no hold time), ramp at 20 °C/min to 320 °C, t_R, 2.42 min. The second used a SCIEX X500R QTOF via electrospray ionization (ESI) (SCIEX, Framingham, MA, USA). The sample was again dissolved in methanol, diluted to ~5 ppm, and then infused manually (100 µL). The data was collected over a 2-min method run. The source temperature was 200 °C and the capillary voltage was –4.5 kV in negative mode.

An additional mass spectrometric experiment was conducted at the University of Wisconsin-Milwaukee, using a Shimadzu GCMS QP2010 instrument with an AOC6000plus autosampler (Shimadzu, Kyoto, Japan). A 30 m × 0.25 mm DB-1 column was used; column flow 3.0 mL/min with helium carrier. The front inlet temperature was 250 °C with a 1:5 split. Headspace sampling conditions involved incubation at 75 °C for 5 min with 250 rpm agitation, syringe temperature 85 °C, injection flow 25 mL/min with helium carrier. The GC temperature program started at 50 °C (1 min hold time), ramp at 25 °C/min to 250 °C, t_R, 5.63 min.

X-ray data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, Department of Chemistry, University of Rochester. X-ray structure manipulation and figure generation were performed using *SHELXTL* [29]. Unless noted otherwise, all structural diagrams containing anisotropic displacement ellipsoids are drawn at 50% probability level. Beyond the text graphics and Tables, additional details about the X-ray studies are found in the Supplementary Materials (Tables S1–S4, Figure S1).

3.2. Experimental

4,4-Dichloro-1,3-dithietane-2-one (1) (CAS 6008-61-3). Thiophosgene, a foul-smelling red liquid, purchased from Aldrich Chemical Company on several occasions in the 1980s, was in an amber glass bottle that was opened intermittently to retrieve aliquots for use in the synthesis of needed organosulfur compounds. The unused portion was stored, with capping, at 4 °C in the original bottle which, when newly purchased, contained 25 g. Despite some ambiguity in lab records, it seems plausible to assume that such storage went on for approximately three decades. Visual inspection in 2015 suggested that none of the thiophosgene originally in the bottle still remained. Instead, solid crystalline material

(~200 mg) was retrieved, without further purification, for characterization: mp 66–68 °C (lit. mp 71 °C [14,15], 68 °C [16], 70 °C with sublimation [17]); Anal. Calcd. for $C_2Cl_2OS_2$ (mol. wt. 173.88): C, 13.72; Cl, 40.50; S, 36.63. Found: C, 13.70; Cl, 40.68; S, 36.51. FTIR: 1768 (s), 1708 (s), 1598 (w), 873 (s), 825 (s), 742 (vs), 728 (vs), 699 (m), 579 (m), 555 (w), 503 (w) cm^{-1} ; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.26 ($CHCl_3$), 1.58 (H_2O), meaning no peaks that could be attributed to the title compound; ^{13}C NMR ($CDCl_3$, 101 MHz) δ 165.1, 70.4 (lit. δ 164.8, 70.5 [24]); GC/MS (Minnesota): t_R , 2.42 min, m/z : obs. 113.9094, theor. 113.9098 ($Cl_2C=S$); obs. 78.9407, theor. 78.9409 ($CClS$); obs. 59.9666, theor. 59.9669 (COS). Direct infusion negative ionization ESI-MS QTOF (Minnesota): theor. 174.8840 ($[M + H]^+$ of $C_2Cl_2S_2O$); not observed. GC/MS (Milwaukee): t_R , 5.63 min, m/z : 174 (M^+ , < 1%), 114 (CCl_2S^+ , 95%), 79 ($CClS^+$, 100%) 76 (CS_2^+ , 44%), 64 (S_2^+ , 6%) 60 (COS^+ , 20%), 44 (CS^+ , 40%). All spectral data can be found in the Supplementary Materials (Figures S2–S5).

3.3. X-Ray Data Collection

A crystal ($0.45 \times 0.40 \times 0.30$ mm³) was placed onto the tip of a thin glass optical fiber and mounted on a Bruker SMART APEX II CCD platform diffractometer for a data collection at 100.0(5) K [30]. A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was carried out using MoK α radiation (graphite monochromator) with a frame time of 10 s and a detector distance of 4.01 cm. A randomly oriented region of reciprocal space was surveyed: twelve major sections of frames were collected with 0.50° steps in ω at twelve different ϕ settings and a detector position of -38° in 2θ . The intensity data were corrected for absorption [31]. Final cell constants were calculated from the xyz centroids of 3839 strong reflections from the actual data collection after integration [32]. Additional crystal and refinement information can be found in Table 1.

3.4. X-Ray Structure Solution and Refinement

The structure was solved using SHELXT [33] and refined using SHELXL [34]. The space group $P2_1/n$ was determined based on systematic absences. Most atoms were correctly assigned from the solution. Full-matrix least squares / difference Fourier cycles were performed which located the remaining atoms. All atoms were refined with anisotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0216$ (F^2 , $I > 2\sigma(I)$) and $wR2 = 0.0554$ (F^2 , all data).

Crystal data for $C_2Cl_2OS_2$ ($M = 175.04$ g/mol): monoclinic, space group $P2_1/n$ (no. 14), $a = 5.8312(5)$ Å, $b = 10.3605(9)$ Å, $c = 9.3858(8)$ Å, $\beta = 94.4572(17)^\circ$, $V = 565.32(8)$ Å³, $Z = 4$, $T = 100.0(5)$ K, $\mu(\text{MoK}\alpha) = 1.752$ mm⁻¹, $D_{\text{calc}} = 2.057$ g/cm³, 41,413 reflections measured ($5.87^\circ \leq 2\theta \leq 77.30^\circ$), 3169 unique ($R_{\text{int}} = 0.0216$, $R_{\text{sigma}} = 0.0088$) which were used in all calculations. The final $R1$ was 0.0216 ($I > 2\sigma(I)$) and $wR2$ was 0.0554 (all data).

Supplementary Materials: Table S1: Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 4,4-dichloro-1,3-dithietane-2-one (**1**); Table S2: Anisotropic displacement parameters [$\text{\AA}^2$] for 4,4-dichloro-1,3-dithietane-2-one (**1**); Table S3: Bond lengths [$\text{\AA}$] and angles [$^\circ$] for 4,4-dichloro-1,3-dithietane-2-one (**1**); Table S4: Torsion angles [$^\circ$] for 4,4-dichloro-1,3-dithietane-2-one (**1**); Figure S1: Unit cell of **1** looking down the [001] direction; Figure S2: ^1H NMR for 4,4-dichloro-1,3-dithietane-2-one (**1**); Figure S3: ^{13}C NMR for 4,4-dichloro-1,3-dithietane-2-one (**1**); Figure S4: FTIR for 4,4-dichloro-1,3-dithietane-2-one (**1**); Figure S5: Mass spectral data for 4,4-dichloro-1,3-dithietane-2-one (**1**).

Author Contributions: Conceptualization and supervision, G.B.; experimental work, M.J.T., E.S.G. and T.R.T.; X-ray crystallography, W.W.B.; original draft preparation, review, and editing, G.B., T.R.T., W.W.B. and E.S.G. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: X-ray data is deposited at the Cambridge Crystallographic Data Centre as 2437635. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre at <http://www.ccdc.cam.ac.uk/structures> (accessed on 31 March 2025).

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Conflicts of Interest: The authors declare no conflicts of interest.

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