Synthesis and reactions of a new cyclobutanethione derivative

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Abstract: The 3,3-dichloro-2,2,4,4-tetramethylcyclobutanethione (4b) was prepared from the parent diketone by successive reaction with PCl5 and Lawesson reagent in pyridine. This new thioketone 4b was transformed into 1-chlorocyclobutanesulfanyl chloride 5 and chloro 1-chlorocyclobutyl disulfide 9 by treatment with PCl5 and SCl2, respectively, in chlorinated solvents (Schemes 1 and 2). These products reacted with S- and P-nucleophiles by substitution of Cl− at the S-atom; e.g., the reaction with 4b yielded the di- and trisulfides 6b and 11, respectively. Surprisingly, only pentasulfide 12 was formed in the reaction of 9 with thiobenzophenone (Scheme 3). In contrast to 5 and 9, the corresponding chloro 1-chlorocyclobutyl trisulfide 13 could not be detected, but reacted immediately with the starting thioketone 4b to give the tetrasulfide 14 (Scheme 4). Oxidation of 4b with 3-chloroperbenzoic acid (mCPBA) yielded the corresponding thione oxides (= sulfine) 15, which underwent 1,3-dipolar cycloadditions with thioketones 3a and 4b (Scheme 5). Furthermore, 4b was shown to be a good dipolarophile in reactions with thiocarbonylium methanides (Scheme 6) and iminium ylides (= azomethine ylides; Scheme 7). In the case of phenyl azide, the reaction with 4b gave the symmetrical trithiolane 25 (Scheme 8).

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Synthesis and Reactions of a New Cyclobutanethione Derivative

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3) Part of the planned Ph.D. thesis of M. W., University of Lodz.
The 3,3-dichloro-2,2,4,4-tetramethylcyclobutanethione (4b) was prepared from the parent diketone by successive reaction with PCl₅ and Lawesson reagent in pyridine. This new thioketone 4b was transformed into α-chloro sulfanylchloride 5 and α-chloro disulfanylchloride 9 by treatment with PCl₅ and SCl₂, respectively, in chlorinated solvents (Schemes 1 and 2). These products reacted with S- and P-nucleophiles by substitution of Cl⁻ at the sulfanyl group; e.g. the reaction with 4b yielded the di- and trisulfane derivatives 6b and 11, respectively. Surprisingly, only pentasulfane 12 was formed in the reaction of 9 with thiobenzophenone (Scheme 3). In contrast to 5 and 9, the corresponding α-chloro trisulfanylchloride 13 could not be detected, but reacted immediately with the starting thioketone 4b to give the tetrasulfane 14 (Scheme 4). Oxidation of 4b with mCPBA yielded the corresponding sulfine 15, which underwent 1,3-dipolar cycloadditions with thioketones 3a and 4b (Scheme 5). Furthermore, 4b has been shown to be a good dipolarophile in reactions with thiocarbonyl methanides and azomethine ylides (Schemes 6 and 7). In the case of phenyl azide, the reaction with 4b gave the symmetrical trithiolane 25 (Scheme 8).
1. Introduction. – Despite their interesting chemical and physico-chemical properties, thioketones were considered as unstable compounds, which are accessible only with difficulty. Whereas aromatic thioketones show enhanced stability, aliphatic representatives are much less stable and easily undergo enolization and oligomerization [1][2][3]. At present, it is known that their stability increases significantly by the introduction of bulky substituents or other steric stabilizing effects. In addition to adamantanethione (1) [3] and the only recently described ‘cage thioketone’ 2 [4], thioxo derivatives of 2,2,4,4-tetramethylcyclobutane-1,3-dione 3 [5][6] belong to the most useful and relatively easily available cycloaliphatic thioketones. Generally, the synthesis of thioketones is carried out by replacement of the O-atom of a carbonyl group by an S-atom using Lawesson’s reagent, a mixture of H₂S and HCl, or P₄S₁₀ as thionating reagents [7].

**Formulae 1–4**

In a recent paper, we reported on the reaction of 2,2,4,4-tetramethylcyclobutane-1,3-dione with PCl₅ which leads to 3,3-dichloro-2,2,4,4-tetramethylcyclobutan-1-one (4a) [8]. Now we present the preparation of the corresponding thione 4b and reactions of this new and stable chlorinated thioketone.

2. Results and Discussion. – Heating of 4a with P₄S₁₀ in pyridine for 6 h led to the thioketone 4b as a red solid, which was stable at room temperature, similar to the thioketones 3a and 3b. Typically, the C=S group of 4b absorbed in the ¹³C-NMR spectrum (CDCl₃) at 273.0 ppm. In analogy to the corresponding reactions of 3a and 3b [9], the new thioketone 4b

4) Furthermore, thioketones are known as substances with very unpleasant odor.
reacted with PCl$_5$ to yield the relatively stable $\alpha$-chlorosulfanyl chloride 5, which was used for further reactions without purification. Treatment of 5 in CH$_2$Cl$_2$ at room temperature with thioketones 3a and 4b led smoothly to the disulfanes 6a and 6b, respectively, in high yield (Scheme 1). In this reaction, the S-atom of the thioketone acts as a soft nucleophile towards the sulfanyl chloride.

Scheme 1

The substitution of chloride in the SCl group was easily achieved by the reaction of 5 with thioacetic acid, which afforded the acetylated disulfane 7 (cf. [9][10]). Compounds of this type have been shown to undergo a deacetylation in the presence of morpholine, and a subsequent intramolecular substitution of chloride is believed to yield a reactive dithirane [11]. Alternatively, the corresponding thiocarbonyl S-sulfide can be formed by elimination of chloride. In the case of 7, the experiment with morpholine led, unexpectedly, to 4b, which probably was formed from the intermediate S-sulfide by elimination of sulfur.

The reaction of 5 with diethyl or triethyl phosphite yielded exclusively 8, which is the substitution product formed by the nucleophilic attack of the phosphite P-atom in analogy to the Arbuzov reaction [12] (Scheme 1).

The treatment of 4b with SCl$_2$ in CH$_2$Cl$_2$ gave the adduct 9, i.e. an $\alpha$-chlorodisulfanyl chloride (Scheme 2). The reaction of the latter with thioacetic acid led to the trisulfane 10 by an extension of the sulfur chain. Similar to the reaction with 5, 9 also underwent an addition with the parent thioketone 4b to give the symmetrical trisulfane 11.
In order to test the ability of aromatic thioketones to form non-symmetric trisulfanes of type 11, an experiment with 9 and thiobenzophenone was carried out. When the reagents were used in a 1:1 molar ratio, only benzophenone was isolated after chromatographic workup. Therefore, the reaction was repeated using an excess of 9 (2:1 ratio) in wet THF. Under these conditions, the symmetrical pentasulfane 12 was isolated along with comparable amounts of benzophenone. A likely reaction pathway leading to 12 is outlined in Scheme 3. The first step is the formation of the thiocarbonylium ion A by a nucleophilic substitution of chloride. In contrast to similar intermediates appearing in reactions with cycloaliphatic thioketones, which lead to the formation of 6 and 11, A is easily hydrolyzed to give benzophenone and the trisulfane derivative B. The excess of 9 intercepts B immediately forming the pentasulfane 12.

The molecular formula of 12 was confirmed by the elemental analysis. As the spectroscopic data were not indicative for the structure, an X-ray crystal-structure determination was performed (Fig. 1).

In accordance with the results obtained with other polysulfanes [14], the S-chain adopts a helical conformation with torsion angles close to 90° and, as observed in a previously described pentasulfane structure [15], it completes one full helical turn along its length.
However, unlike the similar pentasulfane with terminal cyclobutanone groups [15], there is no disorder in the crystal structure.

With the aim of preparing the corresponding trisulfanyl chloride 13, 4b was treated with freshly distilled S₂Cl₂ in CH₂Cl₂ at room temperature. The decoloration of the mixture was significantly slower than in the reaction with SCl₂, and after usual workup, the tetrasulfane 14 was isolated exclusively (Scheme 4). Apparently, the slowly formed 13 instantaneously reacts with thioketone 4b to give the final product in almost quantitative yield.

Scheme 4

The oxidation of thiocarbonyl compounds leads to their S-oxides (sulfines), which differ in stability significantly, depending on the substitution pattern [16]. It is well established that sulfines react smoothly with 1,3-dienes and 1,3-dipoles along the activated C=S bond to give the corresponding six- or five-membered heterocyclic S-oxides [17]. On the other hand, it has been shown recently that sulfines also behave as 1,3-dipoles in [3+2] cycloadditions with thioketones [18][19]. Treatment of 4b with mCPBA in CH₂Cl₂ gave the expected sulfine 15 as a crystalline material (Scheme 5). The reaction of 15 with the parent thioketone 4b and the oxo-analogue 3a, respectively, was carried out by heating a mixture of equimolar amounts of the reagents without solvent to 110°. The red color of the thioketones disappeared within ca. 30 min, and 1,2,4-oxadithiolanes 16 and 17, respectively, were obtained after crystallization from MeOH. The molecular structure of 17 has been established by X-ray crystallography (Fig. 2). The reaction between 4b and the known sulfine 18 [20] was performed in an analogous manner leading to 19, which is an isomer of 17.
The parent thioketone 4b was also tested as a dipolarophile in reactions with thiocarbonyl S-methanides, which were generated by thermal N₂ extrusion from the corresponding 2,5-dihydro-1,3,4-thiadiazoles 20a and 20b (Scheme 6). The analysis of the reaction mixture by ¹H-NMR spectroscopy showed that the cycloaddition occurred regioselectively leading to the 2,2,4,4-substituted-1,3-dithiolanes 21. These products revealed the characteristic CH₂ absorption in the ¹³C-NMR spectrum at 41.9 and 43.3 ppm, respectively. The regioselectivity observed in these reactions fits well with the general rules for [3+2]-cycloadditions of cycloaliphatic S-methanides with cycloaliphatic thioketones [21].

The thermal electrocyclic ring opening of aziridines was widely explored for the synthesis of thiazolidines via [3+2]-cycloadditions of the reactive azomethine ylides with C=S dipolarophiles (cf. [22-24]). Thermolysis of cis-1-methyl-2,3-diphenylaziridine (22) in boiling toluene in the presence of 4b afforded a single product whose structure was again established by X-ray crystallography [25] (Scheme 7). In accordance with the expected reaction course, the Ph groups are trans oriented, i.e., the intermediate 1,3-dipole 23 has been generated by a conrotatory ring opening of 22.
In analogy to a previously reported experiment with 3a and phenyl azide [26], a mixture of 4b and phenyl azide was heated to 80°. The reaction was significantly slower than with 3a and, after evaporation of excess phenyl azide, the residue was analyzed by 1H-NMR spectroscopy. The presence of two sets of singlets located at 1.58/1.51 ppm and 1.49/1.20 ppm revealed the formation of two products in comparable amounts. After chromatographic workup, only the product with the signals at lower field was obtained as a colorless solid, which was identified as the symmetric 1,2,4-trithiolane 25 (Scheme 8). The second set of signals can be attributed to the imine 26, which decomposed during chromatography. In contrast to the reaction with 3a [26], no 1,4,2-dithiazolidine 27 was formed. Obviously, the proposed intermediate thiocarbonyl S-imide 28 undergoes a fast electrocyclic ring closure to give the thiaziridine 29. Sulfur transfer to 4b yields the reactive thiocarbonyl S-sulfide 30 and imine 26. Finally, interception of 30 by 4b leads to the isolated trithiolane 25. This result shows that the replacement of the C=O group of 3a by CCl₂ influences remarkably the reactivity of the intermediate thiocarbonyl S-imide.

Scheme 8

In summary, the presented results show that the new chlorinated thioketone 4b, which can easily be prepared, is an attractive model for studies focused on the reactivity of thiocarbonyl groups. Of special interest are the chlorinated α-chlorosulfanyl chlorides 5 and 9, which are suitable for the preparation of polysulfanes and other sulfur-rich products. The replacement of the C=O group in 3a by the CCl₂ unit (→ 4b) does not change significantly the properties of the C=S function, e.g. the dipolarophilicity of 4b has been demonstrated in cycloadditions with thiocarbonyl ylides, sulfines, and azomethine ylides. However, the lack of
the stabilizing transannular effect of the C=O group influences the reactivity of the thiocarbonyl S-imide 28 in comparison with the analogous 1,3-dipole generated from 3a [27].

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**Experimental Part**

1. General. See [28]. M.p.’s were determined in capillary using a Meltemp 2 apparatus and are uncorrected. $^1$H- and $^{13}$C-NMR spectra were registered in CDCl$_3$ with a Tesla BS 687 instrument (80 and 20 MHz, resp.) or a Bruker 300 spectrometer (300 and 75 MHz, resp.) using TMS ($\delta_{\text{TMS}} = 0$ ppm) as an internal standard. IR spectra (KBr pellets or film) with a Nexus spectrophotometer. MS (EI or CI) on a Finnigan-Mat-90 or Finnigan-SSQ-700 spectrometer. Elemental analyses were performed in the Analytical Laboratory of the University of Zurich or in the Laboratory of the Polish Academy of Sciences (CBMiM) in Lodz.
2. Starting Materials. 2,2,4,4-Tetramethylcyclobutane-1,3-dione was prepared from isobutyryl chloride and Et$_3$N in CH$_2$Cl$_2$ [29]. 2,5-Dihydro-1,3,4-thiadiazoles 20a and 20b were synthetized from the corresponding thioketones and CH$_2$N$_2$ in pentane at 0–5° following known protocols [30][31]. cis-1-Methyl-2,3-diphenylaziridine (22) was available from erythro-N-methyl-1,2-diphenylethanol by treatment with SOCl$_2$ and subsequent cyclisation by using Et$_3$N or KOH as a base [32]. Phenyl azide was prepared by diazotation of phenylhydrazine as described in [33]. Thioacetic acid, diethyl and triethyl phosphite, sulfur chloride (SCl$_2$) and disulfur dichloride (S$_2$Cl$_2$; b.p. 134-136°) have been carefully distilled prior to their use. 2,2,4,4-Tetramethyl-3-thioxocyclobutanone S-oxide (18) was obtained by oxidation of 3a with m-chloroperbenzoic acid (MCPBA) in CH$_2$Cl$_2$ following the protocol in [34].

3. Chlorination of 2,2,4,4-Tetramethylcyclobutane-1,3-dione with PCl$_5$. A mixture of 2,2,4,4-tetramethylcyclobutane-1,3-dione (9.8 g, 0.07 mol) and PCl$_5$ (29.2 g, 0.14 mol) in CCl$_4$ (50 ml) was heated under reflux for 1.5 h. After cooling to r.t., the soln. was diluted with CH$_2$Cl$_2$ (20 ml) and washed with sat. aq. NaHCO$_3$ soln. and H$_2$O (3x). The org. layer was dried (anhydr. MgSO$_4$), and after filtration, the solvent was evaporated. CC on SiO$_2$ with hexane containing increasing amounts of CHCl$_3$ gave two colorless products.


4. Thionation of 4a using P$_2$S$_5$. To a vigorously stirred (magnetic stirrer) soln. of 4a (2.93 g, 0.015 mol) in 15 ml of freshly distilled pyridine, P$_2$S$_5$ (3.33 g, 0.015 mol) was added
in small portions. The mixture was heated to 130° (oil bath) for 6 h. After cooling to r.t. the mixture was poured into H₂O and extracted with hexane (3x 5 ml). The org. layer was separated and washed with 2 N HCl, with H₂O (3x) and dried (anhyd. MgSO₄). After filtration and evaporation, the red solid residue was purified by CC on SiO₂ using hexane with increasing amounts of CH₂Cl₂ as the eluent. Yield of crude 3,3-Dichloro-2,2,4,4-tetramethylcyclobutanethione (4b): 2.79 g (88%). M.p. 140–144°⁰. Crystallization from petroleum ether in dry ice gave red crystals. M.p. 133–135°. IR (KBr): 2990m, 1466m, 1306s, 1145m (C=S), 1003w, 915vs, 827vs. ¹H-NMR: 1.50 (s, 4 Me); 73.1 (s, C(2), C(4)); 98.0 (s, CCl₂); 273.0 (s, C=S). EI-MS: 212 (24), 211 (3), 210 (39), 175 (50), 139 (27), 86 (100, [Me₂C=C=S]+), 71 (55). Anal. calc. for C₈H₁₂Cl₂S (212.15): C 45.50, H 5.73, S 15.19; found: C 45.65, H 5.84, S 15.38.

5. Reaction of 4b with PCl₅. A soln. of 4b (211 mg, 1 mmol) and PCl₅ (416 mg, 2 mmol) in CCl₄ (5 ml) was heated under reflux. After 45 min, another portion of PCl₅ (832 mg, 4 mmol) was added and heating was continued for 15 min until the red color of the soln. disappeared. The mixture was diluted with CCl₄ (10 ml), washed with sat. aq. Na₂CO₃ soln. and with H₂O (2x). After separation, the org. phase was dried (MgSO₄) and filtered, the solvent was evaporated, and the oily residue was used for further reactions without purification: 272.0 mg (96%) of (1,3,3-Trichloro-2,2,4,4-tetramethylcyclobutan-1-yl)sulfanyl chloride (5). Colorless, thick oil. IR (neat): 3007m, 2981s, 2940s, 1469vs, 1453s, 1385vs, 1371s, 1190m, 943m, 871vs, 835vs, 803s. ¹H-NMR: 1.56 (s, 2 Me); 1.58 (s, 2 Me). ¹³C-NMR: 24.3 (q, 2 Me); 27.4 (q, 2 Me); 60.1 (s, C(2), C(4)); 89.6 (s, C(1)); 97.9 (s, CCl₂).

5) During the storage at r.t., a slow decomposition of 4b was observed, and the ¹H-NMR spectrum confirmed the formation of growing amounts of dichloroketone 4a.
6. Reaction of 5 with Cyclobutanethiones 3a and 4b. General Procedure. To a magnetically stirred soln. of freshly prepared 5 (136 mg, 0.48 mmol) in CH₂Cl₂ (2 ml), the red soln. of 0.48 mmol of the corresponding thioketone was added dropwise at r.t. After 30 min, the solvent was evaporated and the oily residue was triturated with MeOH to yield crystalline products. Analytically pure samples were obtained by recrystallisation

3-Chloro-3-(1′,3′,3′-trichloro-2′,2′,4′,4′-tetramethylcyclobutan-1′-yl)disulfanyl-2,2,4,4-tetramethylcyclobutanone (6a). Yield: 57 mg (30%). Colorless crystals. M.p. 116–118° (MeOH). IR (KBr): 2984 w, 2936 w, 1789 v s, 1445 m (br.), 1366 w, 1023 w, 834 m. ¹H-NMR: 1.38, 1.51, 1.52, 1.64 (4 s, 4 Me). ¹³C-NMR (CDCl₃): 23.0, 23.2 (2 q, 4 Me); 26.4, 26.6 (2 q, 4 Me); 60.6 (s, 2 Me₂C); 69.7 (s, 2 Me₂C); 84.8 (s, SCCl); 87.2 (s, SCCl); 98.9 (s, CCl₂); 217.2 (s, C=O). EI-MS: 438 (1), 368 (20), 366 (15), 213 (31), 177 (44), 159 (43), 141 (85), 131 (100), 105 (26), 86 (86). Anal. calc. for C₁₆H₂₄Cl₄OS₂ (438.31): C 43.84, H 5.52, S 14.63; found C 43.72, H 5.56, S 14.65.

Bis(1,3,3-trichloro-2,2,4,4-tetramethylcyclobutan-1-yl)disulfane (6b). Yield 143 mg (60%). Colorless crystals. M.p. 182–184° (MeOH/CH₂Cl₂). IR (KBr): 3012 s, 2984 s, 2936 s, 1466 vs, 1443 vs, 1383 vs, 1370 s, 1197 s, 992 s, 942 s, 868 vs, 833 vs, 796 s, 942 s, 833 s, 796 s, 554 s. ¹H-NMR: 1.49 (s, 4 Me); 1.62 (s, 4 Me). ¹³C-NMR: 26.48, 26.51 (2 q, 4 Me each); 60.5 (s, 4 Me₂C); 87.2 (s, 2 SCCl); 98.7 (s, 2 CCl₂). CI-MS: 459 (72), 457 (100), 455 (61). Anal. calc. for C₁₆H₂₄Cl₄S₂ (493.21): C 38.96, H 4.90, S 13.00; found: C 38.67, H 4.78, S 12.92.

7. Reaction of 5 with Thioacetic Acid. To a stirred soln. of 5 (282 mg, 1 mmol) in CCl₄ (5 ml), thioacetic acid (83 mg, 1.1 mmol) in 2 ml of CCl₄ was added in small portions at r.t. After complete addition, the stirring was continued for 30 min, the solvent was evaporated and the residual thick oil was crystallized from hexane: 59 mg (38%) of 1-[(1,3,3-Trichloro-2,2,4,4-tetramethylcyclobutan-1-yl)disulfanyl]ethan-1-one (7). Colorless crystals. M.p. 48–
50° (hexane). IR (KBr): 2980\,w, 2940\,w, 1740\,s (C=O), 1470\,m, 1110\,s, 943\,m, 870\,m, 833\,m, 595\,s. \(^1\)H-NMR: 1.52 (s, 2 Me); 1.61 (s, 2 Me); 2.49 (s, MeCO). \(^{13}\)C-NMR: 26.1 (q, 2 Me); 27.1 (q, 2 Me); 28.7 (q, MeCO); 60.1 (s, 2 Me\(_2\)C); 89.4 (s, SCCl); 98.3 (s, CCl\(_2\)); 193.5 (s, MeCO). Cl-MS: 340 (5), 338 (5), 289 (16), 287 (72), 286 (13), 285 (100). Anal. calc. for C\(_{10}\)H\(_{15}\)Cl\(_3\)O\(_3\) (321.71): C 37.33, H 4.69, S 19.93; found: C 37.44, H 4.72, S 19.65.

8. **Treatment of 7 with Morpholine.** A soln. of morpholine (652.5 mg, 7.5 mmol) in Et\(_2\)O (3 ml) was cooled to –40° (acetone/dry ice). To the stirred soln. was added dropwise a soln. of 7 (482 mg, 1.5 mmol) in Et\(_2\)O (3 ml). The mixture was stirred at –40° (acetone, dry ice) for 4 h. While warming to r.t., the orange color changed to red. After addition of Et\(_2\)O (15 ml), the mixture was washed with H\(_2\)O (2x 30 ml), the org. phase was dried (anhyd. Na\(_2\)SO\(_4\)), the solvent evaporated, and the residue (180 mg) analyzed by \(^1\)H-NMR spectroscopy. There were no signals of the expected product found. Then, the mixture was separated by prep. TLC (SiO\(_2\), CH\(_2\)Cl\(_2\)/hexane 1:1). Only 4b (68 mg, 21%) and decomposition products were obtained.

9. **Reaction of 5 with Phosphites.** a) **With P(\(\text{OEt}\))\(_3\) (Method A).** To a stirred soln. of 5 (282 mg, 1 mmol) in CH\(_2\)Cl\(_2\) (7 ml) at 0° was slowly added P(\(\text{OEt}\))\(_3\) (166 mg, 1 mmol). The color of the mixture turned to pale red. After additional stirring for 30 min at r.t., the solvent was evaporated to give 8 as a crude oily product (ca. 97%). Crystallization from hexane (–78°) afforded analytically pure 8.

b) **With HP(\(\text{O}\))(\(\text{OEt}\))\(_2\) (Method B).** To a stirred soln. of 5 (501 mg, 1.77 mmol) in CH\(_2\)Cl\(_2\) (3 ml) was added a soln. of HP(\(\text{OEt}\))\(_2\) (166 mg, 1 mmol) in CH\(_2\)Cl\(_2\) (3 ml). After keeping for 3 d at r.t., the solvent was evaporated and the crude oily product was crystallized from hexane in dry ice to give pure 8.
O,O-Diethyl-S-(1,3,3-trichloro-2,2,4,4-tetramethylcyclobutan-1-yl)monothiophosphate (8). Yield: Method A: 282 mg (73%), method B: 186 mg (31%). Colorless crystals. M.p. 48–50° (hexane, dry ice). IR (KBr): 3004m, 2984m, 2942m, 1473s, 1384m, 1263vs, 1161s, 1052vs, 1019vs, 831s, 742vs, 564s, 547s. \(^1\)H-NMR: 1.36 (td, \(J_{H,H} = 7.1, J_{H,P} = 0.8, 2 \text{ MeCH}_2\); 1.57 (s, 2 Me); 1.67 (s, 2 Me); 4.12–4.28 (m, MeC\(\text{H}_2\)). \(^1\)C-NMR: 15.9 (dq, \(J_{C,P} = 7.3, \text{ Me}\); 25.0 (q, 2 Me); 27.4 (q, Me); 60.4 (d, \(J_{C,P} = 5.2, 2 \text{ Me}_2\text{C}\)); 64.3 (td, \(J_{C,P} = 7.1, \text{ MeCH}_2\text{O}\)); 85.4 (s, SCCl); 98.9 (s, CCl\(_2\)). CI-MS: 404 (33), 402 (100), 400 (96), 385 (49), 383 (47). Anal. calc. for C\(_{12}\)H\(_{22}\)Cl\(_3\)O\(_3\)P (383.70): C 37.56, H 5.78, S 8.35, Cl 27.71; found: C 37.58, H 5.63, S 8.17, Cl 27.42.

10. Reaction of 4b with Sulfur Dichloride (SCl\(_2\)). To a stirred soln. of SCl\(_2\) (536 mg, 5.2 mmol) in CH\(_2\)Cl\(_2\) (5 ml), a soln. of 4b (1.0 g, 4.74 mmol) in CH\(_2\)Cl\(_2\) (5 ml) was added dropwise, and the stirring was continued for 30 min. The solvent was evaporated and the crude 1-Chloro-2-(1,3,3-trichloro-2,2,4,4-tetramethylcyclobutan-1-yl)disulfane (9) was obtained as a thick, pale yellow oil. Yield: 1.41 g (95%). Distillation in a Kugelrohr at 100°/0.5 Torr gave a colorless thick oil. IR (neat): 3005s, 2977vs, 2940vs, 1469vs, 1385vs, 1371s, 1200s, 1171m, 994m, 871vs, 834vs, 801s. \(^1\)H-NMR: 1.52 (s, 2 Me); 27.5 (q, 2 Me); 59.9 (s, 2 Me\(_2\text{C}\)); 89.9 (s, SCCl); 98.2 (s, CCl\(_2\)). \(^1\)C-NMR: 26.4 (q, 2 Me); 27.5 (q, 2 Me); 59.9 (s, 2 Me\(_2\text{C}\)); 89.9 (s, SCCl); 98.2 (s, CCl\(_2\)).

11. Reaction of 9 with Thioacetic Acid. To a stirred soln. of freshly distilled 9 (314 mg, 1 mmol) in CH\(_2\)Cl\(_2\) (5 ml) at r.t., thioacetic acid (84 mg, 1.1 mmol) dissolved in CH\(_2\)Cl\(_2\) (2 ml) was added dropwise. After complete addition, stirring was continued for 15 min. at r.t. and the solvent was evaporated. The crude 1-{(1,3,3-Trichloro-2,2,4,4-tetramethylcyclobutan-
1-
-yl)trisulfanyl]ethane-1-one (10) was obtained as a colorless, thick oil, which crystallized slowly. Yield: 243 mg (69%). Colorless crystals. M.p. 72–74°. IR (KBr): 3007w, 2983m, 2941w, 1732vs (C=O), 1466s, 1383m, 1107vs, 944vs, 867vs, 829vs, 800m, 591vs, 564s. 1H-NMR: 1.54 (s, 2 Me); 1.55 (s, 2 Me); 2.47 (s, MeCO). 13C-NMR: 26.3 (q, 2 Me); 27.0 (q, 2 Me); 29.3 (q, MeCO); 60.0 (s, 2 Me2C); 90.3 (s, SCl); 98.2 (s, CCl2); 192.3 (s, MeCO). CI-MS: 319 (78), 317 (100), 287 (28), 285 (38), 200 (77), 175 (53). Anal. calc. for C10H15Cl3OS3 (353.78): C 33.95, H 4.27, S 27.18, Cl 30.06; found: C 34.29, H 4.09, S 26.34, Cl 30.06.

12. Reaction of 9 with 4b. To a stirred soln. of 9 (314 mg, 1 mmol) in CH2Cl2 (4 ml) at r.t., a soln. of 4b (211 mg, 1 mmol) in CH2Cl2 (2 ml) was added in small portions. After additional stirring for 30 min, the colorless soln. was evaporated to give a solid material. Crystallization from MeOH/CH2Cl2 afforded the analytically pure bis(1,3,3-trichloro-2,2,4,4-tetramethylcyclobutan-1-yl)trisulfane (11). Yield: 296 mg (56%). Colorless crystals. M.p. 238–240°. IR (KBr): 3010s, 2978s, 2939s, 1469vs, 1442m, 1385s, 1370s, 1200m, 993m, 946m, 870vs, 833vs, 559s. 1H-NMR: 1.54 (s, 4 Me); 1.55 (s, 4 Me). 13C-NMR: 26.8 (q, 4 Me); 27.1 (q, 4 Me); 60.1 (s, 4 Me2C); 90.7 (s, 2 SCl); 98.3 (s, 2 CCl2). CI-MS: 493 (29), 491 (48), 490 (21), 489 (100), 487 (59), 457 (46), 455 (26). Anal. calc. for C16H24Cl6S3 (525.28): C 36.58, H 4.60, S 18.31, Cl 40.50; found: C 36.58, H 4.49, S 18.07, Cl 40.44.

13. Sulfur Transfer with Thiobenzophenone; Synthesis of Pentasulfane 12. To a stirred soln. of blue colored thiobenzophenone (99 mg, 0.5 mmol) in 1 ml of wet THF (2vol% H2O), a soln. of 9 (314 mg, 1 mmol) in abs. THF (1 ml) was added in small portions. The mixture was cooled in a H2O/ice bath and stirring was continued for 10 min. The colorless soln. was evaporated and the pale yellow, oily residue was crystallized from mixture of MeOH/CH2Cl2 to give 94 mg (32%) of bis(1,3,3-trichloro-2,2,4,4-tetramethylcyclobutan-1-yl)pentasulfane.
Colorless crystals. M.p. 157–159°. IR (KBr): 2997vs, 2974s, 2935m, 1466vs, 1450s, 1383s, 1371s, 1198m, 1170m, 991m, 944m, 870vs, 835vs, 800m, 559s. 1H-NMR: 1.54 (s, 6 Me); 1.55 (s, 2 Me). 13C-NMR: 26.4 (s, 2 Me); 26.5 (s, 2 Me); 27.0 (s, 4 Me); 60.1 (s, 4 Me2C); 89.8 (s, SCCl); 90.1 (s, SCCl); 98.4 (s, 2 CCl2). CI-MS: 555 (2), 523 (14), 519 (10), 197 (26), 195 (39), 177 (37), 176 (12), 175 (100). Anal. calc. for C16H24Cl6S5 (589.41): C 32.60, H 4.10, S 27.20, Cl 36.10; found: C 32.50, H 3.90, S 27.04, Cl 35.70.

Suitable crystals for an X-ray crystal-structure determination were grown from MeOH/CH2Cl2 by slow evaporation of the solvent.

14. Treatment of 4b with S2Cl2; Synthesis of Tetrasulfane 14. A soln. of freshly distilled S2Cl2 (149mg, 1.1 mmol) in CH2Cl2 (1 ml) was added at r.t. in small portions to a stirred soln. of 4b (211 mg, 1 mmol) in CH2Cl2 (1 ml). After complete addition, the solvent was evaporated and the crude Bis(1,3,3-trichloro-2,2,4,4-tetramethylcyclobutan-1-yl)tetrasulfane (14) was obtained as a colorless solid. An analytically pure sample was obtained after crystallization from MeOH/CH2Cl2. Yield: 253 mg (91%). Colorless crystals. M.p. 218–220° (MeOH/CH2Cl2). IR (KBr): 3010s, 2972vs, 2937s, 1467vs, 1442vs, 1384s, 1372s, 1199s, 1169m, 993m, 831vs, 799s, 557s. 1H-NMR: 1.54 (s, 8 Me). 13C-NMR: 26.4 (q, 4 Me); 27.0 (q, 4 Me); 60.0 (s, 4 Me2C); 90.1 (s, 2 SCCl); 98.3 (s, 2 CCl2). CI-MS: 525 (31), 524 (15), 523 (74), 522 (21), 521 (100), 519 (56), 175 (90). Anal. calc. for C16H24Cl6S5 (557.35): C 34.48, H 4.34, S 23.01, Cl 38.17; found: C 34.04, H 4.07, S 23.13, Cl 37.96.

15. Oxidation of 4b with m-Chloroperbenzoic Acid. To a stirred soln. of 4b (1.0 g, 4.7 mmol) in CH2Cl2 (15 ml) at 0° (ice-water bath), mCPBA acid was added in small portions until the red color of the soln. completely vanished. After 10 min, the soln. was diluted with CH2Cl2 (10 ml) and washed with sat. aq. NaHCO3 soln., 2% aq. soln. of NaOH, and finally
with brine. The org. phase was separated and dried (MgSO₄). After evaporation of the solvent, the crude product was obtained as a thick colorless oil. Crystallization from hexane in dry ice afforded colorless, crystalline 3,3-dichloro-2,2,4,4-tetramethylcyclobutanethione S-oxide (15). Yield: 460 mg (43%). Colorless crystals. M.p. 149–152°C (hexane). IR (KBr): 2992s, 2934s, 2868w, 1795m, 1467s, 1450s, 1383m, 1368m, 1299s, 1222m, 1150m, 1072vs, 1015m, 916vs, 825vs, 607m. ¹H-NMR: 1.61 (s, 2 Me); 1.76 (s, 2 Me). ¹³C-NMR: 25.1 (q, 2 Me); 28.8 (q, 2 Me); 57.8, 61.5 (2s, 2 Me₂C); 98.5 (s, CCl₂); 204.1 (s, C=S). CI-MS: 248 (13), 246 (69), 245 (10), 244 (100). Anal. calc. for C₈H₁₂Cl₂OS (227.15): C 42.30, H 5.32, S 14.11; found: C 42.44, H 5.75, S 14.16.

16. 1,3-Dipolar Cycloadditions of Sulfines 15 and 18 with 3a and 4b. General procedure. A soln. of 1 mmol of 15 or 18 and 1 mmol of 3a or 4b in 0.5 ml of toluene was heated to 110°C (oil bath) for 1.5 h. After cooling to r.t., the solvent was evaporated, the residual solid material was triturated with MeOH, and the solid product was filtered and purified by crystallization.

2,2,8,8-Tetrachloro-1,1,3,3,7,7,9,9-octamethyl-10-oxa-5,11-dithiadispiro[3.1.3.2]undecane (16). Yield: 236 mg (54%). Colorless crystals. M.p. 162–163°C (MeOH/CH₂Cl₂). IR (KBr): 2976s (br.), 2938s (br.), 1452s, 1375s, 1056w, 946m, 881vs, 802vs (br.), 778s, 570m. ¹H-NMR: 1.33 (s, 4 Me); 1.47 (s, 2 Me); 1.58 (s, 2 Me). ¹³C-NMR: 21.4 (q, 2 Me); 24.5 (q, 2 Me); 28.3 (q, 2 Me); 28.7 (q, 2 Me); 58.2 (s, 2 Me₂C); 59.4 (s, 2 Me₂C); 81.8 (s, SCS); 98.4, 99.0 (2s, 2 CCl₂); 112.3 (s, OCS). CI-MS: 456 (8), 455 (6), 405 (25), 404 (12), 403 (65), 401 (61), 171 (100). Anal. calc. for C₁₈H₂₄Cl₄O₂S₂ (438.31): C 43.84, H 5.52, S 14.63; found: C 43.64, H 5.48, S 14.79.

6) During storage at r.t., 15 decomposed slowly by elimination of S and converted into 4a.
2,2-Dichloro-1,1,3,3,7,7,9,9-octamethyl-10-oxa-5,11-dithiadispiro[3.1.3.2]undecan-8-one (17). Yield: 242 mg (63%). Colorless crystals. M.p. 100–101°C (MeOH/CH₂Cl₂). IR (KBr): 2974v, 2935s, 1772v (C=O), 1456s, 1376s, 1252m (br.), 1046s, 1012s, 888s, 800s. 

1H-NMR: 1.23 (s, 2 Me); 1.33 (s, 2 Me); 1.37 (s, 2 Me); 1.61 (s, 2 Me). 13C-NMR: 17.4 (q, 2 Me); 24.6 (q, 4 Me); 28.7 (q, 2 Me); 58.4 (s, 2 Me₂C); 66.1 (s, 2 Me₂C); 82.5 (s, SCS); 99.0 (s, CCl₂); 110.2 (s, OCS); 218.7 (s, C=O). CI-MS: 402 (22), 400 (31), 385 (75), 383 (100).

Anal calc. for C₁₆H₂₄Cl₂O₂S₂ (383.40): C 50.12, H 6.31, S 16.73; found: C 49.95, H 6.45, S 16.62.

Suitable crystals for an X-ray crystal-structure determination were grown from MeOH/CH₂Cl₂ by slow evaporation of the solvent.

8,8-Dichloro-1,1,3,3,7,7,9,9-octamethyl-10-oxa-5,11-dithiadispiro[3.1.3.2]undecan-2-one (19). Yield: 196 mg (51%). Colorless crystals. M.p. 103–105°C (MeOH). IR (KBr): 2966s, 2927m, 1790vs (C=O), 1451s (br.), 1374m, 1027w, 943m, 894m, 810m (br.), 771s. 1H-NMR: 1.25 (s, 2 Me); 1.35 (s, 2 Me); 1.44 (s, 2 Me); 1.52 (s, 2 Me). 13C-NMR: 20.9 (q, 2 Me); 21.1 (q, 2 Me); 25.2 (q, 2 Me); 28.4 (q, 2 Me); 59.6 (s, 2 Me₂C); 65.5 (s, 2 Me₂C); 79.2 (s, SCS); 98.5 (s, CCl₂); 113.5 (s, OCS); 217.9 (s, C=O). CI-MS: 402 (4), 401 (3), 400 (5), 189 (100), 175 (20). Anal calc. for C₁₆H₂₄Cl₂O₂S₂ (383.40): C 50.12, H 6.31, S 19.73, Cl 18.49; found: C 49.73, H 6.10, S 16.52, Cl 18.44.

17. Reactions of 4b with Thiocarbonyl S-Methanides. General Procedure. A stirred red soln. of 4b (211 mg, 1mmol) and 1.1 mmol of the corresponding 2,5-dihydro-1,3,4-thiadiazole 20 in abs. THF (1 ml) was heated to 45°C (oil bath). The evolution of N₂ was monitored with a gas burette attached to the reaction flask. After 5 h, the red color disappeared and the evolution of N₂ ceased; the expected volume of N₂ (ca. 25 ml) was collected. After cooling to r.t., the solvent was evaporated and the residue was triturated with
MeOH. After 2 h in the refrigerator, the crude product was filtered and purified by crystallization.

3",3"-Dichloro-2",2",4",4"-Tetramethyldispiro[adamantane-2,2'-{(1,3)dithiolane-4',1"-cyclobutane (21a). Yield: 230 mg (59%). Colorless crystals. M.p. 92–94° (MeOH). IR (KBr): 2997 vs, 2977 vs, 2914 vs (br.), 2854 s, 1470 s, 1382 m, 1097 w, 966 w, 917 m, 879 m, 803 s.

$^1$H-NMR: 1.35 (s, 2 Me); 1.49 (s, 2 Me); 1.71–1.81 (m, 8 H); 2.02–2.17 (m, 6 H); 3.31 (s, CH$_2$). $^{13}$C-NMR: 23.3 (q, 2 Me); 29.1 (q, 2 Me); 26.2, 26.5, 42.1 (3d, 4 CH); 36.4, 36.6, 37.5 (3t, 5 CH$_2$); 41.8 (t, CH$_2$S); 55.0 (s, 2 Me$_2$C); 73.4, 74.5 (s, 2 C$_q$); 100.8 (s, CCl$_2$). CI-MS: 395 (17), 393 (71), 391 (100). Anal. calc. for C$_{19}$H$_{28}$Cl$_2$S$_2$ (391.47): C 58.30, H 7.21, S 16.38, Cl 18.11; found: C 58.19, H 7.21, S 16.53, Cl 18.36.

2,2-Dichloro-1,1,3,3,7,7,9,9-octamethyl-5,10-dithiadispiro[3.1.3.2]undecan-8-one (21b). Yield: 148 mg (39%). Colorless crystals. M.p. 143–145° (hexane). IR (KBr): 2971 vs, 2928 m, 1773 vs (C=O), 1453 s (br.), 1381 m, 1248 w, 1170 w, 1024 s (br.), 906 m, 885 m, 806 s (br.). $^1$H-NMR: 1.29 (s, 2 Me); 1.53 (s, 2 Me); 3.16 (s, CH$_2$). $^{13}$C-NMR: 21.9, 23.5, 25.0, 28.9 (4q, 4 Me); 43.3 (t, CH$_2$); 56.2 (s, 2 Me$_2$C); 66.2 (s, 2 Me$_2$C); 73.1 (s, SCS); 74.3 (s, C$_q$); 100.5 (s, CCl$_2$); 219.9 (s, C=O). CI-MS: 385 (18), 383 (75), 381 (100). Anal. calc. for C$_{17}$H$_{26}$Cl$_2$S$_2$ (381.43): C 53.53, H 6.87, S 16.81, Cl 18.59; found: C 53.59, H 6.98, S 16.58, Cl 18.37.

18. Reaction of 4b with cis-1-Methyl-2,3-diphenylaziridine (22). A soln. of 22 (209 mg, 1 mmol) in abs. toluene (2 ml) was heated under reflux for 30 min. Then, 4b (211 mg, 1 mmol) was added in small portions, and the mixture was heated under reflux for 6 h. The solvent was evaporated and the solid residue was purified by crystallisation: 200 mg (50%) of trans-2,2-dichloro-1,1,3,3,7-pentamethyl-6,8-diphenyl-5-thia-7-azaspiro[3.4]octane (24). Colorless crystals. M.p. 194–196° (MeOH/CH$_2$Cl$_2$). IR (KBr): 3025 m, 2977 m, 2946 s, 2844 m,
19. Reaction of 4b with PhN₃: Synthesis of 1,3,4-Trithiolane 25. A stirred soln. of 4b (422 mg, 2 mmol) in 0.5 ml of freshly distilled PhN₃ was heated to 80° (oil bath). The evolution of N₂ was monitored with a gas burette connected to the reaction flask. After 10 h, the N₂ evolution ceased, and the volume of N₂ was determined to ca. 17 ml (1/3 of the stochiometric amount). The excess of PhN₃ was removed in vacuo using a Kugelrohr (50°/0.1 Torr). The residual oil was analysed by ¹H-NMR spectroscopy, which revealed the presence of two sets of singlet signals located at 1.20/1.49 ppm and 1.51/1.57 ppm, respectively. The first two signals were attributed to the N-phenylimine 26, which decomposed during chromatographic workup on SiO₂. Trithiolane 25 was isolated by prep. TLC using plates precoated with SiO₂ and hexane as the eluent. An analytically pure sample was obtained by recrystallisation. 2,2,8,8-Tetrachloro-1,1,3,3,7,7,9,9-octamethyl-5,10,11-trithiadispiro-[3.1.3.2]undecane (25). Yield: 110 mg (36%). Colorless crystals. M.p. 183–184° (MeOH/CH₂Cl₂). IR (KBr): 2994s, 2979s, 2937m, 1470s, 1452m, 1442m, 1382s, 1368m, 947m, 871s, 800vs, 566m. ¹H-NMR: 1.51 (s, 4 Me); 1.58 (s, 4 Me). ¹³C-NMR: 25.4 (q, 4 Me); 29.4 (q, 4 Me); 59.1 (s, 4 Me₂C); 88.0 (s, 2 SCS); 100.0 (s, 2 CCl₂). CI-MS: 456 (59), 454 (100), 419 (82). Anal. calc. for C₁₆H₂₄Cl₄S₃ (454.38): C 42.30, H 5.32, S 21.17; found: C 42.64, H 5.23, S 19.48.
20. X-Ray Crystal-Structure Determination of 12 and 17 (Table and Figs. 1-2). All measurements were performed on a Nonius KappaCCD diffractometer [36] using graphite-monochromated MoKα radiation (λ 0.71073 Å) and an Oxford Cryosystems Cryostream 700 cooler. The data collection and refinement parameters are given in the Table, and views of the molecules are shown in Figs. 1-3. Data reduction was performed with HKL Denzo and Scalepack [37]. The intensities were corrected for Lorentz and polarization effects, and an absorption correction based on the multi-scan method [38] was applied. Equivalent reflections, other than the Friedel pair for 12, were merged. The structures were solved by direct methods using SIR92 [39], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 Ueq of its parent C-atom (1.5 Ueq for the Me groups). The refinement of each structure was carried out on F² using full-matrix least-squares procedures, which minimized the function \( \Sigma w(F_o^2 - F_c^2)^2 \). Corrections for secondary extinction were not applied. In 12 and 17, three and one reflections, respectively, whose intensities were considered to be extreme outliers, were omitted from the final refinement. Refinement of the absolute structure parameter [40] of 12 yielded a value of –0.03(5), which confidently confirms that the refined coordinates correspond with the true absolute structure. Neutral atom scattering factors for non-H-atoms were taken from [41a], and the scattering factors for H-atoms were taken from [42]. Anomalous dispersion effects

CCDC-271077–271078 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, via www.ccdc.cam.ac.uk/data_request/cif.
were included in $F_c$ [43]; the values for $f'$ and $f''$ were those of [41b]. The values of the mass attenuation coefficients are those of [41c]. All calculations were performed using the SHELXL97 [44] program.

Table. Crystallographic Data for Compounds 12 and 17

REFERENCES


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$^a$ $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ where $P = (F_o^2 + 2F_c^2)/3$
Graphical Abstract

1

2

3a $X = O$

b $X = S$

4a $X = O$

b $X = S$
\textit{Scheme 1}

\begin{align*}
4b & \xrightarrow{\text{PCl}_5, \text{CCl}_4} 5 \\
& \xrightarrow{3a \text{ or } 4b} 6a \\
& \quad X = O \\
& \quad b \quad X = \text{Cl}_2
\end{align*}

\begin{align*}
5 & \xrightarrow{\text{HP(OEt)}_2 \text{ or } P(OB)_3} 7 \\
& \quad \xrightarrow{\text{MeCOSH}} 8
\end{align*}

\textit{Scheme 2}

\begin{align*}
4b & \xrightarrow{\text{SCl}_2, \text{CH}_2\text{Cl}_2} 9 \\
& \xrightarrow{4b} 10
\end{align*}

\begin{align*}
9 & \xrightarrow{\text{PCl}_5, \text{CCl}_4} 11
\end{align*}
Scheme 3

\[
\begin{align*}
\text{9} & \quad \text{THF} \quad \text{H}_2\text{O} \quad \text{12} \\
\text{12} & \quad \text{+ 9} \quad \text{13} \quad \text{+ 9} \quad \text{14}
\end{align*}
\]

Scheme 4

\[
\begin{align*}
\text{4b} & \quad \text{S}_2\text{Cl}_2 \quad \text{CH}_2\text{Cl}_2 \quad \text{13} \quad \text{+ 4b} \quad \text{14}
\end{align*}
\]
Scheme 5

\[ 4b \xrightarrow{mCPBA, \text{CH}_2\text{Cl}_2} 15 \quad + \quad 4b \quad \xrightarrow{\text{neat, } 110^\circ\text{C}} 16 \]

\[ \xrightarrow{\text{neat, } 110^\circ\text{C}} 18 \]

\[ \xrightarrow{\text{neat, } 110^\circ\text{C}} 19 \]

\[ \xrightarrow{\text{neat, } 110^\circ\text{C}} 17 \]

Scheme 6

\[ 20 + 4b \xrightarrow{\text{THF, } 45^\circ\text{C}} - N_2 21 \]

\[ a \quad R, R = \quad \quad b \quad R, R = \]
Scheme 7

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{N} & \quad \downarrow \\
\text{N} & \quad \text{Me} \\
\text{Toluene} & \quad \text{reflux} \\
\end{align*}
\]

22

\[
\begin{align*}
- \quad \text{Ph} & \quad \text{N} & \quad \text{Ph} \\
+ & \quad 4b \\
\end{align*}
\]

23

\[
\begin{align*}
\text{Ph} & \quad \text{N} & \quad \text{Me} \\
\downarrow & \quad \text{S} & \quad \text{Cl} \\
\text{N} & \quad \text{Cl} & \quad \text{Cl} \\
\text{Ph} & \quad \downarrow & \quad \text{Cl} \\
\end{align*}
\]

24

Scheme 8

\[
4b + \text{PhN}_3 \xrightleftharpoons[\text{80}]{\text{N}_2} \text{28} \quad 4b \quad \text{27}
\]

\[
\begin{align*}
\text{S} & \quad \text{N} & \quad \text{Ph} \\
\text{Cl} & \quad \text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} & \quad \text{Cl} \\
\text{29} & \quad \text{26} & \quad \text{30} & \quad \text{25}
\end{align*}
\]