

Formation of a 4*H*-Cyclopenta-1,2,3-thiadiazole by Rearrangement of a Transient *N*-(Thionitroso)cyclopenta-2,4-diene-1-imine

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1-Diazo-2,3,4,5-tetrachlorocyclopenta-2,4-diene, **2**, reacts with sulfur dichloride or with disulfur dichloride to form 4,4,5,6-tetrachloro-4*H*-cyclopenta-1,2,3-thiadiazole, **6**, most likely *via* a transient *N*-(thionitroso)cyclopenta-2,4-diene-1-imine, **4**.

In an attempt to prepare the unknown 2,3,4,5-tetrachlorocyclopenta-2,4-diene-1-thione from disulfur dichloride and 2,3,4,5-tetrachlorocyclopenta-2,4-dien-1-one hydrazone, **1**, according to Okazaki's method¹ we isolated, besides two minor unidentified products, the known diazo compound **2** and 4,4,5,6-tetrachloro-4*H*-cyclopenta-1,2,3-thiadiazole, **6**,[†] which was characterized by a single crystal X-ray structure determination.[‡] This novel compound is a derivative of 5,6-dihydro-4*H*-cyclopenta-1,2,3-thiadiazole, prepared in 1975 by Braun and Meier³ based on a procedure by Hurd and Mori.⁴ In this communication we present a new synthetic access to the cyclopenta-1,2,3-thiadiazole system. In order to account for the formation of **6** a series of theoretical calculations have been performed which imply a transient *N*-thionitrosoimine as the key intermediate.

Treatment of 2,3,4,5-tetrachlorocyclopenta-2,4-dien-1-one hydrazone, **1**, with S₂Cl₂ or SCl₂ in acetonitrile and diisopropylethylamine (Hünig's base) in acetonitrile gave 1-diazo-2,3,4,5-tetrachlorocyclopenta-2,4-diene, **2**, as the minor and

4,4,5,6-tetrachloro-4*H*-cyclopenta-1,2,3-thiadiazole, **6**, as the major product. Further experiments showed that **6** is also formed from the systems 2–S₂Cl₂ and 2–SCl₂. In the reaction of **1** it was found that after treatment with an equimolar amount of S₂Cl₂ or SCl₂ the major product was **2**.[§] Characteristic aspects of the reaction of **1** and **2** with S₂Cl₂/SCl₂ are the formation of the thiadiazole ring and the 1,3-shift of a chlorine atom.

The electron impact induced fragmentation of **6**, as verified by metastable defocusing, is initiated by elimination of a chlorine atom, followed by loss of N₂, which yields the base peak at *m/z* 197. Then follow consecutive eliminations of the three remaining chlorine atoms to give *m/z* 162, 127 and 92. Parallel loss of C₂Cl₂ generates the *m/z* 103 ion. The latter ions probably possess characteristic open-chain structures such as Cl–C≡C–C≡C–C≡S⁺ in the case of the *m/z* 127 ion.

The structure of **6** was determined by an X-ray determination and is shown as an ORTEP drawing in Fig. 1.⁸

[†] 4,4,5,6-Tetrachloro-4*H*-cyclopenta-1,2,3-thiadiazole **6**: m.p. 94–96°C; ¹³C NMR (200 MHz, CDCl₃) δ 166.3, 151.3, 143.7, 124.8, 74.1; MS *m/z* (rel. int.) ion composition, in agreement with the isotopic patterns, 260 (23) M⁺: C₅Cl₄N₂S, 225 (54) C₅Cl₃N₂S, 197 (100) C₅Cl₃S, 162 (8) C₅Cl₂S, 127 (38) C₅ClS, 103 (50) C₃ClS, 92 (25) C₅S, 79 (27) CClS; IR (KBr) ν/cm⁻¹ 1550s, 1440m, 1200s, 950s, 830s, 780m; UV–VIS (ethanol) λ/nm 212.5, 253.0, 323.0; satisfactory elemental analysis.

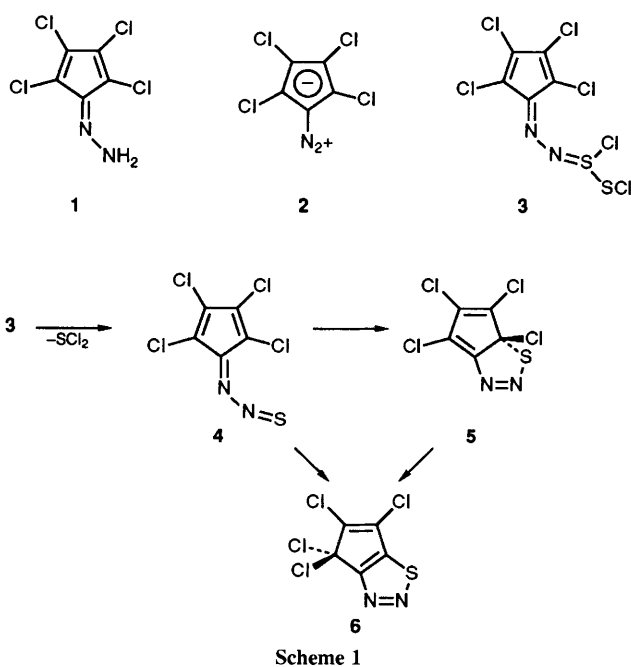
[‡] Crystal data for 4,4,5,6-tetrachloro-4*H*-cyclopenta-1,2,3-thiadiazole, C₅Cl₄N₂S, *M* = 261.94, monoclinic, space group P2₁/m, *a* = 7.333(1), *b* = 6.996(2), *c* = 9.237(2) Å, β = 110.53(1)°, *V* = 443.8 Å³, *Z* = 4, *D*_c = 3.92 g cm⁻³. Data were measured on a HUBER four-circle diffractometer with graphite monochromated Mo-*K*α radiation (λ = 0.71073 Å) in the ω–2θ scan mode, 2θ_{max} = 70°, μ = 14.86 cm⁻¹, crystal dimensions 0.16 × 0.15 × 0.45 mm, range of transmission factors 0.759, 0.839, 2392 ± *h*, ± *k*, *l* reflections measured gave 1408 unique reflections with an internal agreement of 0.025. The structure was solved by direct methods² and refined to *R* = 0.047, *R*_w = 0.060, based on the 885 intensities with *I* ≥ 3σ_{*I*}. Goodness of fit 1.72, 70 parameters.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[§] Procedure 1: A solution of S₂Cl₂ (0.594 g, 4.4 mmol) or SCl₂ (0.453 g, 4.4 mmol) in acetonitrile (20 ml) was added dropwise to a solution of 2,3,4,5-tetrachlorocyclopenta-2,4-dien-1-one hydrazone⁵ (0.506 g, 2.2 mmol) and Hünig's base (diisopropylethylamine) (0.568 g, 4.4 mmol) in acetonitrile (50 ml). The reaction mixture was stirred for 3 days at room temp. Procedure 2: A solution of S₂Cl₂ (0.297 g, 2.2 mmol) or SCl₂ (0.277 g, 2.2 mmol) in acetonitrile (20 ml) was added to a solution of 1-diazo-2,3,4,5-tetrachlorocyclopenta-2,4-diene⁶ (0.506 g, 2.2 mmol) in acetonitrile (50 ml). The reaction mixture was stirred for 2 days at room temperature. Work-up: After filtration and evaporation the reaction mixture was separated by column chromatography (silica gel, light petroleum–dichloromethane eluent system). The fractions eluted in the following order: minor product (only from the S₂Cl₂ reactions) [yellow, MS max. *m/z* 362 (C₅Cl₆N₂S₂); this corresponds to the sum of **2** and S₂Cl₂, *i.e.* maybe the adduct **3**], 1-diazo-2,3,4,5-tetrachlorocyclopenta-2,4-diene, unidentified minor product (green), 4,4,5,6-tetrachloro-4*H*-cyclopenta-1,2,3-thiadiazole. The fourth fraction was further purified by dry flash chromatography (silica gel, CH₂Cl₂–light petroleum 1 : 7) or sublimation (10 mm Hg/50°C) to yield colourless crystals. Yields: Procedure 1 (S₂Cl₂) 0.190 g (33%), procedure 1 (SCl₂) 0.070 g (12%), procedure 2 (S₂Cl₂) 0.220 g (38%), procedure 2 (SCl₂) 0.060 g (10%). Since **2** must be prepared by oxidation of **1** procedure 1 (S₂Cl₂) gives the best overall yield. The known slow reaction between acetonitrile and an excess of S₂Cl₂⁷ does not appear to play a role in our experiments.

Table 1 Calculated total energies and some structural data for 2-6

	Total energy/ eV	Bond length C(5)-N(1)/Å	Bond length N(1)-N(2)/Å	Bond length N(2)-S/Å	Bond length S-C(1)/Å
2	-2546.24	1.32	1.32	—	—
3	-3683.95	1.31	1.28	1.39	—
4	-2739.82	1.30	1.27	1.48	—
5	-2740.34	1.43	1.22	1.71	1.81
6	-2741.01	1.39 (1.346) ^a	1.26 (1.307) ^a	1.69 (1.715) ^a	1.65 (1.674) ^a

^a X-Ray data in brackets.

It is suggested that the first step in the formation of **6** from **1** is the oxidation of **1** to **2**.⁹ The mechanism of this and the following steps has been investigated by means of AM1 calculations.¹⁰ Several reaction paths for the formation of **6** from **1** and S_2Cl_2/SCl_2 can be imagined; a tentative one is outlined in Scheme 1.

The first step in this reaction path is the nucleophilic attack of a sulfur atom of S_2Cl_2 on **2** leading to the adduct **3**. Loss of SCl_2 from **3** creates a transient thionitroso intermediate, **4**. The diazo compound **2** and SCl_2 form an analogous adduct which can give **4** by loss of Cl_2 . The formation of **6** from **4** can take place as a concerted ring closure-[1,3] sigmatropic chlorine shift, or by prior ring closure to **5**, followed by a [1,3] sigmatropic chlorine shift. The geometries of **2-6** as well as those of S_2Cl_2 and SCl_2 have been optimized. The computational optimization of the molecular parameters of **6** leads to a structure which corresponds well with the experimental X-ray structure. A comparison with the X-ray structure is shown in Table 1. It appears from these numbers that the calculated bond lengths of the thiadiazole part are very similar to those obtained by X-ray determination. The only bond length of the calculated structure which differs by more than 0.05 Å compared to the X-ray determined structure is the C(1)-C(5) bond length, which has been calculated to be 0.08 Å longer than that found in the X-ray structure. The calculated total energies and some structural data for **2-5** are also given in Table 1.

It appears from Table 1 that the order of stability of **4-6** is **6** > **5** > **4**. Compound **6** is calculated to be 1.19 eV (≈ 27 kcal; 1 cal = 4.184 J) more stable than the thionitroso compound **4**, with the total energy of **5** lying between that of **4** and **6**. This calculated stability of **6** thus reflects its experimentally

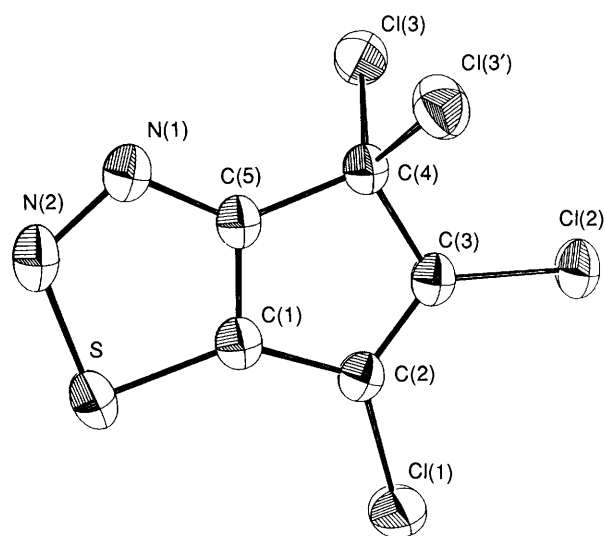
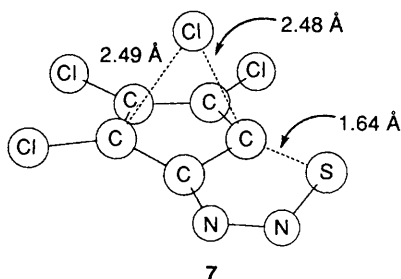


Fig. 1 The molecular structure of **6**, 4,4,5,6-tetrachloro-4H-cyclopenta-1,2,3-thiadiazole, $C_5Cl_4N_2S$, showing 50% thermal ellipsoids (ORTEP⁸). All atoms except C(13) sit on a crystallographic mirror plane. Bond lengths (Å): S-C(1) 1.674(5), S-N(2), 1.715(5), C(2)-Cl(1) 1.697(5), C(3)-Cl(2) 1.691(5), C(4)-Cl(3)≡C(4)-Cl(3') 1.778(3), C(1)-C(2) 1.463(7), C(2)-C(3) 1.338(7), C(3)-C(4) 1.520(7), C(4)-C(5) 1.499(7), C(5)-C(1) 1.362(8), C(5)-N(1) 1.346(7), N(1)-N(2) 1.307(7). Selected bond angles (°): C(1)-S-N(2) 91.9(2), S-N(2)-N(1) 112.0(4), N(2)-N(1)-C(5) 111.4(5), N(1)-C(5)-C(1) 116.7(5), C(5)-C(1)-S 108.0(4), C(5)-C(1)-C(2) 109.3(5), C(1)-C(2)-C(3) 108.3(5), C(2)-C(3)-C(4) 111.1(5), C(3)-C(4)-C(5) 101.3(4), C(4)-C(5)-C(1) 110.0(5), C(1)-C(2)-Cl(1) 124.7(4), C(3)-C(2)-Cl(1) 127.0(4), C(2)-C(3)-Cl(2) 128.1(4), C(4)-C(3)-Cl(2) 120.8(4), C(3)-C(4)-Cl(3) 110.8(2), C(5)-C(4)-Cl(3') 111.9(2), Cl(3)-C(4)-Cl(3') 110.0(3).

observed stability. A comparison of the structure of the diazo part of **2** with the experimental structure of comparable diazo compounds¹¹ shows good agreement. To our knowledge so far no thionitroso compound has been characterized by X-ray crystallography; but the calculated bond lengths and angles of the thionitroso part of **4** compare well with the bond lengths and angles calculated for the thionitroso part of $(Me)_2N-N=S$.¹²

Starting from the proposed transient thionitroso intermediate **4** we have calculated the transition states for the **4** → **5** → **6** and **4** → **6** reaction paths. The calculated transition state energy for the reaction **4** → **5** amounts to 20 kcal, while the corresponding transition state energy for the **5** → **6** rearrangement is found to be 46 kcal. The calculated transition state energy for the reaction path **4** → **6** is 35 kcal. Thus, our computations suggest that the lowest-energy path involves a ring closure concerted with a [1,3] sigmatropic chlorine shift. The optimized transition state structure for the **4** → **6** reaction path is **7**.

The formation of an *N*-thionitrosoamine from a hydrazine, disulfur dichloride and triethylamine has precedent (in the case of *N,N*-diphenylhydrazine¹³), but must of necessity have



a different mechanism. The formation of a transient thio-nitroso compound by loss of chlorine from an iminosulfur dichloride has likewise been implied earlier.¹⁴

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