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A Compound Previously Described as Trichloromethanethiol is in Fact 1,1,2,2-Tetrachloro-1,2-ethanedisulfenyl Dichloride

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Abstract: The reaction of *N*-(4-methylphenyl)-trichloromethanesulfenamide **2a** with base gives 2,3-bis-(4-methylphenyl)-5,5,6,6-tetrachloro-2,3,5,6-tetrahydro-1,4,2,3-dithiadiazine **6a**, which can be cleaved with HCl to give 1,1,2,2-tetrachloro-1,2-ethanedisulfenyl chloride **7**, and not, respectively, 2,5-bis-(4-methylphenyl)-3,3,6,6-tetrachloro-2,3,5,6-tetrahydro-1,4,2,5-dithiadiazine **4a** and trichloromethanethiol **5**.

Trichloromethanethiol **5** has appeared in the literature in two connections. Most references to **5** appear in the secondary literature and stem from the erroneous interpretation of the semitrivial commercial name perchloromethyl mercaptan as **5** rather than the intended trichloromethanesulfenyl chloride **1**.[1]

Early work by Connolly and Dyson[2] involved a reaction sequence (see Scheme 1, Path b) which, from **1** and primary aromatic amines, led to the sulfenamides **2** which in turn could be cyclized by treatment with alcoholic base to yield six-membered heterocycles assumed to possess the 1,4,2,5-dithiadiazine structure **4**. Finally, the alleged **4** could be cleaved with gaseous hydrogen chloride to form a yellow, distillable liquid which, on the basis of the elemental analysis and a number of reactions (*vide infra*) was assigned the structure **5**, irrespective of the fact that true **5** would be expected to decompose spontaneously into thiophosgene and hydrogen chloride and also to possess an extrapolated boiling point far below the observed one of 125 °C (15 mm Hg).

Recently, Potts and Baum[3] showed that the alleged **4** [rigorously demonstrated in the case of the bis-(4-methylphenyl) derivative **4a**] actually constitute head-to-head dimers of the intermediate red thione *S*-imide **3** (responsible for the observed transient red color of the reaction mixture) and thus possess the 1,4,2,3-dithiadiazine structure **6**.

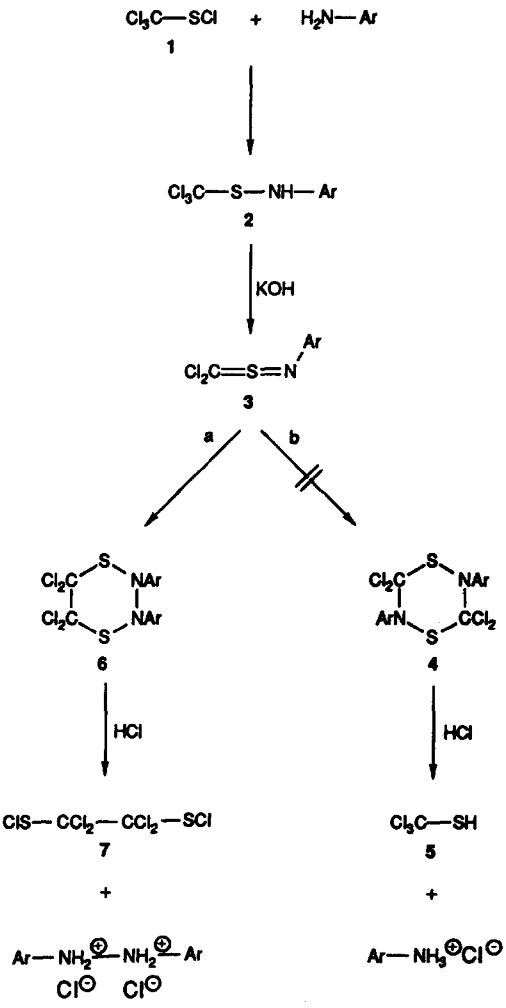
These findings suggested to us that the alleged formation of **5** from **4** and HCl rather must be interpreted as the formation of 1,1,2,2-tetrachloro-1,2-ethanedisulfenyl dichloride **7** from **6** and HCl (Scheme 1, Path a).

A repetition of the experimental procedure of Connolly and Dyson furnished a product with the reported physical properties, but not its reported chemical lability (such as sensitivity to air), and could be shown to possess structure **7**. Thus, correct elemental analyses could be obtained and the spectral properties were in accordance with the revised structure. In a modified procedure it was found advantageous to purify **7** by column chromatography rather than by distillation.[4] Moreover, reaction of **7** with phenylmethanethiol furnishes the corresponding bis-disulfide, $C_6H_5CH_2SSCCl_2CCl_2SSCH_2C_6H_5$ **8**.

Compound **7** is the hypothetical end point of the exhaustive chlorination of 1,2-ethanedithiol **9** which has been investigated by Rees et al.[5,6] and also by us.[7] While a number of less substituted chloro-1,2-ethanedisulfenyl chlorides can be obtained by controlled chlorination[6] we were unable to prepare **7** by exhaustive chlorination of **9** due to uncontrollable HCl elimination and C-S bond cleavage.

$$\underset{\mathbf{9}}{HS-CH_2-CH_2-SH} \xrightarrow{Cl_2} \cancel{\xrightarrow{Cl_2}} \underset{\mathbf{7}}{ClS-CCl_2-CCl_2-SCl}$$

Compound **7** is a new C_2 building block for organic synthesis, for instance in the construction of heterocycles, and a possible precursor for further modified C_2 synthons.



Scheme 1.

References and notes

1. Senning, A. *Sulfur Rep.* **1986**, 7, 45.
2. Connolly, J. M.; Dyson, G. M. *J. Chem. Soc.* **1934**, 822-824.
3. Potts, K. T.; Baum, J. S. *J. Heterocycl. Chem.*. **1991**, 28, 1637-1639.
4. *1,1,2,2-Tetrachloro-1,2-ethanedisulfenyl dichloride 7:* A solution of 2.50 g (5.68 mmol) 2,3-bis(4-methylphenyl)-5,5,6,6-tetrachloro-2,3,5,6-tetrahydro-1,4,2,3-dithiadiazine[2,3] (**6a**) in 125 ml ether is saturated with gaseous HCl. The color changes from colorless to yellow and a white precipitate forms. The flask is stoppered and set aside. After 1-2 d, when the reaction is complete as seen by TLC, the solution is filtered and purified on a silica gel column with petroleum ether as eluent. A yellow, foul smelling oil is obtained (0.55 g, 32 %). Attempts to induce crystallization failed. ^{13}C NMR ($CDCl_3$): δ 101.3 ppm. Elemental analysis: Found C 8.42; H 0.03; Cl 69.89; S 21.23 %. Calculated for $C_2Cl_6S_2$: C 7.98; H 0.00; Cl 70.70; S 21.31 %. MS: *m/z* 266 (M^+- S), 231 (M^+- ClS), 196 (M^+- Cl_2S), 161 (M^+- Cl_3S), 126 (M^+- Cl_4S), etc.
5. Morris, J. L.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1987**, 211-215.
6. Rees, C. W.; Surtees, J. R. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2945-2953.
7. Nielsen, S. B.; Senning, A. unpublished results.

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