# Chlorotropic Rearrangements of an α-Sulfanyl-α-sulfonylalkanesulfenyl Chloride to an α-Chloroalkyl Disulfide and an S-(α-Chloroalkyl) Thiosulfonate

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(1-Adamantylsulfonyl)(pentachlorophenylsulfanyl)chloromethanesulfenyl chloride, 3, can undergo two quantitative chlorotropic rearrangements, the more facile one leading to (1-adamantylsulfonyl)-dichloromethyl pentachlorophenyl disulfide, 4, the less facile one forming S-[(pentachlorophenyl-sulfanyl)dichloromethyl] adamantane-1-thiosulfonate 5.

On a previous occasion it was noted that dichloromethane-disulfenyl dichloride, 1, undergoes a facile chlorotropic rearrangement to 1-chloro-2-(trichloromethyl)disulfane, 2 [reaction (1)].[1] Related chlorotropic rearrangements of sulfanyl



$$\text{1} \longrightarrow \text{2} \qquad (1)$$
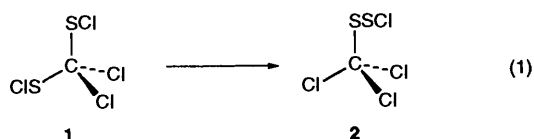
substituted alkanesulfenyl chlorides are well documented.[2-4] This communication reports two new concomitant chlorotropic rearrangements of an α-sulfanyl-α-sulfonylalkanesulfenyl chloride to an α-chloroalkyl disulfide and an S-(α-chloroalkyl) thiosulfonate. 1-Adamantylsulfonyl)(pentachlorophenylsulfanyl)chloromethanesulfenyl chloride, 3, is found to rearrange quantitatively to (1-adamantylsulfonyl)dichloromethyl pentachlorophenyl disulfide, 4, if left in CHCl₃ for a few days [Scheme 1, reaction (2)].



$$\text{3} \longrightarrow \text{4} \qquad (2)$$

$$\text{3} \longrightarrow \text{5} \qquad (3)$$
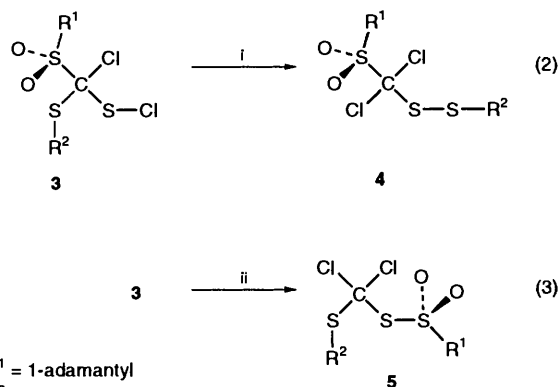
R¹ = 1-adamantyl
R² = C₆Cl₅

**Scheme 1**

However, refluxing an ethereal solution of 3 for 40 min leads to a quantitative yield of the unprecedented, alternative rearrangement product, S-[(pentachlorophenylsulfanyl)di-chloromethyl] adamantane-1-thiosulfonate 5 [Scheme 1, reaction (3)]. It has also been observed that heating 3/4 in boiling diethyl ether for a short time or leaving a CHCl₃ solution of 3/4 for a long time causes quantitative rearrangement to 5.

The structures of 4 and 5 are deduced from their inability to react with tert-butylamine to form the corresponding thio-carbonyl S-imide as does 3[5] and from their characteristic ¹³C
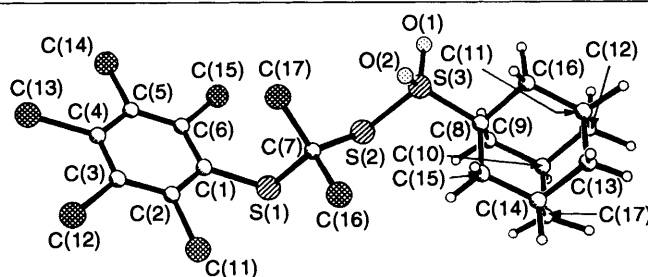


Fig. 1 The molecular structure of S-[(pentachlorophenylsulfanyl)-dichloromethyl] adamantane-1-thiosulfonate, 5, $C_{17}H_{15}Cl_7O_2S_3$. Selected bond lengths (Å): S(1)–C(7) 1.87(1), S(2)–C(2) 1.79(1), S(3)–O(2) 1.421(7), S(1)–C(1) 1.75(1), S(2)–S(3) 2.36(4), S(3)–O(1) 1.457 (9), S(3)–C(8) 1.81(1). Selected bond angles (°): C(1)–S(1)–S(7) 103.1(5), S(3)–S(2)–C(7) 106.7(4), S(2)–S(3)–O(1) 102.1(3), O(1)–S(3)–O(2) 119.1(5), S(2)–S(3)–O(2) 109.6(3), S(2)–S(3)–O(2) 106.9(4), O(1)–S(3)–C(8) 108.3(5), O(2)–S(3)–C(8) 110.1(4).

NMR spectra (see Experimental section). The unexpected structure of 5 has been confirmed by a single crystal X-ray determination and is shown in an ORTEP drawing in Fig. 1.

The rearrangements (2) and (3) in Scheme 1 can either take place in a concerted manner [reactions (4a) and (5a)] or via an ion pair intermediate consisting of a dithiiranium cation, 6, and a chloride anion [reaction (4b)] or via a zwitterion intermediate, 7 [reaction (5b)]. Dithiiranium cations have previously been encountered in rearrangements.[6] The four possible rearrangement paths 3→4 and 3→5 are outlined in Scheme 2. Furthermore, 5 can also be formed from 4; i.e. the following reaction sequence takes place: 3→4→5.

The rearrangements (2) and (3) have been subjected to a theoretical investigation using AM1 calculations[7] in order to shed some light on the mechanism. The dual rearrangement paths for 3 to 4 and 5 outlined in Scheme 2, as well as the reaction sequence 3→4→5 have been investigated.

The structures of 3–7 have been optimized with no geometric restrictions. The optimized geometry for 5 is very similar to the structure found by X-ray crystallography, while the geometry for the others have standard bond lengths and bond angles. The total energy for 3 is calculated to be 6223.88 eV (all other energies are given relative to the energy for 3). The total energies of 4 and 5 are calculated to be 4.4 and 8.4 kcal mol⁻¹,‡ respectively, lower than that of 3. It thus appears that the rearrangement of 3 to 4 and 5 is driven by the thermodynamics of the system. The total energies for 6 + Cl⁻ and for 7 are calculated to be 94.3 and 103.5 kcal mol⁻¹, respectively, larger than that of 3. It thus appears that 3–5 are significantly more stable than ionic intermediates.

‡ 1 cal = 4.184 J.

(4a)



(4b)



(5a)



(5b)

R¹ = 1-adamantyl
R² = C₆Cl₅
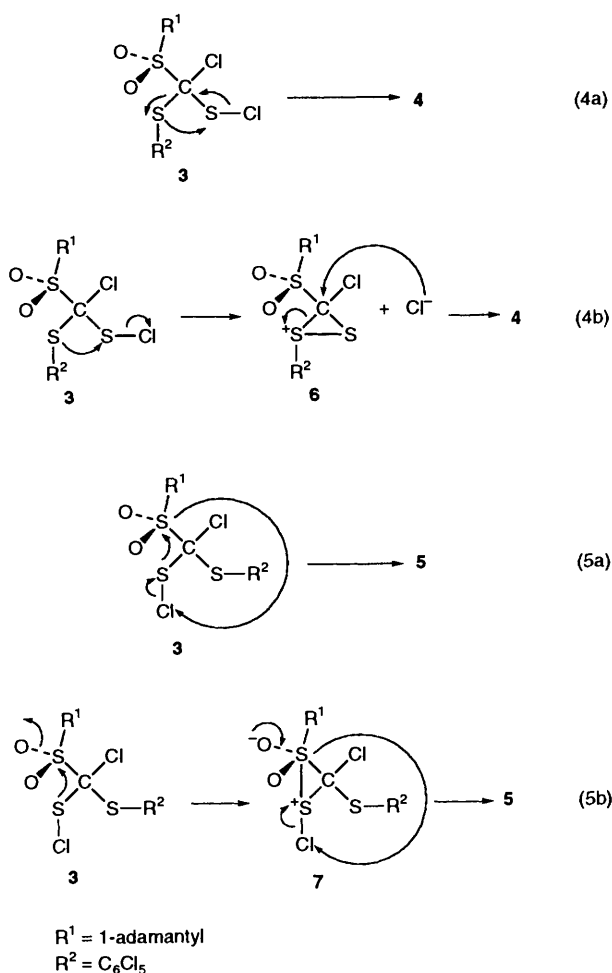
**Scheme 2**

Starting from **3** the transition states for the following reaction paths have been calculated: **3→4**, **3→5** and **4→5**. All transition states were calculated with respect to an intrinsic reaction path coordinate and keeping all the geometrical parameters free. The transition state energies are calculated to be: 23.6 kcal mol⁻¹ for **3→4**; 53.4 kcal mol⁻¹ for **3→5** and 44.7 kcal mol⁻¹ for **4→5**. These results indicate that the concerted rearrangement is more favourable than both the dithiiranium cation and the zwitterion intermediate reaction path, and that the rearrangement probably takes place in the following sequence: **3→4→5**. A concerted rearrangement is not unrealistic from an experimental point of view as the reactions take place in solvents with low polarity.

## Experimental

*Typical Procedures.*—(a) A solution of **3** (1.00 g, 1.7 mmol) in CHCl₃ (50 cm³) was left at room temperature for 5 d. The solution was cooled and **4** (0.96 g, 96%) was precipitated and collected by filtration. (b) An ethereal solution of **3** (1.80 g, 3.0 mmol) was refluxed for 40–60 min and then left overnight. The solvent was evaporated to give **5** (1.76 g, 98%).

(1-Adamantylsulfonyl)(pentachlorophenylsulfanyl)chloro-methanesulfenyl chloride **3**:[5] m.p. 134–136 °C; $\delta_C$(200 MHz; CDCl₃) 141.52, 138.42, 133.01, 130.23, 93.93 (α-C), 73.40, 35.81, 35.54 and 28.95; $\delta_H$(200 MHz; CDCl₃) 1.75 (s, 6 H), 2.16 (s, 6 H) and 2.27 (s, 3 H); m/z (rel. int.) ion composition, in agreement with the isotopic patterns, 592 (<1) M⁺: $C_{17}H_{15}Cl_7O_2S_3$, 560 $C_{17}H_{15}Cl_7O_2S_2$ (1) 323, (1) $C_7Cl_5S_2$, 281 (<1) $C_{11}H_{15}Cl_2O_2S$, 279 (<1) $C_6Cl_5S$, 247 (<1) $C_6Cl_5$ and 135 (100) $C_{10}H_{15}$; v(KBr)/cm⁻¹ 2915s, 2845w, 1337s, 1143s and 690s.

(1-Adamantylsulfonyl)dichloromethyl pentachlorophenyl di-sulfide **4**: m.p. 195–196 °C (from CHCl₃); $\delta_C$(200 MHz; CDCl₃) 137.55, 135.95, 134.83, 132.66, 104.37 (α-C), 73.52, 37.65, 35.39 and 29.13; $\delta_H$(200 MHz; CDCl₃) 1.71 (s, 6 H), 2.20 (s, 6 H) and 2.40 (s, 3 H); m/z (rel. int.) ion composition, in agreement with the isotopic patterns, 560 (3) $C_{17}H_{15}Cl_7O_2S_2$, 323 (2) $C_7Cl_5S_2$, 281 (13) $C_{11}H_{15}Cl_2O_2S$, 279 (7) $C_6Cl_5S$, 247 (11), $C_6Cl_5$ and 135 (100) $C_{10}H_{15}$; v(KBr)/cm⁻¹ 2915s, 2850w, 1340s, 1155s and 697s (Found: C, 34.2; H, 2.5; Cl, 41.7; S, 15.8. Calc. for $C_{17}H_{15}Cl_7O_2S_3$: C, 34.3; H, 2.5; Cl, 41.7; S, 16.1%).

*S*-[(Pentachlorophenylsulfanyl)dichloromethyl] adamant-ane-1-thiosulfonate, **5**: m.p. 159–160 °C (from diethyl ether); $\delta_C$(200 MHz; CDCl₃) 141.41, 138.28, 132.92, 130.22, 93.88 (α-C), 73.34, 35.76, 35.48 and 28.90; $\delta_H$(200 MHz; CDCl₃) 1.75 (s, 6 H), 2.18 (s, 6 H) and 2.28 (s, 3 H); m/z (rel. int.) ion composition, in agreement with the isotopic patterns, 592 (<1) M⁺: $C_{17}H_{15}Cl_7O_2S_3$, 560 (1) $C_{17}H_{15}Cl_7O_2S_2$, 323 (<1) $C_7Cl_5S_2$, 281 (<1) $C_{11}H_{15}Cl_2O_2S$, 279 (<1) $C_6Cl_5S$, 247 (<1) $C_6Cl_5$ and 135 (100) $C_{10}H_{15}$; v(KBr)/cm⁻¹ 2915s, 2845w, 1338s, 1155s and 690s (Found: C, 34.3; H, 2.5; Cl, 41.4; S, 15.9. Calc. for $C_{17}H_{15}Cl_7O_2S_3$: C, 34.3; H, 2.5; Cl, 41.7; S, 16.1%).

*Crystal Data for* S-[*(Pentachlorophenylsulfanyl)dichloro-methyl*] *Adamantane-1-thiosulfonate*, **5**.—$C_{17}H_{15}Cl_7O_2S_3$, M = 595.48, triclinic, space group P$\bar{1}$, a = 6.661(1), b = 10.626(2), c = 16.402(3) Å, α = 87.36(3), β = 81.02(3), γ = 84.96(3)°, V = 1142(1) Å³, Z = 2, $D_c$ = 1.731 g cm⁻³. Data were measured on a Syntex P$\bar{1}$ diffractometer with Mo-Kα radiation (λ = 0.710 69 Å) in the φ/2φ scan mode, $\varphi_{max}$ = 22.5°, crystal dimensions 0.10 × 0.15 × 0.35 mm, 1651 reflections measured gave 1479 unique reflections with an internal agreement of 0.0. The structure was solved by direct methods and refined to R = 0.060, $R_w$ = 0.072. Goodness of fit 2.78, 323 parameters. The crystals were strongly twinned which might explain the rather high R value and standard deviations.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallo-graphic Data Centre.*

## Acknowledgements

* For details of the deposition scheme, see 'Instructions for Authors', J. Chem. Soc., Perkin Trans. 1, 1994, Issue 1.

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