Tetrahedron Letters, Vol. 34, No. 27, pp. 4289-4292, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

SULFENYL CHLORIDE CHEMISTRY. SULFUR TRANSFER TO DOUBLE BONDS.

Imad A. Abu-Yousef, Rosemary C. Hynes and David N. Harpp*

Department of Chemistry, McGill University,
Montreal, Quebec, Canada H3A 2K6

Abstract: *When triphenylmethanesulfenyl chloride* (1) *(or its thio homolog* 2*) are treated with various bicycles, 1,2 addition reactions take place. Final products occur via an episulfide intermediate. The stereochemistry of addition has been determined by x-ray analysis. Finally, evidence has been obtained for the delivery of diatomic sulfur, likely via intermediate* 3.

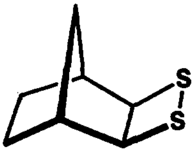
The chemistry of sulfenyl halides has been studied extensively.[1] Much less examined however, is the chemistry of triphenylmethanesulfenyl chloride (1) and its thio homolog 2.[2] We recently reported an interesting reaction of 1 where its sulfur atom is quantitatively and catalytically extruded by a reaction with thioketones.[3a] In another investigation, the reaction of 2 with 1,3 dienes affords a 1,4 addition product which subsequently produces cyclic di- and tetrasulfides (4, 5) in good, overall yield.[3b]

$(C_6H_5)_3C\text{-}S\text{-}Cl$

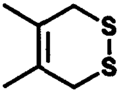
1

$(C_6H_5)_3C\text{-}S\text{-}S\text{-}Cl$

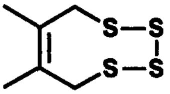
2



3



4

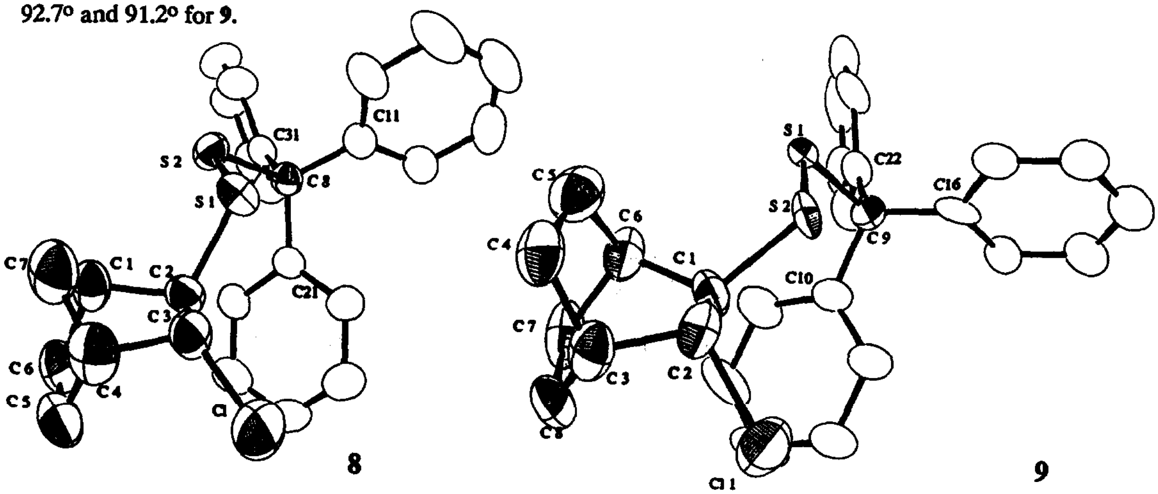


5

The net effect of the latter transformation is to deliver a 2- and 4-sulfur fragment to the diene. We have initiated a study of some of the chemistry of this type of addition in hopes to develop a useful pathway to dithietanes such as 3 as potentially stable intermediates or diatomic sulfur precursors.

The reaction of 1 with norbornene (6) has been investigated[4] previously. Indeed, other similar types of sulfenyl halides have been shown to add to double bonds; this has resulted in preparative methods for episulfides.[5] In the case of the reaction of 1 with 6, a number of products were reported[4] but details were lacking and neither their stereochemistry nor the mechanism of reaction were demonstrated.

In order to establish the structure of the product(s) and the likely pathway of this type of addition reaction, sulfenyl chloride **1** was mixed at room temperature with norbornene (*6*) and bicyclo [2.2.2] octene (**7**) respectively. In each case, adducts were formed in *ca.* 65% isolated yield. MS and elemental analyses revealed each product contained two sulfur atoms. X-ray crystal analysis revealed the regiochemistry of **8**; the symmetry of **9** permits only one isomer (Figure 1).[6] The S-S bond length for **8** was 2.026(3)Å and 2.046(5)Å and 2.022(5)Å for the two orientations of **9**.[7] The C-S-S-C dihedral angles were 95.6° for **8** and 92.7° and 91.2° for **9**.

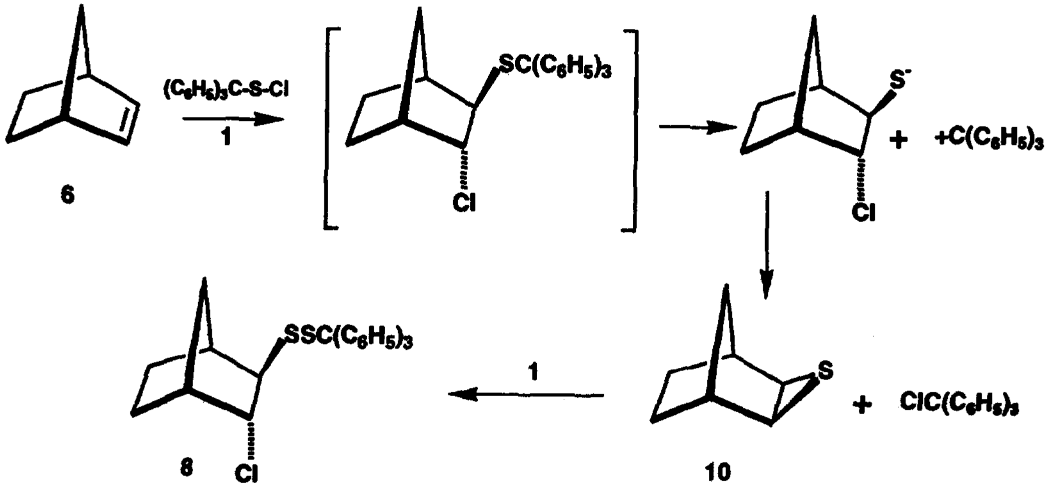


8

9

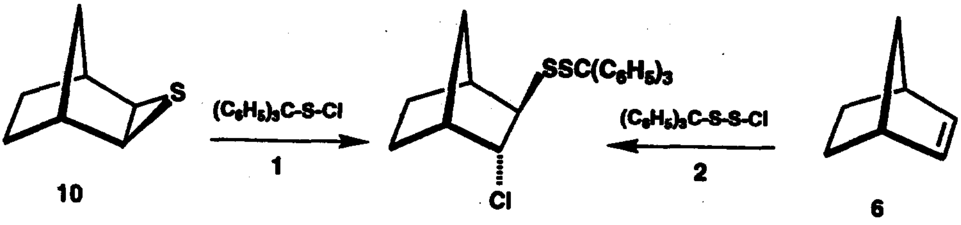
Figure 1

A plausible, general mechanism showing the most probable explanation for the presence of the second sulfur atom is indicated by the pathway in Scheme 1.



Scheme 1

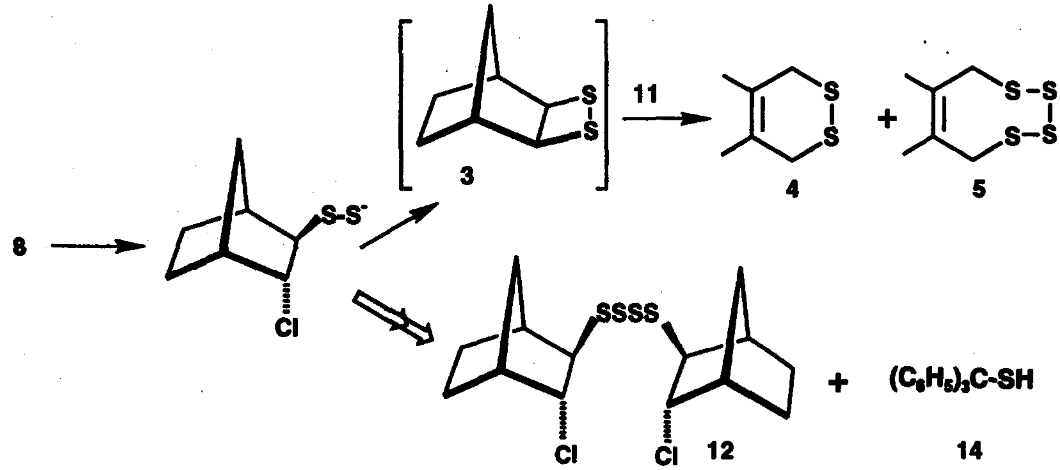
We independently prepared exo episulfide 10[5b] and treated it with sulfenyl halide 1. Adduct 8 was isolated in 90% yield. This experiment clearly verifies the likely pathway displayed in Scheme 1. In addition, when the thiosulfenyl chloride 2 and norbornene 6 were mixed, both regioisomers were formed (^{13}C NMR) and adduct 8 was eventually isolated in 75% yield (Scheme 2). When bicycle 7 was treated with either sulfur chlorides 1 or 2, a single, pure compound was isolated in 62% yield.



Scheme 2

It was hoped to be able to induce disulfur adducts 8 or 9 to cleanly give up diatomic sulfur perhaps *via* intermediate 3 (Scheme 3). When 8 was heated in ethyl acetate with a standard diatomic sulfur trap, 2,3-dimethylbutadiene (11)[8], both 4 and 5 were detected by ^1H NMR. Eventually, the tetrasulfide adduct was isolated but only in 4% yield (^1H NMR δ 1.70, 3.64 ppm).[3b] It is likely that intermediate 3 transfers its two sulfur atoms to the diene trap to form 4. As has been noted by ourselves[8a,b,f] and in other labs,[8c,d] a likely second trap of a two sulfur unit takes place forming tetrasulfide 5.

The major product of the reaction is formed by an intermolecular pathway when 8 is heated in EtOAc eventually giving the corresponding tetrasulfide (12) in 60% yield.[9] A possible pathway to explain this result is suggested in Scheme 3. In addition, starting material was isolated (*ca.* 15%) and triphenylmethanethiol 14 (*ca.* 12%). Work is continuing in this area.



Scheme 3

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada and the F. C. A. R. (Quebec) for financial support.

References

1. K. D. Gundermann, *Angew Chem. Int. Ed. Engl.*, **2**, 674 (1963); W. R. Hardstaff and R. F. Langler in "Sulfur in Organic and Inorganic Chemistry," A. Senning (Ed.), Marcel Dekker Inc., New York, Vol. 4, (1982), p 193; G. H. Schmid and D. G. Garratt, "The Chemistry of the Double Bonded Functional Groups", S. Patai (Ed.), John Wiley and Sons, New York, (1982) Chapter 9.
2. D. N. Harpp and D. K. Ash, *Int. J. Sulfur Chem.* Part A, **1**, 211, 1971.
3. a) C. R. Williams and D. N. Harpp, *Tetrahedron Lett.*, **32**, 7633 (1991); b) C. R. Williams and D. N. Harpp, *Tetrahedron Lett.*, **32**, 7651 (1991).
4. J. M. Majewski and J. Zakrzewski, *Tetrahedron Lett.*, **22**, 3659 (1981).
5. a) T. Fujisawa and T. Kobori, *Chemistry Lett.*, 935, 1065 (1972); b) M. U. Bombala and S. V. Ley, *J. Chem. Soc., Perkin I*, 3031 (1979).
6. **X-Ray Data for 8.** Empirical Formula $C_{26}H_{25}ClS_2$, M = 437.05, monoclinic, space group $P2_1/c$ (# 14), a = 10.1400(20), b = 12.860(3), c = 17.407(14) Å, β = 99.38(3)°, V = 2239.6(19)Å^3, Z = 4, D_c = 1.296Mgm^{-3}, μ = 0.36 mm^{-1}, F(000) = 921.62. Data collected at 293K on a Rigaku diffractometer using MoKα radiation and $\theta/2\theta$ scans to a 2θ max of 45°. Reflections measured: 3114; unique reflections: 2921; reflections with I > 2.5σ (I): 1600. Solution by direct methods; hydrogens calculated. Last least-squares with 54 atoms, 263 parameters and 1600/2921 reflections gave R_f = 0.057, R_w = 0.058; GoF = 1.80. **X-Ray Data for 9.** Empirical Formula $C_{27}H_{27}ClS_2$, M = 451.08, triclinic, space group P1 (# 2), a = 9.1129(14), b = 11.6262(21), c = 22.2218(23) Å, α = 87.829(14), β = 89.966(12), γ = 78.904(14)°. V = 2308.6(6)Å^3, Z = 4, D_c = 1.298Mgm^{-3}, μ = 0.35 mm^{-1}, F(000) = 951.91. Data collected at 115K on a Rigaku diffractometer using MoKα radiation and $\theta/2\theta$ scans to a 2θ max of 47°. Reflections measured: 7304; unique: 6807; number of reflections with I > 2.5σ (I): 4439. Solved as above. Last least-square with 110 atoms, 595 parameters and 4439/6807 reflections gave R_f = 0.109, R_w = 0.129 and GoF = 5.39. The structure is disordered around the S-S bond with two orientations present in a 3:1 ratio. Minor positions of S and Cl atoms were identified but disorder of the carbons showed up as unreasonable thermal parameters, even at low temperature causing the poor refinement.
7. These values are *ca.* 10° greater than most disulfides and *ca.* 20° less than the dihedral angle for ditrityldisulfide; C. R. Williams and D. N. Harpp, manuscript submitted; M. Ostrowski, J. Jeske, P. G. Jones and W.-W. du Mont, manuscript submitted.
8. For similar trapping reactions see: a) S. Tardif, C. R. Williams and D. N. Harpp, unpublished results; b) W. Chew and D. N. Harpp, *Sulfur Letters*, **16**, 0000 (1993), *in press*; c) T. L. Gilchrist and J. R. Wood, *J. Chem. Soc., Chem. Commun.*, 1460 (1992); d) K. C. Nicolaou, S. A. DeFrees, C.-K. Hwang, N. Stylianides, P. J. Carroll and J. P. Snyder, *J. Am. Chem. Soc.*, **112**, 3029 (1990); e) K. Steliou, Y. Gareau, G. Milot and P. Salama, *J. Am. Chem. Soc.*, **112**, 7819 (1990); f) D. N. Harpp and J. G. MacDonald, *J. Org. Chem*, **53**, 3812 (1988); g) K. Steliou, P. Salama, D. Brodeur and Y. Garneau, *J. Am. Chem. Soc.*, **109**, 926 (1987); h) M. Schmidt and U. Görl, *Angew. Chem. Int. Ed. Engl.*, **26**, 887 (1987); i) K. Steliou, Y. Garneau and D. N. Harpp, *J. Am. Chem. Soc.*, **106**, 799 (1984).
9. For 12: oil; Anal. Calcd for $C_{14}H_{20}Cl_2S_4$: C, 43.40; H, 5.20; S, 33.10. Found: C, 43.46; H, 4.85; S, 33.09. Compound 13 was isolated from the heating of 9 in EtOAc. Trapped products 4 and 5 were not detected due to overlapping ^{1}H NMR signals: 13 is an oil; Anal. Calcd for $C_{16}H_{24}Cl_2S_4$: C, 46.25; H, 5.82; S, 30.87. Found: C, 46.10; H, 5.65; S, 30.63.

(Received in USA 8 April 1993; accepted 12 May 1993)