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SULFENYL CHLORIDE CHEMISTRY. PRECURSORS FOR DIATOMIC SULFUR TRANSFER.

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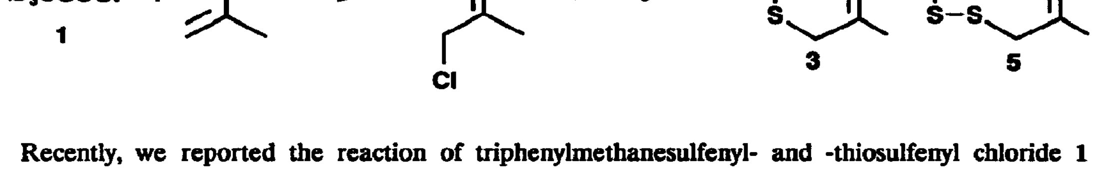
Abstract: *Triphenylmethanethiosulfenyl chloride* 1 *[$(C_6H_5)_3CSSCl$] (and its dithio homolog* 2 *[$(C_6H_5)_3CSSSCl$]) give stable addition products (ca. 85% yield) with cyclopentene and cyclohexene. When these adducts are warmed with a diene, they deliver diatomic sulfur-trapped derivatives. These tetrasulfides are quantitatively converted to the corresponding disulfide* 3 *with triphenylphosphine; this affords cyclic disulfides in > 50% isolated yield from the diene. In addition, evidence has been obtained implicating dithietane intermediate* 4.

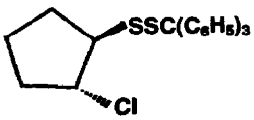
We have examined the chemistry of the surprisingly stable triphenylmethanethiosulfenyl chloride 1.[1,2,3] The reaction of 1 with 1,3-dienes affords a 1,4 addition product which, by warming in a solvent, produces cyclic di- and tetrasulfides (3, 5) in *ca.* 65% yield by an addition-elimination mechanism (Scheme 1).[2] We have initiated an examination of this type of chemistry in the hopes of developing a delivery system for diatomic sulfur, possibly by way of dithietanes such as 4.

SCHEME 1

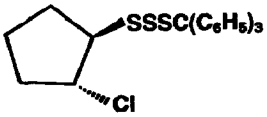


Recently, we reported the reaction of triphenylmethanesulfenyl- and -thiosulfenyl chloride 1 with norbornene and bicyclo[2.2.2]octene.[3] Stable 1,2 addition products were formed and while diatomic sulfur transfers took place from them to a diene acceptor, the yield of final products was quite low.

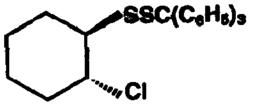
In contrast, the addition products (**8**, **9** from **1**; **10**, **11** from **2**)[4,5] are effective in transferring sulfur to a diene trap. When adducts **8**-**11** were each heated in the presence of 2,3-dimethyl-1,3-butadiene in a variety of solvents varying temperature, time and concentration, trapped tetrasulfide **5** was isolated in 10-63% yield (^{1}H NMR δ 1.79, 3.63 ppm; ^{13}C NMR δ 18.16, 42.70, 130.28 ppm).[2,3,6] In the case of dithio reagent **9**, two decomposition avenues are possible (Scheme 2). Dithietane intermediate **4** either directly transfers its two sulfur atoms to the diene trap to form **3** or undergoes a cycloreversion to cyclohexene and $^1S_2$ which is then trapped. Conversely, intermediate **12** could fragment directly to deliver $^1S_2$ which is then trapped. *In addition, we find cyclohexene in the crude reaction mixture*; it is difficult to rationalize the presence of this molecule except by the decomposition of dithietane **4** or by a concerted expulsion of $^1S_2$ from intermediate **12** (Scheme 2). A second capture of a two sulfur unit apparently takes place which results in cyclic tetrasulfide **5** as the major product. The formation of **5** parallels experiments noted in our[3,6] and other labs.[7] Tetrasulfide **5** can be converted quantitatively to disulfide **3** by an *in situ* treatment with triphenylphosphine; thus this methodology serves to transfer a two sulfur unit to a diene in over 50% isolated yield (Table).



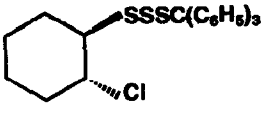
8



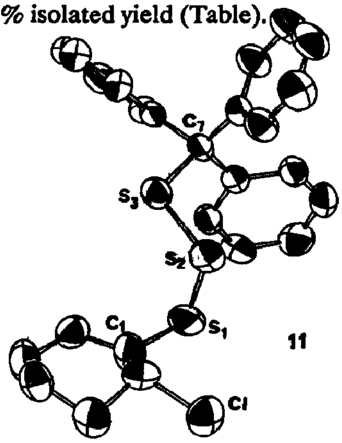
10



9



11



11

By-products **13** and **14** (10-62%)[8] are likely formed by an intermolecular pathway; in addition, chlorotriphenylmethane was isolated in each experiment along with starting material (*ca.* 10%) and triphenylmethanethiol (13-51%).[9] At this time, it is not completely clear why disulfide **3** is absent since it is found in other similar trapping experiments concerning diatomic sulfur transfer[3,6,7,10] however, using an excess of precursors **8**-**11**, (which deliver diatomic sulfur) would account for the production of **5** from **3**. In addition, preliminary experiments in our lab have shown that **3** is substantially converted to tetrasulfide **5** by heating in certain solvents.[11]

SCHEME 2

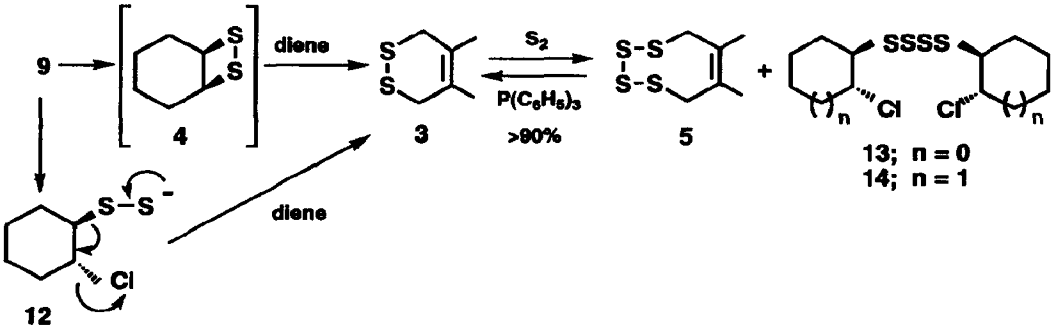


Table. Summary of Trapping Experiments of Adduct 9 with 2,3 -Dimethyl-1,3-Butadiene[a]

Run #	Ratio 9:diene	Solvent	T °C	Time (h)	% Yield 5	% Yield 14
1	1:3	EtOAc	reflux	12	27	41
2	3:1	EtOAc	reflux	10	54[b]	16
3	3:1	CH_2Cl_2	reflux	15	10	62
4	3:1	$CHCl_3$	reflux	15	26	42
5	3:1	C_6H_5Cl	reflux	2	48	20

[a] Over 30 other, similar experiments were carried out with these solvents using adducts **8**, **10** and **11**. Isolated yields of tetrasulfide **5** were somewhat higher with 6-ring adducts **9** and **11**; **11** gave somewhat higher yields of **5** than did **9**. [b] using a 3:1 or 5:1 ratio of **11**:diene gave 63% of **5**.

Acknowledgements

We thank the Natural Science and Engineering Research Council of Canada and the F. C. A. R. (Quebec) for financial support. We are grateful to Dr. Anne-Marie Lebuis (McGill University) for solving the x-ray structures of **10** and **11**.

References

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2. Williams, C. R.; Harpp, D. N.; *Tetrahedron Lett.*, **1991**, *32*, 7651.
3. Abu-Yousef, I. A.; Hynes, R. C.; Harpp, D. N. *Tetrahedron Lett.*, **1993**, *34*, 4289.
4. The x-ray crystallographic structures for the reaction products (**10**, **11**) are reported for the first time; bond angles and lengths are not exceptional; see reference 5. Spectral data for compound **8**: recrystallizing solvent, *n*-pentane; yield, 82%; mp. 99-101°C; ^{1}H-NMR ($CDCl_3$) δ: 1.27-2.40 (m, 7H), 4.30-4.40 (m, 1H), and 7.21-7.70 (m, 15H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 22.02, 28.89, 33.66, 55.25, 65.79, 71.38, 126.95, 127.85, 130.04, and 143.57. Anal. Calc'd for $C_{24}H_{23}ClS_2$: C, 70.18; H, 5.60; S, 15.59. Found: C, 70.65; H, 5.60; S, 16.02. Compound **9**: recrystallizing solvent, *n*-hexane; yield, 85%; mp. 103-104°C; ^{1}H-NMR ($CDCl_3$) δ: 0.85-2.11 (m, 9H), 3.70-3.85 (m, 1H), and 7.15-7.55 (m, 15H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 22.54, 22.75, 28.62, 32.76, 52.78, 62.26, 71.44, 127.00, 127.95, 130.18, and 143.77 ppm. Anal. Calc'd for $C_{25}H_{25}ClS_2$: C, 70.69; H, 5.89; S, 15.08. Found: C, 70.35; H, 6.08; S, 15.09. Compound **10**: recrystallizing solvent, *n*-pentane; yield, 92%; mp 73-74°C; ^{1}H-NMR ($CDCl_3$) δ: 1.52-2.25 (m, 6H), 3.30-3.41 (m, 1H), 4.40-4.42 (m, 1H), and 7.22-7.43 (m, 15H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 22.07, 29.69, 34.33, 59.39, 65.08, 73.29, 127.21, 127.96, 130.34, and 143.23 ppm. Anal. Calc'd for $C_{24}H_{23}ClS_3$: C, 65.11; H, 5.19; S, 21.71. Found: C, 65.32; H, 5.10; S, 21.99. Compound **11**: recrystallizing solvent, *n*-hexane; yield, 87% ; mp. 138-139°C. ^{1}H-NMR ($CDCl_3$) δ: 1.30-1.71 (m, 6H), 2.11-2.21 (m, 2H), 2.83-2.85 (m, 1H), 3.99-4.03 (m, 1H), and 7.17-7.37 (m, 15H) ppm; ^{13}C-NMR ($CDCl_3$) δ : 23.51, 23.88, 30.33, 34.30, 56.49, 61.51, 73.42, 127.14, 127.91, 130.37, and 143.33 ppm. Anal. Calc'd for $C_{25}H_{25}ClS_3$: C, 65.74; H, 5.48; S, 21.04. Found: C, 65.66; H, 5.72; S, 20.70.

5. **X-Ray Data for 11.** Empirical Formula $C_{25}H_{25}ClS_3$, M = 457.11. Monoclinic space group $P2_1/c$, a = 13.934(2), b = 18.171(1), c = 9.518(1) Å, β = 106.607(9)°. V = 2309.4(9) Å^3, Z = 4, D_c = 1.315 Mgm^{-3}, μ = 4.04mm^{-1}, F(000) = 960. Data collected at 295°K on a Nonius CAD4 diffractometer using graphite monochromatized Cu Kα radiation and w-2θ scans to a 2θ max: 144.2°. Reflections measured: 9181; unique: 5114; number of reflections with $I > 3.0\sigma$ (I): 3636. Solution by direct methods; the six-membered ring is disordered over two orientations; hydrogens refined isotropically (except on the disordered ring). The two rings show the same trans stereochemistry. Refinement by full-matrix least-squares 359 parameters and 3636 reflections gave R_f = 0.064, R_w = 0.075 and GoF = 2.75. Compound **10** has also been solved. Selected bond distances and angles: S_1-S_2 = 2.032(2)Å; S_2-S_3 = 2.041(2)Å; S_1-S_2-S_3 = 108.47(8)°; dihedral S_1-S_2-S_3-C_7 = -103.7(2)°; C_1-S_1-S_2-S_3 = 89.2(2)°.

6. a) Harpp, D. N.; MacDonald, J. G. *J. Org. Chem.*, **1988**, *53*, 3812; b) Chew, W.; Harpp, D. N. *Sulfur Letters*, **1993**, *16*, 19; c) Tardif, S. L.; Williams, C. R.; Harpp, D. N., unpublished results.

7. a) Nicolaou, K. C.; Hwang, C.-K.; Duggan, M. E.; Carroll, P. J. *J. Am. Chem. Soc.*, **1987**, *109*, 3801; Nicolaou, K. C.; DeFrees, S. A.; Hwang C. K.; Stylianides, N.; Carroll, P. J.; Snyder, J. P. *J. Am. Chem. Soc.*, **1990**, *112*, 3029; b) Gilchrist, T. L.; Wood, J. E. *J. Chem. Soc. Chem. Commun.*, **1992**, 1460.

8. Spectral data for a) compound **13**: oil; ^{1}H-NMR ($CDCl_3$) δ: 1.56-2.08 (m, 4H), 2.26-2.58 (m, 2H), 3.73-3.88 (m, 1H) and 4.51-4.69 (m, 1H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 22.59, 30.22, 34.79, 59.59 and 65.35 ppm; Anal. Calc'd for $C_{10}H_{16}Cl_2S_4$: C, 35.85; H, 4.78; S, 38.24. Found: C, 35.50; H, 4.49; S, 38.35; b) compound **14**: oil; ^{1}H-NMR ($CDCl_3$) δ: 1.29-1.95 (m, 6H), 2.19-2.40 (m, 2H), 3.18-3.32 (m, 1H) and 4.19-4.25 (m, 1H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 23.87, 24.29, 30.60, 35.07, 56.99, and 61.71 ppm; Anal. Calc'd for $C_{12}H_{20}Cl_2S_4$: C, 39.70; H, 5.51; S, 35.29. Found: C, 40.08; H, 5.33; S, 35.00. It should be pointed out that *3*-sulfur transfers to olefin systems have been reported: Ghosh, T.; Bartlett, P. D. *J. Am. Chem. Soc.*, **1988** *110*, 7499; ref. 10d.

9. Independent experiments show that only about 15% of the theoretical amount of cholortriphenylmethane emerges from silica gel chromatography; the trityl group is likely retained by reaction with siloxy functions in the silica gel. The path by which **10** gives **5** + **13** and **11** gives **5** + **14** is not entirely clear.

10. a) Steliou, K.; Gareau, Y.; Harpp, D. N. *J. Am. Chem. Soc.*, **1984**, *106*, 799; b) Steliou, K.; Salama, P.; Brodeur, D. P.; Gareau, Y. *J. Am. Chem. Soc.*, **1987** *109*, 926; c) Schmidt, M.; Görl, U. *Angew. Chem. Int. Ed. Engl.*, **1987**, *26*, 887; d) Sato, R.; Satoh, S.; Saito, M. *Chem. Lett.*, **1990**, 139.

11. It is clear that cyclic disulfide **3** can undergo cycloreversion to diatomic sulfur and 2,3-dimethyl-1,3-butadiene which, in turn, forms some Diels-Alder addition product; Tardif, S. L.; Harpp, D. N. submitted.

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