

Catalytic Transformations of Thiiranes by the $W(CO)_5$ Grouping. A New Route to Cyclic Polydisulfides

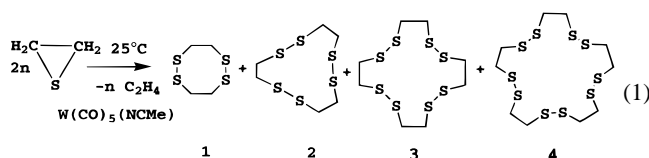
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It is well-known that thiiranes are readily polymerized when treated with a variety of Lewis acids and Lewis bases.¹ When heated, they are readily desulfurized to yield the corresponding olefin.^{1b–d} Desulfurization reactions are promoted by a variety of transition metal complexes and metal surfaces.²

We have now discovered some interesting new transformations of thiirane, 2(*R*),3(*S*)-dimethylthiirane (*cis*-DMT), and 2(*R*),3(*R*)(2(*S*),3(*S*))-dimethylthiirane (*trans*-DMT) by the $W(CO)_5$ group. The reaction of an excess of thiirane with $W(CO)_5(NCMe)$ leads to the formation of the cyclic polydisulfides $(CH_2-CH_2SS)_n$, **1–4**, $n = 2–5$ plus ethylene catalytically, eq 1.^{3,4} Compound **1** is the major product.³ Over a 6 h period at 25



°C, the reaction produced 37.2 turnovers of **1** at a turnover frequency (TOF) of 6.2 h⁻¹. From the reaction, we have been able to isolate the thiirane complex $W(CO)_5(SCH_2CH_2)$ (**5**).⁵ In the presence of the free thiirane, **5** produces the formation of **1–4** at rates comparable to that of $W(CO)_5(NCMe)$; however, no catalysis was observed when $W(CO)_6$ was substituted for the $W(CO)_5(NCMe)$.

(1) (a) Korotneva, L. A.; Belonovskaya, G. P. *Russ. Chem. Rev.* **1972**, *41*, 83. (b) Zoller, U. In *Small Ring Heterocycles*; Hassner, A., Ed.; Interscience: New York, 1983; Part I, Chapter 3. (c) Sander, M. *Chem. Rev.* **1966**, *66*, 297. (d) Dittmer, D. C. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon Press: London, 1984; Vol. 7, Section 5.06.

(2) (a) Adams, R. D.; Babin, J. E.; Tasi, M. *Inorg. Chem.* **1986**, *25*, 4514. (b) Morrow, J. R.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1985**, *4*, 745. (c) Lorenz, I.-P.; Messelauser, J.; Hiller, W.; Conrad, M. *J. Organomet. Chem.* **1986**, *316*, 121. (d) Shunn, R. A.; Fritchie, C. J.; Prewitt, C. T. *Inorg. Chem.* **1966**, *5*, 892. (e) King, R. B. *Inorg. Chem.* **1963**, *2*, 326. (f) Beck, W.; Danzer, W.; Theil, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 582. (g) Roberts, J. T.; Friend, C. M. *J. Am. Chem. Soc.* **1987**, *109*, 7899.

(3) A solution consisting of 2.0 mL of thiirane, 1.0 mL of CH_2Cl_2 , and 10.0 mg of $W(CO)_5(NCMe)$ was allowed to stir at 25 °C for 6 h. After the volatile components were removed, the residue was extracted with CH_2Cl_2 to yield 290.1 mg of residue after removal of the solvent. Separation by TLC on silica gel yielded the following compounds: 190.1 mg of $(CH_2-CH_2SS)_2$,^{4a} **1**; 45.3 mg of $(CH_2CH_2SS)_3$,^{4b} **2**; 17.0 mg of $(CH_2CH_2SS)_4$,^{4c} **3**; 15.2 mg of $(CH_2CH_2SS)_5$, **4**. For **1**, the amount of product is equivalent to 37.2 catalytic turnovers and a turnover frequency of 6.2 h⁻¹. The known compounds **1–3** have been characterized by mass and ¹H NMR spectroscopies.⁴ Compound **4** is new. Spectral data for **4**: ¹H NMR (δ in $CDCl_3$) 3.03 (20 H, s); MS, found (calcd) 460 (460).

(4) (a) Goodrow, M. H.; Musker, W. K. *Synthesis* **1981**, 457. (b) Goodrow, M. H.; Olmstead, M. M.; Musker, W. K. *Tetrahedron Lett.* **1982**, 23, 3231. (c) Crank, G.; Makin, M. I. H. *Aust. J. Chem.* **1984**, *37*, 2331.

(5) $W(CO)_5(SCH_2CH_2)$ (**5**) was obtained in 12% yield from the reaction of $W(CO)_5(NCMe)$ with thiirane in hexane solvent for 48 h at 25 °C by column chromatography using a CH_2Cl_2 /hexane solvent. Spectral data for **5**: IR (ν_{CO} (cm⁻¹) in hexane) 2077(w), 1947(s), 1936(m); ¹H NMR (δ in $CDCl_3$) 2.96 (4 H, ³*J*_{H-Hcis} = 7.75 Hz, ³*J*_{H-Htrans} = -2.72 Hz, ²*J*_{H-H} = 8.23 Hz), 2.68 (4 H, ³*J*_{H-Hcis} = 7.75 Hz, ³*J*_{H-Htrans} = -2.72 Hz, ²*J*_{H-H} = 8.23 Hz).

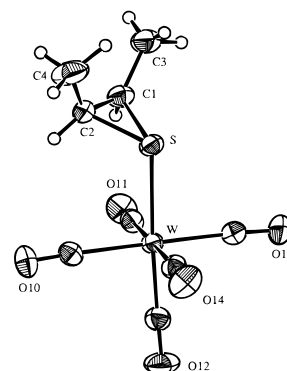
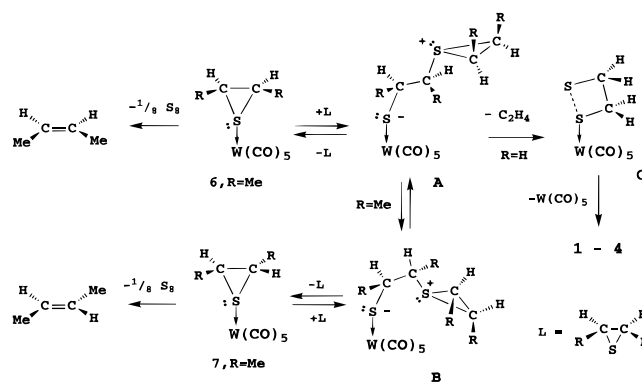


Figure 1. An ORTEP diagram of (2(*R*),3(*S*)-SCHMeCHMe) $W(CO)_5$, **6** showing 40% probability thermal ellipsoids.

Scheme 1



The compounds $W(CO)_5(cis\text{-SCHMeCHMe})$ (**6**) and $W(CO)_5(trans\text{-SCHMeCHMe})$ (**7**) have been obtained from the reactions of $W(CO)_5(NCMe)$ with the appropriate thiirane.⁶ Compound **6** was characterized crystallographically and was found to contain an S-coordinated *cis*-DMT ligand with a pyramidal coordination at the sulfur atom (Figure 1). Pyramidally coordinated thiirane ligands have been characterized previously.⁷ In solution, compounds **6** and **7** slowly decompose to yield sulfur and the corresponding olefin only; however, in the presence of the free thiiranes, compounds **6** and **7** produce a combination of catalytic isomerization and desulfurization to yield mixtures of *cis*- + *trans*-2-butenes.⁸

All of the transformations can be understood within the framework of a series of rearrangements initiated by the addition of a free thiirane to a thiirane ligand in a $W(CO)_5$ complex as shown in Scheme 1. Backside addition of *cis*-DMT to **6** would yield a thiiranium/thiolate zwitterion such as intermediate A.

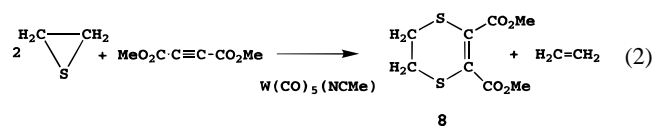
(6) $W(CO)_5(cis\text{-SCHMeCHMe})$ (**6**) was obtained in 37% yield from the reaction of $W(CO)_5(NCMe)$ with 2(*R*),3(*S*)-dimethylthiirane in hexane solvent for 19 h at 25 °C by column chromatography by using a CH_2Cl_2 /hexane solvent. Spectral data for **6**: IR (ν_{CO} (cm⁻¹) in hexane) 2075(w), 1940(vs), 1931(m); ¹H NMR (δ in $CDCl_3$) 3.28 (2H, ³*J*_{H-CH3} = 6.09 Hz, ⁴*J*_{H-CH3} = -0.26, *J*_{CH3-CH3} = 0.05, *J*_{H-H'} = 8.04), 1.55 (6H, ³*J*_{H-CH3} = 6.09 Hz, ⁴*J*_{H-CH3} = -0.26, *J*_{CH3-CH3} = 0.05, *J*_{H-H'} = 8.04). Crystal data: space group = $P2_1/n$, $a = 5.8281(6)$ Å, $b = 18.204(2)$ Å, $c = 11.999(2)$ Å, $\beta = 91.67(1)^\circ$, $Z = 4$, 1720 reflections, $R = 0.024$.

(7) (a) Abel, E.; Cooley, N. A.; Kite, K.; Orrell, K. G.; Sik, V.; Hursthouse, M. B.; Dawes, H. M. *Polyhedron* **1989**, *8*, 887. (b) Amarasekera, J.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1988**, *110*, 2332.

(8) A 20.0 mg amount of **6** was placed in an NMR tube with 500 μ L of CD_2Cl_2 and 500 μ L of 2(*R*),3(*S*)-dimethylthiirane and placed in a water bath at 25 °C for 48 h. The formation of *cis*- and *trans*-2-butene and *trans*-DMT were measured by ¹³C NMR spectroscopy by integration of the appropriate resonances: *cis*-2-butene (127 mg, 2.26 mmol), $\delta = 124.0$ -(2C), 12.4(2C); *trans*-2-butene (25 mg, 0.44 mmol); *trans*-DMT (143 mg, 1.62 mmol). At the end of the period, the NMR tube was emptied and the volatiles were removed. The residue (88.3 mg) was separated by TLC to yield S_8 (40.3 mg, 0.16 mmol), $W(CO)_6$ (4.1 mg), and **6** (10.1 mg).

Rotation about the C–C single bond would yield the intermediate **B** which could generate **7** by release of the *cis*-DMT.⁹ Ligand substitution reactions would release the thiirane isomer. Alternatively, loss of C₂H₄ from **A** (R = H) would yield a SCH₂CH₂S tungsten complex (**C**). Previous studies have shown that thiiranium ions readily eliminate alkene.¹⁰ Although SCH₂CH₂S has not been isolated in the free state,¹¹ a bis-CpMn(CO)₂ complex of SCH₂CH₂S has been described, and it was shown to exhibit a diradical character.¹² The formation of SCH₂CH₂S ligands has also been observed in the reactions of thiirane with the cluster complexes Os₆(CO)_{18–n}(NCMe)_n, *n* = 1, 2.¹³

Evidence for a transient existence of SCH₂CH₂S was obtained by performing this reaction in the presence of MeO₂C≡CCO₂Me.¹⁴ Under these conditions the heterocycle SCH₂CH₂SC(CO₂Me)C(CO₂Me) (**8**) was obtained as the principal product, TOF = 1.5 h⁻¹, eq 2.¹⁴ In the absence of trapping agents, the



SCH₂CH₂S groupings could condense with loss of W(CO)₅ to form the cyclic polydisulfides **1–4**.

(9) Studies have shown that nucleophiles generally add to thiiranes with inversion of configuration,^{14,17} although in our case a *cis*-addition (**6** to **B**) followed by rotation to **A** and *trans*-elimination to yield **7** would produce the same result and cannot be ruled out at this time.

Cyclic disulfides have been shown to exhibit a variety of antimicrobial properties.¹⁶ The ease of this new catalytic thiirane reaction indicates that it could be a practical route for the synthesis of large quantities of these and other cyclic polydisulfides.

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Supporting Information Available: Details of the reactions and characterization of the products, tables of final atomic positional parameters and anisotropic thermal parameters are available for the structural analysis (12 pages). See any current masthead page for ordering and Internet access instructions.

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(10) Bolster, J.; Kellogg, R. M. *J. Chem. Soc., Chem. Commun.* **1978**, 630.

(11) Snyder, J. P.; Carlsen, L. *J. Am. Chem. Soc.* **1977**, 99, 2931.

(12) Braunwarth, H.; Lau, P.; Huttner, G.; Minelli, M.; Günauer, D.; Zsolnai, L.; Jibril, I.; Evertz, K. *J. Organomet. Chem.* **1991**, 411, 383.

(13) Adams, R. D.; Chen, G.; Sun, S.; Wolfe, T. A. *J. Am. Chem. Soc.* **1990**, 112, 868.

(14) It was shown in an independent experiment that the cyclic disulfide **1** does not react with MeO₂C≡CCO₂Me to form **8**.

(15) Troyanskii, E. I.; Strelenko, Y. A.; Demchuk, D. V.; Lutsenko, A. I.; Nikishin, G. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1990**, 5, 1195.

(16) (a) Steliou, K.; Gareau, Y.; Milot, G.; Salma, P. *Phosphorus, Sulfur Silicon Relat. Elem.* **1989**, 43, 209. (b) St. Georgiev, V. *Med. Res. Rev.* **1990**, 10, 371. (c) Nicolaou, K. C.; DeFrees, S. A.; Hwang, C.-K.; Stylianides, N.; Carroll, P. J.; Snyder, J. P. *J. Am. Chem. Soc.* **1990**, 112, 3029. (d) Gmelin, R.; Susilo, R.; Fenwick, G. R. *Phytochemistry* **1981**, 20, 2521. (e) *Merck Index*, 10th ed.; Merck & Co., Inc.: Rahway, NJ, 1983; entries 4301 and 9166 and references therein.

(17) Helmkamp, G. K.; Schnautz, N. *Tetrahedron* **1958**, 2, 304.