ries.[10,11] The electron count for **3b** is the same as for **2a**, but the Os_4SC_2 cluster core has adopted the form of a capped trigonal prism with the atom C(13) serving as the capping atom.[14] Surprisingly, this cluster also does not obey the EAN rule.[10c]

The changes in the metal atom framework that accompany the overall transformation **2** → **3** → **4** are shown schematically in Figure 3. This novel rearrangement begins by the cleavage of the diametrically opposed metal–metal bonds Os(1)–Os(4) and Os(2)–Os(3) in **2**. For **2a** → **3a** the transformation is spontaneously reversible, but the energy barrier is surprisingly large, ΔG^*_{295} = 18.6 kcal/mol. The transformation of the compounds **3** into **4** is accomplished by the loss of 1 mol of CO and the formation of the Os(2)–Os(4) bond. A major consequence of the transformation is that the alkyne and sulfido ligands are shifted to opposite sides of the cluster in **4**. Also, it is significant to observe that the metal atoms which exhibited the order 1-2-3-4 in **2** were permuted into the order 1-2-4-3 by the rearrangement.

In a recent report Johnson proposed a theory based on single-edge cleavage processes to explain the polyhedral interconversion of cluster compounds. The facile double-edge cleavage observed in the transformation of **2** into **4** shows that more complex mechanisms must also be considered.[16]

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Supplementary Material Available: Tables of crystal data, atomic coordinates and thermal parameters, and selected interatomic distances and angles for both structural analyses (14 pages); tables of structure factor amplitudes (54 pages). Ordering information is given on any current masthead page.

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(14) Compound **3b** contains 18 cluster valence electrons and both the trigonal prismatic and the dodecahedral polyhedra are consistent with this electron count. The addition of the capping vertex to the cluster of **3b** should not change the electron count.[15]

(15) Mingos, D. M. P.; Forsyth, M. I. *J. Chem. Soc., Dalton Trans.* **1977**, 610.

(16) Johnson, B. F. G. *J. Chem. Soc., Chem. Commun.* **1986**, 27.

Diatomic Sulfur (S_2)

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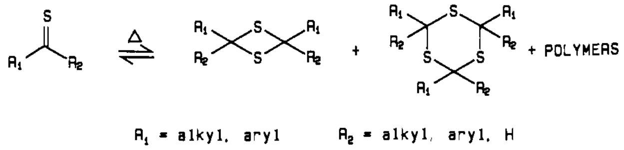
Recently, we described a group 14 metal assisted procedure for the preparation and Diels–Alder trapping of S_2,[1] a highly reactive diatomic form of elemental sulfur. Our continuing efforts in this area have led us to develop an alternate synthetic method that affords this reactive dienophile by, to our knowledge, an unprecedented intramolecular carbon–carbon bond-forming reaction.

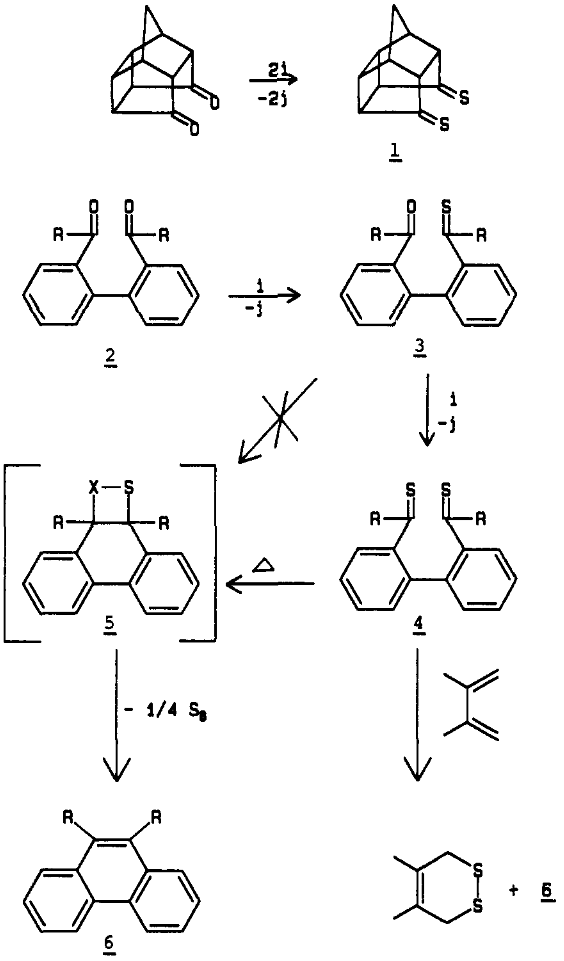
Although nonenolizable thiones, and in particular thioaldehydes, thermally undergo reversible dimerization or trimerization in "head to tail" fashion (Scheme I),[2] thermal condensations resulting from "head to head" combinations are not known to take place.[2a,b,e] In anticipation that certain conformationally restricted bis(thiocarbonyl) derivatives could be encouraged to experience such additions, we developed methodology[3] for the specific preparation of this novel class of compound (Scheme II). Unfortunately, caged dithiones such as **1**[3] were discovered to be too labile for any useful synthetic study.

Scheme I



R_1 = alkyl, aryl R_2 = alkyl, aryl, H

Scheme II



i = $(Me_3Si)_2S$ + 2/3 BCl_3 j = 2 Me_3SiCl + 1/3 B_2O_3

a) R = Ph, X = S   b) R = p-C_6H_4OMe, X = S

c) R = OMe, X = S   d) R = Ph, X = O

Table I. Calculated (Observed) Heats of Formation from AMPAC[6a,b]

struct	Hamiltonian	ΔH	struct	Hamiltonian	ΔH
S=O		(1.50)[6c]	**5a**	MINDO/3	184.80
S=S		(30.68)[6c]	**5c**	MINDO/3	-17.17
3a	MINDO/3	128.26	**5d**	MINDO/3	126.88
4a	MINDO/3	184.66	**6a**	AM1	116.89
4c	MINDO/3	-20.13	**6c**	AM1	-12.39

We have been able to apply this sulfurating methdology to the preparation of the novel *o,o'*-biphenyl thione derivatives **3**[4] and **4**[4] (Scheme II). Monothione derivatives **3a** and **3b** (blue) are quite

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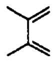
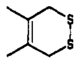
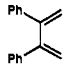
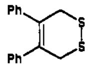
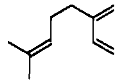
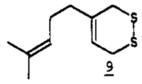
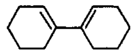
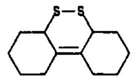
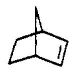
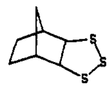
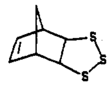
(1) Steliou, K.; Gareau, Y.; Harpp, D. N. *J. Am. Chem. Soc.* **1984**, *106*, 799.

(2) (a) Field, L. *Synthesis* **1978**, 713. (b) Fraser, P. S.; Robbins, L. V.; Chilton, W. S. *J. Org. Chem.* **1974**, *39*, 2509. (c) Campaigne, E. *Chem. Rev.* **1946**, *39*, 1. (d) Duus, F. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: New York, 1978; Vol. 3, p 373. (e) Vedejs, E.; Eberlein, T. H.; Mazur, D. J.; McClure, C. K.; Perry, D. A.; Ruggeri, P. R.; Schwartz, E.; Stults, J. S.; Varie, D. L.; Wilde, R. G.; Wittenberger, S. *J. Org. Chem.* **1986**, *51*, 1556 and references cited therein.

(3) Steliou, K.; Mrani, M. *J. Am. Chem. Soc.* **1982**, *104*, 3104.

Table II. S_2 Products Prepared According To Scheme II

olefin	product	isolated[4] % yield	mp, °C
	 7	60	oil
	 8	85	101-102
	 9	75	oil
	 10	70	oil
	 11	85	oil
	 12	75	30-31

stable. However, upon formation, their corresponding bis(thiocarbonyl) analogues **4a** and **4b** (intense blue) spontaneously eject S_2 to give, through the likely intermediacy of **5a** and **5b**, a quantitative yield of the 9,10-biphenylsubstituted derivatives **6a**[4] and **6b**,[4] respectively.

Our expectation that this carbon–carbon bond-forming reaction[5] would yield the formation of S_2, and possibly even the formation of S=O, was based on molecular modeling[6a] and calculated[6b] heats of formation for compounds **3**–**6**, S_2, and S=O (see Table I). For example, a ΔH of −37.09 kcal/mol is predicted for the conversion of **4a** into **6a** and S_2. The postulated intermediate **5a** (surprisingly calculates to virtually the same ΔH as **4a**) could not be isolated for complete characterization.[7a] In order to obtain a derivative of **4** that could be isolated and then subsequently and independently converted into **6** and S_2, dithione ester **4c**[4,7b] (yellow) was prepared. However, even after refluxing in xylene for 48 h, **4c** could not be converted into **6d**. Indeed, a ΔH of 38.00 kcal/mol is calculated to be required for extrusion of S_2 from this compound. On the other hand, even though a ΔH of −9.87 kcal/mol is calculated for the conversion of **3a** into **6a** and S=O, this reaction also failed to proceed in refluxing toluene for 3 days to any measurable extent. Although intermediate **5d** (similar to what was found for **5a**) is calculated to have nearly the same ΔH as its precursor **3a**, the entropy values for these processes cannot be ascertained and it is likely, due to lesser degrees of freedom and ring strain, that the actual energy barrier (ΔG) posed by intermediates **5** is poorly estimated when considering only the heats of formation.[7c] Nonetheless, the results of the above experiments suggest that this type of calculation can serve as a good predictive indicator for the feasibility of the overall reaction process and hopefully will help lead us to the design of a stable dithione derivative that could also, upon gentle heating, be used to generate S_2 at will.

As with the organometallic route,[1] evidence for the formation of diatomic sulfur was obtained by Diels–Alder trapping (Table II). Since S_2 is generated from **4a** or **4b** at the temperature at which these dithiones are prepared (80–131 °C), the Diels–Alder trapping is considerably more efficacious than that observed at the temperature range (0–44 °C) possible by the organometallic route. For example, S_2 generated according to Scheme II in refluxing toluene reacts with 2,3-diphenylbutadiene to give an 85% isolated yield of 3,6-dihydro-4,5-diphenyl-1,2-dithiin. This is a substantial improvement to the 20% yield obtained by the previous method.[1] Similarly, at these higher temperatures (80–110 °C), S_2 smoothly reacts with norbornene and norbornadiene to afford trisulfides **11** and **12** in 85% and 75% isolated yields (based on S_2), respectively. Interestingly, no trace of the possible [4 + 2]-type adduct with norbornadiene and S_2 (one of many products obtained from the reaction with "activated" elemental sulfur)[8] was noted. This further supports our findings that the chemistry of diatomic sulfur is clean and different from that observed from the multitude of reactive sulfur species formed in "activated" elemental sulfur.[5c–e]

The ability to generate S_2 conveniently, and at temperatures more conductive to Diels–Alder trapping, makes it synthetically more attractive to use. The present procedure should therefore, find widespread application in the synthesis of 1,2-dithiins.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Natural Sciences and Engineering Research Council of Canada for support of this research.

Registry No. 3a, 105930-72-1; **3b**, 105930-73-2; **4a**, 105930-74-3; **4b**, 105930-75-4; **4c**, 105930-78-7; **5a**, 105930-76-5; **5b**, 105930-77-6; **5c**, 105930-80-1; **5d**, 105930-81-2; **6a**, 602-15-3; **6b**, 103162-61-4; **6c**, 13935-65-4; **7**, 18655-88-4; **8**, 34804-73-4; **9**, 73188-23-5; **10**, 88157-92-0; **11**, 38738-37-3; **12**, 105930-79-8; S_2, 23550-45-0; $CH_2{=}C(CH_3)C(CH_3){=}CH_2$, 513-81-5; $CH_2{=}C(Ph)C(Ph){=}CH_2$, 2548-47-2; $(CH_3)_2C{=}CH(CH_2)_2C({=}CH_2)CH{=}CH_2$, 123-35-3; 1-(1-cyclohexenyl)cyclohexene, 1128-65-0; norbornene, 498-66-8; norbornadiene, 121-46-0.

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(4) New compounds were analyzed by combustion or HRMS analyses.

(5) (a) Although metal[5b] or photochemically[5c,d] induced reactions of this type are known, this is the first example of carbon–carbon bond formation by extrusion of trapable S_2 (characterized by Diels-Alder trapping).[5e] An analogous example for O_2 elimination (unseccessfully trapped) has been reported by Vogel.[5f] (b) See, for example: Bran J.; Lazzlo, P. *Tetrahedron Lett.* **1985**, *26*, 5135. Campaigne, E.; Reid, W. B., Jr. *J. Am. Chem. Soc.* **1946**, *68*, 769. (c) See, for example: Jahn, R.; Schmidt, U. *Chem. Ber.* **1975**, *108*, 630. (d) Orahovatz, A.; Levinson, M. I.; Caroll, P. J.; Lakshmikantham, M. V.; Cava, M. P. *J. Org. Chem.* **1985**, *50*, 1550. (e) Although others claim to have processes that yield S_2, no evidence for the formation of this reactive species by chemical trapping has been demonstrated. In the Schmidt[5c] reaction, the sulfurated products obtained are more consistent with those expected from "activated" elemental sulfur (see references cited in ref 1). (f) Vogel, E.; Markowitz, G.; Schmalstieg, L.; Itô, S.; Breuckmann, R.; Roth, R. W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 719.

(6) (a) MODEL (an enhanced graphics interactive version of Allinger's MM2 molecular mechanics program (Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127)) and MMPM (obtained from Serena Software, Bloomington, IN 47701) were used to generate preminimized structures for the AMPAC (Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902; available from Indiana's University Quantum Chemistry Program Exchange as program number 506) calculations. (b) We have found that the AM1 Hamiltonian in the AMPAC program gives better heats of formation for hydrocarbons and for compounds containing single carbon–sulfur bonding. Although the AM1 Hamiltonian is not parameterized for sulfur, the default MNDO parameters that are used for this element, in conjunction with the AM1 parameters for H, C, and O, appear to give good values (compared to reported values) for the heats of formation of a plethora of organo sulfides that we have looked at. On the other hand, the MINDO/3 Hamiltonian performs better for compounds containing C=S, S—S, S—O, and S=O type bonds (cf.: Harpp, D. N., presented in part at the XII Symposium on Organic Sulfur Chemistry, Nijmegen, The Netherlands, June 1986). (c) *Handbook of Chemistry and Physics*, 67th ed., Weast, R. C., Ed.; C. R. C.: Cleveland, OH, 1986–1987; p D-87.

(7) (a) Although these compounds show up on TLC as a bright blue spot that is slightly more mobile than that of the corresponding monosulfurated analogues, isolation results in rapid loss of the blue color and the product collected analyzes as a mixture of elemental sulfur (S_8) and the corresponding 9,10-biphenyl substituted derivative. (b) This compound was prepared in low yield (5%) by using Lawesson's reagent (Pedersen, B. S.; Scheibye, S.; Clausen, K.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 293) in refluxing xylene. Our sulfurating methodology[1] tolerates the presence of this functionality which is often a desirably used protecting group. (c) A recent report (Lown, J. W.; Koganty, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 3811) involving a 1,2-oxathietane intermediate shows that such a species undergoes rapid cycloreversion in which carbonyl and thiocarbonyl fragments are preferentially formed.

(8) We thank Prof. P. D. Bartlett (Texas Christian University) for sharing with us some of his unpublished results.