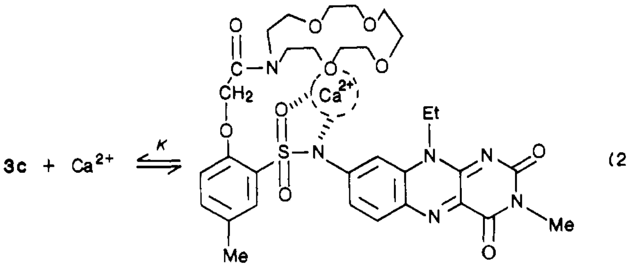
Table I. Quantum Yields (Φ_{ox}) for Photooxidation of Benzyl Alcohol by **3** and 3-Methyl-10-ethylisoalloxazine[a]

solvent	$[Ca(ClO_4)_2]$/ mM	Φ_{ox}/% 3c	3a	3-methyl-10-ethylisoalloxazine
water (pH 3.5)	0	0.60	0.64[b]	3.34
water (pH 7.5)	0	0.04	ca. 1 × 10^{-3}[b]	2.47
MeCN	0	0.05	0.04	0.08
MeCN	0.199	0.08	0.07	
MeCN	1.01	0.13	0.07	
MeCN	2.55	0.20	0.08	

[a] Three-Milliliter aliquots of the substrate solutions in a 1-cm quartz cell were deaerated and were irradiated under nitrogen at room temperature with a 300-W high-pressure Hg lamp. The extraneous lines of the lamp other than 366 nm were filtered out:[21] [**3**] = 2.00 × 10^{-4} M, [benzyl alcohol] = 5.00 × 10^{-2} M. [b] Neutral **3a** was sparingly soluble in water, so that the photooxidation was carriedout in 40 vol % aqueous acetonitrile.

nm for **3c**), while in alkaline aqueous solution they gave a red color similar to roseoflavin (λ_{max} 476 nm for **3a**, 478 nm for **3b**, and 485 nm for **3c**). The pK_a values for the dissociation of the 8-sulfonamide groups (eq 1) were determined spectrophotometrically at 30 °C: pK_a = 4.85 for **3a**, 4.93 for **3b**, and 5.54 for **3c**. The results show that the higher the pK_a, the more the λ_{max} shifts to longer wave-lengths.[19]

In an aqueous system the absorption spectra of **3a–c** were unaffected by the addition of alkali and alkaline earth metal cations. In acetonitrile the absorption spectra of **3a** and **3c** were scarcely affected by the addition of these metal cations (as perchlorate salts) but **3c** gave a new absorption band at 452 nm on the addition of $Ca(ClO_4)_2$ which increased with increasing Ca^{2+} concentration (Figure 1). This is probably due to the "lariat effect" by which the dissociation of the 8-sulfonamide group is facilitated to serve as a cap for the Ca^{2+} ion bound to the crown cavity. The association constant (K) was estimated to be 4.27 × 10^4 M^{-1} from a plot of OD_{452} vs. $[Ca(ClO_4)_2]$.



(2)

In order to examine the potential correlation between the spectral change and the oxidizing ability, we carried out the anaerobic photooxidation of benzyl alcohol.[20] The results (Table I) indicate that (i) in an aqueous system the quantum yields (Φ_{ox}) for neutral **3a** and **3c** (at pH 3.5) were greater by 16–640-fold than those for the corresponding anionic species (at pH 7.5), whereas the Φ_{ox} for 3-methyl-10-ethylisoalloxazine was scarcely affected by mediam pH; (ii) the Φ_{ox} values in acetonitrile are smaller by more than 1 order of magnitude than those in an aqueous system; and (iii) most importantly, the Φ_{ox} for **3c** increases with increasing Ca^{2+} concentration but that for **3a** increases only slightly. Fact i suggests that the photooxidizing ability of the anionic **3** is significantly quenched by the intramolecular charge transfer from the dissociated 8-sulfonamide group. On the other hand, fact iii is well correlated with the spectral data: that is, Ca^{2+} ion bound to the crown cavity of **3c** induces the spectral change and enhances the photooxidizing ability.[22] Conceivably, Ca^{2+} ion can suppress the intramolecular charge transfer through the interaction with the 8-sulfonamide anion serving as a cap for this metal cation.

In conclusion, this paper demonstrated that in **3c** the crown ether moiety serving as an allosteric site can induce the activity change in the flavin moiety serving as a catalytic site. The close imitation of natural control mechanisms suggests that in a sense **3c** is a well-constructed miniature of "allosteric" enzymes.

Acknowledgment. We are indebted to Dr. M. Ohnishi for the quantum-yield determinations. We thank Professor M. Takagi for helpful discussions. This research was supported by a grant from the Ministry of Education of Japan.

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(19) We also found that the absorption and fluorescence spectra are sensitively affected by the solvent effect. For example, a plot of the fluorescence quantum yield (Φ_f) for neutral **3c** vs. $E_T(30)$ showed a linear relationship (r = 0.98) as expressed by $\Phi_f = 1.07E_T(30) - 0.017$.

(20) A standard actinometer (potassium trioxalatoferrate(III)) was used for the quantum-yield determinations on the photochemical reaction of **3** (2.00 × 10^{-4} M) and benzyl alcohol (5.00 × 10^{-2} M). The further details of the experimental method were described previously.[21]

(21) Shinkai, S.; Nakao, H.; Ueda, K.; Manabe, O.; Ohnishi, M. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1632.

(22) It is known that conventional flavins interact with certain metal cations such as Mg^{2+} and Zn^{2+} in aprotic solvents (e.g., acetone and acetonitrile).[23-27] However, the association constants are so small (K = ca. 10^2 M^{-1}) that the effects are observed only in the presence of a large excess of the metal cations (ca. 0.10 M).

(23) Hemmerich, P.; Müller, F.; Ehrenberg, A. In *Oxidase and Related Redox Systems*; King, T. E., Mason, H. S., Morrison, M., Eds.; Wiley: New York, 1965; p 157.

(24) Shinkai, S.; Nakao, H.; Ueda, K.; Manabe, O. *Tetrahedrrn Lett.* **1984**, *25*, 5295.

(25) Shinkai, S.; Nakao, H.; Tsuno, T.; Manabe, O.; Ohno, A. *J. Chem. Soc., Chem. Commun.* **1984**, 849.

(26) Shinkai, S.; Nakao, H.; Honda, N.; Manabe, O. *J. Chem. Soc., Perkin Trans. 1*, in press.

(27) Fukuzumi, S.; Kuroda, S.; Tanaka, T. *J. Am. Chem. Soc.* **1985**, *107*, 3020.

Cluster Framework Rearrangements. An Unusual Transformation of a Butterfly Cluster into a Rhombus. The Crystal and Molecular Structures of $Os_4(CO)_{12}(\mu_3\text{-}S)(\mu\text{-}HC_2R)$, R = Ph and CO_2Me

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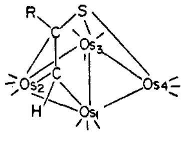
The ability of transition-metal cluster compounds to undergo structural transformations of their metal frameworks has been shown to play an intimate and important role in their chemistry.[1,2] Most frequently these transformations are induced by ligand additions or eliminations, but they can also be induced by ligand transformations. Some recent reports have been described unusual examples of dynamically rapid degenerate rearrangements.[3]

In our recent studies we have observed the formation of the unusual butterfly cluster complexes $Os_4(CO)_{12}[\mu_4\text{-}\eta^3\text{-}SC(R){=}CH]$ (**1a,b** R = Ph, CO_2Me) by the insertion of terminal alkynes into a metal–sulfur bond in the cluster compound $Os_4(CO)_{12}(\mu_3\text{-}S)$.[4] When refluxed in octane solvent, these compounds are decarbo-



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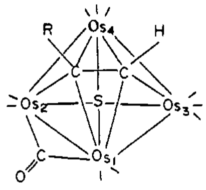

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(1) Vahrenkamp, H. *Adv. Organomet. Chem.* **1983**, *22*, 169.

(2) Johnson, B. F. G.; Lewis, J. *Philos. Trans. R. Soc. London, A* **1982**, *No. 308*, 5.

(3) (a) Adams, R. D.; Horvath, I. T.; Wang, S. *Inorg. Chem.* **1986**, *25*, 1617. (b) Martin, L. R.; Einstein, F. W. B.; Pomeroy, R. K. *J. Am. Chem. Soc.* **1986**, *108*, 338.

(4) Adams, R. D.; Wang, S. *Organometallics* **1985**, *4*, 1902.

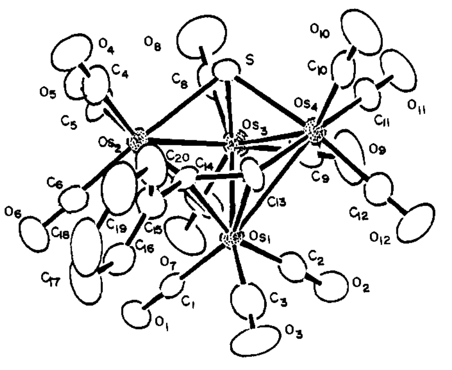

Figure 1. ORTEP diagram of $Os_4(CO)_{12}(\mu_3\text{-}S)(\mu_3\text{-}HC_2Ph)$ (**2a**) showing 50% probability thermal ellipsoids.

nylated and are transformed into the new complexes $Os_4(CO)_{11}(\mu_4\text{-}S)(\mu_4\text{-}HC_2R)$ (**4a**,**b**, R = Ph, CO_2Me) that contain a rhombohedral arrangement of metal atoms with quadruply bridging sulfido and alkyne ligands on opposite sides of the cluster.[5]

We have now isolated and characterized two intermediates that show in great detail a remarkable rearrangement of the metal atom framework that has accompanied the transformation of **1** into **4**. When an octane solution of compound **1a** was heated to reflux for 20 min, two red isomers with the formula $Os_4(CO)_{12}(\mu_3\text{-}S)(\mu\text{-}HC_2R)$, R = Ph, **2a** (33%) and **3a** (8%), in addition to **4a** (50%), were obtained.[6] When the solution is heated, **2a** and **3a** can both be converted into **4a**. Compound **3a** can be regenerated rapidly by the addition of CO to **4a**.[6] **2a** and **3a** slowly interconvert in solution and exist in a 1.0/3.1 equilibrium mixture at 22 °C. However, they can be separated in a pure form chromatographically. When an octane solution of **1b** was heated to reflux for 1 h, it was converted into a mixture of **2b** (25%) and **4b** (62%), R = CO_2Me.[7] Only traces of compound **3b** were observed, but **3b** was made in 97% yield by the addition of CO to **4b**. The structural similarities of **2a** with **2b** and **3a** with **3b** are indicated by their IR and ^1H NMR spectra.

The molecular structure of **2a** was established by a single-crystal X-ray diffraction analysis. An ORTEP drawing of its structure is shown in Figure 1.[8] The molecule consists of a "butterfly" cluster of four osmium atoms with triply bridging sulfido and alkyne ligands on the two open triangular faces.[9] If one defines the cluster to include the four metal atoms, the sulfur atom, and the two acetylenic carbon atoms, it has the form of a deltahedron with one vertex missing, specifically, a *nido*-dodecahedron. This structure can be rationalized by the polyhedral skeletal electron pair (PSEP) theory (SEP = 9)[10] or the topological electron-counting (TEC) theory (TEC = 72)[11] but cannot be explained by use of the effective atomic number (EAN) rule.[10c]

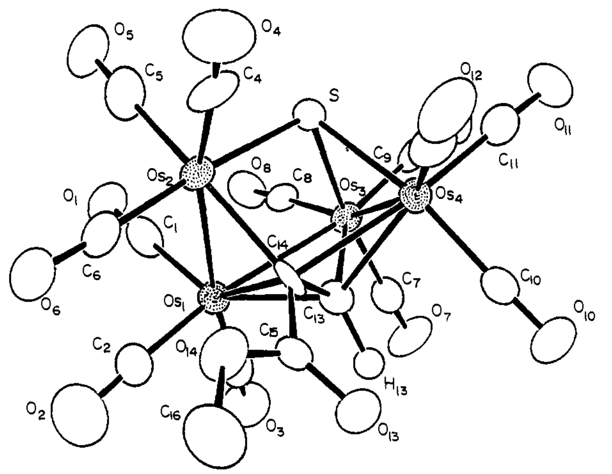

Figure 2. ORTEP diagram of $Os_4(CO)_{12}(\mu_3\text{-}S)(\mu_4\text{-}HC_2CO_2Me)$ (**3b**) showing 50% probability thermal ellipsoids.

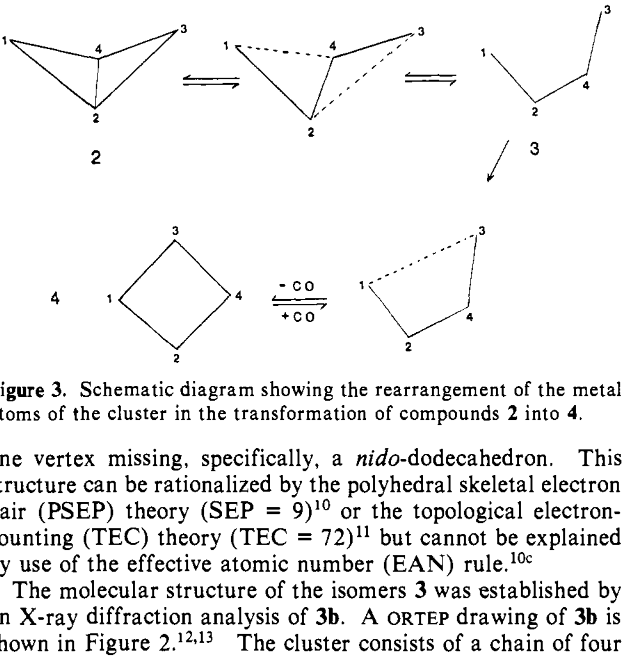

Figure 3. Schematic diagram showing the rearrangement of the metal atoms of the cluster in the transformation of compounds **2** into **4**.

The molecular structure of the isomers **3** was established by an X-ray diffraction analysis of **3b**. A ORTEP drawing of **3b** is shown in Figure 2.[12,13] The cluster consists of a chain of four metal atoms connected by three metal–metal bonds. The interactions Os(1)–Os(2) = 2.784 (1) Å, Os(1)–Os(3) = 2.907 (1) Å, and Os(3)–Os(4) = 2.802 (1) Å are at normal bond lengths, but the interactions Os(1)···Os(4) = 3.813 (1) Å, Os(2)···Os(3) = 4.056 (1) Å, and Os(2)···Os(4) = 3.420 Å are too long to permit a significant amount of bonding. The sulfido ligand is triply bridging, but the alkyne ligand is a quadruple bridge. The structure of **3b** can be rationalized by the PSEP and TEC theo-

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[5] Adams, R. D.; Wang, S. *Organometallics* **1986**, *5*, 1272.

[6] The products were separated by TLC on silica gel with a 20% CH_2Cl_2/80% hexane solvent mixture. IR spectra are as follows (ν(CO) cm^{-1} in hexane): **2a**, 2105 w, 2070 vs, 2064 s, 2058 s, 2042 vw, 2018 m, 2006 m, 1997 m; **3a**, 2103 vw, 2075 s, 2065 vs, 2051 vw, 2043 s, 2017 vs, 2001 w, 1985 w, 1974 w. ^1H NMR (δ in $CDCl_3$): **2a**, 10.38 (s, 1 H), 7.02–7.77 (m, 5 H); **3a**, 11.79 (s, 1 H), 7.16–7.66 (m, 5 H). Compounds **2a** and **3a** slowly isomerize to a 1.0/3.1, **2a**/**3a** equilibrium mixture in $CDCl_3$ at 22 °C over several days. The addition of CO (at 1 atm) to **4a** proceeds rapidly (10 min in CH_2Cl_2) to yield **3a** (100%).

[7] The products were separated by TLC on silica gel with a 30% CH_2Cl_2/70% hexane solvent mixture. IR spectra (ν(CO) cm^{-1} in hexane): **2b**, 2109 w, 2075 vs, 2068 s, 2061 s, 2028 m, 2021 m, 2004 m, 1992 w, 1984 w, 1715 vs br; **3b**, 2109 w, 2090 w, 2081 s, 2069 vs, 2046 s, 2028 w, 2018 s, 2004 w, 1991 vw, 1980 vw, 1710 w br. ^1H NMR (δ in $CDCl_3$): **2b**, 11.11 (s, 1 H), 3.92 (s, 3 H); **3b**: 11.61 (s, 1 H), 3.79 (s, 3 H). The addition of CO (1 atm) to a CH_2Cl_2 solution of **4b** at 25 °C resulted in the formation (10 min) of **3b** (97%).

[8] Red crystals of **2a** were grown from hexane solutions at 0 °C. Space group: $P2_1/c$, $a = 7.7164$ (6) Å, $b = 17.552$ (2) Å, $c = 18.727$ (3) Å, $\beta = 99.62$ (1)°, $Z = 4$, $\rho_{calcd} = 3.27$ g/cm³. Diffraction data were collected on an Enraf-Nonius CAD-4 automatic diffractometer using Mo Kα radiation. The structure was solved by direct methods (MULTAN) and was refined (2625 reflections) to the final values of the residuals $R = 0.035$ and $R_w = 0.037$. Structure-solving programs from the Enraf-Nonius SDP-Plus program library were used on a Digital Equip. Corp. PDP 11/60 computer. The data were corrected for absorption.

[9] Selected interatomic distances (Å) are as follows: Os(1)–Os(2) = 2.904 (1), Os(1)–Os(3) = 2.911 (1), Os(1)–Os(4) = 2.943 (1), Os(2)–Os(3) = 2.908 (1), Os(3)–Os(4) = 3.083 (1), Os(1)–C(13) = 2.284 (14), Os(1)–C(14) = 2.277 (14), Os(4)–C(13) = 2.103 (12), Os(2)–C(14) = 2.102 (14), Os(2)–S = 2.432 (3), Os(3)–S = 2.382 (4), Os(4)–S = 2.406 (4), C(13)–C(14) = 1.43 (2).

[10] (a) Wade, K. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: New York, 1980. (b) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311. (c) Johnson, B. F. G.; Benfield, R. E. In *Topics in Stereochemistry*; Geoffroy, G. L.; Wiley: New York, 1981; Vol. 12.

[11] (a) Teo, B. K. *Inorg. Chem.* **1984**, *23*, 1251. (b) Teo, B. K. *Inorg. Chem.* **1984**, *23*, 1257.

[12] Red crystals of **3b** were grown from CH_2Cl_2/hexane solutions by cooling to 0 °C. Space group: $P2_1/n$, $a = 9.949$ (2) Å, $b = 13.709$ (8) Å, $c = 16.816$ (4) Å, $\beta = 92.24$ (2)°, $Z = 4$, $\rho_{calcd} = 3.52$ g/cm³. Diffraction data were collected on an Enraf-Nonius CAD4 automatic diffractometer. Data processing was performed by using the Enraf-Nonius SDP program library on a Digital Equipment Corp. VAX 11/782 computer. The structure was solved by direct methods and was refined (2695 reflections) to the final values of the residuals $R = 0.035$ and $R_w = 0.038$. The data were corrected for absorption.

[13] Selected interatomic distances (Å) and angles (deg) for **3b** are as follows: Os(1)–Os(2) = 2.784 (1), Os(1)–Os(3) = 2.907 (1), Os(3)–Os(4) = 2.802 (1), Os(1)···Os(4) = 3.813 (1), Os(2)···Os(3) = 4.056 (1), Os(2)···Os(4) = 3.420 (1), Os(1)–C(13) = 2.179 (4), Os(1)—C(14) = 2.286 (13), Os(2)–C(14) = 2.171 (15), Os(3)–C(13) = 2.156 (13), Os(4)–C(13) = 2.288 (13), Os(4)–C(14) = 2.378 (13), C(13)–C(14) = 1.45 (2); Os(2)–Os(1)–Os(3) = 84.09 (2), Os(1)–Os(3)–Os(4) = 90.52 (2).

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]

Acknowledgment. These studies were supported by the Office of Basic Energy Sciences of the US Department of Energy. We thank Johnson-Matthey for a loan of osmium tetraoxide.

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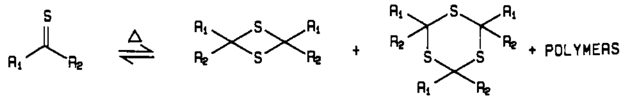
Recently, we described a group 14 metal assisted procedure for the preparation and Diels–Alder trapping of S_2,[1] a highly reactive diatomic form of elemental sulfur. Our continuing efforts in this area have led us to develop an alternate synthetic method that affords this reactive dienophile by, to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

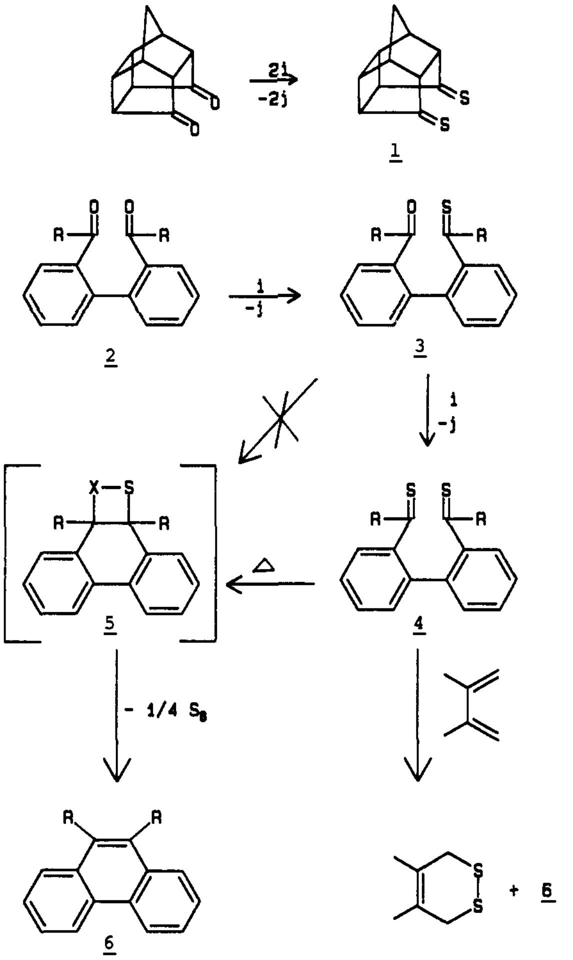
We have been able to apply this sulfurating methdology to the preparation of the novel *o,o'*-biphenyl thione derivatives **3**[4] and **4**[4] (Scheme II). Monothione derivatives **3a** and **3b** (blue) are quite

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

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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.

0002-7863/87/1509-0926$01.50/0