MHz, $CDCl_3$) δ 7.15 (dd, 1 H, J = 5.2, 1.2 Hz, C-5 thiophene H), 6.93 (dd, 1 H, J = 3.4, 5.2 Hz, C-4 thiophene H), 6.84 (ddd, 1 H, J = 3.4, 1.2, 1.9 Hz, C-3 thiophene H), 4.61, 4.60 (AB, 2 H, J = 6.6 Hz, OCH_2O), 3.81-3.74 (m, 2 H, CH_2OMOM), 3.36 (s, 3 H, OCH_3), 3.02, 2.98 (AB, 2 H, J = 14.6 Hz, $CH_2C(2)$), 2.94 (s, 1 H, OH), 1.98-1.73 (m, 2 H, CH_2CH_2OMOM), 1.23 (s, 3 H, CCH_3); ^{13}C NMR (500 MHz, $CDCl_3$) 139.7, 127.4, 127.0, 124.8, 97.0, 72.4, 65.1, 55.9, 43.3, 39.8, 26.9.

Acknowledgment. This work was supported by research grant CHE-8912745 from the National Science Foundation to whom we are grateful. We thank Professor Rick Danheiser for calling our attention to the relevant work of Arens and co-workers.

Registry No. **1**, 35761-83-2; **2d**, 693-02-7; **2f**, 78592-82-2; **2g**, 73448-13-2; **3f**, 132462-00-1; **4f**, 132462-01-2; **5a**, 132461-84-8; **5b**, 132461-85-9; **5c**, 132461-86-0; **5d**, 138659-72-0; **5e**, 132461-87-1; **5f**, 132462-02-3; **5i**, 138059-73-1; **6a**, 132461-88-2; **6b**, 132461-89-3; **6c**, 132461-91-7; **6d**, 138659-74-2; **6dD**, 138059-75-3; **6e**, 132491-02-2; **6j**, 132461-92-8; **7l**, 593-60-2; **8l**, 138059-76-4; **9l**, 138059-77-5; **10l**, 138059-78-6; **10m**, 138059-79-7; **10n**, 138059-80-0; **11l**, 138059-81-1; **11m**, 138059-82-2; **11n**, 138059-83-3; **12m**, 138059-84-4; **12n**, 116118-62-8; **13l**, 138059-85-5; **13m**, 138059-86-6; **13n**, 138059-87-7; **14**, 78592-73-1; **15**, 138059-88-8; **16**, 138059-89-9; **17**, 138059-90-2; **18**, 132461-98-4; **19**, 132461-99-5; **21**, 138059-91-3; **22**, 138059-92-4; **23**, 138059-93-5; (*Z*)-**25**, 132461-95-1; (*E*)-**25**, 132461-94-0; (*E*)-**26**, 132461-96-2; (*Z*)-**26**, 132461-97-3; **27**, 598-19-6; **28**, 138059-94-6; **29**, 138089-50-6; **30**, 138059-95-7; **31**, 138059-96-8; **32**, 138059-97-9.

Supplementary Material Available: Experimental procedures for **3c**, **3d**, **3g**, **3h**, **4c**, **4d**, **4g**, **4h**, **5b-d**, **5g-i**, **6c**, **6e**, **8m**, **8n**, **9m**, **9n**, **10m**, **10n**, **11m**, **11n**, **12n**, **13m**, and **13n** (9 pages). Ordering information is given on any current masthead page.

Does Diatomic Sulfur (S_2) React as a Free Species?

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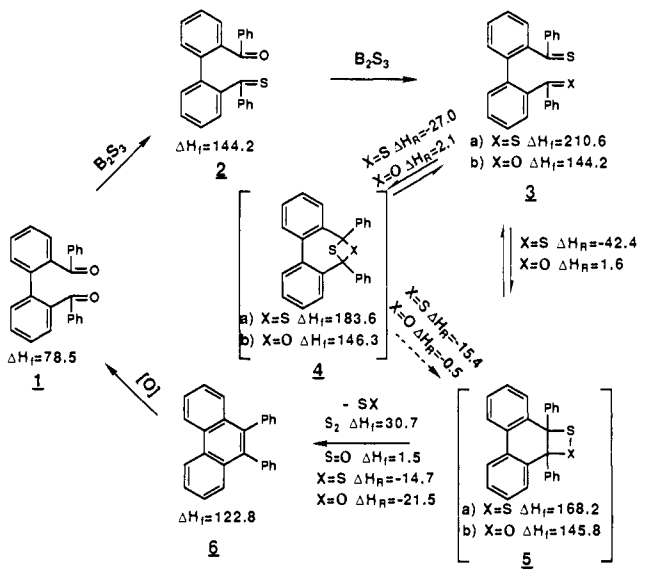
Contribution from the Department of Chemistry, University of Montreal, Montreal, Quebec, Canada H3C 3J7. *Received August 28, 1991*

Abstract: A detailed study into the design and synthesis of stable 1,2-dithietane derivatives for the generation of diatomic sulfur (S_2) was undertaken. Computer-aided evaluation of enthalpic differences was used to direct the synthesis of target compounds and, although all of the compounds calculated to afford S_2 that were prepared did yield diatomic sulfur, an isolable 1,2-dithietane other than dithiatopazine failed to materialize. The results of this study provide convincing evidence that the computational procedure outlined can be successfully used to predict the course of S_2 extrusion pathways from potential dithionocarbonylated derivatives. To determine if the disulfide moiety found in the Diels-Alder adduct derived from the addition of diatomic sulfur to conjugated 1,3-dienes is due to a transference mechanism involving the transient 1,2-dithietane intermediate, a chiral nonracemic binaphthyl source of S_2 was prepared. Reactions of S_2 from this source with chiral nonracemic and prochiral conjugated 1,3-dienes indicate that the added disulfide moiety would be inconsistent with a transference mechanism and that a "free" acting S_2 unit is more likely to be involved.

Recently we described a synthetically useful method[1] based on favorable enthalpic considerations (Scheme I) for generating diatomic sulfur (S_2). Although the proposed pathway for the S_2 extrusion implicated a transient 1,2-dithietane intermediate **5a** derived from the labile 2,2'-bis(thiobenzoyl)biphenyl (**3a**), evidence for the formation of the 4-membered cyclic disulfide (an unknown class of compounds) was by inference only.[1] Nicolaou and co-workers,[2] however, were subsequently able to prepare and isolate the first example of a stable 1,2-dithietane (Scheme II), dithiatopazine (**7**), and show by trapping experiments using 2,3-diphenylbutadiene that it also extrudes the S_2 fragment. Unfortunately, other sulfurated products (**10**) which are not produced using the biphenyl route and which may be construed as having been derived from the addition of activated elemental sulfur,[1,3] an alternate mode of sulfur extrusion,[4] are also formed in significant yield.

In both the biphenyl route[1] and the Nicolaou[2] approach, it is possible that the S_2 fragment added to 1,3-dienes might be entirely due to a transference process that directly involves the 1,2-dithietane intermediate as opposed to a "free" acting S_2 species (Scheme III). A similar type of exchange (Scheme IV) has recently been proposed by Ghosh and Bartlett[5] to be operative in the addition of S_3 to norbornene. If the transference mechanism is correct, it would have important and useful stereochemical implications in the construction of chiral 1,2-dithiins. Since several examples of 1,2-dithiins are reported to have anti-AIDS properties[6]

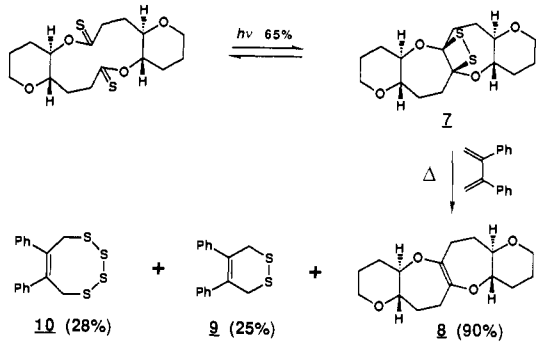
Scheme I



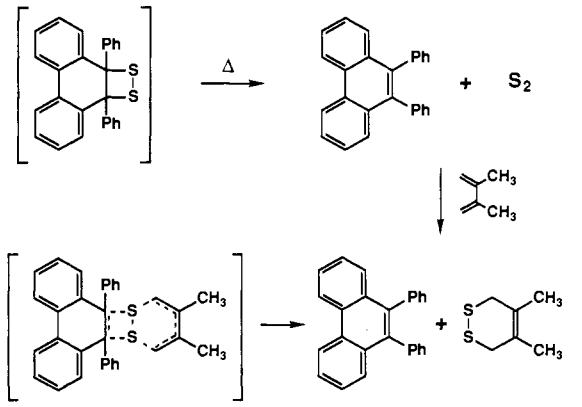
(1) Steliou, K.; Salama, P.; Brodeur, D.; Gareau, Y. *J. Am. Chem. Soc.* **1987**, *109*, 926.
(2) Nicolaou, K. C.; Hwang, C.-K.; Duggan, M. E.; Carroll, P. J. *J. Am. Chem. Soc.* **1987**, *102*, 3801.
(3) Elvidge, J. A.; Jones, S. P.; Peppard, T. L. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1089.
(4) Harpp, D. N. *Perspectives in the Organic Chemistry of Sulfur*; Zwanenburg, B., Klunder, A. J. H., Eds.; Elsevier: Amsterdam, 1987; pp 1-22.
(5) Ghosh, T.; Bartlett, P. D. *J. Am. Chem. Soc.* **1988**, *110*, 7499.

0002-7863/92/1514-1456$03.00/0

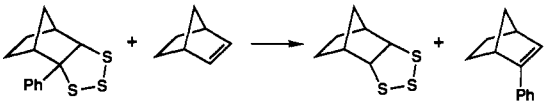
Scheme II



Scheme III



Scheme IV

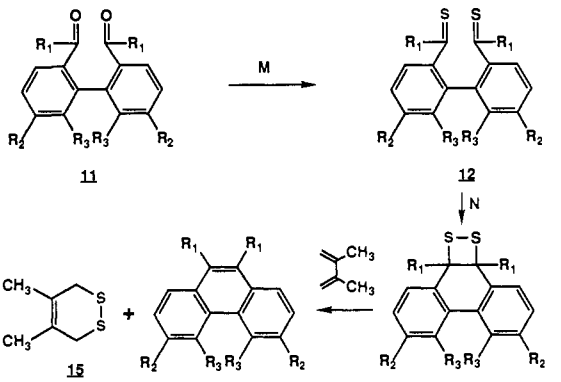


and since interest in the fundamental aspects of S_2 chemistry is now becoming widespread,[7-14] we designed and carried out the following set of experiments in an attempt to prepare other 1,2-dithietanes potentially capable of S_2 extrusion and report herein on the results of this study.

Results and Discussion

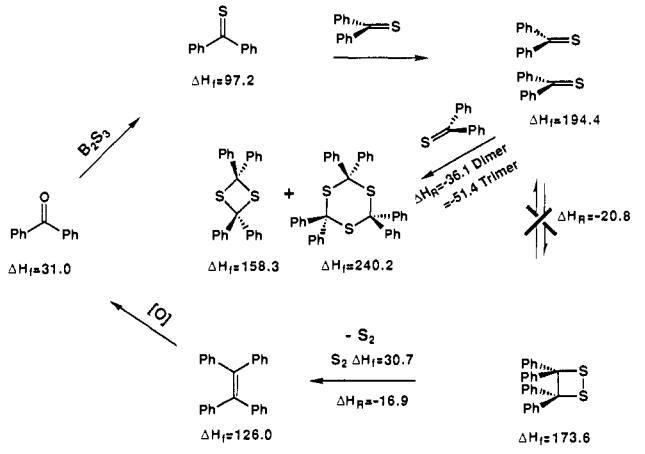
The biphenyl route to S_2 offers several possible sites for modulating the S_2 extrusion process, and we chose to concentrate our efforts on steric and/or electronic effects. Thus, biphenylated derivatives **11a–i** (Scheme V) were prepared and sulfurated using activated B_2S_3[15] for the ketonyl derivatives and Lawesson's[16a]

Scheme V



	R_1	R_2	R_3	M	N	% 15
a)	Ph	H	H	B_2S_3	Δ	70
b)	Ph	H	Me	B_2S_3	Δ	65
c)	1-naphthyl	H	H	B_2S_3	Δ	60
d)	9-anthracyl	H	H	B_2S_3, L.R.	Δ	0
e)	*p*-Cl-C_6H_4	H	H	B_2S_3	Δ	65
f)	*p*-MeO-C_6H_4	H	H	B_2S_3	Δ	65
g)	Ph	-C_4H_4-		B_2S_3	Δ	30
h)	*p*-Me_2N-C_6H_4H		H	B_2S_3	Δ	60
i)	*p*-Me-C_6H_4-S	H	H	L.R.	Δ	0
j)	EtO	H	H	L.R	*hv*	0

Scheme VI

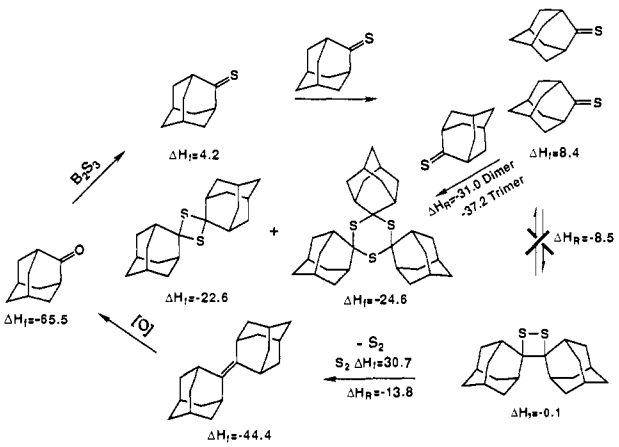


reagent (or a modification of it)[16b] for the carboxylated analogues which are inert to B_2S_3 thionation. (Compound **11d** could not be sulfurated by either method.) All of the biphenylated thioketonyl derivatives **12a–h** (except **12d**, which could not be made) thermally eject an S_2 fragment that can be captured in Diels–Alder fashion with 2,3-dimethyl-1,3-butadiene. Although the thermal ejection of S_2 from **12i** also occurs, the ejected S_2 fragment could not be trapped in this example because Lawesson's reagent preferentially reacts with the 1,3-diene[16a] during the in situ thionation process. With compound **12j**, S_2 extrusion requires photochemical conditions.[7,14] However, even though **12j** desulfurates in high yield, in our hands, no sulfurated adduct could be made in the presence of the conjugated diene. Also, and unfortunately, none of the biphenylated analogues in Scheme V led to a 1,2-dithietane (**13**) that could be isolated or spectroscopically identified in the reaction mixture. Therefore, we next considered making modifications to the biphenyl system itself.

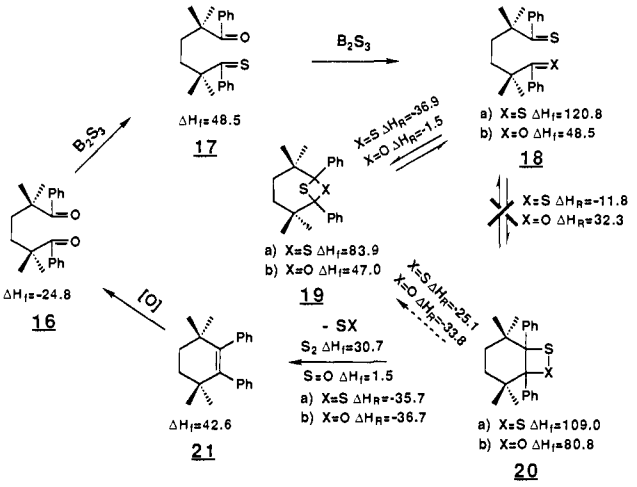
Since a random approach to such modifications would be fortuitously dependent and an exhaustive systematic substitution pattern impractical to undertake, the computer-aided technique that successfully led to the design of the biphenyl route to S_2 extrusion was used to help guide and select our synthetic targets.

(6) (a) Steliou, K.; Gareau, Y.; Milot, G.; Salama, P. *Phosphorus, Sulfur Silicon Relat. Elem.* **1989**, *43*, 209. (b) Freeman, F.; Kim, D. S. H. L.; Rodriguez, E. *Sulfur Rep.* **1989**, *9*, 207.
(7) Steliou, K.; Gareau, Y.; Harpp, D. N. *J. Am. Chem. Soc.* **1984**, *106*, 799.
(8) Jahn, R.; Schmidt, U. *Chem. Ber.* **1975**, *108*, 630.
(9) Orahovatz, A.; Levinson, M. I.; Carroll, P. J.; Lakshmikanthan, M. V.; Cava, M. P. *J. Org. Chem.* **1985**, *50*, 1550.
(10) Bartlett, P. D.; Ghosh, T. *J. Org. Chem.* **1987**, *52*, 4937.
(11) Schmidt, M.; Görl, U. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 887.
(12) (a) Ando, W.; Kumamoto, Y.; Tokitoh, N. *Tetrahedron Lett.* **1987**, *28*, 4833. (b) Ando, W.; Sonobe, H.; Akasaka, T. *Tetrahedron Lett.* **1987**, *28*, 6653.
(13) Harpp, D. N.; MacDonald, J. G. *J. Org. Chem.* **1988**, *53*, 3812.
(14) (a) Nicolaou, K. C.; Hwang, C.-K.; de Frees, S. D.; Stylianides, N. A. *J. Am. Chem. Soc.* **1988**, *110*, 4868. (b) Niolaou, K. C.; de Frees, S. D.; Hwang, C.-K.; Stylianides, N. A.; Carroll, P. J.; Snyder, J. P. *J. Am. Chem. Soc.* **1990**, *112*, 3029. (c) Nicolaou, K. C.; Hwang, C.-K.; Marron, B. E.; de Frees, S. D.; Couladouros, E. A.; Abe, Y.; Carroll, P. J.; Snyder, J. P. *J. Am. Chem. Soc.* **1990**, *112*, 3041.
(15) Steliou, K.; Mrani, M. *J. Am. Chem. Soc.* **1982**, *104*, 3104.
(16) (a) Pedersen, B. S.; Scheibye, S.; Clausen, K.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 293. (b) Yokoyma, M.; Hasegawa, Y.; Hatanaka, H.; Kawazoe, Y.; Imamoto, T. *Synthesis* **1984**, 827.

Scheme VII



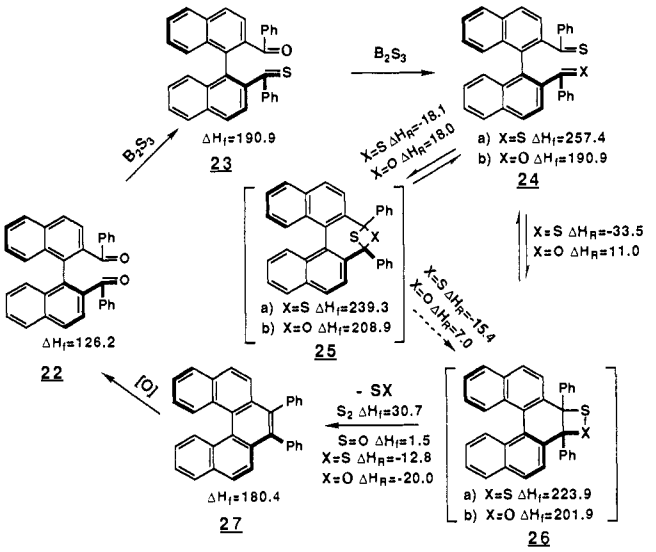
Scheme VIII



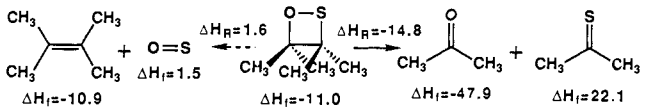
The computational protocol[1,14b,c] for S_2 extrusion is one that we are the first to advocate[1] and entails the following procedure. Each intermediate is conformationally searched for its global minimum conformer on the MM2-based[17] energy hypersurface using the algorithms of the MODEL[18] set of programs. The geometry of this conformer, with no further optimization, is then subjected to an enthalpic evaluation in the AMPAC[19] program using the AM1 Hamiltonian. The significance of this procedure of calculation is that, on a digital MicroVAX II work station, it generally takes CPU minutes instead of CPU hours and days if further geometry "optimization" is requested. More importantly, the AMPAC "optimized" results do not correlate with the experimental observations as depicted.

The expected preference for the head-to-tail dimerization (**4a**, Scheme I) of the thiocarbonyl units in **3a**, on the basis of literature precedent,[20] is correctly calculated to be less favored than the head-to-head (1,2-dithietane **5a**) dimerization inferred. To verify that the calculated enthalpic stability of the 1,2-dithietanes over the corresponding 1,3 isomers is not coincidental, benzothiophenone (Scheme VI) and adamantanethione (Scheme VII), which are known to dimerize and trimerize in strict head-to-tail fashion,[20] were subjected to the same computational procedure. Both systems yield the observed products by calculation. To further test the integrity of the computational method, structural

Scheme IX



Scheme X



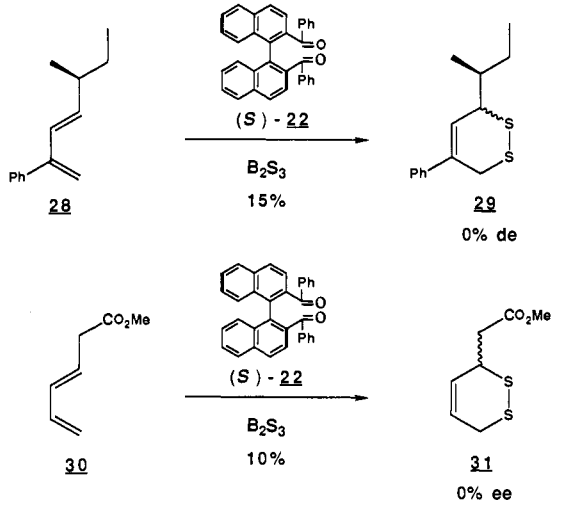
modifications (Schemes VIII and IX) founded on the successful biphenyl analogy were experimentally undertaken. Whenever the 1,3-dithietane is calculated to be enthalpically more stable than the 1,2 isomer (**19a** vs **20a**, Scheme VIII), S_2 extrusion from these systems cannot be experimentally achieved.[21] On the other hand, in the examples where the 1,2-dithietane (**5a** vs **4a**, Scheme I and **26a** vs **25a**, Scheme IX) is computed to be preferred, S_2 extrusion occurs spontaneously. It is also worth noting that the monothiocarbonyl intermediates in these thermally directed reactions can also undergo dimerization, and where they are calculated to be more stable than the uncoupled material (**18b** vs **19b**, Scheme VIII), the resulting oxathietane derivatives can indeed by isolated.[21] Although, in principle, the 1,2-oxathietane coupled product can also extrude S=O, with these examples, this does not take place. The uncoupled material or the 1,3-oxathietane (as calculated) is always found to be the more stable entity. Again, it can be demonstrated that the calculated predictions are not coincidental. Consistent with experimental findings,[22] 3,3,4,4-tetramethyl-1,2-oxathietane is correctly predicted (Scheme X) to favor cycloreversion (−14.8 kcal/mol) into acetone and thioacetone. The formation of tetramethylethylene with concomitant S=O extrusion (1.6 kcal/mol) is not observed.

Thus, the calculations in each case correlate well with experiment and suggest that this procedure can be used to successfully predict elimination, dimer-/trimerization, or cycloreversion. However, one should keep in mind that the computational analysis evaluates only systemic thermodynamic properties and offers no insight as to what the intermediate kinetic or entropic preferences for the ultimate reaction process might be.

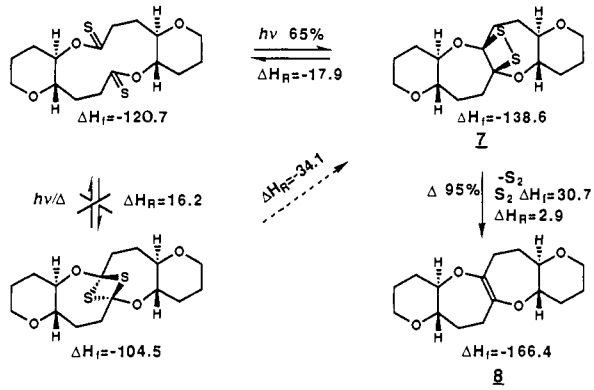
Since the above-designed systems did not yield an isolable 1,2-dithietane, the binaphthyl strategy shown in Scheme IX was specifically conceived to take advantage of the inherent dissymmetry of the binaphthyl molecule and thereby offer an alternative method for testing the plausibility of the transference mechanism. If a free S_2 species is first ejected and then trapped by addition to the diene, an optically active form of the binaphthyl 1,2-dithietane intermediate **26a** (Scheme IX) would exert no preference

(17) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. QCPE 395.
(18) Prof. K. Steliou, Department of Chemistry, University of Montreal, Montreal, Quebec, Canada H3C 3J7.
(19) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. QCPE 506.
(20) (a) Field, L. *Synthesis* **1978**, 713. (b) Fraser, P. S.; Robins, L. V.; Chilton, W. S. *J. Org. Chem.* **1974**, *39*, 2509. (c) Mikolajczyk, M.; Kielbasinski, P. *J. Org. Chem.* **1977**, *42*, 2347. (b) Sundermeyer, W. *Synthesis* **1988**, 349.
(21) During the course of our investigation in this series of compounds, an unsuccessful attempt to generate S_2 using this logic was published. See: Ishii, A.; Nakayama, J.; Ding, M. X.; Kotaka, N.; Hishino, M. *J. Org. Chem.* **1990**, *55*, 2421.
(22) Lown, J. W.; Koganty, R. P. *J. Am. Chem. Soc.* **1986**, *108*, 3811.

Scheme XI



Scheme XII



toward any diastereomeric or enantiomeric selectivity with chiral or prochiral 1,3-dienes. On the other hand, if the S_2 is intimately transferred to the diene, as suggested by Scheme III, then some diastereomeric and/or enantiomeric selectivity would be reasonable to expect.

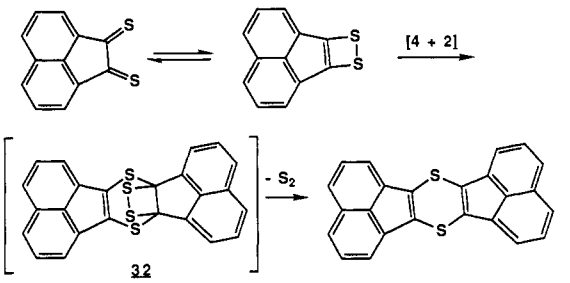
Thus, when the (*S*)-binaphthyl diketone **22** was treated with activated B_2S_3[15] in the presence of the (+) enantiomer of diene **28** (Scheme XI), the expected Diels–Alder adduct **29** was obtained in 15% yield with no preferential diastereomeric excess. Similarly, the prochiral diene **30** gave a 10% yield of a racemic mixture of the adduct **31**. (The low chemical yield for the S_2 adducts is due to the poor sulfuration yield of the binaphthyl diketone **22**. The yields are 60 and 50%, respectively, if the biphenyl diketone **1** is used instead.) The same results were obtained with the *R* enantiomeric form of the binaphthyl reagent so that any mismatched "reagent-like" control can be ruled out.[23] Therefore, from these experimental observations, it is unlikely that the transference mechanism is viable, and a "free" acting S_2 species is more likely to be the sulfurating agent involved.

The only known example of a non-biphenyl type 1,2-dithietane that extrudes trappable S_2 is dithiatopazine **7** (Scheme XII).[14b,c] It should be noted that Cava and co-workers[8] were actually the first group to describe a thioketal type intermediate (**32**) in which S_2 is ejected (Scheme XIII), but they did not record any trapping evidence for this form of sulfur.

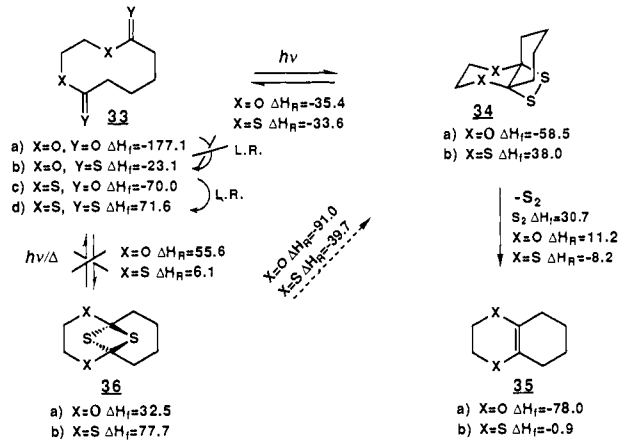
In anticipation that other stable dithiatopazine-like analogues for S_2 extrusion could be made, a series of synthetically accessible acyclic and cyclic esters were prepared by the coupling of various α,ω-diols with acid chlorides. Although several of the targeted thionoesters are predicted to extrude S_2, in our hands, except for the phenyl esters (entries **1j**, **1u**, and **1ee** in Table I), the required

(23) Masamune, S.; Choy, W.; Petersen, J. S.; Sita, L. R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1.

Scheme XIII



Scheme XIV



perthionation of the remaining esters could not be achieved. The bis-thionated phenyl esters which could be made, surprisingly, do not undergo the photochemical coupling (possibly due to unfavorable entropy factors). On the other hand, since thionation of thiol esters is less problematic than esters, compound **33c**[24] (Scheme XIV) and the thiol ester analogues of entries **1d**, **1k** **1o**, and **1v** listed in Table I were prepared and successfully perthionated with Lawesson's reagent.[16a] However, once again, photochemical or thermal coupling of the thiocarbonyl units, even under prolonged (48 h) conditions, does not occur. Thus, for reasons not yet clearly understood, the stability of dithiatopazine[2,14] is unique to the 1,2-dithietane class of compound.

Summary

The results of this study demonstrate that computational techniques can be successfully applied to formulating strategies for S_2 extrusion from 1,2-dithietane intermediates. Although a stable 1,2-dithietane (other than dithiatopazine) remains elusive, the experimental observations with the chiral binaphthyl system, described herein, do not support a transference mechanism for S_2 additions to 1,3-dienes. A "free" reactive S_2 species, on the other hand, would be consistent with all of the experimental results obtained from this work and with those from previous studies.[25]

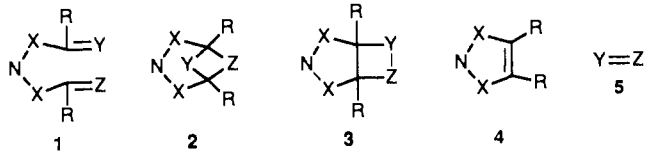
Experimental Section

All reactions were carried out under an atmosphere of argon. Solvents and reagents were used as obtained from commercial sources. Nuclear magnetic resonance spectra were recorded on a Varian VXR-300 spectrometer, and chemical shifts are reported as δ values (ppm) relative to internal tetramethylsilane. Significant ^{1}H NMR data are tabulated in the following order: number of protons, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad), and coupling constants (in hertz). Infrared spectra were recorded on a Perkin-Elmer Model 781 grating spectrometer, calibrated with the 1602 cm^{-1} band of a polystyrene film. Optical rotations were measured on a Perkin-Elmer Model 241 automatic polarimeter using the D band of sodium for the light source. Mass spectra were obtained with a VG Micromass-1212 (chemical ion-

(24) Although dilute reaction conditions were used to prepare these diolides, careful mass spectral analyses indicated that the cyclic compounds formed are dimers and not monomers.

(25) Steliou, K.; Gareau, Y.; Milot, G.; Salama, P. *J. Am. Chem. Soc.* **1990**, *112*, 7819.

Table I. Enthalpy Calculations of Dithiatopazine Analogues



						ΔH_f, kcal/mol				
entry	N	R	X	Y	Z	1	2	3	4	5
a	C_2H_4	Me	O	O	O	−179.8				
b	C_2H_4	Me	O	O	S	−103.3	−82.3	−71.0	−70.4	1.5
c	C_2H_4	Me	O	S	S	−26.7	−33.8	−42.3	−70.4	30.7
d	C_2H_4	Me	S	S	S	60.8	42.5	43.5	8.6	30.7
e	C_2H_4	CF_3	O	O	O	−455.2				
f	C_2H_4	CF_3	O	O	S	−375.3	−356.6	−345.0	−351.6	1.5
g	C_2H_4	CF_3	O	S	S	−295.4	−303.0	−310.9	−351.6	30.7
h	C_2H_4	Ph	O	O	O	102.3				
i	C_2H_4	Ph	O	O	S	−22.6	−6.3	9.4	5.2	1.5
j	C_2H_4	Ph	O	S	S	58.3	42.4	41.1	5.2	30.7
k	C_2H_4	Ph	S	S	S	137.2	113.5	121.6	76.0	30.7
l	C_3H_6	Me	O	O	O	−186.7				
m	C_3H_6	Me	O	O	S	−110.1	−85.1	−70.8	−72.0	1.5
n	C_3H_6	Me	O	S	S	−33.3	−38.8	−44.2	−72.0	30.7
o	C_3H_6	Me	S	S	S	52.2	38.6	41.7	14.4	30.7
p	C_3H_6	CF_3	O	O	O	−462.5				
q	C_3H_6	CF_3	O	O	S	−382.7	−360.8	−345.0	−354.6	1.5
r	C_3H_6	CF_3	O	S	S	−302.6	−309.8	−312.6	−354.6	30.7
s	C_3H_6	Ph	O	O	O	−109.2				
t	C_3H_6	Ph	O	O	S	−28.7	−8.0	8.8	3.1	1.5
u	C_3H_6	Ph	O	S	S	51.4	38.1	36.0	3.1	30.7
v	C_3H_6	Ph	S	S	S	130.0	110.4	122.6	75.9	30.7
w	C_6H_4	Me	O	O	O	−119.9				
x	C_6H_4	Me	O	O	S	−40.4	−29.3	−20.4	−13.9	1.5
y	C_6H_4	Me	O	S	S	38.5	23.4	8.7	−13.9	30.7
z	C_6H_4	CF_3	O	O	O	−391.0				
aa	C_6H_4	CF_3	O	O	S	−308.1	−300.8	−289.9	−292.2	1.5
bb	C_6H_4	CF_3	O	S	S	−228.1	−244.2	−255.7	−292.2	30.7
cc	C_6H_4	Ph	O	O	O	−39.4				
dd	C_6H_4	Ph	O	O	S	40.0	46.7	57.9	59.0	1.5
ee	C_6H_4	Ph	O	S	S	120.9	99.2	89.5	59.0	30.7

ization (CI); low resolution) and an AEI MS-902 or Kratos MS-50 TCSA (electron impact and FAB; high resolution) mass spectrometers. Significant mass spectra data are tabulated as m/z (intensity expressed as percent total ion current). Flash chromatography was performed according to the literature procedure[26] using E. Merck silica gel 230–400 mesh size. Satisfactory combustion analyses and/or high-resolution mass spectral data were obtained for all of the new compounds prepared.

Conformational searches were performed using MODEL ver KS 2.96 for interactively generating an MM2[17] MODEL minimized structure that was fed into the BAKMDL (ver KS 2.96) sister program using the default settings for a mixed (bonds and Cartesians) Monte Carlo search.[18] All nonterminal rotatable bonds in acyclic components of a structure (having no hydrogens or lone pairs) and all ring bonds for the cyclic components were selected for analysis. MODEL was then used to submit the global minimum conformer found from each of these searches (using a Cartesian format with no geometry optimization under the AM1 Hamiltonian) to the AMPAC[19] program.

2,2′-Dibenzoylbiphenyl (11a) was prepared according to the method of Bacon and Lindsay,[27a] and 2,2′-dibenzoyl-6,6′-dimethylbiphenyl (**11b**) according to Yamada and Akimoto.[27b]

2,2′-Bis(1-naphthoyl)biphenyl (11c). To a solution of 1-bromonaphthalene (600 μL, 4.2 mmol) in anhydrous THF (30 mL) kept under an atmosphere of argon at −78 °C (dry ice/acetone) was added 1.7 mL (4.4 mmol) of a 2.6 M hexanes solution of *n*-butyllithium. After the mixture was stirred for 30 min, a THF (10 mL) solution of diphenic acid dichloride[27c] (560 mg, 2 mmol) was quickly added and the reaction mixture allowed to warm to ambient temperature. The reaction mixture was quenched with H_2O (20 mL), and the whole was transferred to a separatory funnel. The organic phase was separated and washed with H_2O until neutral, dried ($MgSO_4$), and flash evaporated. Recrystallization of the resulting residue in CH_2Cl_2/hexanes afforded 460 mg (50%) of a white solid: mp 190–192 °C (lit.[27d] mp 200 °C); IR ($CHCl_3$) 1660 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 195.4 (C=O); MS (CI) m/z $M^+ + 1$, 463.

2,2′-Bis(9-anthroyl)biphenyl (11d) was prepared as per **11c** in a similar yield: mp >250 °C dec; IR ($CHCl_3$) 1670 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 200.03 (C=O), 143.95, 136.24, 135.04, 133.57, 132.65, 130.95, 130.07, 128.70, 128.29, 128.04, 127.17, 126.33, 125.67, 125.29; HRMS calcd for $C_{42}H_{26}O_2$ m/z 562.1933, found 562.1906.

2,2′-Bis(4-chlorobenzoyl)biphenyl (11e)[27d] was prepared (yield 40%) by the general method described by Mullins:[27m] mp 132–134 °C (lit.[27d] mp 139–140 °C); IR ($CHCl_3$) 1665 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 196.03 (C=O), 139.91, 139.27, 137.57, 135.39, 131.57, 131.43, 130.28, 129.05, 128.21, 126.85; ^1H NMR ($CDCl_3$) δ 7.21–7.37 (16 H, m); $HRMS_{FAB}$ calcd for $C_{26}H_{16}Cl_2O_2$ m/z 431.0534, found 431.0606.

2,2′-Bis(4-methoxybenzoyl)biphenyl (11f)[27e] was prepared (yield 45%) by the general method described by Mullins:[27m] mp 147–147.5 °C (lit.[27e] mp 147 °C); IR ($CHCl_3$) 1660 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 195.9 (C=O), 163.1 (COMe), 139.6–113.1 (11 C), 55.2; HRMS calcd for $C_{28}H_{22}O_4$ m/z 422.1518, found 422.1527.

2,2′-Dibenzoyl-1,1′-binaphthyl (11g, 22). A solution of (*S*)-1,1′-binaphthyl-2,2′-dicarboxylic acid[27f] (2.11 g, 6 mmol) in thionyl chloride (30 mL) was refluxed for 5 h. Excess thionyl chloride was removed under vacuum, and the residue was taken in dry methylene chloride (10 mL), transferred to a flask containing a cooled (0 °C) solution of 2-pyridinethiol (1.66 g, 15 mmol) and Et_3N (5 mL, 30 mmol) in dry methylene

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chloride (50 mL), and left to sit overnight. The reaction mixture was then transferred to a separatory funnel and washed with 1.0 N NaOH (2 × 15 mL) and H_2O (3 × 15 mL). The organic phase was separated, dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The resulting residue was then flash chromatographed ($AcOEt/C_6H_6$ 2:8) to afford 2.15 g (85%) of the dithiol ester as a yellow solid: mp 143–145 °C dec; IR ($CHCl_3$) 1700 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 189.6 (C=O), 151.62, 150.0, 136.9, 135.61, 134.66, 134.55, 133.1, 130.47, 128.93, 127.99, 127.93, 127.70, 127.28, 124.20, 123.21; $[\alpha]^{23}_D$ +60° (c = 1.0, $CHCl_3$) for the *S* enantiomer, $[\alpha]^{23}_D$ −57.5° (c = 1.0, $CHCl_3$) for the *R* enantiomers; HRMS calcd for $C_{32}H_{20}N_2O_2S_2$ m/z 528.0966, found 528.0950.

To a cooled (−10 °C) solution of the above dithiol ester (2.15 g, 4.07 mmol) in dry THF (100 mL) was added 9 mL (9 mmol) of a 1 M THF solution of PhMgBr. After the reaction was stirred for 1 h at −10 °C, the excess Grignard was destroyed by the dropwise addition of 10 mL of a saturated aqueous solution of NH_4Cl, and the reaction mixture was concentrated by rotary evaporation. The resulting residue was then taken up in CH_2Cl_2 (50 mL), transferred to a separatory funnel, and washed with 6 N HCl (2 × 15 mL), 3 N NaOH (2 × 15 mL), and H_2O (2 × 15 mL). The organic phase was separated, dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. Recrystallization of the resulting residue in CH_2Cl_2/hexanes afforded 1.16 g (62%) of a colorless solid, and concentration of the mother liquor followed by flash chromatography of the residue afforded an additional 0.34 g (18%) for a total of 1.50 g (80%) of the desired diketone: mp 128–129 °C; IR ($CHCl_3$) 1670 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 196.99 (C=O), 137.28, 136.51, 136.0, 133.90, 133.63, 132.07, 129.83, 128.13, 127.91, 127.46, 127.33, 127.10, 126.71, 125.52; $[\alpha]^{23}_D$ −152.4° (c = 1.0, $CHCl_3$) for the *S* enantiomer, $[\alpha]^{23}_D$ +155.0° (c = 1.0, $CHCl_3$) for the *R* enantiomer; HRMS calcd for $C_{34}H_{22}O_2$ m/z 462.1617, found 462.1612. Anal. Calcd for $C_{34}H_{22}O_2$: C, 88.28; H, 4.8. Found: C, 87.8; H, 4.8.

2,2′-Bis[4-(*N*,*N*-dimethylamino)benzoyl]biphenyl (11h):[27g] yield 22%; mp 200–202 °C; IR ($CHCl_3$) 1640 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 195.71 (C=O), 152.95, 139.41, 139.13, 135.08, 132.59, 131.09, 128.58, 128.36, 126.23, 110.09, 39.69; HRMS calcd for $C_{30}H_{28}O_2N_2$ m/z 448.2151, found 448.2159.

***S*,*S*-Bis(*p*-methylphenyl) Diphenthioate (11i)**.[27h] To a benzene (50 mL) solution of diphenic acid dichloride[27c] (1.12 g, 4 mmol) kept at 0 °C were added *p*-thiocresol (1 g, 8 mmol) and triethylamine (1 g, 10 mmol). After stirring for 3 h, the reaction mixture was filtered, and the filtrate was transferred to a separatory funnel and washed with 1 N NaOH (5 × 5 mL) and brine (2 × 5 mL). The organic layer was separated, dried ($MgSO_4$), and rotary evaporated to remove the solvent, and the resulting residue was recrystallized from hexanes to give 1.27 g (96%) of a white solid: mp 91–92 °C (lit.[27h] mp 89 °C); IR ($CHCl_3$) 1680 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 191.74 (C=O), 139.55, 139.34, 137.22, 134.66, 131.38, 131.16, 129.92, 128.31, 127.73, 124.44, 21.31; $HRMS_{FAB}$ calcd for $C_{28}H_{22}O_2S_2$ m/z 455.1089, found 455.1139.

Diethyl Diphenoate (11j).[27i] To an ethanolic (150 mL) solution of diphenic acid (5 g, 20.64 mmol) was slowly added 5 mL of concentrated sulfuric acid, and the mixture was refluxed for 3 h. After the solution was cooled to ambient temperature, excess solvent was removed by flash evaporation, and the residue was taken up in ether (150 mL), transferred to a separatory funnel, and washed with a saturated aqueous solution of $NaHCO_3$ (3 × 15 mL) and H_2O (2 × 15 mL). The organic layer was separated, dried ($MgSO_4$), and rotary evaporated to remove the solvent, and the resulting residue was recrystallized from hexanes to give 1.27 g (96%) of a white solid: mp 40–41 °C (lit.[27i] mp 41–42 °C); IR ($CHCl_3$) 1720 cm^{-1}.

2,2′-Bis[Ethoxy(thiocarbonyl)]biphenyl (12j) was prepared according to the general procedure of Lawesson et al.:[16a] yield 32%; ^{13}C NMR ($CDCl_3$) δ 214.52 (C=S), 139.86, 139.50, 131.36, 130.22, 129.93, 126.65, 68.78, 12.61; ^1H NMR ($CDCl_3$) δ 8.08–7.13 (8 H, m), 4.22 (4 H, q, J = 7 Hz) 0.88 (6 H, t, J = 7 Hz); HRMS calcd for $C_{18}H_{18}O_2S_2$ m/z 330.0750, found 330.0755.

S_2 Additions to 2,3-Dimethyl-1,3-butadiene According to Scheme V: A Typical Reaction with 2,2′-Dibenzoylbiphenyl (11a) and B_2S_3.[1] To a solution of 2,2′-dibenzoylbiphenyl (200 mg, 0.55 mmol) in dry benzene (10 mL) kept under an atmosphere of argon were added hexamethyldisilathiane (300 μL, 1.43 mmol), 950 μL (0.95 mmol) of a 1 M solution of BCl_3 in hexanes, and 2,3-dimethyl-1,3-butadiene (113 μL, 1 mmol). The resulting yellow solution was refluxed for 4 h, cooled to ambient temperature, and then concentrated by flash evaporation. The residue was flash chromatographed (hexanes, benzene/hexanes 1:4) to afford, in order, 49 mg (61%) of 4,5-dimethyl-3,6-dihydro-1,2-dithiin (**15**)[1] as a yellowish oil (^{13}C NMR ($CDCl_3$) δ 125.1, 34.2, 20.8; ^1H NMR ($CDCl_3$) δ 3.20 (2 H, m), 1.75 (3 H, s)) and 168 mg (93%) of 9,10-diphenylphenanthrene (**14a**) as a white solid: mp 235–237 °C (lit.[27a] mp 238 °C); HRMS calcd for $C_{26}H_{18}$ m/z 330.1408, found 330.1423. **14b**: HRMS calcd for $C_{28}H_{22}$ m/z 358.1720, found 358.1800. **14c**: mp >250 °C dec; ^{13}C NMR ($CDCl_3$) δ 137.022, 136.337, 132.916, 132.865, 132.106, 130.024, 127.994, 127.992, 127.180, 126.763, 126.671, 126.593, 126.483, 125.657, 125.302, 124.884, 122.466; HRMS calcd for $C_{34}H_{22}$ m/z 430.1721, found 430.1729. **14e**: mp 245–247 °C (lit.[27j] mp 248 °C); HRMS calcd for $C_{26}H_{16}Cl_2$ m/z 398.0629, found 398.0589. **14f**: mp 255–257 °C (lit.[27k] mp 256–258 °C); HRMS calcd for $C_{28}H_{22}O_2$ m/z 390.1619, found 390.1625. **14g**: mp >250 °C dec; $HRMS_{FAB}$ calcd for $C_{34}H_{23}$ m/z 431.1800, found 431.1747. **14h**: mp >250 °C dec; HRMS calcd for $C_{30}H_{28}N_2$ m/z 416.2252, found 416.2266.

S_2 Addition to 2,3-Dimethyl-1,3-butadiene via Dithiono Ester 12i. An attempt to prepare the dithiono ester from **11i** by the method of Lawesson et al.[16a] resulted only in the monothionated product (IR ($CHCl_3$) 1680 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 231.81 (C=S), 191.93 (C=O), 146.13, 140.58, 139.59, 139.23, 137.92, 136.98, 134.79, 134.54, 131.97, 130.99, 130.82, 130.43, 129.98, 129.46, 128.45, 128.29, 127.86, 127.78, 127.70, 124.53, 21.49, 21.32; ^1H NMR ($CDCl_3$) δ 7.48–7.01 (16 H, m), 2.37 (3 H, s), 2.33 (3 H, s); MS (CI) m/z M^+ + 1, 471) and the eliminated product **14i** (mp 139–141 °C; ^{13}C NMR ($CDCl_3$) δ 138.18, 134.83, 134.48, 132.52, 131.50, 129.48, 129.14, 127.74, 127.34, 126.96, 122.65, 20.87; ^1H NMR ($CDCl_3$) δ 8.74 (4 H, d, J = 7.6 Hz), 7.63 (4 H, q, J = 6.6 Hz), 8.92 (4 H, s), 2.21 (6 H, s); HRMS calcd for $C_{28}H_{28}S_2$ m/z 390.1618, found 390.1623) being formed in low yields.

S_2 Addition to 2,3-Dimethyl-1,3-butadiene via Dithiono Ester 12j. A solution of dithiono ester **12j** (66 mg, 0.2 mmol) and 2,3-dimethyl-1,3-butadiene (565 μL, 5 mmol) in degassed cyclohexane (20 mL) was photolyzed at 300 nm in a Rayonette apparatus for 30 min. The reaction mixture was concentrated by flash evaporation, and the residue was flash chromatographed to give 51 mg (95%) of 9,10-diethoxyphenanthrene (**14j**) as an oil: ^{13}C NMR ($CDCl_3$) δ 142.96, 129.63, 128.52, 126.58, 125.55, 122.44, 69.20, 16.03; ^1H NMR ($CDCl_3$) δ 8.70–8.60 (1 H, m), 8.33–8.23 (1 H, m), 7.67–7.57 (2 H, m), 4.33 (4 H, q, J = 7.0 Hz), 1.53 (6 H, t, J = 7.0 Hz); HRMS calcd for $C_{18}H_{18}O_2$ m/z 266.1307, found 266.1307. No trace of dithiin **15** could be noted.

5(*S*)-Methyl-2-phenyl-1,3-heptadiene (28). To a suspension of (β-methylstyryl)triphenylphosphonium bromide (460 mg, 1 mmol) in anhydrous THF (25 mL) kept under an atmosphere of argon at room temperature was added 400 μL (1 mmol) of a 2.5 M hexanes solution of *n*-BuLi. The mixture was vigorously stirred for 15 min and then cooled to −78 °C using a dry ice/acetone bath. (*S*)-2-Methylbutanal (107 μL, 1 mmol) was then added neat to the reaction mixture, and the stirring was continued for 1 h at −78 °C. The reaction mixture was allowed to reach ambient temperature and stirred for an additional hour. Excess solvent was removed by flash evaporation, and the resulting residue was triturated with hexanes. The extracts were combined, passed through a pad of silica (5 g), and then concentrated by flash evaporation followed by high vacuum to remove any last traces of solvent. This afforded 156 mg (84%) of a 4:1 *E*/*Z* mixture of the diene as a colorless liquid, which could not be separated by chromatography but could easily be distinguished by ^1H NMR analysis and was used in this form: ^1H NMR ($CDCl_3$) δ 7.34–7.29 (5 H, m), 6.26 (1 H, d, J = 16 Hz), 6.08 (1 H, d, J = 11 Hz), 5.54 (1 H, t, J = 8 Hz), 5.50 (1 H, d, J = 2 Hz), 5.46 (1 H, t, J = 11 Hz), 5.182 (1 H, d, J = 2 Hz), 5.14 (1 H, t, J = 2 Hz), 5.06 (1 H, d, J = 2 Hz), 2.47 (1 H, m, allyl), 2.12 (1 H, septuplet, allyl, J = 11 Hz), 1.37–1.23 (2 H, m), 0.99 (3 H, d, J = 7 Hz), 0.95 (3 H, d, J = 7 Hz), 0.86 (3 H, t, J = 7 Hz), 0.83 (3 H, t, J = 7 Hz); $[\alpha]^{23}_D$ +51.5° (c = 1.35, $CHCl_3$); HRMS calcd for $C_{14}H_{18}$ m/z 186.1409, found 186.1404.

Preparation of 1,2-Dithiin 29. A solution of (*S*)-2,2′-dibenzoyl-1,1′-binaphthyl (150 mg, 0.325 mmol), hexamethyldisilathiane (165 μL, 0.79 mmol), 520 μL of a 1 M hexanes solution of BCl_3 (0.52 mmol), and 92.85 mg (0.5 mmol) of diene **28** from the above preparation in dry toluene (10 mL) under an atmosphere of argon was refluxed for 6 h. After cooling to ambient temperature, the reaction mixture was concentrated by flash evaporation, and the resulting residue was passed through a pad of silica (5 g) washing with benzene/hexanes (1:4). The filtrate was concentrated to rotary evaporation, and the residue was flash chromatographed (hexanes) to afford 12 mg (15% based on the diketone) of disulfide **29** as a yellow oil. With reagent **11a** a 60% yield was obtained. The disulfide expressed no optical rotation in the polarimeter. **29**: ^1H NMR ($CDCl_3$) δ 7.25–7.42 (5 H, m), 6.11 (1 H, quintuplet, J = 1.8 Hz), 6.08 (1 H, quintuplet, J = 1.8 Hz), 3.43–3.71 (3 H, m, allyl), 1.90 (1 H, m), 1.66 (1 H, m), 1.35 (1 H, m), 1.09 (3 H, d, J = 6.8 Hz), 1.05 (3 H, d, J = 6.8 Hz), 0.89–0.99 (3 H, m); ^{13}C NMR ($CDCl_3$) δ 143.22, 143.16, 137.24, 137.46, 129.06, 128.40, 128.06, 127.41, 125.94, 48.22, 48.08, 40.35, 40.01, 31.53, 27.02, 26.59, 16.60, 16.21, 11.71; HRMS calcd for $C_{14}H_{18}S_2$ m/z 250.0850, found 250.0835.

Preparation of 1,2-Dithiin 31. A solution of (*R*)-2,2′-dibenzoyl-1,1′-binaphthyl (230 mg, 0.5 mmol), bis(tricyclohexylstannyl) sulfide[7] (845 mg, 1.1 mmol), 730 μL of a 1 M hexanes solution of BCl_3 (0.73 mmol),

and 63.0 mg (0.5 mmol) of diene **30**[27] from the above preparation in dry toluene (10 mL) under an atmosphere of argon was refluxed for 6 h. After cooling to ambient temperature, the bluish green colored reaction mixture was transferred to a separatory funnel and shaken vigorously with 100 mL of a saturated aqueous solution of KF. The layers were partitioned, and the organic phase was saved. The aqueous mixture was then extracted with 2 × 30 mL ether. The extracts were combined with the saved organic phase, dried ($MgSO_4$), and concentrated by rotary evaporation. The nonvolatile residue was distilled under high vacuum (60 °C, 0.1 mmHg) to collect 10 mg (10.5%) of the disulfide as an amber oil, which expressed no optical rotation in the polarimeter. With reagent **11a** a 50% yield was obtained: IR ($CHCl_3$) 1739 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.96 (2 H, m), 3.72 (3 H, s), 3.58 (1 H, m), 3.50 and 3.44 (1 H, dd, J_1 = 2.0, J_2 = 7.0 Hz), 3.06–2.74 (3 H, m); ^{13}C NMR ($CDCl_3$) δ 171.15, 129.15, 126.51, 51.71, 39.25, 34.94, 27.92; HRMS calcd for $C_7H_{10}O_2S_2$ m/z 190.0118, found 190.0106.

Preparation of Diolides 33a and 33c. To a vigorously stirred solution of dry CH_2Cl_2 (400 mL) kept under an atmosphere of argon in a 1-L three-necked flask were simultaneously added dropwise, with the aid of two dropping funnels, a solution of 2 mL (25 mmol) of anhydrous ethylene glycol and 7 mL (50 mmol) of dried Et_3N in 100 mL of dry CH_2Cl_2 in one dropping funnel and 4.3 mL (30 mmol) of freshly distilled adipyl chloride in 100 mL of dry CH_2Cl_2 in the other over a period of 2 h. After the addition, the mixture was stirred for 1 h, transferred to a 2-L separatory funnel charged with 500 mL of H_2O, and shaken. The organic layer was separated, dried ($MgSO_4$), and concentrated by rotary evaporation. Flash chromatography (EtOAc/hexanes 1:4) of the resulting residue afforded 500 mg (10%) of dimer **33a** as colorless solid: mp 46–49 °C; ^1H NMR ($CDCl_3$) δ 4.28 (4 H, m), 2.35–2.39 (4 H, m), 1.66–1.70 (4 H, m); ^{13}C NMR ($CDCl_3$) δ 172.81, 61.90, 33.42, 23.99; HRMS calcd for $C_{16}H_{24}O_8$ m/z 344.1464, found 344.1434. **33c** was similarly prepared: mp 80–83 °C; ^1H NMR ($CDCl_3$) δ 3.16 (4 H, m), 2.56–2.39 (4 H, m), 1.73–1.78 (4 H, m); ^{13}C NMR ($CDCl_3$) δ 198.26, 61.90, 43.18, 28.78, 24.49; MS (CI) m/z M^+ + 1, 408.

Preparation of Esters Listed in Table I. Entry **1a** is commercially available, and **1e**,[28a] **1h**,[28c] **1s**,[28b] and **1w**[28d] were prepared according to literature methods. Entries **1c**, **1f**, **1g**, **1i**, **1j**, **1dd**, and **1ee** could not (in our hands) be prepared by the general procedure of Lawesson et al.,[16a] and no attempt to synthetically prepare entries **1o**, **1p**, **1q**, **1r**, **1v**, **1z**, **1aa**, and **1bb** was made. Entries **1b**, **1d**, **1k**, **1m**, **1n**, **1t**, **1u**, **1x**, and **1v** were prepared by the general procedure of Lawesson et al.[16a] **1b**: yield 18%; ^1H NMR ($CDCl_3$) δ 4.62 (2 H, t, J = 5 Hz), 4.41 (2 H, t, J = 2 Hz), 2.61 (3 H, s), 2.10 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 219.49 (C=S), 170.50 (C=O), 69.22, 61.38, 34.11, 20.61; HRMS calcd for $C_6H_{10}O_3S$ m/z 162.0353, found 162.0348. **1d**: yield 24%; mp 74–76 °C; ^1H NMR ($CDCl_3$) δ 3.50 (4 H, s), 2.84 (6 H, s); ^{13}C NMR ($CDCl_3$) δ 232.04 (C=S), 39.03, 34.04; HRMS calcd for $C_6H_{10}S_4$ m/z 209.9666, found 209.9646. **1k**: yield 7%; mp 96–97 °C; ^1H NMR ($CDCl_3$) δ 8.02–7.36 (10 H, m), 3.78 (4 H, s); ^{13}C NMR ($CDCl_3$) δ 227.19 (C=S), 144.64, 132.54, 128.27, 126.80, 34.14; HRMS calcd for $C_{14}H_{14}S_4$ m/z 309.9978, found 309.9984. **1m**: yield 16%; ^1H NMR ($CDCl_3$) δ 4.52–4.49 (2 H, m), 4.22–4.15 (2 H, m), 2.58 (3 H, s), 2.15–2.10 (2 H, m), 2.07 (3 H, s); HRMS calcd for $C_7H_{12}O_3S$ m/z 176.0509, found 176.0500. **1n**: yield 40%; ^1H NMR ($CDCl_3$) δ 4.54 (4 H, t, J = 6 Hz), 2.59 (6 H, s), 2.57 (2 H, quintuplet, J = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 219.59 (C=S), 68.65, 34.21, 26.90; HRMS calcd for $C_7H_{12}O_2S_2$ m/z 192.0282, found 192.0290. **1t**: yield 19%; ^1H NMR ($CDCl_3$) δ 8.21–7.35 (10 H, m), 4.87 (2 H, t, J = 6 Hz), 4.57 (2 H, t, J = 6 Hz), 2.42 (2 H, t, J = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 211.12 (C=S), 166.33 (C=O), 138.02, 132.90, 132.68, 129.85, 129.45, 128.60, 128.25, 127.96, 69.09, 61.67, 27.77; HRMS calcd for $C_{17}H_{16}O_3S$ m/z 300.0821, found 300.0814. **1u**: yield 72%; ^1H NMR ($CDCl_3$) δ 8.17–7.28 (10 H, m), 4.81 (4 H, t, J = 6 Hz), 2.54 (2 H, t, J = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 210.72 (C=S), 137.75, 132.51, 128.43, 127.77, 68.96, 27.20; HRMS calcd for $C_{17}H_{16}O_2S_2$ m/z 316.0592, found 316.0585. **1x**: yield 33%; mp 65–67 °C; ^1H NMR ($CDCl_3$) δ 7.31–7.10 (4 H, m), 2.78 (3 H, s), 2.26 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 217.80 (C=S), 168.03 (C=O), 145.53, 141.67, 127.10, 126.57, 123.57, 123.36, 33.67, 20.52; HRMS calcd for $C_{10}H_{10}O_3S$ m/z 210.0353, found 210.0369. **1v**: yield 4%; mp 70–71 °C; ^1H NMR ($CDCl_3$) δ 7.37–7.15 (4 H, m), 2.76 (6 H, s); ^{13}C NMR ($CDCl_3$) δ 217.56 (C=S), 145.31, 127.26, 123.73, 33.73; HRMS calcd for $C_{10}H_{10}O_2S_2$ m/z 226.0124, found 226.0126.

Preparation of Catechol Dibenzoate (1cc). A 200-mL round-bottom flask was charged with 80 mL of dry CH_2Cl_2 and 16.8 mL (145 mmol) of freshly distilled benzoyl chloride. The mixture was cooled to 0 °C under an atmosphere of argon and stirred vigorously while a solution of catechol (7.9 g, 71.7 mmol) and Et_3N (21.1 mL, 150 mmol) in dry CH_2Cl_2 was added dropwise. After complete addition, the reaction mixture was allowed to reach ambient temperature, and the solvent was removed by flash evaporation. The crude residue was recrystallized from EtOH (95%) to afford 20.5 g (90%) of the desired ester as colorless crystals: mp 46–49 °C; ^1H NMR ($CDCl_3$) δ 8.07–8.04 (4 H, m), 7.53–7.31 (10 H, m); ^{13}C NMR ($CDCl_3$) δ 164.06 (C=O), 142.39, 133.45, 129.92, 128.58, 128.28, 126.51, 123.40; HRMS calcd for $C_{20}H_{14}O_4$ m/z 318.0892, found 318.0897.

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