MHz) δ 0.73 (3 H, d, J = 7.7 Hz), 0.78 (3 H, d, J = 6.9 Hz), 0.82 (3 H, d, J = 6.5 Hz), 1.00 (3 H, d, J = 7.2 Hz), 1.06 (9 H, s), 1.32 (3 H, s), 1.36 (3 H, s), 1.37 (3 H, s), 1.42 (3 H, s), 1.45–1.70 (2 H, m), 1.85 (1 H, m), 1.98 (1 H, m), 3.40–3.56 (3 H, m), 3.63–3.75 (2 H, m), 3.80 (1 H, dd, J = 6.3, 2.1 Hz), 3.84 (1 H, dd, J = 8.0, 1.8 Hz), 7.41 (6 H, m), 7.68 (4 H, m); HRMS (CI, M + 1) calcd for $C_{35}H_{54}O_5Si(H)$ 583.3821, found 583.3791.

3(*R*)-[1(*R*)-Methyl-2-[(*tert*-butyldimethylsilyl)oxy]ethyl]-4(*S*)-methyl-5(*R*)-[1(*S*)-methyl-2-[(*tert*-butyldiphenylsilyl)oxy]ethyl]dihydro-2(3*H*)-furanone (52). Olefinic lactone **24** (74.2 mg, 0.15 mmol) was ozonized, reduced, and silylated by using the procedure for the conversion of **38** to **39b** giving the *bis*(silyl ether) **52** in 89% yield: ^{1}H NMR (250 MHz) δ 0.06 (6 H, s), 0.89 (3 H, d, J = 6.7 Hz), 0.91 (9 H, s), 1.02 (3 H, d, J = 6.7 Hz), 1.08 (9 H, s), 1.27 (3 H, d, J = 6.6 Hz), 1.86 (2 H, m), 2.54 (2 H, m, C_3-H), 3.52 (2 H, m), 3.79 (2 H, m), 4.11 (1 H, dd, J = 10.7, 3.5 Hz, C_5-H), 7.41 (6 H, m), 7.67 (4 H, m); IR (CCl_4) 1781 cm^{-1}; $[\alpha]_D$ −4.2° (c 2.2, $CHCl_3$). Anal. ($C_{33}H_{52}O_4Si_2$) C, H.

7-[(*tert*-Butyldimethylsilyl)oxy]-1-[(*tert*-butyldiphenylsilyl)oxy]-5-oxo-2(*S*),4(*R*),6(*S*)-trimethylheptan-3(*S*)-ol (53). Lactone **52** (35 mg, 0.061 mmol) was converted to β-hydroxy ketone **53** in 82% yield by using the procedure described above: ^{1}H NMR (250 MHz) δ 0.02 (3 H, s), 0.03 (3 H, s), 0.86 (9 H, s), 0.93 (3 H, d, J = 6.9 Hz), 1.02 (3 H, d, J = 7.0 Hz), 1.06 (9 H, s), 1.13 (3 H, d, J = 7.1 Hz), 1.77 (1 H, m), 2.78 (1 H, m), 3.06 (1 H, m), 3.39 (1 H, d, J = 2.8 Hz), 3.58 (1 H, dd, J = 9.6, 5.3 Hz), 3.82 (3 H, m), 4.02 (1 H, m), 7.41 (6 H, m), 7.68 (4 H, m); IR (CCl_4) 3528, 1704 cm^{-1}; $[\alpha]_D$ +24.7° (c 2.4, $CHCl_3$). Anal. ($C_{32}H_{52}O_4Si_2$) C, H.

7-[(*tert*-Butyldimethylsilyl)oxy]-1-[(*tert*-butyldiphenylsilyl)oxy]-2(*S*),4(*S*),6(*S*)-trimethylheptane-3(*S*),5(*R*)-diol (54a) and 7-[(*tert*-Butyldimethylsilyl)oxy]-1-[(*tert*-butyldiphenylsilyl)oxy]-2(*S*),4(*S*),6(*S*)-trimethylheptane-3(*S*),5(*S*)-diol (55a). Ketone **53** (30.0 mg, 0.054 mmol) was reduced with Dibal as described above. Chromatography (20% ethyl acetate/hexanes) gave the less polar, *anti*-diol **55a** (44%) and the more polar, *syn*-diol **54a** (36%): Diol **55a**: ^{1}H NMR (250 MHz) δ 0.10 (6 H, s), 0.84 (6 H, d, J = 6.8 Hz), 0.91 (9 H, s), 1.07 (9 H, s), 1.07 (3 H, d, J = 6.9 Hz), 1.82 (2 H, m), 2.07 (1 H, m), 3.55 (1 H, m), 3.67–3.82 (4 H, m), 3.97 (1 H, d, J = 9.8 Hz), 4.23 (1 H, s), 4.52 (1 H, d, J = 3.9 Hz), 7.41 (6 H, m), 7.69 (4 H, m); IR (CCl_4) 3458 cm^{-1}; $[\alpha]_D$ +10.9° (c 0.5, $CHCl_3$); HRMS (CI, M + 1) calcd for $C_{32}H_{54}O_4Si_2(H)$ 559.3641, found 559.3642. Diol **54a**: ^{1}H NMR (250 MHz) δ 0.05 (3 H, s), 0.06 (3 H, s), 0.69 (3 H, d, J = 6.8 Hz), 0.90 (9 H, s), 0.99 (3 H, d, J = 6.7 Hz), 1.02 (3 H, d, J = 7.5 Hz), 1.07 (9 H, s), 1.84 (2 H, m), 1.93 (1 H, m), 3.56–3.82 (6 H, m), 3.83 (1 H, s), 4.23 (1 H, s), 7.44 (6 H, m), 7.68 (4 H, m); IR (CCl_4) 3479 cm^{-1}; $[\alpha]_D$ +15.8 (c 0.3, $CHCl_3$); HRMS (CI, M + 1) calcd for $C_{32}H_{54}O_4Si_2(H)$ 559.3641, found 559.3640.

6(*R*)-[1(*S*)-Methyl-2-[(*tert*-butyldimethylsilyl)oxy]ethyl]-4(*R*)-[1-(*S*)-methyl-2-[(*tert*-butyldiphenylsilyl)oxy]ethyl]-2,2,5(*S*)-trimethyl-1,3-dioxane (54b). Diol **54a** (9.1 mg, 0.01 mmol) was ketalized as previously described. Chromatography (3% ether/hexanes) gave 7.8 mg (82%) of the acetonide **54b**: ^{1}H NMR (250 MHz) δ 0.06 (6 H, s), 0.87 (3 H, d, J = 6.8 Hz), 0.92 (9 H, s), 0.97 (3 H, d, J = 6.9 Hz), 1.00 (3 H, d, J = 6.6 Hz), 1.06 (9 H, s), 1.37 (6 H, s), 1.60–1.80 (3 H, m), 3.47–3.62 (3 H, m), 3.68 (1 H, dd, J = 10.1, 1.7 Hz), 3.82–3.93 (2 H, m), 7.41 (6 H, m), 7.69 (4 H, m); $[\alpha]_D$ +15.1 (c 0.4, $CHCl_3$); HRMS (CI, M + 1) calcd for $C_{35}H_{58}O_4Si_2(H)$ 599.3954, found 599.3917.

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Diastereoselectivity in the Diels–Alder Reactions of Thioaldehydes

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Abstract: The Diels–Alder reaction of thioaldehydes with cyclopentadiene occurs with a preference for the endo isomer. The highest selectivity is observed for thioaldehydes RCHS where R is a bulky alkyl group such as *tert*-butyl or isopropyl. Thioaldehydes having α-alkoxy, acetoxy, or siloxy substituents also react with useful endo selectivity. Secondary orbital overlap is a small factor in these reactions since α-oxo thioaldehydes react with relatively low endo selectivity. Steric effects are primarily responsible for the endo preferences observed. The Diels–Alder reactions of chiral α-oxygen substituted thioaldehydes also occur with useful thioformyl face selectivity. A Cornforth transition state **5** is most likely for the selectivity observed for α-alkoxy or acetoxy thioaldehydes, but the α-hydroxy analogue **23** reacts with the opposite facial preference. The highest face selectivity is obtained with the acetonide of thioglyceraldehyde, generated by photolysis of the phenacyl sulfide **15b**.

We have been interested in synthetic applications of thioaldehyde Diels–Alder additions.[1-5] The high intrinsic reactivity and polarizability of the thioformyl group makes possible the formation of new carbon bonds with excellent control of regiochemistry (eq 1 vs 2, Scheme I).[2] An important additional requirement for exploring synthetic applications of this cycloaddition is to define the stereochemical aspects of the bond-forming step. As in any Diels–Alder process, the reaction may choose between "exo" and "endo" transition states **3** vs **4**, resulting in adducts **1** or **2**, respectively. If the thioaldehyde fragment is chiral, then there is the added feature of diastereomer excess to consider (eq 5 vs 6), and each of the endo or exo pathways may produce two isomeric products. For the endo approach in the cyclopentadiene example as illustrated, a chiral thioaldehyde can react at either thiocarbonyl face (**5** or **6**) to give the product diastereomers **7A** or **7B**. The corresponding exo approach (not shown) can produce **8A,B**. Given the many options for removal or modification of the sulfur substituent, useful methodology for control of remote stereochemistry would result if there is a strong bias for a single combination of the selectivity factors that con-

(1) Vedejs, E.; Eberlein, T. H.; Varie, D. L. *J. Am. Chem. Soc.* **1982**, *104*, 1445.
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(4) Vedejs, E. *Acc. Chem. Res.* **1984**, *17*, 358. Vedejs, E.; Reid, J. G. *J. Am. Chem. Soc.* **1984**, *106*, 4617.
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Scheme I

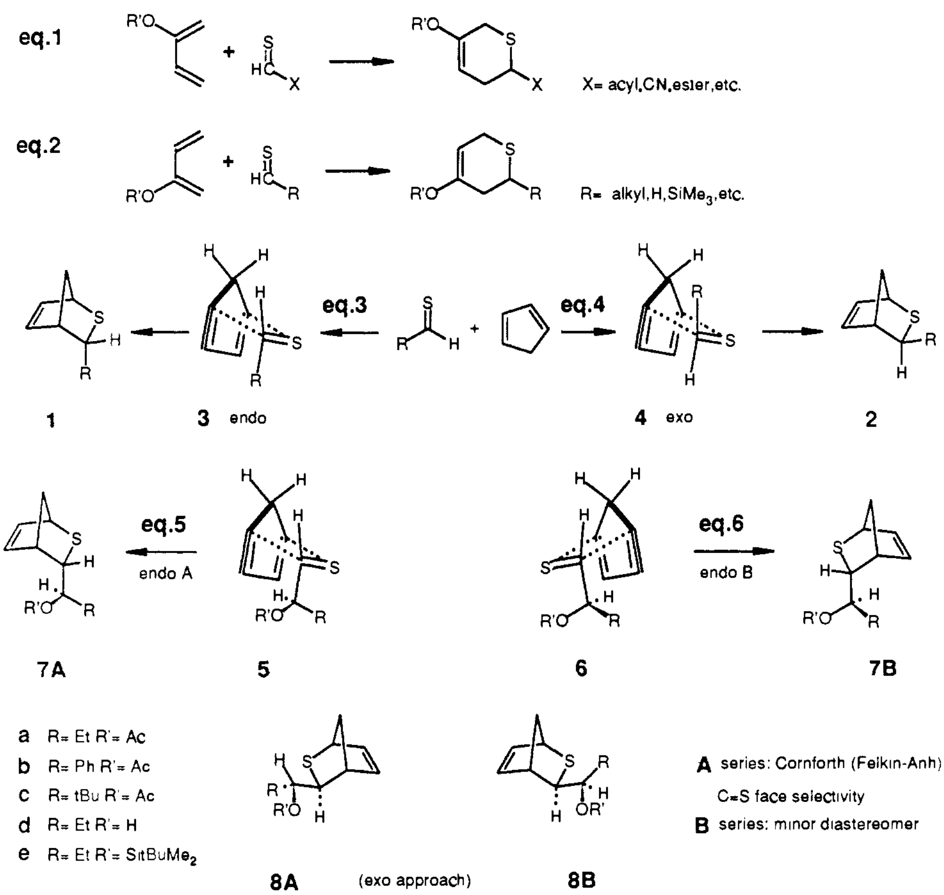


Table I. Thioaldehyde/Cyclopentadiene Diels–Alder Reactions

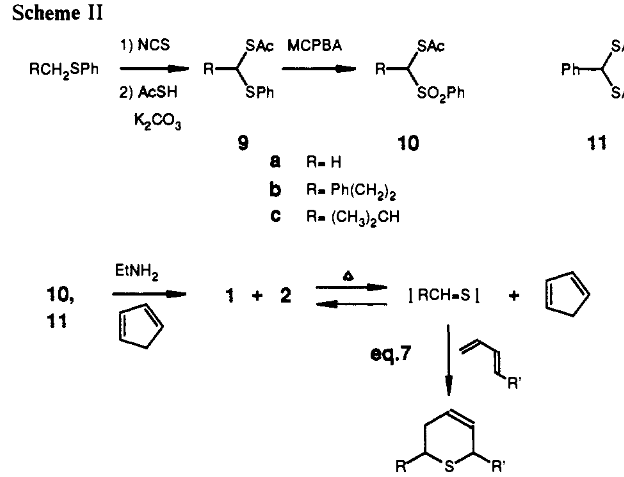
entry	R in RCHS	yield, %	endo/exo ratio (**1**/**2**)	ref
1	CO_2CH_3	84	2.3:1	*a,b*
2	$COCH_3$	59	4.0:1	*c*
3	COC_2H_5	27	3.7:1	*b*
4	COPh	86	3.0:1	*b*
5	$Ph_2P{=}O$	60	2.7:1	*b*
6	$PhSO_2$	84	4.0:1	*b*
7	Ph	84	4.0:1	*c,d*
8	$CH{=}CH_2$	30	2.0:1	*b*
9	Me_3Si	65	5.5:1	*c*
10	CH_3	41	3.0:1	*b,e*
11	$Ph(CH_2)_2$	83	3.6:1	*b,c*
12	*i*-Pr	49	16:1	*b,d*
13	*t*-Bu	75	>50:1	*b*
14	$AcOCH_2$	93	6.6:1	*b*
15	AcOCHEt	55	13:1	*b*

[a] The same ratio was reported for the ethyl ester generated by a base-induced elimination method (ref 6). [b] This work. [c] Reference 2a. [d] An endo/exo ratio of 7:1 is reported (ref 7) with a disulfide precursor. [e] An endo/exo ratio of 3.3:1 is reported (ref 7) with a disulfide precursor.

tribute to possible transition states.

Endo vs Exo Selectivity. Previous studies have encountered an apparent preference for the formation of "endo" adducts when cyclopentadiene is used to trap thioaldehydes.[6,7] This is a convenient system for stereochemical assignments and turns out to have major preparative implications as well. To allow systematic comparisons, we have examined a large number of thioaldehydes generated by the highly versatile photochemical method from phenacyl sulfides.[1,2] When the experiment is performed in the

Scheme II



presence of cyclopentadiene at room temperature, good to excellent yields of the adducts can be obtained from numerous thioaldehydes. Adduct stereochemistry is based on NOE studies in several cases, on the related findings by Kirby et al.[6] and Krafft et al.[7] and on highly consistent NMR chemical shift and coupling correlations in all of the cyclopentadiene adducts. Thus, the proton α to sulfur in the endo adduct **1** experiences a ca. 3–4 Hz coupling with the adjacent bridgehead proton and appears as a doublet in the absence of other coupling. In the exo adduct **2**, the corresponding proton is a singlet at higher field due to shielding by the nearby double bond (see the Experimental Section). The results of the current investigation are summarized in Table I together with some of the earlier examples using the method of photochemical thioaldehyde generation.

In general, the exo/endo ratios in the tables are similar to previously reported data from other methods of thioaldehyde generation,[6,7] but there are some differences (entries 7, 12). To confirm that our results represent the kinetically determined

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(7) Krafft, G. A.; Meinke, P. T. *Tetrahedron Lett.* **1985**, *26*, 1947.

Table II. Thioaldehyde Generation from Thioacetal S-Acetates **10a–c**, **11**

entry	R in RCHS	yield, %	exo/endo fron acetal	exo/endo by $h\nu$
1	H	51		
2	$Ph(CH_2)_2$	77	5:1	3.6:1
3	i-Pr	29	16:1	16:1
4	Ph	15	3.5:1	4.0:1

Table III. Thioaldehyde/Cyclopentadiene Adduct Equilibration

entry	R in RCHS	temp, °C	endo/exo starting	equil.
1	CH_3	140	3.0:1	1.1:1
2	$Ph(CH_2)_2$	140	3.6:1	1.3:1
3	i-Pr	140	16:1	1.9:1
4	t-Bu	140	>50:1	1:1.4
5	Ph	140	4.0:1	1.4:1
6	CO_2CH_3	100	40:1	1:2.8
7	CO_2CH_3	100	1:16	1:2.8

product ratios and that they are not influenced by secondary photochemical reactions or equilibration by other means, several control experiments were performed.

First, the exo/endo ratios were compared with those obtained from a new nonphotochemical method of thioaldehyde generation. As shown in Scheme II, several thioaldehydes could be released by cleavage of readily available S-acetyl thioacetals. The thiobenzaldehyde precursor **11** was already known,[8] while **10a–c** were obtained from phenyl alkyl sulfides via α-chlorination and thiolacetate displacement. Cleavage of **10–11** with diethylamine at room temperature with excess cyclopentadiene present gave thioaldehyde adducts (Table II). In two of the three relevant cases (**10b**,**c**, **11**), the exo/endo ratios from both the thioacetal and the photochemical methods were well within experimental error. In the third case (entry 2, Table II), a small difference in product ratios between the photochemical and base-induced methods may be due to medium effects. The same factors may explain the differences between some of our exo/endo ratios compared to the earlier study,[7] but it is clear that there is a strong kinetic bias for the endo product in all cases.

Further confirmation that Tables I and II do indeed represent the kinetic exo/endo ratios of the thioaldehydes was obtained by studying the equilibration of the isomers. The exo/endo isomers were quite stable at room temperature, but prolonged heating in sealed tubes at 80–140 °C resulted in the interconversion of isomers and eventually gave a constant product ratio (Table III). This experiment has been performed in many of the examples listed in Tables I and II, and in every case the thermodynamic mixture contained more of the exo isomer than did the kinetic mixture. In the entries 6 and 7, Table III, two samples containing very different ratios of exo/endo isomers were shown to reach the same equilibrium mixture of 1:2.8 endo/exo at 100 °C, and no new products were detected during the equilibration. Kirby and Lochead report a 1:2.3 endo/exo equilibrium mixture for the corresponding ethyl ester with the same thermal equilibration method.[6] In general, the simple alkanethial adducts required a temperature of 140 °C for equilibration within 20–30 h, and the thermodynamic product ratios were close to 1:1 exo/endo. Adducts derived from electron-deficient thioaldehydes XCH=S were more readily equilibrated (2–6 h at 100 °C), and there was a greater trend for the exo product in the final mixture.

The mechanism for thermal equilibration undoubtedly involves the equivalent of retro-Diels–Alder reaction.[6] This was demonstrated directly in the case of Table III, entry 4, by heating the thiopivaldehyde–cyclopentadiene adduct at 250 °C in a nitrogen stream and trapping the products at liquid nitrogen temperature. The condensate had the characteristic pink-magenta color of thiopivaldehyde,[3] and warming to room temperature afforded the known trimers (75%). Also relevant is the observation initially reported by Kirby et al. that heating the cyclopentadiene adducts with an excess of a 1,3-diene results in the formation of crossover Diels–Alder adducts.[6] We have found that this process occurs in good to excellent yield with many of the cyclopentadiene–thioaldehyde adducts (eq 7), and in some cases the technique becomes the method of choice for preparation of other cycloadducts.[5a–c] The practical advantages depend on a subtle balance of reactivity factors, salient features of which are discussed below.

As is well known, simple thioaldehydes decompose rapidly at room temperature to polymeric material. The formation of trimers was previously believed to occur spontaneously, but it is more likely due to catalysis by protic or Lewis acids, as demonstrated in the thiopivaldehyde case.[3] The observation that cyclopentadiene adducts **1** or **2** can be heated for many hours with isomer interconversion, but without significant decomposition to trimers or to thioaldehyde polymers, has interesting implications. Since the thioaldehydes are obviously present in an equilibrating system as demonstrated by crossover and trapping experiments, the presence of cyclopentadiene in the sealed-tube reactions must be responsible for preventing the formation of intractable thioaldehyde polymers. It is likely that the polymerization process involves the readily reversible formation of soluble oligomers that are unstable relative to **1** or **2**. The insoluble polymers formed when thioaldehydes are generated without suitable trapping agents present do not accumulate under these conditions, nor do the relatively stable thioaldehyde trimers.

In effect, the presence of cyclopentadiene assures the prolonged survival of **1** and **2**. Significant decomposition (as evidenced by the formation of cyclopentadiene dimer) requires heating for days at 140 °C or above. On the other hand, if a 1,3-diene is present, the crossover Diels–Alder reaction (eq 7) occurs over several hours, accompanied by conversion of **1** + **2** into cyclopentadiene and its dimer together with a new thioaldehyde Diels–Alder adduct. This procedure can be most useful for the preparation of adducts from the relatively unreactive alkanethials, especially in the case of simple 1,3-dienes, which are not efficient as thioaldehyde trapping agents.[5a–c,6] The method can also be recommended in cases where the photochemical thioaldehyde generation technique is precluded due to photochemical side reactions of the diene or of the desired adduct.

Tables I–III reveal interesting selectivity trends. Essentially all of the thioaldehyde Diels–Alder reactions with cyclopentadiene favor the endo product kinetically, but by far the highest endo selectivity is seen for alkanethials having one or more substituents in the α-position. The endo preference drops significantly from R = t-C_4H_9 (>50:1) to i-C_3H_7 (16:1) to unbranched alkyl (ca. 3–7:1) or to α-oxo substituted alkyl (2–4:1). When the α-carbon atom is replaced by bulky heteroatom substituents (trimethylsilyl, phenylsulfonyl, diphenylphosphinyl) having relatively long bonds to thioformyl carbon, a modest 3–6:1 endo preference is observed. There is little indication of an important role for secondary orbital interactions or other electronic effects in these results. The primary source of endo selectivity appears to be associated with steric bulk held near the thioformyl group.

It is instructive to compare the thioaldehyde results of Table I with the corresponding all-carbon examples.[9,10] There are several reports of remarkable endo selectivity in the Diels–Alder reaction of cyclopentadiene with simple alkenes (allyl alcohol,[9a,10f] norbornene,[10a] cyclopentene,[10b,10c] cyclopropene,[10d] allyl bromide,[10f]

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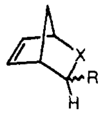
Table IV. MACROMODEL MM2 Energies of Cyclopentadiene + RCH═X Adducts



entry	R	X	steric energy, kcal	
			exo	endo
1	CH_3	CH_2	27.1	26.9
2	i-Pr	CH_2	29.9	28.9
3	*t*-Bu	CH_2	32.6	32.6
4	$(CH_2)_3$	CH	35.3	36.0
5	CH_3	S	18.6	18.4
6	*i*-Pr	S	21.4	20.4
7	*t*-Bu	S	24.2	23.8
8	CO_2CH_3	S	19.1	19.1

propene,[10f] etc.). Only one of these examples (cyclopentene + cyclopentadiene) has been studied sufficiently to deduce contrasting kinetic (ca. 2:98 exo/endo at 200 °C, estimated by IR analysis) and thermodynamic (ca. 72:28 exo/endo at 300 °C) trends from the data.[10c] However, the consistent endo preference in all of the examples argues against equilibration. Kinetic control is more firmly established in the case of acrylate dienophiles, and in this series there are many examples of the steric endo effect, especially for methacrylate esters where the endo preference of α-methyl dominates over that of the ester.[10e,g,h] As in the thioaldehyde reactions, the endo effect due to secondary orbital overlap is small in the cyclopentadiene Diels–Alder reactions.

A steric explanation for the endo preference of simple alkene dienophiles was originally proposed by Martin and Hill,[9c,11] and an adaptation of their argument explains the trends seen with alkanethials (Table I). A relatively advanced, productlike transition state for the 2 + 4 cycloaddition is ruled out by the equilibration studies because the kinetic ratios are quite different from the thermodynamic ratios (Table III). Therefore, the transition state comes early, and there is relatively little rehybridization. The cyclopentadiene ring is nearly flat, and the choice is between endo-selective **3** or exo-selective **4**. Geometry **4** experiences interactions between dienophile (thioaldehyde) R and the saturated CH_2 bridge, while **3** has the less demanding interaction of R with a sp^2-hybridized center. This favors **3** relative to **4**. As bonding proceeds, the separation between bridging CH_2 and R increases, and the thermodynamic difference between endo and exo isomers in the final products is modest. On the other hand, the kinetic difference in the early transition state can be quite large for R = *tert*-butyl ($\Delta\Delta G^* > 1.5$ kcal) and is still substantial for R = singly branched alkyl (entries 12 and 15, Table I).

Since simple alkenes are less reactive dienophiles than are the thioaldehydes, their Diels–Alder reactions with cyclopentadiene presumably involve more advanced transition states. To evaluate the role of productlike interactions, we have performed MACROMODEL MM2[12] calculations on several representative norbornenes and thianorbornenes (Table IV). Surprisingly good agreement was found between the MM2 energies and the equilibrium ratios of the thioaldehyde adducts (Table III). Only the cases where R = t-C_4H_9 or CO_2Me deviated significantly, as might be expected given the difference in closely interacting atom types between exo and endo isomers. The MM2 calculations should be more reliable for the all-carbon examples (entries 1 to 4, Table IV). Here, the endo isomers were favored marginally for R = CH_3 and more so for R = i-C_3H_7. In the case of the cyclopentene adduct, the exo isomer was calculated to be slightly more stable, again in reasonable agreement with the (tentative) 72:28 equilibrium ratio that is implied by the data of Cristol et al.[10c] The 5-alkylnorbornenes apparently do not have an overwhelming thermodynamic preference for the exo geometry. In the absence of a strong bias for either product, even a relatively advanced transition state might be controlled by the simple steric endo argument.[9c,11]

In the thioaldehyde examples, the transition states are earlier and product stability issues are probably unimportant. However, the steric endo effect may be diluted by distortions resulting from the longer carbon–sulfur bond and its smaller steric demand. The steric argument is consistent with the considerably larger endo/exo ratio reported for the adduct of thiopyruvaldehyde[2a] or thioglyoxylate[6] with cyclohexadiene (ca. 20:1 endo/exo) compared to the corresponding reactions with cyclopentadiene (2–4:1). The endo transition state encounters a similar CH═CH unit in the case of cyclohexadiene, but the exo analogue must now contend with the two carbon (CH_2CH_2) bridge. The magnitude of this effect suggests that the thiopyruvaldehyde methyl is close to the CH_2CH_2 bridge in the case of the exo transition state, a result that is consistent with a thiopyruvaldehyde geometry where the C═S and α-C═O groups are kept far apart to minimize unfavorable lone pair and dipole interactions.

Thioaldehyde Facial Selectivity. From the results of Table I, we conclude that stereocontrol in the exo/endo sense requires α branched or α doubly branched thioaldehydes. The former are useful substrates for diastereoselective synthesis subject to the directive influence of α-heteroatom substituents. Similar concepts have been explored extensively by Danishefsky et al. for the Lewis acid catalyzed Diels–Alder reactions of α-alkoxy aldehydes such as **12a** or **12b**.[13] Diastereoselectivity with **12b** is especially high and tends to correlate with the arrangement where the α-heteroatom is kept away from developing bonds as in the Felkin–Anh model for nucleophilic addition.[14] The same result would be predicted by turning the α-heteroatom away from thiocarbonyl unshared (*n*) electron pairs as in the Cornforth model.[15,10h] Technially, the Felkin–Anh model should not apply to cycloadditions because its basis is in the Dunitz trajectory for nucleophilic addition of anions resulting in a *single* bond. However, this terminology is commonly used for classification purposes and can be understood to refer to aldehyde facial selectivity where the details of transition-state geometry are not specified.

In thioaldehyde Diels–Alder reactions, the effect of α-heteroatom substituents on facial selectivity need not follow the same patterns as in the above aldehyde examples. The transition-state geometry of the C═S dienophile should be more sensitive to lone pair interactions between sulfur 3p and α-alkoxy 2p orbitals, in particular because the thioaldehyde reaction does not involve Lewis acid catalysis. In the carbonyl case, the reactive dienophile uses one carbonyl lone pair for coordination to the catalyst, an interaction that has no parallel in the simple sulfur analogue. Differences in selectivity may also result because the Lewis acid/CH═O complex is formally a disubstituted dienophile with more evenly balanced steric demands compared to the (monosubstituted) thioformyl group. To probe these issues, a series of thioaldehyde precursors **14a–e** was prepared having systematically varied substitutents α to the eventual thioformyl carbon.

As shown in Scheme III, the various phenacyl sulfides **14** were made by cleavage of an oxirane with thiolacetate followed by spontaneous S to O acyl transfer[16] and alkylation with phenacyl chloride. The more highly functionalized **15a** was obtained directly from the mercaptan[17] by S-alkylation. Photolysis of **14** in the

(11) Houk, K. N. *Tetrahedron Lett.* **1970**, 2621. (b) Fox, M. A.; Cardona, R.; Kiwiet, N. J. *J. Org. Chem.* **1987**, *52*, 1469.

(12) MACROMODEL 1.5 was kindly provided by Prof. W. C. Still of Columbia University. Default parameters were used for the MM2 minimization of the norbornene or 2-thianorbornene skeleton. Substituents were then incorporated and were manually adjusted by 60° dihedral angle increments and the structures minimized again.

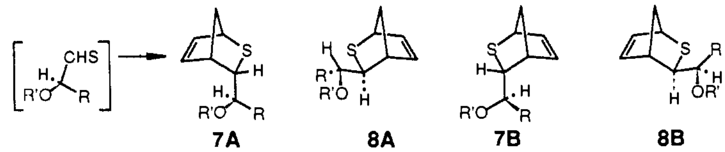
(13) (a) Danishefsky, S. J.; Pearson, W. H.; Harvey, D. F.; Maring, C. J.; Springer, J. P. *J. Am. Chem. Soc.* **1985**, *107*, 1256. (b) Danishefsky, S.; Kobayashi, S.; Kerwin, J. F. *J. Org. Chem.* **1982**, *47*, 1981.

(14) Anh, N. T.; Eisenstein, O. *Nouv. J. Chem.* **1977**, *1*, 61.

(15) (a) Cornforth, J. W.; Cornforth, R. H.; Mathew, K. K. *J. Chem. Soc.* **1959**, 112. (b) Reetz, M.; Kesseler, K. *J. Org. Chem.* **1985**, *50*, 5434. (c) Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1984**, *96*, 542.

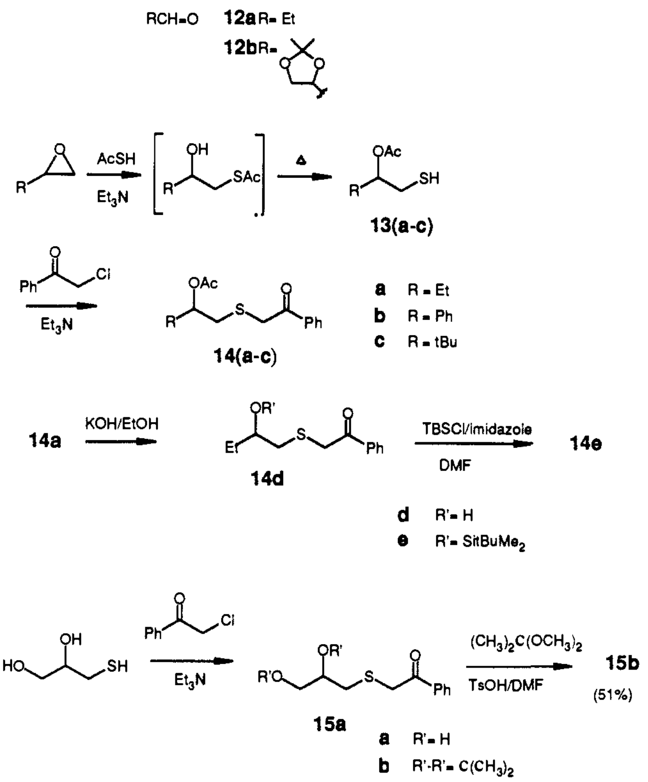
(16) Vedejs, E.; Buchanan, R. A. *J. Org. Chem.* **1984**, *49*, 1840. (b) Vedejs, E.; Powell, D. W. *J. Am. Chem. Soc.* **1982**, *104*, 2046 and references therein.

Table V. α-Alkoxy Thial/Cyclopentadiene Diels–Alder Reactions

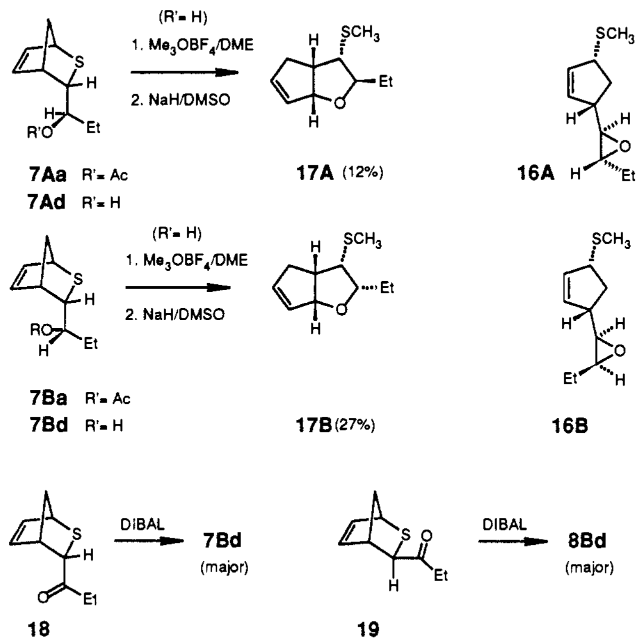


R	R′	sulfide	products (% total products)				yield, %
Et	Ac	**14a**	**7Aa** (75)	**8Aa** (5)	**7Ba** (18)	**8Ba** (2)	55
Ph	Ac	**14b**	**7Ab** (62)	**8Ab** (8)	**7Bb** (25)	**8Bb** (5)	76
tBu	Ac	**14c**	**7Ac** (82)	**8Ac** (6)	**7Bc** (9)	**8Bc** (3)	100
Et	H	**14d**	**7Ad** (30)	**8Ad** (4)	**7Bd** (56)	**8Bd** (10)	72
Et	TBS	**14e**	**7Ae** (79)	**8Ae** (10)	**7Be** (10)	**8Be** (1)	82

Scheme III



Scheme IV



presence of cyclopentadiene as usual gave a mixture of four adduct diastereomers in each case. As expected, there was a large preference for endo over exo products as evidenced by the characteristic C_3–C_4 coupling constant of the endo isomers **7**, and the endo/exo ratio (**7**:**8**) showed only minor variation (86–93% endo; Table V). The three related acetoxy thioaldehydes generated by photolysis of **14a**, **14b**, and **14c** gave similar endo/exo ratios with cyclopentadiene, and there was little indication that changes in the thioaldehyde alkyl substituent affected this aspect of stereoselectivity. Therefore, detailed stereochemical correlations were performed only in the case of the adducts derived from **14a**. On the basis of methods discussed below, the product ratio was found to be 75:18:5:2 **7Aa**:**7Ba**:**8Aa**:**8Ba** where A and B designate the facial selectivity of thioaldehyde trapping. Overall, the endo selectivity is 93:7 while the A-face selectivity (Felkin–Anh or Cornforth) is ca. 4:1 for endo adducts and ca. 3:1 for the exo adducts.

The first attempts to prove the stereochemistry of the thioaldehyde adducts **7** were based on literature precedents for the conversion of α-hydroxy sulfonium salts into epoxides with strong base.[18] Saponification of **7Aa** or **7Ba** gave the corresponding alcohols **7Ad** and **7Bd**, but S-methylation followed by base treatment for conversion into epoxides **16A** and **16B** was complicated by the formation of isomeric tetrahydrofurans **17A** and **17B** (Scheme IV). The epoxides could not be obtained pure, but vicinal coupling constants for protons α to S and O in the NMR spectra of **17A,B** were in good agreement with values obtained using the NMR analysis submode of MACROMODEL.[19] Further evidence was sought by correlation with ketones **18** and **19**. The latter were available by the usual thioaldehyde trapping route (Table I, entry 5) and the endo/exo assignments were clear. Reduction of α-sulfenyl ketones is known to occur with Felkin–Anh selectivity in a variety of acyclic and cyclic systems.[20] Thus, reduction of **1**, with diisobutylaluminum hydride (DIBAL) in toluene or with lithium triethylborohydride or potassium tri-*sec*-butylborohydride in tetrahydrofuran gave 2–3:1 ratios of two

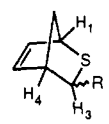
(17) Smith, L.; Sjoberg, B. *Chem. Ber.* **1936**, *69B*, 678.

(18) Kano, S.; Yokomatsu, T.; Shibuya, S. *J. Chem. Soc., Chem. Commun.* **1978**, 785.

(19) To simplify the choice of side-chain conformations, energy minimization using the default parameters of MACROMODEL was performed on analogues of **17A,B** having the *C*-ethyl branchpoint replaced by *C*-methyl. Various envelope conformers were generated from an unsubstituted bicyclic ether, and the appropriate carbon and sulfur substituents were then added and minimized. One reasonable conformer of the methyl analogue of **17A** (steric energy 16.3 kcal) was found; the next best was >2 kcal less stable. Coupling constant analysis using the NMR submode of MACROMODEL indicated $J_{3,4}$ = 10.4 Hz (obsd for **17A**, 10.2 Hz). In the isomeric *C*-methyl analogues of **17B**, three conformers of similar energy (ca. 18.5 kcal) were found, with a mean *J* value of 4.7 Hz (obsd $J_{3,4}$ = 5.6 Hz for **17B**). We are grateful to a referee for noting an error in the original computations.

(20) Shimagaki, M.; Maeda, T.; Matsuzaki, Y.; Hori, T.; Nakata, T.; Oishi, T. *Tetrahedron Lett.* **1984**, *25*, 4775. Nakata, T.; Tanaka, T.; Oishi, T. *Tetrahedron Lett.* **1983**, *24*, 2653. Vedejs, E.; Buchanan, R. A.; Conrad, P.; Meier, G. P.; Mullins, M. J.; Watanabe, Y. *J. Am. Chem. Soc.* **1987**, *109*, 5878.

Table VI. NMR[a] Data: Thioaldehyde-Cyclopentadiene Adducts



R	H_1 (br s)	H_3	H_4 (br s)	HC=CH[b]
endo-CO_2CH_3[c]	3.59	4.20 (d, J = 3.5 Hz	3.39	6.23, 6.02
exo-CO_2CH_3	3.63	3.41 (s)	3.30	6.05, 5.57
endo-$COCH_3$[c]	4.12	4.42 (d, J = 4.0 Hz)	3.75	6.43, 5.86
exo-$COCH_3$	4.12	3.41 (s)	3.53	6.39, 5.99
endo-COC_2H_5-**18**[d]	4.08	4.40 (d, J = 3.8 Hz)	3.73	6.38, 5.38
exo-COC_2H_5-**19**	4.08	3.37 (s)	3.50	6.35, 5.96
endo-COPh[e]	4.06	5.10 (d, J = 3.5 Hz)	3.78	6.36, 6.13
exo-COPh	4.14	4.04 (s)	3.65	6.45, 6.07
endo-$POPh_2$[c,f,g]	4.07	4.35 (m)	3.75	6.15, 5.73
exo-$POPh_2$[f,h]	4.12	3.53 (m)	3.31 (br d, J_{P-H} = 3.8 Hz)	6.34, 5.95
endo-SO_2Ph[c]	4.06	4.98 (d, J = 3.5 Hz)	3.87	6.98, 6.05
exo-SO_2Ph	4.16	3.97 (s)	3.83	6.47, 5.98
endo-Ph[c,e]	3.75	4.75 (d, J = 3.5 Hz)	3.15	6.24, 5.31
exo-Ph	3.95	3.83 (s)	2.92	6.17, 5.79
endo-$CH=CH_2$[c]	4.00	4.25 (dd, J = 9.0, 3.8 Hz)	3.40	6.42, 5.77
exo-$CH=CH_2$	4.08	3.35 (obsc 3.38)		6.31 (obsc)
endo-$SiMe_3$[c]	4.01	2.72 (d, J = 4.0 Hz)	3.52	6.17, 5.65
exo-$SiMe_3$	4.10	obsc	3.22	6.07, 5.89
endo-CH_3[e]	3.80	3.67 (qd, J = 6.8, 3.6 Hz)	2.88	6.29, 5.58
exo-CH_3	3.87	2.77 (q, J = 6.8 Hz)	2.56	6.16, 5.78
endo-CH_2CH_2Ph[c]	3.96	3.69 (ddd, J = 3.7, 3.6, 3.6 Hz)	3.32	6.4, 5.76
exo-CH_2CH_2Ph	4.02	3.02 (m)	2.8 (obsc)	6.28, 5.90
endo-$CH(CH_3)_2$[e]	3.90	3.70 (dd, J = 10.6, 3.7 Hz)	3.40	6.37, 5.75
exo-$CH(CH_3)_2$[f]	3.94	2.49 (d, J = 9.9 Hz)	3.17	6.26, 5.92
endo-$C(CH_3)_3$[i]	3.85	3.73 (d, J = 3.3 Hz)	3.40	6.29, 5.75
exo-$C(CH_3)_3$[f]	3.70	2.72 (s)	3.60	6.06, 5.80
endo-CH_2OAc[c]	4.00	obsc	3.45	6.38, 5.77
exo-CH_2OAc	obsc	3.01 (dd, J = 8.4, 6.3 Hz)	3.25	6.32, 5.92

[a] All spectra in $CDCl_3$, δ, unless otherwise noted; all adducts were obtained as oils except in the diphenylphosphinyl case. [b] Characteristic norbornene-like pattern, two dd, J = 5.5 and ca. 2-3 Hz. [c] Reference 2a. [d] Preparation of phenacyl sulfide described in the Experimental Section. [e] Reference 22. [f] NMR spectrum in C_6D_6. [g] Solid, crystallized from ethyl acetate, mp 151-154 °C. [h] Solid, crystallized from ethyl acetate, mp 163-164 °C. [i] Reference 3.

alcohols **7Bd**:**7Ad**, which were identical with the saponification products from **7Ba** and **7Aa**, respectively. Similarly, reduction of **19** with Dibal in toluene afforded the alcohols **8Bd** and **8Ad** (4.9:1 ratio) with the stereochemistry of the exo adducts **8Ba** and **8Aa**. The major Diels-Alder products in both the exo and endo adduct series with **14** as the starting material therefore correspond to the Felkin-Anh or Cornforth model facial selectivity.

Although the stereochemistry of the other entries in Table V was not proved in detail, the NMR spectra of isomeric adducts were sufficiently similar to allow reasonably safe assignment by analogy. All of the adducts from the α-acetoxy thioaldehydes were formed with a preference for bonding at the A face. Substantially increased A face selectivity could be associated with increasing bulk in the thioaldehyde alkyl (*tert*-butyl) group of **14c**. Also, the ether **14e** reacted with a higher A face preference (8:1 A:B for endo adducts) then did the corresponding acetate **14a** (4:1 A:B for endo adducts). The differences are not large, but increased selectivity with the α-siloxy substituent compared to the α-acetoxy group is more consistent with a role for lone pair repulsions in a Cornforth geometry.

Most interesting was the Diels-Alder addition of the thioaldehyde precursor **14d**, containing a free α-hydroxyl group. The thioaldehyde intermediate could be generated by the usual photochemical method and gave adducts in a ratio of **7Ad**:**7Bd**:**8Ad**:**8Bd** = 30:56:4:10. The endo selectivity was still high (86:14), but the thioaldehyde face preference was inverted (A:B = 1:1.8 for endo products; 1:2.5 for exo products) compared to the reactions of the O-protected **14** derivatives **a-c** or **e**. Assuming a Cornforth-like transition state **5** (Scheme I) for the O-protected thioaldehydes from precursors **14a-c** and **14e**, the behavior of the α-hydroxy thioaldehyde **23** from **14d** suggests that an internally hydrogen bonded geometry **24** (Scheme V) is most important. This geometry and the resulting thiocarbonyl facial selectivity are reminiscent of the chelation model for diastereoselective Diels-Alder reactions of α-alkoxy aldehydes.[21] Hydrogen bonding in **24** serves to restrict the conformation of the chiral center with respect to the adjacent π system as does a bidentate Lewis acid in the typical catalyzed reaction of α-alkoxy aldehydes.

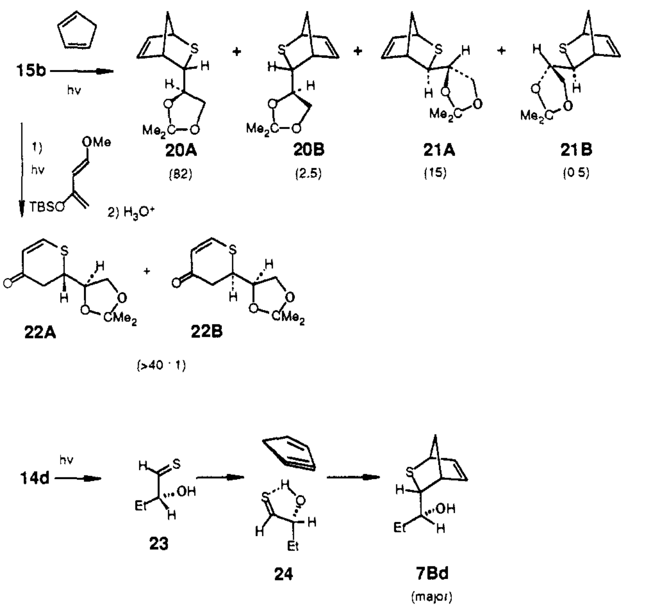
Considerably higher facial discrimination was observed starting with the thioglyceraldehyde acetonide precursor **15b**. In this case, the ratio of **20A**:**20B**:**21A**:**21B** was 82:2.5:15:0.5 (assignment by NMR analogy), indicating an excellent facial selectivity of >30:1 A:B for either the endo or the exo pathway. A similar product ratio of >40:1 was obtained when **15b** was photolyzed in the presence of the Danishefsky diene, followed by acidic workup to induce elimination to the enones **22A,B**. The oxygen analogue has been reported to react with comparably high selectivity by Danishefsky et al.[13] Since the exo/endo issue disappears along with the methoxy substituent in the conversion to enone, the product ratio corresponds to the thioaldehyde facial selectivity.

On the basis of the above findings, we conclude that thioaldehydes can participate in diastereoselective Diels-Alder reactions provided that sufficient steric bulk is incorporated at the α-carbon. Best results are obtained with α-alkoxy thioaldehydes, suggesting that the favored transition state involves maximal separation of sulfur and oxygen lone pairs in a Cornforth geometry such as **5**. A similar geometry has been proposed for the Diels-Alder reaction of related acrylate dienophiles (4,5-di-*O*-isopropylidenepent-2-enoates) with cyclopentadiene.[10h] In the thioaldehyde case, high dienophile reactivity compared to the carbon (acrylate) or oxygen (aldehyde) analogues allows greater flexibility in choice of substrates and reaction conditions and suggests applications of the thioaldehyde Diels-Alder reaction

(21) For a discussion of chelation control in Lewis acid catalyzed Diels-Alder reactions of aldehydes, see ref 13a; for a general review of chelation control, see ref 15c.

(22) Long, L. M. *J. Am. Chem. Soc.* **1946**, *68*, 2859.

Scheme V



for remote stereocontrol in complex synthesis. These issues will be addressed in future publications.

Experimental Section

Cyclopentadiene–Thioaldehyde Adducts (Table VI). The phenacyl sulfides used in this study were prepared according to literature procedures (references in Table VI). The photolytic method for thioaldehyde generation has been described in detail and was used without modification.[2a] Separation of exo and endo isomers was achieved by HPLC or analytical TLC over silica gel in the case of the oxygen-, phenylsulfonyl-, or diphenylphosphinyl-substituted adducts, and the endo isomer in these examples was eluted after the exo isomer. For the alkyl- or silicon-substituted adducts, the two isomers were inseparable. In these examples, NMR assignments could be made by comparing the kinetic adduct mixture (rich in endo isomer) with the mixture after thermal equilibration to increase the content of the exo isomer Satisfactory exact mass data was established by high-resolution mass spectroscopy in all cases.

Independent Generation of Thioaldehydes from Thioacetal *S*-Acetate Derivatives. Acetal Sulfones 10. General Procedure. The alkyl phenyl sulfide (**10a–c**, 1 mmol) was dissolved in CCl_4 (5 mL), and *N*-chlorosuccinimide (Aldrich, 1 mmol) was added. After overnight stirring, the precipitated succinimide was filtered, and the CCl_4 filtrate and washings were concentrated to an oil at 30 °C (aspirator). A solution of thiolacetic acid (Aldrich, 1 mmol) in CH_3CN (1 mL) was then added, followed by powdered K_2CO_3 (2 mmol). The reaction was stirred 2.5 h and filtered, and solvents were evaporated (aspirator). Flashchromatography on silica gel (20% CH_2Cl_2/hexane) to remove the less polar starting sulfide or vinyl sulfide elimination products then gave **9** as the more polar major fraction, 65–75%, sufficiently pure for the next step.

The sulfide **9** (1 mmol) was dissolved in dichloromethane (7 mL) at 0 °C, and MCPBA (Aldrich, 2 mmol) was added in one portion. After 1 h at 0 °C, the was mixture was extracted with saturated aqueous $NaHCO_3$ (2 × 10 mL), the aqueous layer was washed with CH_2Cl_2 (2 × 10 mL), and the combined organic phase was dried ($MgSO_4$) and concentrated to an oil (aspirator). Flash chromatography over silica gel (25% ethyl acetate/hexane) gave a single major fraction containing **10** after a small forerun of nonpolar impurities.

10b: (73%) solid; mp 82–83 °C (crystallized from ethyl acetate–hexane); MS, *m/found* for M + 1 335.0779, calcd 335.0776, error 1.1 ppm; IR ($CDCl_3$, cm^{-1}) 1700 (C(O)S), 1260 (SO_2); 200-MHz NMR ($CDCl_3$) δ 7.96–7.88 (2 H, m), 7.66–7.48 (3 H, m), 7.28–7.18 (3 H, m), 7.10–7.00 (2 H, m), 5.06 (1 H, dd, J = 10.9, 3.2 Hz), 2.96–2.80 (1 H, m), 2.72–2.52 (2 H, m), 2.22 (3 H, s), 2.21–2.04 (1 H, m).

10c: (91%) solid; mp 82–83 °C (crystallized from ethyl acetate–hexane); MS, *m/e* found M + 1 273.0610, calcd 273.0619, error 13.1 ppmf IR ($CDCl_3$, cm^{-1}) 1700 (C(O)S), 1320 (SO2), 1152 (SO2); 200-MHz NMR ($CDCl_3$) δ 7.98–7.88 (2 H, m), 7.67–7.48 (3 H, m), 4.76 (1 H, d, J = 2.4 Hz), 2.95 (1 H, qqd, 6.8, 6.6, 2.4 Hz), 2.22 (3 H, s), 1.15 (3 H, d, J = 6.8 Hz), 0.99 (3 H, d, J = 6.6 Hz).

Thioaldehyde Generation from 10b, 10c, and 11. The sulfones **10b** or **10c** or the thioacetal **11** were reacted under the same conditions to release the corresponding thioaldehyde. In a representative procedure, **10c** (9.7 mg, 0.036 mmol) and cyclopentadiene (0.02 mL, 0.24 mmol, 7 equiv) were dissolved in methylene chloride (0.1 mL) at −5 °C. Diethylamine (Kodak, 8 μL, 0.072 mmol) was added, and the reaction mixture was stirred overnight at −5 °C. The methylene chloride and excess cyclopentadiene were evaporated at reduced pressure. The residue was purified by PTLC on silica gel plates (20% methylene chloride–hexane) to give 1.5 mg (29%) of Diels–Alder adducts **1** + **2** (R = isopropyl), identical with the adducts prepared by the photochemical method (Table I) according to NMR spectroscopy at 200 MHz. Integration of the olefinic or bridgehead protons established an exo/endo ratio of 1:16.

Thermal Equilibration of 1 and 2. The cyclopentadiene thioaldehyde adducts were dissolved in benzene-d_6 (0.3 mL) and transferred to a thick-walled NMR tube. The benzene solution was frozen at −78 °C, the tube was exposed to high vacuum for 2 min, and the benzene was then allowed to melt. After three freeze–thaw cycles, the benzene was refrozen, and the tube was sealed under vacuum. The contents of the NMR tube were then heated in an oil bath at 100 °C for entries 6 and 7, Table III, or at 140 °C for the other entries. Periodically, the sample tubes were withdrawn, cooled, and analyzed by NMR. No further change in product ratios (Table III) was detected after the following times: entry 1, 31 h (140 °C); entry 2, 32 h (140 °C); entry 3, 18 h (140 °C); entry 4, 40 h (140 °C); entry 5, 3 h (140 °C, change first detected at 80 °C); entries 6 and 7, 21 h (100 °C).

Thermal Cracking of *endo*-3-*tert*-Butyl-2-thiabicyclo[2.2.1]hept-5-ene to Thiopivaldehyde. The kinetic adduct **1** (R = *tert*-butyl) was placed in a round-bottom flask connected to a 20-cm length of thick-walled Pyrex tubing (1 mm i.d.). At the other end of the tube, a U-shaped trap was attached as the receiver. The Pyrex tube was then placed within a resistance heater at ca. 250 °C surface temperature, and the U-trap was immersed in a liquid nitrogen bath. A slow nitrogen stream (capillary bleed inlet) was allowed to sweep adduct **1** (R = *tert*-butyl) through the furnace, and a pink condensate collected in the trap. Upon warming, the color slowly faded as the sample reached room temperature. Analysis by NMR revealed the presence of unreacted starting material, cyclopentadiene dimer, and both of the stereoisomeric thiopivaldehyde trimers (2,4,6-tri-*tert*-butyl-1,3,5-trithianes)[2a] in a molar ratio of dicyclopentadiene:trimers = 2:1 (theoretical = 1.5:1) according to NMR integration.

2-Acetoxybutyl Phenacyl Sulfide (14a). Freshly distilled 1,2-epoxybutane (10 mL, 116 mmol) was added to a stirred solution of triethylamine (16.2 mL, 116 mmol) and thiolacetic acid (8.3 mL, 116 mmol) in THF (150 mL). The mixture was heated to reflux for 4 h, cooled, and stirred overnight. A THF solution of phenacyl chloride (18.0 g, 116 mmol) was then added dropwise by cannula, and the solution was stirred for 3 h. The mixture was diluted with water (500 mL) and extracted with two 200-mL portions of CH_2Cl_2. The extract was dried ($MgSO_4$) and evaporated, and the residual oil was separated by flash chromatography to afford 20.2 g (75.8 mmol, 65%) of product, contaminated with a small amount (ca. 5%) of phenacyl thiolacetate. A pure sample of the phenacyl sulfide **14a** was obtained by HPLC as an oil: analytical TLC (silica gel F254), 1:1:8 CH_2Cl_2–EtOAc–hexane, R_f 0.20; MS, *m/e* exact mass calcd for $C_{14}H_{18}O_3S$ 266.0972, found 266.097, error 0.8 ppm; IR ($CHCl_3$, cm^{-1}) 1730 (C=O), 1680 (C=O); 200-MHz NMR ($CDCl_3$) δ 7.97–7.92 (2 H, m), 7.61–7.41 (3 H, m), 5.02–4.89 (1 H, m), 3.89 (1 H, d, J = 14.3 Hz), 3.78 (1 H, d, J = 14.3 Hz), 2.77 (1 H, dd, J = 14.0, 5.0 Hz), 2.65 (1 H, dd, J = 14.0, 7.2 Hz), 2.03 (3 H, s), 1.73–1.55 (2 H, m), 0.88 (3 H, t, J = 7.4 Hz).

Photolysis of 14a. The usual photolysis procedure[2a] was employed with 3.33 g (12.50 mmol) of sulfide **14a** and 32.00 mL (356 mmol) of freshly distilled cyclopentadiene. After 7-h photolysis, evaporation, filtration through silica gel (hexane, then 30% EtOAc–hexane), and HPLC (1:1:8 CH_2Cl_2–EtOAc–hexane), the following fractions were obtained: 1.09 g of major endo product **7Aa** (41%), 74.8 mg of major exo product **8Aa** (3%), 27.4 mg of minor exo adduct **8Ba** (1%), and 265.2 mg of minor endo product **7Ba** (10%). The major product **7Aa** was sufficiently pure for further analysis as an oil: analytical TLC (silica gel F254), 1:1:8 CH_2Cl_2–EtOAc–hexane, R_f 0.34; MS, *m/e* exact mass calcd for $C_{11}H_{16}O_2S$ 212.0867, found 212.0864, error 1.4 ppm; IR ($CHCl_3$, cm^{-1}) 1720 (C=O); 270-MHz NMR ($CDCl_3$) δ 6.36 (1 H, dd, J = 5.5, 2.9 Hz), 5.70 (1 H, dd, J = 5.5, 3.1 Hz), 4.28 (1 H, ddd, J = 10.9, 7.7, 3.5 Hz), 3.91 (1 H, br s), 3.77 (1 H, dd, J = 10.9, 3.8 Hz), 3.35 (1 H, br s), 2.07 (3 H, s), 1.69–1.34 (4 H, m), 0.80 (3 H, t, J = 7.1 Hz).

Hydrolysis of Acetate 14a. Sulfide acetate **14a** (883 mg, 3.31 mmol) was dissolved in 8.5 mL of 0.5 M ethanolic KOH, and 1 mL of water was added. The mixture was stirred for 2 h and then partitioned between water and CH_2Cl_2. The organic phase was dried over $MgSO_4$ and evaporated, and the residue was separated by flash chromatography to afford the product **14d** (592 mg, 2.64 mmol, 80%) as a pure oil: analytical TLC (silica gel F254), 20% EtOAc–hexane, R_f 0.12; MS, *m/e* exact mass calcd for $C_{12}H_{16}O_2S$ 224.0867, found 224.0871, error 1.8 ppm; IR ($CHCl_3$, cm^{-1}) 3480 (O–H), 1680 (C=O); 270-MHz NMR

($CDCl_3$) δ 7.97–7.93 (2 H, m), 7.60–7.43 (3 H, m); 3.90 (1 H, d, J = 14.5 Hz), 3.83 (1 H, d, J = 14.5 Hz), 3.64–3.58 (1 H, m), 2.77 (1 H, dd, J = 13.9, 3.1 Hz), 2.63 (1 H, br d, J = 3.6 Hz), 2.50 (1 H, dd, J = 13.9, 8.8 Hz), 1.51 (2 H, dq, J = 13.7, 7.4 Hz), 0.94 (3 H, t, J = 7.4 Hz).

Photolysis of 14d. Trapping of 2-Hydroxybutanethial with Cyclopentadiene. 2-Hydroxybutyl phenacyl sulfide (**14d**) (436 mg, 1.94 mmol) was dissolved in 10 mL of benzene, and 5 mL of freshly distilled cyclopentadiene was added. The mixture was photolyzed[2a] for 6 h. Evaporation and flash chromatography afforded 206 mg of partially separated cycloadducts (1.21 mmol, 62%) and ca. 15% recovered starting material. HPLC (20% EtOAc–hexane) then separated the four diastereomeric alcohols **8Bd**, **7Bd**, **8Ad**, and **7Ad**, in the ratio 10:56:4:30. **8Bd**: oil; analytical TLC (silica gel F254), 20% EtOAc–hexane, R_f 0.33; MS, m/e exact mass calcd for $C_9H_{14}OS$ 170.0762, found 170.0768, error 3.5 ppm; IR ($CHCl_3$, cm^{-1}) 3550 (O—H); 200-MHz NMR ($CDCl_3$) δ 6.29 (1 H, dd, J = 5.4, 2.7 Hz), 6.00 (1 H, dd, J = 5.4, 3.3 Hz), 4.01 (1 H, br s), 3.70–3.59 (1 H, m), 3.12 (1 H, br s), 2.91 (1 H, d, J = 5.1 Hz), 2.60 (1 H, br s), 1.88 (1 H, d, J = 7.8 Hz), 1.81 (1 H, d, J = 9.3 Hz); 1.79–1.43 (2 H, m), 0.99 (3 H, t, J = 7.3 Hz). **7Bd**: oil; analytical TLC (silica gel F254), 20% EtOAc–hexane, R_f 0.31; MS, m/e exact mass calcd for $C_9H_{14}OS$ 170.0762, found 170.0773, error 6.5 ppm; IR ($CHCl_3$, cm^{-1}) 3550 (O—H); 200-MHz NMR ($CDCl_3$) δ 6.34 (1 H, dd, J = 5.5, 2.9 Hz), 5.72 (1 H, dd, J = 5.5, 3.1 Hz), 3.92 (1 H, br s), 3.86 (1 H, dd, J = 7.5, 3.7 Hz), 3.35–3.32 (1 H, m), 3.20–3.15 (1 H, m), 1.81 (1 H, d, J = 5.8 Hz), 1.62–1.21 (4 H, m), 0.94 (3 H, t, J = 7.4 Hz). **8Ad**: oil; analytical TLC (silica gel F254), 20% EtOAc–hexane, R_f 0.25; MS, m/e no peak match, parent; found M – 17, 153.0746, calcd 153.0738, error 5.2 ppm; formula $C_9H_{14}OS$; IR ($CHCl_3$, cm^{-1}) 3550 (O—H); 200-MHz NMR ($CDCl_3$) δ 6.29 (1 H, dd, J = 5.4, 2.6 Hz), 5.97 (1 H, dd, J = 5.4, 3.3 Hz), 4.00 (1 H, br s); 3.62–3.49 (1 H, m), 3.48 (1 H, br s); 3.20–2.42 (4 H, m), 1.81–1.44 (2 H, m), 1.00 (3 H, t, J = 7.4 Hz). **7Ad**: oil; analytical TLC (silica gel F254), 20% EtOAc–hexane, R_f 0.21; MS, m/e exact mass calcd for $C_9H_{14}OS$ 170.0762, found 170.0779, error 10 ppm; IR ($CHCl_3$, cm^{-1}) 3550 (O—H); 200-MHz NMR ($CDCl_3$) δ 6.35 (1 H, dd, J = 5.5, 2.9 Hz), 5.84 (1 H, dd, J = 5.5, 3.0 Hz), 3.93 (1 H, br s), 3.68 (1 H, dd, J = 9.1, 3.7 Hz), 3.59 (1 H, br s), 3.00–2.21 (2 H, m), 1.67–1.21 (4 H, m), 0.93 (3 H, t, J = 7.3 Hz).

2-(*tert*-Butyldimethylsiloxy)butyl Phenacyl Sulfide (14e). The alcohol **14d** (592 mg, 2.64 mmol) was dissolved in 5 mL of DMF under N_2 and cooled to 0 °C. Imidazole (272 mg, 4.00 mmol) was then added in one portion, followed by a solution of *tert*-butyldimethylsilyl chloride (532 mg, 3.53 mmol) in DMF (5 mL) delivered by cannula. The bath was removed, and the mixture was stirred for 4 h and then poured into ether. The ether phase was washed twice with water, dried over $MgSO_4$, and evaporated. The residual oil was filtered trough a short plug of silica gel with ether, and the eluent was evaporated to afford 809 mg (2.39 mmol, 91%) of pure sulfide silyl ether **14e**: oil; analytical TLC (silica gel F254), 20% EtOAc–hexane, R_f 0.50; MS, m/e no peak match, parent; found M – 15, 323.1506, calcd 323.1501, error 1.5 ppm, formula $C_{18}H_{30}O_2SSi$; IR ($CHCl_3$, cm^{-1}) 1680 (C=O); 200-MHz NMR ($CDCl_3$) δ 7.99–7.92 (2 H, m), 7.59–7.39 (3 H, m), 3.79 (2 H, s), 3.79–3.69 (1 H, m); 2.63 (2 H, d, J = 5.8 Hz), 1.63–1.42 (2 H, m), 0.85 (9 H, s), 0.84 (3 H, t, J = 7.4 Hz), .04 (3 H, s), 0.02 (3 H, s).

Photolysis of 2-(*tert*-Butyldimethylsiloxy)butyl Phenacyl Sulfide (14e). Sulfide **14e** (275 mg, 0.81 mmol) and 2.00 mL (24.3 mmol) of cyclopentadiene was photolyzed in benzene in the usual manner, followed by filtration through silica gel and HPLC (10% CH_2Cl_2–hexane) to afford the four diastereomeric products (190 mg total, 0.67 mmol, 82%) in the ratio 79:10:10:1. The three largest fractions were sufficiently pure for further analysis. Major endo adduct **7Ae**: oil; analytical TLC (silica gel F254), 10% CH_2Cl_2–hexane, R_f 0.29; MS, m/e no peak match, parent; found M – 29, 255.1231, calcd 255.1239, error 3.1 ppm, formula $C_{15}H_{28}OSSi$; IR ($CHCl_3$, cm^{-1}) 1040 (SiO); 200-MHz NMR ($CDCl_3$) δ 6.40 (1 H, dd, J = 5.5, 2.9 Hz), 5.79 (1 H, dd, J = 5.5, 3.1 Hz), 3.89 (1 H, br s), 3.80 (1 H, dd, J = 10.4, 3.6 Hz), 3.54 (1 H, br s), 3.13 (1 H, ddd, J = 10.4, 4.0, 3.2 Hz), 1.69–1.23 (4 H, m), 0.92 (9 H, s), 0.89 (3 H, t, J = 7.5 Hz), 0.08 (3 H, s), 0.04 (3 H, s). Minor endo adduct **7Be**: oil; analytical TLC (silica gel F254), 10% CH_2Cl_2–hexane, R_f 0.27; MS, m/e no peak match, parent; found M – 29, 255.1231, calcd 255.1239, error 3.1 ppm, formula $C_{15}H_{28}OSSi$; IR ($CHCl_3$, cm^{-1}) 1040 (SiO); 200-MHz NMR ($CDCl_3$) δ 6.28 (1 H, dd, J = 5.4, 2.8 Hz), 5.95 (1 H, dd, J = 5.4, 3.3 Hz), 3.97 (1 H, br s), 3.73 (1 H, dt, J = 9.8, 4.0 Hz), 3.39 (1 H, br s), 2.80 (1 H, d, J = 9.8 Hz), 1.70–1.49 (4 H, m), 0.92 (9 H, s), 0.88 (3 H, t, J = 7.4 Hz), 0.07 (3 H, s), 0.06 (3 H, s). Major exo adduct **8Ae**: oil; analytical TLC (silica gel F254), 10% CH_2Cl_2–hexane, R_f 0.25; MS, m/e no peak match, parent; found M – 29, 255.1231, calcd 255.1239, error 3.1 ppm, formula $C_{15}H_{28}OSSi$; IR ($CHCl_3$, cm^{-1}) 1040 (SiO); 200-MHz NMR ($CDCl_3$) δ 6.37 (1 H, dd, J = 5.5, 2.8 Hz), 5.63 (1 H, dd, J = 5.5, 3.1 Hz), 3.93–3.85 (2 H, m), 3.25–3.14 (2 H, m), 1.69–1.54 (4 H, m), 0.97 (3 H, t, J = 7.5 Hz), 0.85 (9 H, s), 0.02 (3 H, s), –0.03 (3 H, s).

***endo*-3-Ethyl-*endo*-4-(methylthio)-2-oxabicyclo[3.3.0]oct-7-ene (17B).** Alcohol sulfide **7Bd** (163 mg, 0.96 mmol) was dissolved in 10 mL of DME and added to 308 mg (2.08 mmol) of solid trimethyloxonium tetrafluoroborate. The mixture was stirred vigorously for 1 h, and excess oxonium salt was quenched by adding 0.5 mL of methanol and stirring for 1 h. The solvent was evaporated and replaced with 5 mL of DMSO, and the solution was added by cannula into a DMSO suspension of sodium hydride (53 mg, 2.20 mmol). After stirring overnight, this mixture was poured into saturated aqueous NH_4Cl and extracted with two portions of CH_2Cl_2. The extract was dried over $MgSO_4$ and evaporated, and the residue was separated by flash chromatography to afford three fractions: 30 mg of an uncharacterized forerun, 50 mg of fractions containing the forerun and a second nonpolar material that may be the epoxide **16B**, and 48 mg (0.26 mmol, 27%) of **17B**: oil; analytical TLC (silica gel F254), 1:1:8 CH_2Cl_2–EtOAc–hexane, R_f 0.29; MS, m/e exact mass calcd for $C_{10}H_{16}OS$ 184.0918, found 184.0925, error 3.8 ppm; IR ($CHCl_3$, cm^{-1}) 1220 (C—O); 200-MHz NMR ($CDCl_3$) δ 5.82–5.80 (2 H, m), 5.00 (1 H, br d, J = 7.8 Hz), 3.91 (1 H, ddd, J = 8.5, 5.7, 5.6 Hz), 3.27 (1 H, dd, J = 8.5, 5.6 Hz), 3.18–3.08 (1 H, m), 2.89–2.77 (1 H, m), 2.41 (1 H, dd, J = 18.3, 9.0 Hz), 2.08 (3 H, s), 1.61–1.52 (2 H, m), 0.94 (3 H, t, J = 7.3 Hz).

***exo*-3-Ethyl-*endo*-4-(methylthio)-2-oxabicyclo[3.3.0]oct-7-ene (17A).** The procedure reported above for **7Bd** was repeated with the isomer **7Ad**. Thus, 600 mg (3.52 mmol) of **7Ad** was alkylated with 783 mg (5.29 mmol) of trimethyloxonium tetrafluoroborate and added to 346 mg of sodium hydride. After 2 h, $^1/_4$ of the reaction mixture was worked up as before and separated by HPLC (5:5:90 CH_2Cl_2–EtOAc–hexane) to afford a forerun, 6.4 mg, that may contain epoxide **16A**, and then 22.1 mg of pure **17A** as an oil: analytical TLC (silica gel F254), 20% EtOAc–hexane, R_f 0.28; MS, m/e exact mass calcd for $C_{10}H_{16}OS$ 184.0918, found 184.0918, error 0 ppm; IR ($CHCl_3$, cm^{-1}) 1590 (C=C), 1220 (C—O); 270-MHz NMR ($CDCl_3$) δ 5.95–5.92 (1 H, m), 5.64 (1 H, ddd, J = 5.6, 4.5, 2.3 Hz), 5.11 (1 H, td, J = 7.0, 2.1 Hz), 3.23 (1 H, ddd, J = 10.2, 7.8, 3.1 Hz), 3.03 (1 H, dddd, J = 9.1, 8.3, 7.1, 3.7 Hz), 2.80 (1 H, dd, J = 10.2, 8.1 Hz), 2.75 (1 H, ddq, J = 17.9, 3.7, 2.4 Hz), 2.37 (1 H, ddtd, J = 17.9, 9.1, 2.3, 0.5 Hz), 2.10 (3 H, s), 1.82 (1 H, dqd, J = 14.0, 7.5, 3.1 Hz), 1.47 (1 H, ddq, J = 14.0, 7.8, 7.4 Hz), 0.97 (3 H, t, J = 7.4 Hz).

Oxidation of Alcohol 14d. Preparation of Phenacyl 2-Oxobutyl Sulfide. The method of Swern et al.[23] was employed. A solution of oxalyl chloride (1.10 mL, 12.3 mmol) in 15 mL of CH_2Cl_2 was cooled to –78 ° under N_2, and a mixture of 1.70 mL (24.0 mmol) of DMSO in 5 mL of CH_2Cl_2 was added by cannula. After 0.5 h, 2.12 g (9.46 mmol) of alcohols **14d** in 5 mL of CH_2Cl_2 was added dropwise. After 1 h, 4.40 mL (31.5 mmol) of triethylamine was added by syringe, and the mixture was warmed to 20 °C and poured into water. The aqueous layer was extracted with CH_2Cl_2, and the organic phases were combined, dried over $MgSO_4$, and evaporated. The residue was separated by flash chromatography to afford the title phenacyl sulfide (868 mg, 3.90 mmol, 41%) as an oil: analytical TLC (silica gel F254), 30% EtOAc–hexane, R_f 0.35; MS, m/e exact mass calcd for $C_{12}H_{14}O_2S$ 222.0711, found 222.0712, error 0.4 ppm; IR ($CHCl_3$, cm^{-1}) 1708 (C=O), 1674 (C=O); 200-MHz NMR ($CDCl_3$) δ 7.96–7.91 (2 H, m), 7.57–7.41 (3 H, m), 3.88 (2 H, s), 3.36 (2 H, s), 2.58 (2 H, q, J = 7.3 Hz), 1.07 (3 H, t, J = 7.3 Hz).

Reduction of Ketone 18 or 19. The keto sulfide **18** (87 mg, 0.51 mmol) was dissolved in 5 mL of toluene and cooled to –78 °C under N_2. Then, 1.00 mL of a 1.0 M solution of diisobutylaluminum hydride was added slowly by syringe. The mixture was allowed to stir for 2 h and then added by cannula to a 10% aqueous THF slurry being stirred at –78 °C. The mixture was warmed and partitioned between saturated brine and CH_2Cl_2. The organic phase was washed with dilute aqueous HCl, dried over $MgSO_4$, and evaporated. The residue was eluted through a small column of silica gel (ether), and the eluent was evaporated to afford 87.2 mg (0.51 mmol, 100%) of a clear, colorless oil. The oil was analyzed by NMR spectroscopy, which showed a 2.2:1 mixture of alcohols **7Bd** and **7Ad**, respectively, by comparison with the products isolated from trapping of 2-hydroxybutanethial, above. Under the same conditions, **19** gave a 4.9:1 ratio of **8Bd** and **8Ad**, 91% yield.

Photolysis of 2-Acetoxy-2-phenylethyl Phenacyl Sulfide (14b). The usual photolysis procedure was employed for 352 mg (1.12 mmol) of sulfide **14b** and 3 mL (36.4 mmol) of cyclopentadiene. After 6-h photolysis, the reaction mixture was evaporated, and the residual oil was filtered through silica gel (hexane and then CH_2Cl_2). The CH_2Cl_2 eluent was evaporated, and the oil was separated by HPLC (1:2:17 EtOAc–CH_2Cl_2–hexane) to afford 223 mg (0.86 mmol, 76%) of cycloadducts

(23) Mancuso, A. J.; Huang, S.-L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480.

7Ab, **8Ab**, **7Bb**, and **8Bb** in the ratio 62:8:25:5. The two endo adducts were separated, but the exo isomers could not be resolved and their ratio was estimated by NMR. Major adduct (**7Ab**): oil; analytical TLC (silica gel F254), CH_2Cl_2, R_f 0.45; MS, m/e exact mass calcd for $C_{15}H_{16}O_2S$ 260.0867, found 260.0872, error 1.9 ppm; IR (neat, cm^{-1}) 1740 (C=O); 270-MHz NMR ($CDCl_3$) δ 7.35–7.25 (5 H, m), 6.47 (1 H, dd, J = 5.5, 2.9 Hz), 5.85 (1 H, dd, J = 5.5, 3.0 Hz), 5.11 (1 H, d, J = 11.0 Hz), 4.22 (1 H, dd, J = 11.0, 3.6 Hz), 3.90 (1 H, br s), 3.56 (1 H, br s), 2.07 (3 H, s), 1.74 (1 H, dt, J = 9.1, 2.2 Hz), 1.64 (1 H, br d, J = 9.1 Hz). Minor endo adduct **7Bb**: oil; analytical TLC (silica gel F254), CH_2Cl_2, R_f 0.42; MS, m/e exact mass calcd for $C_{15}H_{16}O_2S$ 260.0867, found 260.0872, error 1.9 ppm; IR (neat, cm^{-1}) 1740 (C=O); 270-MHz NMR ($CDCl_3$) δ 7.41–7.31 (5 H, m), 6.48 (1 H, dd, J = 5.5, 2.9 Hz), 5.80 (1 H, dd, J = 5.5, 3.0 Hz), 5.07 (1 H, d, J = 11.0 Hz), 4.24 (1 H, dd, J = 11.0, 3.6 Hz), 3.99 (1 H, br s), 2.83 (1 H, br s), 1.96 (3 H, s), 1.61–1.58 (2 H, m).

2-Acetoxy-3,3-dimethylbutyl Phenacyl Sulfide (14c). A 20-mL solution of mCPBA (1.63 g, 80–85%, 7.6 mmol) in dichloromethane was reacted with 2 mL (15.5 mmol) of 3,3-dimethyl-1-butene overnight. The solution was filtered and washed with saturated aqueous Na_2CO_3. The organic phase was dried over $MgSO_4$ and concentrated under a Vigreux column to afford a clear, colorless oil. This was dissolved in 30 mL of THF, and 1.00 mL (14.0 mmole of thiolacetic acid and 2.00 mL (14.3 mmol) of triethylamine were added. The mixture was refluxed for 8 h, cooled, and stirred for an additional 8 h. The mixture was then partitioned between saturated aqueous NaCl and CH_2Cl_2, and the organic phase was dried over $MgSO_4$ and evaporated. The semisolid residue was applied to a coarse silica gel plug, eluted with CH_2Cl_2, the eluent was evaporated, and the residue was dissolved in 20 mL of THF. Next, 1.00 mL of triethylamine (7.17 mmol) and 617 mg (3.99 mmol) of phenacyl chloride were added, and the mixture was stirred for 6 h. Aqueous CH_2Cl_2 workup gave an extract, which was dried over $MgSO_4$ and evaporated, and the residue was eluted on a plug of silica gel (10% EtOAc–hexane). The eluent containing the product was evaporated and separated further by HPLC to afford 133 mg (0.45 mmol) of phenacyl sulfide **14c** as an oil: analytical TLC (silica gel F254), 20% EtOAc–hexane, R_f 0.27; MS, m/e exact mass calcd for $C_{16}H_{22}O_3S$ 294.1284, found 294.1284, error 0.1 ppm; IR ($CHCl_3$, cm^{-1}) 1730 (C=O), 1680 (C=O); 200-MHz NMR ($CDCl_3$) δ 7.97–7.92 (2 H, m), 7.60–7.40 (3 H, m), 4.89 (1 H, dd, J = 10.8, 2.3 Hz), 3.85 (1 H, d, J = 14.1 Hz), 3.72 (1 H, d, J = 14.1 Hz), 2.85 (1 H, dd, J = 14.1, 2.3 Hz), 2.50 (1 H, dd, J = 14.1, 10.8 Hz), 2.07 (3 H, s), 0.90 (9 H, s).

Photolysis of 14c. The usual photolytic/trapping procedure was employed for 66 mg (0.22 mmol) of sulfide **14c** and 2.00 mL (24.3 mmol) of cyclopentadiene in 10 mL of benzene. After 6-h photolysis, evaporation, filtration through a silica gel plug, and HPLC separation, two fractions were obtained: 49.8 mg (0.21 mmol, 89%) and 6.1 mg (0.026 mmol, 11%). The major fraction proved to be endo and exo diastereomers (82:6 by NMR integration) **7Ac** and **8Ac**; the minor fraction was the other endo/exo pair (**7Bc** and **8Bc**, 9:3). The major endo product **7Ac** was characterized further as an oil: analytical TLC (silica gel F254), 10% EtOAc–hexane, R_f 0.35; MS, m/e exact mass calcd for $C_{13}H_{20}O_2S$ 240.1179, found 240.1185, error 2.4 ppm; IR ($CHCl_3$, cm^{-1}) 1720 (C=O), 1370 (C(Me)$_2$); 270-MHz NMR ($CDCl_3$) δ 6.40 (1 H, dd, J = 5.5, 2.9 Hz), 5.62 (1 H, dd, J = 5.5, 2.9 Hz), 4.31 (1 H, d, J = 10.3 Hz), 3.88 (1 H, br s), 3.85 (1 H, dd, J = 10.3, 3.5 Hz), 3.43 (1 H, br s), 2.11 (3 H, s), 1.57 (1 H, br d, J = 9.1 Hz), 1.48 (1 H, br d, J = 9.1 Hz), 0.90 (9 H, s).

2,3-Dihydroxypropyl Phenacyl Sulfide (15a). Phenacyl chloride (5.61 g, 36.3 mmol) and 3-mercapto-1,2-propanediol[17] (3.00 mL, 35.9 mmol) were dissolved in 40 mL of THF, and cooled to 0 °C under N_2. Triethylamine (6.00 mL, 43.0 mmol) was added, and the mixture was warmed and stirred for 10 h. The precipitated amine hydrochloride was removed by filtration, and the filtrate was evaporated. The resulting yellow oil was filtered through a plug of silica gel (10% EtOAc–hexane to remove excess phenacyl chloride then EtOAc), and the EtOAc eluent was evaporated to afford diol sulfide **15a** (7.99 g, 35.3 mmol, 98%e as an oil: analytical TLC (silica gel F254), EtOAc, R_f 0.30; MS, m/e exact mass calcd for $C_{11}H_{14}O_3S$ 226.066, found 226.0663, error 1.4 ppm; IR ($CHCl_3$, cm^{-1}) 3400 (O–H), 1675 (C=O); 270-MHz NMR ($CDCl_3$) δ 7.94–7.90 (2 H, m), 7.57–7.39 (3 H, m), 3.87 (2 H, s) 3.87 (3 H, br s), 3.56–3.52 (1 H, m), 3.12 (1 H, br s), 2.70 (1 H, dd, J = 13.9, 4.7 Hz), 2.61 (1 H, dd, J = 13.9, 7.5 Hz).

Preparation of Acetonide 15b. A 20-mL DMF solution of sulfide diol **15a** (2.54 g, 11.2 mmol), dimethoxypropane (2.00 mL, 16.3 mmol), and toluenesulfonic acid monohydrate (500 mg, 2.63 mmol) was stirred for 10 h under N_2 and poured into ether. The ether phase was washed three times with water, dired over $MgSO_4$, and evaporated. The residual oil was separated by flash chromatography to afford (in order) 815 mg of a byproduct and 1.52 g (5.70 mmol, 51%) of acetonide **15b**. **15b**: colorless oil; analytical TLC (silica gel F254), 20% EtOAc–hexane, R_f 0.23; MS, m/e exact mass calcd for $C_{14}H_{18}O_3S$ 266.0972, found 266.0976, error 1.5 ppm; IR ($CHCl_3$, cm^{-1}) 1680 (C=O); 270-MHz NMR ($CDCl_3$) δ 7.96–7.92 (2 H, m), 7.57–7.42 (3 H, m), 4.30–4.25 (1 H, m), 4.05 (1 H, dd, J = 8.3, 6.1 Hz), 3.92 (1 H, d, J = 14.4 Hz), 3.85 (1 H, d, J = 14.4 Hz), 3.67 (1 H, dd, J = 8.3, 6.4 Hz), 2.89 (1 H, dd, J = 13.6, 7.3 Hz), 2.68 (1 H, dd, J = 13.6, 6.1 Hz), 1.38 (3 H, s), 1.32 (3 H, s).

Photolysis of 15b and Trapping with Cyclopentadiene. The usual photolytic trapping procedure was employed for 116 mg of sulfide **15b** (0.43 mmol) and 2.00 mL of cyclopentadiene (24.3 mmol) in 10 mL of benzene. After 5-h photolysis, silica gel filtration (hexane and then 20% EtOAc–hexane) and HPLC gave the following fractions: (1) a mixture of unresolved major exo and endo adducts **20A** and **21A** (5.6:1, 65.8 mg, 0.31 mmol, 72%) and (2) the other endo/exo pair **20B** and **21B** (4:1, 2.1 mg, 0.01 mmol, 2%). The major endo adduct **20A** was isolated by collecting the tail of the major fraction. **20A**: oil; analytical TLC (silica gel F254), 20% EtOAc–hexane, R_f 0.50; MS, m/e exact mass calcd for $C_{11}H_{16}O_2S$ 212.0867, found 212.0872, error 2.4 ppm; IR ($CHCl_3$, cm^{-1}) 1570 (C=C), 1240 (C–O); 200-MHz NMR ($CDCl_3$) δ 6.35 (1 H, dd, J = 5.5, 2.9 Hz), 5.84 (1 H, dd, J = 5.5, 3.1 Hz), 3.98–3.38 (6 H, m), 1.66 (1 H, dt, J = 9, 3 Hz), 1.52 (1 H, br d, J = 9 Hz), 1.42 (3 H, s), 1.28 (3 H, s).

Thioaldehyde Generation from 15b in the Presence of Danishefsky's Diene. The typical photolysis/trapping procedure was followed, with use of 299 mg (1.12 mmol) of acetonide sulfide **15b** and 862 mg (5.00 mmol) of 1-methoxy-3-(trimethylsiloxy)-1,3-butadiene in 20 mL of benzene. After 6-h photolysis, benzene was evaporated and 10% aqueous THF was added. After 10 h of stirring, the mixture was partitioned between water–dichloromethane. The organics were dried ($MgSO_4$) and evaporated (aspirator), and the residue was purified by filtration through a silica gel plug followed by HPLC separation. Two products were detected, but the less polar minor product was not obtained pure (2 mg, presumed to contain **22B**). The more polar fraction (219 mg, 1.02 mmol, 91%) was the major product **22A**: oil; analytical TLC (silica gel F254), 30% EtOAc–hexane, R_f 0.17; MS, m/e exact mass calcd for $C_{10}H_{14}O_3S$ 214.066, found 214.0661, error 0.6 ppm; IR (neat, cm^{-1}) 1660 (C=O); 27-MHz NMR ($CDCl_3$) δ 7.32 (1 H, d, J = 10.2 Hz), 6.18 (1 H, d, J = 10.2 Hz), 4.24 (1 H, ddd, J = 7.9, 6.1, 5.3 Hz), 4.09 (1 H, dd, J = 8.3, 6.1 Hz), 3.83 (1 H, dd, J = 8.8, 5.3 Hz), 3.49 (1 H, ddd, J = 7.9, 6.4, 2.9 Hz), 2.87 (1 H, dd, J = 15.4, 2.9 Hz)8 2.79 (1 H, dd, J = 15.4, 6.4 Hz), 1.41 (3 H, s), 1.32 (3 H, s).

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