(30 mL) was added 2-[(2-aminoethyl)amino]ethanol (118 mg, 1.13 mmol) whereupon the solution immediately turned dark purple. After 12 h at room temperature, no starting material remained by TLC analysis. The pyridine was removed in vacuo, and the dark purple residue was chromatographed on flash silica gel column (75:25 $CHCl_3/CH_3OH$ as eluant). The highly polar product was finally eluted from the silica gel by adding a small amount of concentrated NH_4OH solution to the eluant. In this way, after concentration and drying in vacuo, a deep purple semisolid (54 mg) was obtained, melting over a broad range and decomposing above 150 °C: IR (KBr) 3600–3200 (br, s), 2920 (w), 1720 (w), 1600 (s), 1520 (w), 1440 (br, m), 1230 (br, m) cm^{-1}; ^1H NMR (500 MHz) δ 9.65 (t, disappears with D_2O wash, 1 H), 7.54 (str m, 2 H), 7.02 (q, 1 H), 5.28 (d, 1 H), 3.72 (t, 2 H), 3.45 (q, collapses to triplet with D_2O wash, 2 H), 3.06 (t, 2 H), 3.02 (AB q, J_{AB} = 18 Hz with higher field component partially obscured, 2 H), 2.43 (s, 3 H), 2.25 (AB q, $\Delta\nu$ = 115 Hz, J_{AB} = 20 Hz with higher field component split into doublet, 2 H); ^{13}C NMR δ 215.8, 186.7, 185.7, 154.3 (2 C), 150.5, 136.1, 135.1, 132.5 (2 C), 119.0, 116.6, 111.7, 110.6 (2 C), 77.0, 61.1, 56.9, 49.9, 46.1, 38.8, 35.8, 31.7, 24.6; FAB, *m/e* 471 (0.21% of base peak).

(−)-1,4-Bis[[2-[*N*-(hydroxyethyl)amino]ethyl]amino]-4-demethoxydaunomycinone (19). To a solution of (+)-4-demethoxy-1,4-difluorodaunomycinone (10 mg, 0.025 mmol) in pyridine (0.25 mL) was added 2-[(2-aminoethyl)amino]ethanol (0.124 mL of a 1.0 M pyridine solution), and the resulting mixture was stirred for 2 h at 75 °C. The pyridine was then removed in vacuo, and the residue was deposited on silica gel and chromatographed ($CHCl_3/CH_3OH$ as eluant) until the product band remained behind. This was then eluted with an 80:20 mixture of $CHCl_3/CH_3OH$ containing 2.5% concentrated NH_4OH. Concentration of the main fractions and drying in vacuo afforded the title compound [8.1 mg (57%)] as a deep blue hygroscopic semisolid with a broad melting range (100–150 °C): $[\alpha]^{436}_{25}$ −188° (1:1 $CHCl_3/CH_3OH$); IR (KBr) 3600–3200 (br, s), 2920 (m), 2850 (w), 1720 (m), 1640 (m), 1600 (s), 1565 (s), 1200 (br, s) cm^{-1}; ^1H NMR (500 MHz, pyridine-d_5) δ 10.74 (s, 2 H), 7.23 (d, 2 H), 5.69 (s, 2 H), 3.99 (s, 4 H), 3.56 (s, 4 H), 3.47 (AB q, $\Delta\nu$ = 139 Hz, J_{AB} = 18 Hz, 2 H), 3.01 (d, 8 H), 2.52 (s, 3 H), 2.47 (AB q, $\Delta\nu$ = 158 Hz, J_{AB} = 14 Hz, 2 H); FAB, *m/e* 573 (0.52% of base peak); UV (1:1 $CHCl_3/CH_3OH$) 680 nm (ϵ 16486), 626 (ϵ 12657).

Testing in Mice against the P388 Lymphocytic Leukemia Model. Test compounds were dissolved in 0.9% saline. Female CDF_1 and DBA_2 (Harlan Laboratory, Indianapolis, IN) housed in gang cages were fed Purina Laboratory Chow and water ad libitum and adapted to this regime for at least 1 week before use. The P388 tumor was maintained by continuous passage in DBA_2 mice. On day 0, ascitic fluid was removed and diluted with Hank's balanced salt solution, cells were counted, and 10^6 tumor cells were implanted ip in a total volume of 0.1 mL. Twenty-four hours later, mice were randomly segregated into treatment groups, and drug was given ip to groups of seven mice for each dilution. The mice were observed for 30 days and T/C (percent) values were determined from the survival rate as compared to the controls.[21]

Acknowledgment. This research was supported by Adria Laboratories and The Ohio State University. G. W.M. thanks the Graduate School, The Ohio State University, for a fellowship (1984–1985).

(21) For data interpretation, see: Geran, R. I.; Greenberg, N. H.; McDonald, M. H.; Schumacher, A. M.; Abbott, B. S. *Cancer Chemother. Rep., Part 3* **1972**, *3*, 1.

Asymmetric Induction in the Addition Reactions of Chiral Sulfinylallyl Anions (Ambident Nucleophiles) with Enones (Ambident Electrophiles). Ring Closure of Enol Thioether Ketones[1]

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The regio- and stereochemical aspects of reactions of sulfinylallyl anions possessing chiral sulfur with various cyclic enones are reported. The 1,4-γ-adducts (Michael-type adducts) were obtained with excellent enantioselectivity in most cases (70–96% ee). Hydrolytic desulfurization followed by intramolecular cyclization of the adducts were demonstrated. These two methods constitute a mild and versatile method for the synthesis of chiral cyclic molecules.

The regiospecific addition reactions of cyclopentenones with carbanions of allylic sulfoxides constitute a mild and versatile method for the formation of carbon–carbon bonds. Kraus and Frazier[2] were the first to disclose the Michael additions of allylic sulfone anions to α,β-unsaturated ketones and esters. The addition reactions of allylic sulfide[3] and racemic allylic sulfoxide[4-6] anions with cyclic enones were then reported. The present paper describes the asymmetric induction exhibited in the conjugate addition reaction of the carbanion derived from allylic sulfoxides possessing chiral sulfur with various cyclic enones and the intramolecular cyclization of the adduct enol

(1) Part of this work has been previously communicated: (a) Hua, D. H.; Sinai-Zingde, G.; Venkataraman, S. *J. Am. Chem. Soc.* **1985**, *107*, 4088. (b) Hua, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 3835. (c) Hua, D. H.; Takusagawa, F.; Badejo, I., McCann, P. J., submitted for publication in *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*

(2) Kraus, G. A.; Frazier, K. *Synth. Commun.* **1978**, *8*, 483.

(3) (a) Binns, M. R.; Haynes, R. K.; Houston, T. L.; Jackson, W. R. *Tetrahedron Lett.* **1980**, 573. (b) Binns, M. R.; Haynes, R. K. *J. Org. Chem.* **1981**, *45*, 3790.

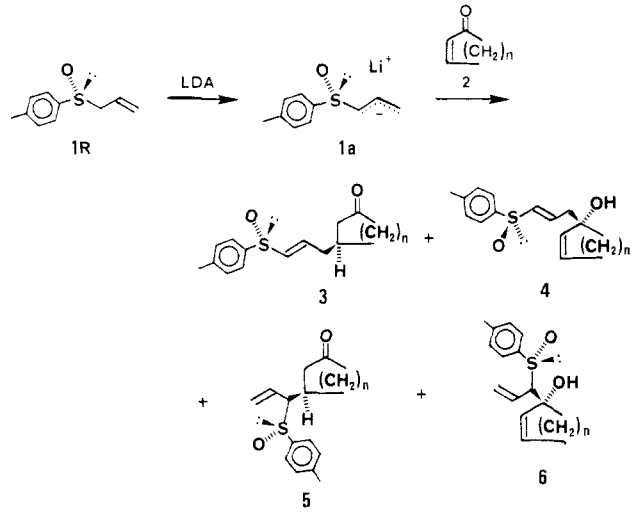
(4) (a) Binns, M. R.; Haynes, R. K.; Houston, T. L.; Jackson, W. R. *Aust. J. Chem.* **1981**, *34*, 2465. (b) Binns, M. R.; Haynes, R. K.; Katsifis, A. A.; Schober, P. A.; Vonwiller, S. C. *Tetrahedron Lett.* **1985**, 1565. (c) Binns, M. R.; Chai, O. L.; Haynes, R. K.; Katsifis, A. A.; Schober, P. A.; Vonwiller, S. C. *Tetrahedron Lett.* **1985**, 1569.

(5) (a) Nokami, J.; Ono, T.; Iwao, A.; Wakabayasho, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3043. (b) Nokami, J.; Ono, T.; Wakabayashi, S.; Hazato, A.; Kurozumi, S. *Tetrahedron Lett.* **1985**, 1985.

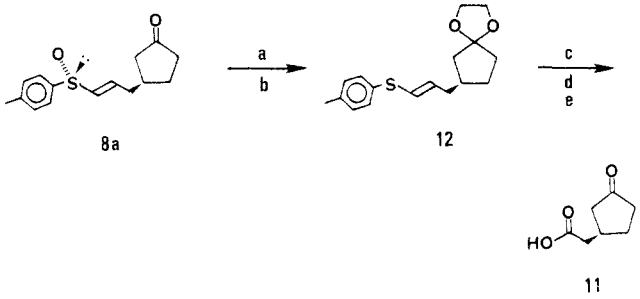
(6) (a) Vasil'eva, L. L.; Mel'nikova, V. I.; Gainullina, E. T.; Pivnitskii, K. K. *J. Org. Chem. USSR (Engl. Transl.)* **1983**, *19*, 835. (b) Vasil'eva, L. L.; Mel'nikova, V. I.; Pivnitskii, K. K. *Zh. Org. Khim.* **1984**, *20*, 690.

0022-3263/87/1952-0719$01.50/0

Scheme I



Scheme II[a]



[a] (a) Zn–AcOH, room temperature; (b) $HOCH_2CH_2OH$–pyridinium tosylate; (c) O_3–CH_2Cl_2, −78 °C; (d) n-Bu_4NMnO_4–CH_2Cl_2; (e) $NaHSO_3$–HCl–H_2O.

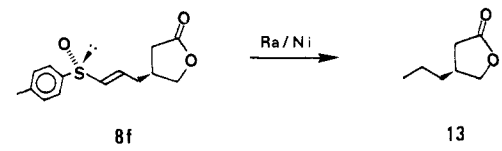
thioether ketones[1] as a part of our program concerned with asymmetric synthesis of chiral cyclic molecules. The addition reaction of allylic sulfoxide anion **1a** with enones **2** in theory could provide 1,4-γ-adducts **3**, 1,2-γ-adducts **4**, 1,4-α-adducts **5**, and 1,2-α-adducts **6** (Scheme I); however, we found mainly 1,4-γ-adducts **3** and in few cases the 1,2-γ-adducts **4**.

Results and Discussion

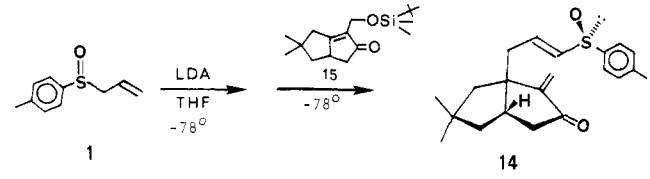
I. Addition Reactions of Chiral Sulfinylallyl Anions with Enones. The results of reactions of the carbanion derived from (+)-(*R*)-allyl *p*-tolyl sulfoxide (**1R**)[7] with various cyclic enones are summarized in Table I. The general procedure for these reactions consists in treating (+)-(*R*)-allyl *p*-tolyl sulfoxide (**1R**)[7] with lithium diisopropylamide (LDA) in THF at −78 °C for 1 h followed by 1 equiv of the cyclic enones **2** at −78 °C. The absolute configurations at the newly created chiral centers (e.g., C-3 of 1,4-γ-adduct **8a**) of the 1,4-γ-adducts were proven in three cases (entries 1 and 6 and enone **15**) by degradation to known compounds or X-ray diffraction.

The 1,4-γ-adduct **8a** was degraded to the known acid, (+)-(*R*)-3-oxocyclopentaneacetic acid (**11**),[8] $[\alpha]^{21}_D$ +109° (lit.[8c] $[\alpha]$ −115.5° for *S* configuration), by the (i) reduction of the sulfoxide group of **8a** with zinc in acetic acid at room temperature for 12 h to the corresponding sulfide, 95% yield, (ii) protection of the carbonyl group with ethylene glycol–pyridinium tosylate to ketal **12**, 96% yield, (iii) ozonolysis of the double bond in CH_2Cl_2 at −78 °C, and (iv) oxidation of the resulting aldehyde group with n-Bu_4NMnO_4 in CH_2Cl_2 at room temperature followed by $NaHSO_3$–HCl workup[9] (70% yield in two steps) (Scheme II).

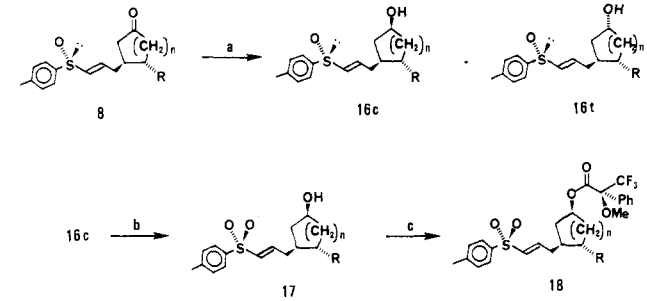
Scheme III



Scheme IV



Scheme V[a]



[a] (a) $NaBH_4$–MeOH; (b) MCPBA–CH_2Cl_2; (c) (+)-MTPAC–Et_3N–DMAP.

1,4-γ-adduct **8f** (entry 6) was transformed to the known lactone, (*S*)-β-propyl-γ-butyrolactone (**13**)[10] (80% yield), $[\alpha]^{25}_D$ −7.3° (lit.[10b] $[\alpha]$ +6.7° for *R* configuration, >90% ee) by reacting with Raney nickel (W-2) in refluxing acetone (Scheme III).

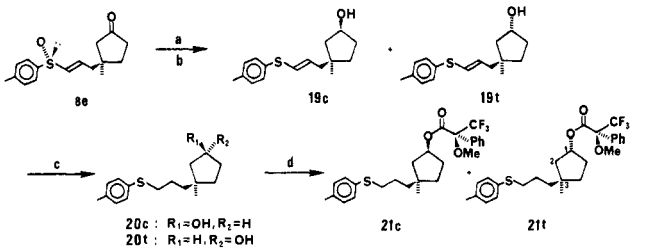
The relative stereochemistry at C-1, C-5, and sulfur of the 1,4-γ-adduct, [1(*S**),5(*S**),*S*(*R**)]-1-[3-(*p*-tolylsulfinyl)-2-propenyl]-2-methylene-7,7-dimethylbicyclo[3.3.0]octan-3-one (**14**), from the reaction of the carbanion derived from racemic *p*-tolyl allyl sulfoxide (**1**) with 2-[((*tert*-butyldimethylsilyl)oxy)methyl]-7,7-dimethylbicyclo[3.3.0]-1-octen-3-one (**15**), was determined by X-ray diffraction (Scheme IV).[1c]

In all cases but one (entry 6) the 1,4-γ- and 1,4-α-adducts were transformed to either the corresponding hydroxy sulfones or hydroxy sulfides, and the optical purities were determined from the ^1H and/or ^{19}F NMR spectra of the corresponding Mosher's derivatives.[11]

For entries 1–3 and 8–11, the 1,4-γ-adducts were reduced with $NaBH_4$ in MeOH at −10 °C to give alcohols **16c** and **16t** in 95% yield (Scheme V). These two alcohols were separated by preparative thin-layer chromatography (PTLC) or column chromatography. Oxidation of sulfoxide alcohol **16c** (in most cases mixtures of **16c** and **16t** could be used without separation) with 1 equiv of *m*-chloro-

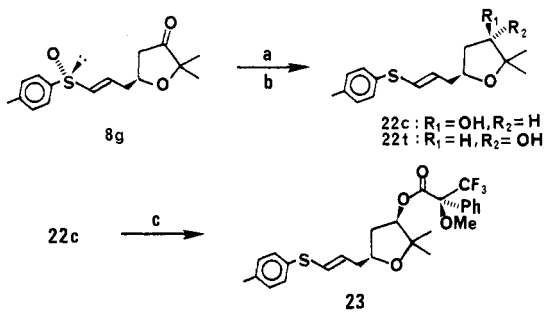
(7) Bickart, P.; Carson, F. W. *Jacobus*, J.; Miller, E. G.; Mislow, K. *J. Am. Chem. Soc.* **1968**, *90*, 4869.
(8) (a) Demole, E.; Stoll, M. *Helv. Chim. Acta* **1962**, *45*, 692. (b) Hill, R. K.; Edwards, A. G. *Tetrahedron* **1965**, *21*, 1501. (c) Kuritani, H.; Takaoka, Y.; Shingu, K. *J. Org. Chem.* **1979**, *44*, 452.
(9) Sala, T.; Sargent, W. V. *Chem. Commun.* **1978**, 253.
(10) (a) Ceder, O.; Nilsson, H. G. *Acta Chem. Scand., Ser. B* **1977**, *B31*, 189. (b) Mukaiyama, T.; Fujimoto, K.; Hirose, T.; Takeda, T. *Chem. Lett.* **1980**, 635.
(11) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.

Scheme VI[a]



[a] (a) Zn–AcOH, room temperature; (b) $NaBH_4$–MeOH; (c) H_2–Pd/C, room temperature; (d) (+)-MTPAC–Et_3N–DMAP.

Scheme VII[a]



[a] (a) $NaBH_4$–MeOH; (b) Zn–AcOH, room temperature; (c) (+)-MTPAC–Et_3N–DMAP.

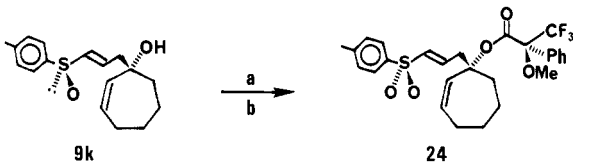
peroxybenzoic acid in CH_2Cl_2 at 0 °C for 4 h gave sulfone alcohol **17** in 90% yield. Treatment of **17** with 1.2 equiv of (+)-(*R*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (MTPAC), 2 equiv of Et_3N, and 0.4 equiv of 4-(dimethylamino)pyridine (DMAP) in toluene at room temperature provided 88% yield of the Mosher derivative **18**. The vinylic protons (SO_2CH=C) of the diastereomers of **18** have different ^1H NMR chemical shifts. For comparison, in all cases racemic sulfoxide **1** was used to generate racemic **17** and the respective Mosher esters were prepared.

Entries 2, 3, 8, and 9 show examples of kinetic resolution. For instance, when 2 equiv of racemic 4-[(α,α-dimethylbenzyl)oxy]-2-cyclopentenone was allowed to react with the carbanion derived from **1R**, only the (*S*)-enones reacted, indicating that the carbanion approaches 2-cyclopentenone from the *si* face.[12]

Adduct **8f** (entry 5) was reduced with zinc–AcOH at room temperature for 24 h followed by $NaBH_4$–MeOH at −10 °C to form a mixture of the sulfide alcohols **19c** and **19t** in 70% yield (two steps) (Scheme VI). Hydrogenation of **19c** and **19t** with H_2–10% Pd/C at room temperature produced the saturated sulfide alcohols **20c** and **20t**, respectively (90% yield), which upon esterification with (+)-(*R*)-MTPAC–Et_3N–DMAP–toluene at 50 °C gave 92% yield of **21c** and **21t**. The C-3 methyl groups of all four diastereomers have different chemical shifts in the 400-MHz ^1H NMR spectra (δ 0.9498, 0.9299, 0.9214, and 0.8923).

1,4-adduct **8g** (entry 7) was converted to alcohols **22c** and **22t** (2:1 ratio) by (i) reduction (of carbonyl) with $NaBH_4$–MeOH at −10 °C (95% yield) and (ii) reduction (of sulfoxide) with Zn–AcOH at room temperature (85% yield) (Scheme VII). These two alcohols were separated by column chromatography. Treatment of alcohol **22c** with (+)-(*R*)-MTPAC–Et_3N–DMAP–toluene at 50 °C

Scheme VIII[a]



[a] (a) MCPBA–CH_2Cl_2; (b) (+)-MTPAC–Et_3N–DMAP.

provided 90% yield of ester **23**. The vinylic protons (SC-*H*=C) of the diastereomers of **23** have different ^1H NMR chemical shifts spectra (δ 6.0289 and 6.1155).

Adduct **8f** (entry 6) was degraded to lactone **13** (vide supra), and the optical purity of **13** was measured by ^1H NMR analysis using optically active shift reagent tris-[3-((heptafluoropropyl)hydroxymethylene)-*d*-camphorato]europium(III) as described.[10b]

The optical purities of the 1,2-γ-adducts **9i** (entry 9), **9j** (entry 10), and **9k** (entry 11) were measured by using Mosher's method[11] by oxidation of the sulfoxide group with 1 equiv of MCPBA in CH_2Cl_2 at 0 °C followed by esterification with (+)-(*R*)-MTPAC–Et_3N–DMAP in toluene (Scheme VIII). The vinylic protons (SO_2CH=C) of the diastereomers have different ^1H NMR chemical shifts. Although the absolute configuration of these three adducts has not been proven, we assume the (*R*)-sulfinylallyl anion attacks the C=O of the cyclic enones from the *si* face as in the above 1,4-addition reaction. From a synthetic point of view, the 1,4-addition product is more useful than the 1,2-addition product.

In the five-memebered ring system, only 1,4-γ-adducts were formed except with enone **7i**[13] (entry 9), where two bulky (*tert*-butyldimethylsilyl)oxy groups are appended to C-4 and C-5 in a trans juxtaposition. Steric effect from the C-5 substituent increases the activation energy for the 1,4-γ-addition so that some 1,2-addition reaction occurs. It is clear that the chiral sulfinylallyl anion (formed from **1R** by treatment with LDA in THF at −78 °C) attacks cyclopentenones from the *si* face and the allylic carbanion exists as trans configuration. The "trans-fused ten-membered" cyclic transition state proposed by Haynes[4b] offers an explanation of this highly stereoselective reaction.

Six- and seven-membered cyclic enones provided both 1,4-γ- and 1,2-γ-adducts. The larger ring gave more of the 1,2-γ-adduct; e.g., with the seven-membered ring, a 58% yield of the 1,2-γ-adduct **9k** was isolated. Furthermore, these 1,4- and 1,2-addition reactions appear to be kinetically controlled. The same product (in five-membered ring system) or product ratio was found when the addition reactions were performed at −100, −78, or −50 °C, and the 1,2-γ- and 1,4-γ-adducts did not interconvert under the reaction conditions or even at 25 °C. The lower 1,4-reactivity found for the larger ring enones is consistent with the results obtained in the reactions of cyclic enones with the carbanion derived from methyl (methylthio)methyl sulfoxide.[14] The percentages of enantiomeric excess of those adducts formed from the six- and seven-membered rings are substantially lower than that from the five-membered ring enones. This result with the larger cyclic enones may be due to the comparable activation energy for the anion to approach from the "*si*" and "*re*" faces of the enones.

The formation of the cis adducts **8bc** and **8cc** (entries 2 and 3) probably results from the chelation of lithium counterion by C-4 oxygen.

(12) The Izumi-Tai nomenclature is employed: Izumi, Y.; Tai, A. *Stereodifferentiating Reactions*; Kodansha Ltd.: Tokyo; Academic Press: New York, 1977; pp 68–69.

(13) Hua, D. H.; Venkataraman, S. *Tetrahedron Lett.* **1985**, 3765.

(14) Ogura, K.; Yamashita, M.; Tsuchihashi, G.-I. *Tetrahedron Lett.* **1978**, 1303.

Table I. Yields and Optical Purities of the Adducts from the Reaction of Enones with Lithiated (*R*)-(*p*-Tolylsulfinyl)allyl Anion

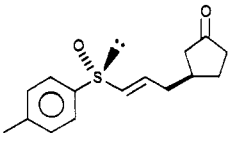
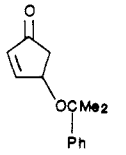
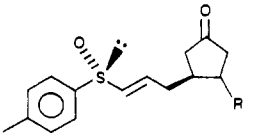
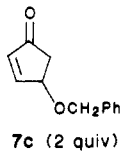
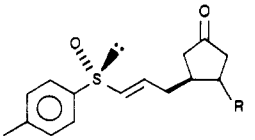
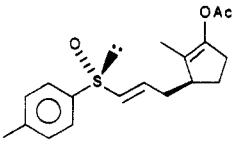
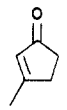
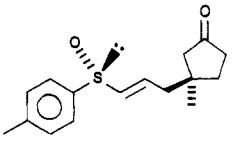
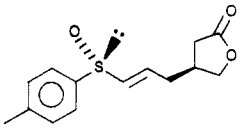
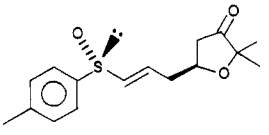
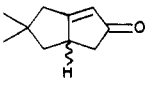
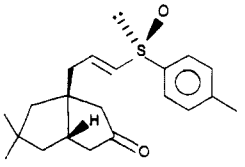
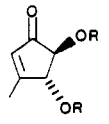
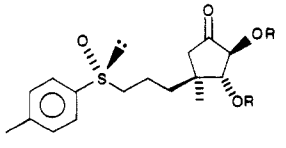
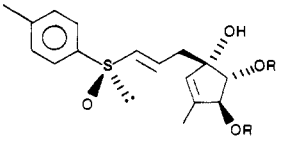
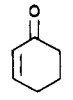
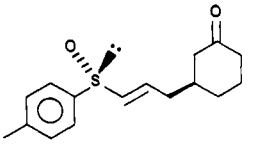
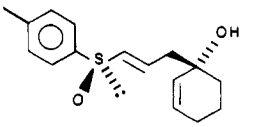
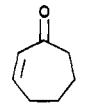
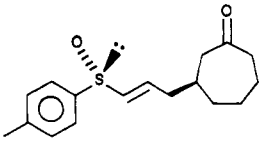
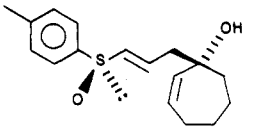
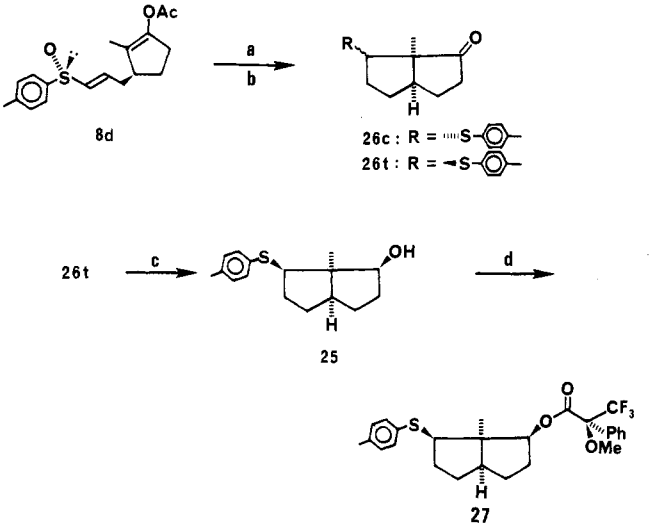
		1,4-γ-adduct		1,2-γ-adduct	
entry	enones		% yield (% ee)		% yield (% ee)
1	 **7a**	 **8a**	91 (96)	none	
2	 **7b** (2 equiv)	 **8bt**, R = ≡OCMe$_2$Ph **8bc**, R = ◀OCMe$_2$Ph	68 (95) 7 (90)	none	
3	 **7c** (2 equiv)	 **8ct**, R = ≡OCH$_2$Ph **8cc**, R = ◀OCH$_2$Ph	48 (60) 32 (86)	none	
4	 **7d**	 **8d**	84 (95)[a]	none	
5	 **7e**	 **8e**	80 (95)	none	
6	 **7f**	 **8f**	70 (95)	none	
7	 **7g**	 **8g**	82 (70)	none	
8	 **7h** (2 equiv)	 **8h**	83 (74)	none	
9	 **7i**, R = SiMe$_2$-*t*-Bu, racemic (2 equiv)	 **8i**	51 (85)	 **9i**	34 (88)

Table I (Continued)

entry	enones	1,4-γ-adduct	% yield (% ee)	1,2-γ-adduct	% yield (% ee)
10	 7j	 8j	79 (50)	 9j	14 (50)
11	 7k	 8k	25 (50)	 9k	58 (50)

[a] The resulting enolate ion was treated with acetyl chloride at −78 °C.

Scheme IX[a]



[a] (a) Zn–AcOH, room temperature; (b) $TiCl_4$–AcOH–H_2O, room temperature; (c) $NaBH_4$–MeOH; (d) (+)-MTPAC–Et_3N–DMAP.

II. Ring Closures of Enol Thioether Ketones. For the determination of the optical purity of the adduct from the reaction of the chiral sulfinylallyl anion with 2-methyl-2-cyclopentenone (entry 4), the adduct was transformed into bicyclo[3.3.0]octanol **25** by the following sequence: (i) in situ O-acetylation with acetyl chloride (AcCl) at −78 °C of the enolate ion formed in the reaction of **1R** and 2-methyl-2-cyclopentenone, (ii) reduction with Zn–AcOH at room temperature, 95% yield, (iii) intramolecular cyclization of the enol acetate with the vinylic sulfide moiety in the presence of 1 equiv of $TiCl_4$ in AcOH and 4 equiv of H_2O at room temperature for 15 min to give hexahydropentalenones **26c** and **26t** (1:4), 86% yield, and (iv) reduction of isomer **26t** with $NaBH_4$ in MeOH at −10 °C for 1 h, 95% yield. Ester **27** was prepared (vide supra) from **25** and (+)-MTPAC, and the ^{19}F NMR method[11] was applied to **27** to determine its optical purity (Scheme IX).

The intramolecular cyclizations involving enolic acetates or ketones and vinylic sulfide moieties have not been reported. However, ring closures involving a vinylic sulfide moiety and aromatic ring[15a] or β-keto ester[15b] have been described. This reaction with enol acetate apparently involves the conversion of enol acetate to enol, protonation of the vinylic sulfide to form α-arylthio carbocation and rapid attack by the enol on the carbocation. Enolization involving the more substituted side of ketone is thermodynamically preferred. Other systems have been explored to examine the general application of this cyclization reaction. Under the same conditions ($TiCl_4$–AcOH–H_2O, room temperature), but with a longer reaction time, sulfide **28b** did not provide any product; only starting material was recovered. Structure **28b**, without an α-methyl group provides insignificant amounts of the enol tautomer. Hence, other reaction conditions were sought for the cyclization reactions. Table II summarizes the results of the hydrolytic ring closure of enol thioether ketones. All the starting sulfides are prepared from zinc–AcOH (room temperature) reduction of the corresponding sulfoxides.

The difficulty of hydrolyzing vinyl sulfides possessing an α-CH to the corresponding aldehydes with $HgCl_2$ or under strongly acidic conditions has been reported.[16] Vinyl sulfide **28b** underwent hydrolysis to eliminate *p*-toluenethiol followed by rapid intramolecular cyclization with the ε-enol moiety when treated with 88% HCO_2H and a catalytic amount of CF_3CO_2H at 70 °C for 3 h to give mainly bicyclo[3.3.0]octanone **29** (70%) and some of the disulfide **31b** (7%). Disulfide **31b** was formed from the capture of the α-arylthio carbocation by the eliminated *p*-toluenethiol. Indeed, in more concentrated reaction condition, **31b** was formed as the major product. Dilution and higher temperature (optimum at 70 °C) favor the ring-closure product **29b**.

In the bicyclic systems[1b] (entries 15 and 16), cyclizations at α- as well as α′-carbons of the ketone took place, and the pentalenene structure, **29e** (cyclization at α-C) was isolated as the major product (60%). A recent study[17] on the intramolecular aldolization of this class of tricyclic structure also demonstrated the formation of both products. The corresponding alcohol **30d** was formed from the hydrolysis of the formate **29d** under the reaction conditions.

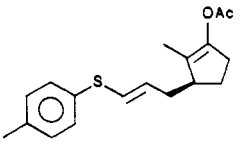
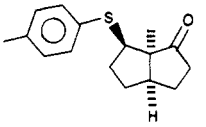
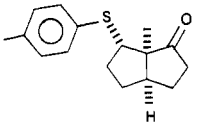
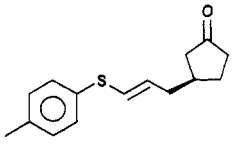
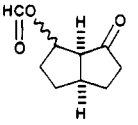
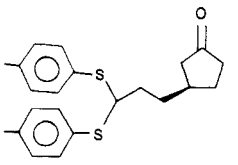
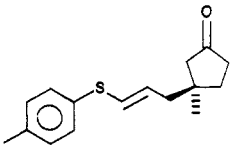
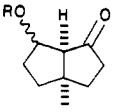
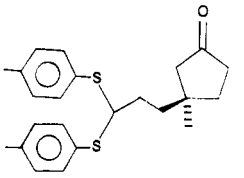
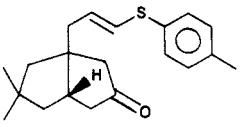
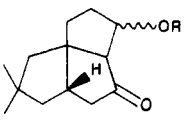
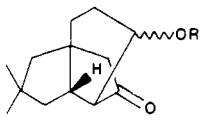
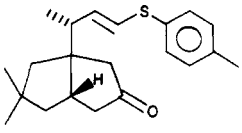
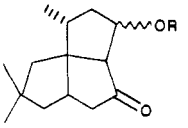
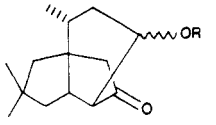
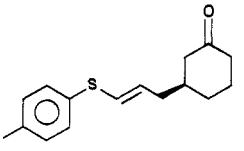
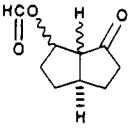
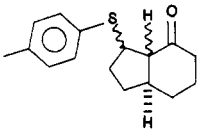
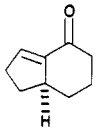
The structure of **31e** was proven by hydrolysis with 1 equiv of K_2CO_3–MeOH at room temperature for 15 min to alcohol **32e** followed by oxidation with pyridinium chlorochromate–CH_2Cl_2 to the corresponding diketone (C-4, C-6). ^1H NMR spectrum of this diketone shows four doublets of δ 2.60 (J = 20 Hz, C-4 H), 2.18 (J = 20 Hz, C-4

(15) (a) DeWaard, E. R.; Reus, H. R.; Huisman, H. O. *Tetrahedron Lett.* **1973**, 4315. (b) Kende, A. S.; Schneider, J. A. *Synth. Commun.* **1979**, *9*, 419.

(16) Mura, A. J., Jr.; Majetich, G.; Grieco, P. A.; Cohen, T. *Tetrahedron Lett.* **1975**, 4437.

(17) Paquette, L. A.; Lau, C. J. *Synth. Commun.* **1986**, *16*, 103.

Table II. Hydrolytic Ring Closure of Enol Thioether Ketones

entry	sulfide	reacn conditions	products (% yield)		
12	 **28a**	*a*	 **26t** (69)	 **26c** (17)	
13	 **28b**	*b*	 **29b** (70)	 **31b** (7)	
14	 **28c**	*b*	 **29c**, R = CHO (65) **30c**, R = H (10)	 **31c** (7)	
15	 **28d**	*b*	 **29d**, R = CHO (50) **30d**, R = H (9)	 **31d**, R = CHO (30) **32d**, R = H (7)	
16	 **28e**	*b*	 **29e**, R = CHO (60) **30e**, R = H (8)	 **31e**, R = CHO (20) **32e**, R = H (4)	
17	 **28f**	*b*	 **29f** (16)	 **30f** (13)	 **31f** (50)

[a] $TiCl_4$–AcOH–H_2O, room temperature, 30 min. [b] 88% HCO_2H–CF_3CO_2H (catalyst), 70 °C, 3 h.

H), 1.83 (J = 14 Hz, C-1 H), and 1.50 (J = 14 Hz, C-1 H). Formate **29e** has been transformed to (+)-pentalenene.[1b] The relative stereochemistry (3aα,5aβ,6β,8β,8aβ) of the major formate **29e** (6β is the major component) was proven by X-ray analysis of the corresponding *N,N,N',N'*-tetramethyldiamidophosphonate derivative of alcohol **30e**.[1b,18]

The asymmetric induction reaction of chiral sulfinylallyl anion with enones provides a facile enantioselective synthesis of substituted cyclic ketones. The subsequent hydrolytic ring closure of the resulting enol thioether ketones is a synthetically desirable transformation which further enhances the utility of this method in ring construction and should prove to be a valuable new reaction tool in other syntheses.

We are currently studying applications of this work in natural product synthesis.

Experimental Section

General Methods. Proton magnetic resonance spectra were obtained in deuteriochloroform on Bruker WM-400 (400 MHz) spectrometer and are reported in ppm (δ units) downfield of internal tetramethylsilane (Me_4Si). Infrared spectra were recorded on a Perkin-Elmer 1330 spectrophotometer. Mass spectra were determined on a Finnigan 4000 automated gas chromatograph/EI-CI mass spectrometer. High-resolution MS were performed by Dr. Sadahiko Iguchi of Ono Pharmaceutical Co., Japan, and the Midwest Center for Mass Spectrometry, University of Nebraska—Lincoln. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. The solvents used in most of the experiments were dried and distilled under argon. Flash chromatography was performed by using E. Merk silica gel 60 (230–400 mesh) and Davisil silica gel, grade 643 (200–425 mesh). E. Merk precoated TLC plates, silica gel 60 F-254 were used in preparative thin-layer chromatography.

(+)-(*R*)-Allyl *p*-tolyl sulfoxide (**1R**) was prepared,[7] purified at 0 °C and used immediately.

The following experiment serves as the general procedure for the reaction of sulfoxide ***1R*** *with cyclic enones.*

(*E*)-[3(*S*),*S*(*R*)]-3-[3-(*p*-Tolylsulfinyl)-2-propen-1-yl]-cyclopentanone (8a). To a solution of 0.90 g (5.0 mmol) of (+)-(*R*)-allyl *p*-tolyl sulfoxide (**1R**) in 16 mL of THF at −78 °C under argon was added a cold (−78 °C) solution of lithium diisopropylamide (LDA) prepared at −30 °C from 0.73 mL (5.2 mmol) of diisopropylamine and 3.3 mL (5.2 mM) of *n*-butyllithium in 8 mL of THF. The yellow-colored solution obtained was stirred

(18) Ireland, R. E.; Muchmore, D. C.; Hengartner, U. *J. Am. Chem. Soc.* **1972**, *94*, 5098.

at −78 °C for 1 h, and then 0.42 mL (5 mmol) of 2-cyclopentenone was added. After the solution was stirred at −78 °C for 5 min, 0.72 g (12 mmol) of acetic acid in 2 mL of ether was added. The reaction mixture was warmed to room temperature, poured into saturated aqueous NH_4Cl solution, and extracted three times with ether. The combined extracts were washed with brine, dried ($MgSO_4$), concentrated, and column chromatographed on silica gel to give 1.205 g (91% yield) of ketone **8a** as an oil: $[\alpha]^{21}_D$ +207° (*c* 1.23, $CHCl_3$); IR (neat) 1730 (C=O), 1620 (C=C), 1040 (S=O); ^1H NMR ($CDCl_3$) δ 7.49 (d, *J* = 8 Hz, 2 H, ortho H), 7.3 (d, *J* = 8 Hz, 2 H, meta H), 6.56 (dt, *J* = 15, 7 Hz, 1 H, =CHC), 6.25 (d, *J* = 15 Hz, 1 H, SCH=), 2.4 (s, 3 H, *p*-CH_3), 2.3–1.5 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 217.18, 140.80, 140.20, 136.13, 136.04, 129.39, 123.85, 43.69, 37.44, 36.77, 35.42, 28.307, 20.698; MS, *m/e* (relative intensity) 262 (M^+, 5), 246 (M − 16, 4), 214 (32), 163 (8), 140 (10), 131 (100), 123 (40), 91 (50), 79 (25); HRMS calcd for $C_{15}H_{18}O_2S$ 262.1023, found 262.10 583. Anal. Calcd for $C_{15}H_{18}O_2S$: C, 68.67; H, 6.92; S, 12.22. Found: C, 68.72; H, 6.95; S, 12.16.

[3(*S*),4(*S*),*S* (*R*)]-3-(Cumyloxy)-4-[(*E*)-3-(*p*-tolylsulfinyl)-2-propen-1-yl]cyclopentanone (8bt): $[\alpha]^{22}_D$ +112° (*c* 0.95, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 7.25–7.47 (m, 9 H, Ar), 6.34 (dt, *J* = 14, 6.8 Hz, 1 H, =CHC), 6.12 (d, *J* = 14 Hz, 1 H, SCH=), 3.64 (q, *J* = 6.8 Hz, 1 H, CHO), 2.41 (s, 3 H, para CH_3), 2.53–1.52 (m, 7 H), 1.56 (s, 6 H, CCH_3); ^{13}C NMR ($CDCl_3$) δ 214.21, 145.16, 141.13, 137.44, 136.78, 136.14, 129.75, 127.87, 127.15, 125.80, 124.15, 76.79, 73.52, 46.66, 42.53, 41.73, 34.17, 28.41, 28.02, 21.10; HRMS calcd for $C_{24}H_{28}O_3S$ 396.17517, found 396.17763. Anal. Calcd for $C_{24}H_{28}O_3S$: C, 72.69; H, 7.12; S, 8.09. Found: C, 72.72; H, 7.24; S, 7.92.

[3(*R*),4(*S*),*S* (*R*)]-3-(Cumyloxy)-4-[(*E*)-3-(*p*-tolylsulfinyl)-2-propen-1-yl]cyclopentanone (8bc): ^1H NMR ($CDCl_3$) δ 7.20–7.40 (m, 9 H, Ar), 6.52 (dt, *J* = 15, 7 Hz, 1 H, =CHC), 6.27 (d, *J* = 15 Hz, 1 H, SCH=), 4.11 (q, *J* = 6 Hz, 1 H, CHO), 2.41 (s, 3 H, *p*-CH_3), 2.70–2.0 (m, 7 H), 1.54 (s, 3 H, CCH_3), 1.52 (s, 3 H, CCH_3); ^{13}C NMR ($CDCl_3$) δ 215.03, 145.74, 140.58, 140.49, 136.28, 135.98, 129.74, 127.87, 126.98, 125.42, 76.30, 71.04, 45.96, 41.73, 40.68, 31.55, 28.56, 28.11, 27.83, 21.11; HRMS calcd for $C_{24}H_{28}O_3S$ 396.17517, found 396.17334. Anal. Calcd for $C_{24}H_{28}O_3S$: C, 72.69; H, 7.12; S, 8.09. Found C, 72.70; H, 7.21; S, 7.98.

The cis and trans stereochemical assignments at C-3 and C-4 of **8bt**, **8bc**, **8ct**, and **8cc** were confirmed by comparing ^1H NMR chemical shifts and coupling constants of C-3 H's of the above compounds with those of the cis and trans adducts from the 1,4-addition reaction of lithium dibutylcuprate with enone **7c**.[19]

[3(*S*),4(*S*),*S* (*R*)]-3-(Benzyloxy)-4-[(*E*)-3-(*p*-tolylsulfinyl)-2-propen-1-yl]cyclopentanone (8ct): $[\alpha]^{22}_D$ −127° (*c* 0.7, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.4–7.2 (m, 9 H, Ar), 6.55 (dt, *J* = 15, 7.1 Hz, 1 H, =CHC), 6.25 (d, *J* = 15 Hz, 1 H, SCH=), 4.55 (d, *J* = 11.7 Hz, 1 H, O-CH_2), 4.46 (d, *J* = 11.7 Hz, 1 H, OCH_2), 3.87 (q, *J* = 6 Hz, 1 H, CHO), 2.4 (s, 3 H, *p*-CH_3), 2.5–1.8 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 214.0, 141.59, 140.53, 137.54, 137.12, 136.04, 130.04, 128.46, 127.90, 127.71, 124.45, 79.66, 71.65, 43.89, 42.31, 41.33, 34.91, 21.31; HRMS calcd for $C_{22}H_{24}O_3S$ 368.14397, found 368.14354. Anal. Calcd for $C_{22}H_{24}O_3S$: C, 71.71; H, 6.56; S, 8.70. Found: C, 71.50; H, 6.51; S, 8.31.

[3(*R*),4(*S*),*S* (*R*)]-3-(Benzyloxy)-4-[(*E*)-3-(*p*-tolylsulfinyl)-2-propen-1-yl]cyclopentanone (8cc): $[\alpha]^{22}_D$ −170° (*c* 0.27, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.48 (d, *J* = 8 Hz, 2 H, ortho H), 7.4–7.2 (m, 7 H, Ar), 6.54 (dt, *J* = 15, 7 Hz, 1 H, =CHC), 6.27 (d, *J* = 15 Hz, 1 H, SCH=), 4.48 (d, *J* = 12 Hz, 1 H, OC*H*Ph), 4.21 (d, *J* = 12 Hz, 1 H, OC*H*-Ph), 4.11 (t, *J* = 4.2 Hz, 1 H, O-CH), 2.40 (s, 3 H, para CH_3), 2.70–2.10 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 215.62, 141.55, 104.9, 137.7, 136.95, 136.76, 130.08, 128.42, 127.80, 127.54, 124.42, 77.0, 70.82, 44.48, 41.36, 41.18, 31.87, 21.39; HRMS calcd for $C_{22}H_{24}O_3S$ 368.14397, found 368.14337. Anal. Calcd for $C_{22}H_{24}O_3S$: C, 71.71; H, 6.56; S, 8.70. Found: C, 71.62; H, 6.50; S, 8.43.

[3(*S*),*S* (*R*)]-1-Acetoxy-2-methyl-3-[(*E*)-3-(*p*-tolylsulfinyl)-2-propen-1-yl]-1-cyclopentene (8d): $[\alpha]^{22}_D$ + 75° (*c* 0.5, CH_2Cl_2); IR (neat) 1750 (C=O), 1630 (C=C), 1050 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.51 (d, *J* = 8 Hz, 2 H, *o*-H), 7.3 (d, *J* = 8 Hz, 2 H, meta H), 6.5 (dt, *J* = 15, 7.1 Hz, 1 H, =CHC), 6.25 (d, *J* = 15.1 Hz, 1 H, =CHS), 2.40 (s, 3 H, *p*-CH_3), 2.15 (s, 3 H =CCH_3), 2.2–1.2 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 168.53, 145.16, 141.42, 137.97, 136.78, 134.99, 130.0, 124.65, 114.09, 43.83, 36.14, 29.79, 26.01, 21.39, 20.74, 10.34; HRMS calcd for $C_{18}H_{22}O_3S$ 318.12837, found 318.12804. Anal. Calcd for $C_{18}H_{22}O_3S$: C, 67.89; H, 6.96; S, 10.07. Found: C, 67.95; H, 6.90; S, 9.91.

[3(*S*),*S* (*R*)]-3-Methyl-3-[(*E*)-3-(*p*-tolylsulfinyl)-2-propen-1-yl]-1-cyclopentanone (8e): $[\alpha]^{22}_D$ +32° (*c* 0.09, $CHCl_3$); IR (neat) 1720 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.49 (d, *J* = 7 Hz, 2 H, ortho H), 7.31 (d, *J* = 7 Hz, 2 H, meta H), 6.58 (dt, *J* = 15, 7.7 Hz, 1 H, =CHC), 6.29 (d, *J* = 15 Hz, 1 H, SCH=), 2.32 (s, 3 H, para CH_3), 2.29–1.2 (m, 8 H), 1.11 (s, 3 H, CCH_3); ^{13}C NMR ($CDCl_3$) δ 217.20, 140.80, 140.15, 137.38, 134.27, 129.39, 123.87, 50.70, 42.67, 39.01, 35.84, 34.01, 24.69, 20.69; HRMS calcd for $C_{16}H_{20}O_2S$ 276.11787, found 276.11723. Anal. Calcd for $C_{16}H_{20}O_2S$: C, 69.53; H, 7.29; S, 11.60. Found: C, 69.20; H, 7.37; S, 11.50.

[3(*S*),*S* (*R*)]-2-Oxo-4-[(*E*)-3-(*p*-tolylsulfinyl)-2-propen-1-yl]tetrahydrofuran (8f): $[\alpha]^{22}_D$ +195° (*c* 0.225, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 7.48 (d, *J* = 8 Hz, 2 H, ortho H), 7.32 (d, *J* = 8 Hz, 2 H, meta H), 6.47 (dt, *J* = 15, 7.1 Hz, 1 H, =CHC), 6.30 (d, *J* = 15 Hz, 1 H, SCH=), 4.41 (m, 1 H, OCH), 3.97 (m, 1 H, OCH), 2.7–2.1 (m, 5 H), 2.42 (s, 3 H, para CH_3); ^{13}C NMR ($CDCl_3$) δ 176.04, 141.93, 140.39, 138.15, 133.69, 130.22, 124.54, 72.23, 35.17, 34.56, 33.84, 21.39; HRMS calcd for $C_{14}H_{16}O_3S$ 264.08157, found 264.08014. Anal. Calcd for $C_{14}H_{16}O_3S$: C, 63.61; H, 6.10; S, 12.13. Found: C, 63.72; H, 6.20; S, 11.99. $C_{14}H_{16}O_3S$: C, 63.61; H, 6.10; S, 12.13. Found: C, 63.72; H, 6.20; S, 11.99.

[5(*S*),*S* (*R*)]-2,2-Dimethyl-3-oxo-5-[(*E*)-3-(*p*-tolylsulfinyl)-2-propen-1-yl]tetrahydrofuran (8g): $[\alpha]^{22}_D$ +112° (*c* 0.112, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.51 (d, *J* = 8 Hz, 2 H, ortho H), 7.31 (d, *J* = 8 Hz, 2 H, meta H), 6.60 (dt, *J* = 14.1, 7.8 Hz, 1 H, =CHC), 6.36 (d, *J* = 14.1 Hz, SCH=), 4.32 (m, 1 H, CHO), 2.41 (s, 3 H, para CH_3), 2.6–2.2 (m, 4 H), 1.28 (s, 3 H, CCH_3), 1.21 (s, 3 H, CCH_3); ^{13}C NMR ($CDCl_3$) δ 216.22, 141.25, 140.34, 137.80, 133.50, 129.72, 124.37, 124.28, 80.58, 70.80, 40.49, 37.32, 37.23, 23.87, 21.38, 21.02; HRMS calcd for $C_{16}H_{20}O_3S$ 292.11277, found 292.11293. Anal. Calcd for $C_{16}H_{20}O_3S$: C, 65.72; H, 6.89; S, 10.97. Found: C, 65.45; H, 6.94; S, 10.94.

(*E*)-[1(*R*),5(*S*),*S* (*R*)]-1-[3-(*p*-Tolylsulfinyl)-2-propen-1-yl]-7,7-dimethylbicyclo[3.3.0]octan-3-one (8h): $[\alpha]^{22}_D$ +66° (*c* 0.20, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.5 (d, *J* = 8 Hz, 2 H, ortho H), 7.3 (d, *J* = 8 Hz, 2 H, meta H), 6.5 (dt, *J* = 15, 7 Hz, 1 H, C=CH), 6.25 (d, *J* = 15 Hz, 1 H, SCH=), 2.5 (m, 1 H, CH), 2.4 (s, 3 H, para CH_3), 2.36–1.3 (m, 10 H), 1.1 (s, 3 H, CH_3), 1.06 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 218.7, 141.4; 140.5, 138.1, 135.1, 129.9, 124.3, 52.7, 50.6, 50.2, 48.3, 45.3, 43.4, 42.6, 39.4, 30.8, 30.3, 21.2; HRMS calcd for $C_{20}H_{26}O_2S$ 330.16467, found 330.16790. Anal. Calcd for $C_{20}H_{26}O_2S$: C, 72.69; H, 7.93; S, 9.70. Found: C, 72.32; H, 7.94; S, 9.44.

[2(*S*),3(*R*),4(*S*),*S* (*R*)-2,3-Bis[(*tert*-butyldimethylsily)oxy]-4-methyl-4-[(*E*)-3-(*p*-tolylsulfinyl)-2-propen-1-yl]cyclopentanone (8i): $[\alpha]^{22}_D$ −58° (*c* 0.111, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.50 (d, *J* = 8.2 Hz, 2 H, ortho H), 7.32 (d, *J* = 8.2 Hz, 2 H, meta H), 6.58 (dt, *J* = 15.4, 7.1 Hz, 1 H, =CHC), 6.30 (d, *J* = 15.4 Hz, 1 H, SCH=), 3.96 (m, 1 H, O=CCHO), 3.80 (d, *J* = 5.9 Hz, 1 H, CHO), 2.50 (dd, *J* = 14, 8 Hz, 1 H, =CCH), 2.43 (d, *J*) = 18 Hz, 1 H, CHC=O), 2.42 (s, 3 H, para CH_3), 2.32 (dd, *J* = 18, 8 Hz, 1 H, =CCH), 2.01 (d, *J* = 18 Hz, 1 H, CHC=O), 1.14 (s, 3 H, CH_3), 0.92 (s, 9 H, *t*-Bu), 0.91 (s, 9 H, *t*-Bu), 0.145 (s, 3 H, CH_3Si), 0.130 (s, 3 H, CH_3Si), 0.127 (s, 3 H, CH_3Si), 0.115 (s, 3 H, CH_3Si); ^{13}C NMR ($CDCl_3$) δ 213.2, 141.5, 140.80, 138.22, 135.62, 130.05, 124.50, 82.83, 80.41, 46.64, 40.90, 38.35, 25.86, 25.81, 24.86, 21.33, 18.16, 17.98, −3.89, −4.27, −4.47, −4.60; HRMS calcd for $C_{28}H_{48}O_4SSi_2$ 536.27978, found 536.27841. Anal. Calcd for $C_{28}H_{48}O_4SSi_2$: C, 62.64; H, 9.01; S, 5.97; Si, 10.46. Found: C, 62.50; H, 9.11; S, 5.91; Si, 10.23.

[1(*S*),4(*S*),5(*R*),*S* (*R*)]-4,5-Bis[(*tert*-butyldimethylsilyl)oxy]-3-methyl-1-[(*E*)-3-(*p*-tolylsulfinyl)-2-propen-1-yl]-2-cyclopenten-1-ol (9i): $[\alpha]^{22}_D$ −87° (*c* 0.198, $CHCl_3$); mp 153 °C; ^1H NMR ($CDCl_3$) δ 7.50 (d, *J* = 8 Hz, 2 H, ortho H), 7.30 (d, *J* = 8 Hz, 2 H, meta H), 6.64 (dt, *J* = 15.3, 7.8 Hz, 1 H, =CHC), 6.28 (d, *J* = 15.3 Hz, 1 H, SCH=), 5.38 (s, 1 H, =CH), 4.11 (d, *J* = 4.1 Hz, 1 H, OCCHO), 3.89 (d, *J* = 4.3 Hz, 1 H, CHO), 2.52 (dd, *J* = 14.3, 7.0 Hz, 1 H, =CCHCO), 2.40 (s, 3 H, para CH_3),

(19) Sih, C. J.; Salomon, R. G.; Price, P.; Sood, R.; Peruzzotti, G. *J. Am. Chem. Soc.* **1975**, *97*, 857. The cis adduct (4% yield), *cis*-3-butyl-4-(benzyloxy)cyclopentanone was also isolated.

2.35 (dd, J = 14.3, 8.0 Hz, 1 H, =CCHCO), 1.79 (s, 1 H, OH), 1.68 (s, 3 H, CH_3), 0.91 (s, 9 H, t-Bu), 0.90 (s, 9 H, t-Bu), 0.140 (s, 3 H, CH_3Si), 0.113 (s, 3 H, CH_3Si), 0.106 (s, 3 H, CH_3Si), 0.102 (s, 3 H, CH_3Si); ^{13}C NMR ($CDCl_3$) δ 143.48, 141.34, 141.22, 137.95, 136.52, 130.02, 129.75, 124.66, 88.69, 82.31, 82.24, 38.20, 26.13, 25.89, 21.40, 18.05, 17.94, 14.73, -3.56, -3.82, -4.03, -4.28; HRMS calcd for $C_{28}H_{48}O_4SSi_2$ 536.27987, found 536.27783. Anal. Calcd for $C_{28}H_{48}O_4SSi_2$: C, 62.64; H, 9.01; S, 5.97; Si, 10.46. Found: C, 62.37; H, 9.07; S, 5.79; Si, 10.41.

(*E*)-[3(*S*),*S*(*R*)]-3-[3-(*p*-Tolylsulfinyl)-2-propen-1-yl]-cyclohexanone (8j): $[\alpha]^{22}_D$ +152.0° (c 0.129, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.5 (d, J = 8 Hz, 2 H, ortho H), 7.3 (d, J = 8 Hz, 2 H, meta H), 6.56 (dt, J = 15, 7.1 Hz, 1 H, C=CH), 6.55 [dt, J = 15, 7.1 Hz, 1 H, C=CH, for the diastereomer, 3(*R*),*S*(*R*)], 6.25 (d, J = 15 Hz, 1 H, SCH=, 6.23 (d, J = 15 Hz, 1 H, SCH=, for the diastereomer), 2.4 (s, 3 H, para CH_3), 2.37-1.4 (m, 11 H); ^{13}C NMR ($CDCl_3$) δ 210.4, 141.5, 137.3, 136.4, 136.1, 130.0, 124.5, 47.5, 41.1, 38.6, 38.2, 30.7, 24.8, 21.3; HRMS calcd for $C_{16}H_{20}O_2S$ 276.11787, found 276.12074. Anal. Calcd for $C_{16}H_{20}O_2S$: C, 69.53; H, 7.29; S, 11.60. Found: C, 69.22; H, 7.25; S, 11.80.

[1(*R*),*S*(*R*)]-1-[(*E*)-3-(*p*-Tolylsulfinyl)-2-propen-1-yl]-2-cyclohexen-1-ol (9j): $[\alpha]^{22}_D$ +83° (c 0.20, $CHCl_3$); IR (neat) 3400 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.5 (d, J = 8 Hz, 2 H, ortho H), 7.3 (d, J = 8 Hz, 2 H, meta H), 6.67 (dt, J = 15, 7 Hz, 1 H, CH=CS), 6.26 (d, J = 15 Hz, 1 H, SCH=), 5.8 (m, 1 H, =CH), 5.62 (d, J = 10 Hz, 1 H, =CHCO), 2.88 (s, 1 H, OH), 2.45 (d, J = 8 Hz, 2 H, $=CCH_2CO$), 2.4 (s, 3 H, para CH_3), 2.1-1.15 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 141.1, 140.0, 137.5, 136.5, 131.5, 130.4, 129.8, 124.4, 69.0, 44.5, 35.6, 24.9, 21.2, 18.9; HRMS calcd for $C_{16}H_{20}O_2S$ 276.11787, found 276.11388. Anal. Calcd for $C_{16}H_{20}O_2S$: C, 69.53; H, 7.29; S, 11.60. Found: C, 69.36; H, 7.20; S, 11.57.

(*E*)-[3(*S*),*S*(*R*)]-3-[3-(*p*-Tolylsulfinyl)-2-propen-1-yl]-cycloheptanone (8k): $[\alpha]^{22}_D$ +138° (c 0.110, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.49 (d, J = 8 Hz, 2 H, ortho H) 7.3 (d, J = 8 Hz, 2 H, meta H), 6.52 (dt, J = 15, 7 Hz, 1 H, C=CH), 6.25 (d, J = 15 Hz, 1 H, SCH=), 2.4 (s, 3 H, para CH_3), 2.5-1.2 (m, 13 H); ^{13}C NMR ($CDCl_3$) δ 213.1, 141.4, 140.7, 137.3, 137.0, 130.0, 124.5, 49.3, 43.8, 39.4, 36.3, 35.5, 28.2, 24.1, 21.3; HRMS calcd for $C_{17}H_{22}O_2S$ 290.13347, found 290.13450. Anal. Calcd for $C_{17}H_{22}O_2S$: C, 70.31; H, 7.64; S, 11.04. Found: C, 70.17, H, 7.69; S, 11.12.

[1(*R*),*S*(*R*)]-1-[(*E*)-3-(*p*-Tolylsulfinyl)-2-propen-1-yl]-2-cyclohepten-1-ol (9k): $[\alpha]^{22}_D$ +61° (c 0.341, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.5 (d, J = 8 Hz, 2 H, ortho H), 7.35 (d, J = 8 Hz, 2 H, meta H), 6.67 (dt, J = 15, 7 Hz, 1 H, CH=CS), 6.29 (d, J = 15 Hz, 1 H, SCH=), 5.76 (dt, J = 11, 6 Hz, 1 H, =CHC), 5.59 (d, J = 11 Hz, 1 H, =CHCO), 2.4 (s, 3 H, para CH_3), 2.55-1.5 (m, 11 H); ^{13}C NMR ($CDCl_3$) δ 141.3, 140.8, 137.9, 137.7, 136.2, 131.0, 129.9, 124.6, 75.4, 43.8, 38.8, 27.6, 27.2, 23.9, 21.3; HRMS calcd for $C_{17}H_{22}O_2S$ 290.13347, found 290.13872.

The following experiment serves as the general procedure for the reduction of the sulfoxides to the sulfides.

(*E*)-[3(*S*)]-3-[(3-(*p*-Tolylthio)-2-propen-1-yl]cyclopentanone (8s). A mixture of 2.93 g (0.0112 mol) of sulfoxide **8a** and 20 g of activated zinc[20] in 220 mL (3.85 mol) of acetic acid was stirred at room temperature for 10 h, and the reaction was monitored by TLC. The reaction mixture was diluted with ether, filtered through Celite and neutralized with 5 N NaOH. The organic layer was separated and the aqueous layer extracted twice with ether. The combined ether layers were washed with brine, dried ($MgSO_4$), concentrated, and column chromatographed on silica gel to give 2.6 g (95% yield) of sulfide **8s**: $[\alpha]^{22}_D$ +42° (c 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.25 (d, J = 8 Hz, 2 H, meta H), 7.0 (d, J = 8 Hz, 2 H, ortho H), 6.15 (d, J = 15 Hz, 1 H, SCH=), 5.8 (dt, J = 15, 7.1 Hz, 1 H, =CHC), 2.31 (s, 3 H, para CH_3), 2.25-1.5 (m, 9 H); HRMS calcd for $C_{15}H_{18}OS$ 246.1074, found 246.10674.

(*E*)-[3(*S*)]-1,1-(Ethylenedioxy)-3-[3-(*p*-tolylsulfinyl)-2-propen-1-yl]cyclopentane (12). To a flask equipped with Dean-Stark apparatus under argon were added 1.8 g (7.3 mmol) of ketone **8s**, 0.37 g (1.46 mmol) of pyridinium tosylate, 0.82 mL (14.6 mmol) of ethylene glycol, and 100 mL of benzene. The reaction mixture was heated under reflux for 12 h, then cooled and diluted with ether. The organic layer was washed with aqueous $NaHCO_3$, brine, dried ($MgSO_4$), concentrated, and column chromatographed to give 2.0 g (96% yield) of **12**: ^1H NMR ($CDCl_3$) δ 7.25 (d, J = 8 Hz, 2 H, meta H), 7.0 (d, J = 8 Hz, 2 H, ortho H), 6.15 (d, J = 15 Hz, 1 H, SCH=), 5.8 (dt, J = 15, 7 Hz, 1 H, =CHC), 3.9 (m, 4 H, OCH_2CH_2O), 2.31 (s, 3 H, para CH_3), 2.25-1.5 (m, 9 H); HRMS calcd for $C_{17}H_{22}O_2S$ 290.13347, found 290.13238.

(+)-(*R*)-3-Oxocyclopentaneacetic Acid (11). To 270 mL of CH_2Cl_2 saturated with ozone (10 mmol) at -78 °C was added a solution of 0.9 g (3.1 mmol) of sulfide **12** in 15 mL of CH_2Cl_2 and 1.3 mL of MeOH. It was stirred at -78 °C for 30 min. Argon was bubbled through the solution to expel excess of ozone. Dimethyl sulfide (2.7 mL, 31 mmol) was added and the solution warmed to 0 °C over a period of 2 h. The solvent was evaporated leaving a yellow oil. The crude material was filtered through 20 g of silica gel to remove less polar compounds, and the more polar fractions were combined and used in the next experiment.

To a well-stirred solution of the above crude aldehyde in 2 mL of CH_2Cl_2 containing 0.3 mL of MeOH was added a solution of 2.42 g of freshly prepared n-Bu_4NMnO_4[9] in 5 mL of CH_2Cl_2, which was precooled to 0 °C. The brown solution obtained was stirred at room temperature for 30 min. 1 N HCl (5 mL) was added followed by solid $NaHSO_3$ until the solution became colorless. It was extracted with ethyl acetate three times. The combined extracts were washed with brine and dried ($MgSO_4$), and the solvent was removed by simple distillation. The crude material was dissolved in 3 mL of MeOH and 3 mL of H_2O. KOH (0.1 g) was added and the solution stirred at room temperature for 3 h, diluted with H_2O, and extracted once with ether. The aqueous layer was acidified with 5 N HCl and extracted with ether until the aqueous layer contained no more of the desired acid (TLC). The combined extracts were washed with brine, dried ($MgSO_4$), distilled under normal pressure to remove solvent, and dried in vacuo, leaving 0.308 g (70% yield) of **11**: $[\alpha]^{22}_D$ +109° (c 1.23, $CHCl_3$) (lit.[8c] [α] -115.5° for *S* configuration); ^1H NMR ($CDCl_3$) δ 10.6 (s, 1 H, COOH), 2.7-1.5 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 218.6, 177.6, 44.4, 39.2, 38.2, 33.0, 29.0; HRMS calcd for $C_7H_{10}O_3$ 142.0627, found 142.0616.

(-)-(*S*)-β-Propyl-γ-butyrolactone (13). To 0.45 g (1.7 mmol) of sulfoxide **8f** in 20 mL of acetone under argon was added 5 g of Raney Nickel (W-2). The reaction mixture was stirred under reflux for 4 h, cooled, and diluted with ether. The mixture was filtered through Celite, concentrated, and column chromatographed to give 0.175 g (80% yield) of lactone **13**: $[\alpha]^{22}_D$ -7.3° (c 2.66, EtOH) (lit.[10b] [α] +6.7° for *R* configuration, >90% ee); ^1H NMR ($CDCl_3$) δ 4.42 (dd, J = 7.7 Hz, 1 H, OCH), 3.93 (dd, J = 7.7 Hz, 1 H, OCH), 2.63-1.19 (m, 7 H), 0.94 (t, J = 7.1 Hz, 3 H, CH_3);[10a] ^{13}C NMR ($CDCl_3$) δ 177.0, 73.28, 35.69, 35.20, 32.58, 29.25, 20.97; HRMS calcd for $C_7H_{12}O_2$ 128.0834, found 128.0827.

The following experiments serve as the general procedure for the reduction of the keto group and subsequent oxidation of the sulfoxide group to hydroxy sulfone.

(*E*)-[3(*S*),*S*(*R*)]-3-[3-(*p*-Tolylsulfinyl)-2-propen-1-yl)-cyclopentanol (16ac and 16at). To a solution of 0.10 g (0.38 mmol) of ketone **8a** in 3 mL of MeOH at -20 °C was added 29 mg (0.76 mmol) of $NaBH_4$. After the mixture was stirred at -20 °C for 30 min, 1 mL of 1 N HCl was added. The mixture was diluted with H_2O and extracted three times with ether. The combined extracts were washed with brine, dried ($MgSO_4$), concentrated, and column chromatographed on silica gel to give 0.06 g of the cis alcohol (**16ac**) and 0.04 g of the trans alcohol (**16at**) (100% yield).

Cis alcohol **16ac**: ^1H NMR ($CDCl_3$) δ 7.5 (d, J = 8 Hz, 2 H, ortho H), 7.3 (d, J = 8 Hz, 2 H, meta H), 6.5 (dt, J = 15, 7 Hz, 1 H, =CHC), 6.25 (d, J = 15 Hz, 1 H, =CHS), 4.29 (m, 1 H, CHO), 2.4 (s, 3 H, para CH_3), 2.3-1.1 (m, 10 H). HRMS calcd for $C_{15}H_{20}O_2S$ 264.11787, found 264.11638.

Trans alcohol **16at**: ^1H NMR ($CDCl_3$) δ 7.5 (d, J = 8 Hz, 2 H, ortho H), 7.3 (d, J = 8 Hz, 2 H, meta H), 6.52 (dt, J = 15, 7 Hz, 1 H, =CHC), 6.27 (d, J = 15 Hz, 1 H, =CHS), 4.35 (m, 1 H, CHO), 2.4 (s, 3 H, para CH_3), 2.3-1.1 (m, 10 H); HRMS calcd for $C_{15}H_{20}O_2S$ 264.11787, found 264.11716.

(*E*)-[1(*S*),3(*S*)]-3-[3-(*p*-Tolylsulfonyl)-2-propen-1-yl]-cyclopentanol (17ac). To a solution of 0.1 g (0.38 mmol) of sulfoxide **16ac** in 9 mL of CH_2Cl_2 at -20 °C was added 0.078 g (0.38 mmol) of *m*-chloroperoxybenzoic acid (MCPBA). The

(20) Tsuda, J.; Ohki, E.; Nozoe, S. *J. Org. Chem.* **1963**, *28*, 783.

mixture was stirred at 0 °C for 5 h. It was diluted with ether, washed with saturated $NaHCO_3$ and brine, dried ($MgSO_4$), concentrated, and column chromatographed to give 0.094 g (89% yield) of sulfone **17ac**: ^1H NMR ($CDCl_3$) δ 7.74 (d, J = 8 Hz, 2 H, o-H), 7.32 (d, J = 8 Hz, 2 H, meta H), 6.92 (dt, J = 15, 7 Hz, 1 H, =CHC), 6.3 (d, J = 15 Hz, 1 H, =CHS), 4.29 (m, 1 H, CHO), 2.43 (s, 3 H, para CH_3), 2.3–1.1 (m, 10 H); HRMS calcd for $C_{15}H_{20}O_3S$ 280.11277, found 280.11192.

The following experimental procedure for the preparation of Mosher derivatives from alcohol ***17ac*** *is representative.*

[1(*S*),3(*S*),1′(*R*)]-1-[α-Methoxy-α-(trifluoromethyl)-phenylacetoxy)-3-[(*E*)-3-(*p*-tolylsulfonyl)-2-propen-1-yl]-cyclopentane (18a). A mixture of 0.1 g (0.351 mmol) of alcohol **17ac**, 42.6 mg (0.351 mmol) of 4-(dimethylamino)pyridine (DMAP), 0.15 mL (1.05 mmol) of triethylamine, and 0.15 mL (0.702 mmol) of (+)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (MTPAC) in 3 mL of toluene was stirred at room temperature for 12 h. The reaction mixture was poured into water and extracted twice with ether. The combined extracts were washed with saturated $CuSO_4$ solution and brine, dried ($MgSO_4$), concentrated, and column chromatographed to give 0.156 g (90% yield) of ester **18a**: ^1H NMR ($CDCl_3$) δ 7.74–7.3 (m, 9 H, Ar), 6.9 (dt, J = 15, 7 Hz, 1 H, =CHC), 6.21 (d, J = 15 Hz, 1 H, SCH=), 6.18 (d, J = 15 Hz, 1 H, SCH= for the minor diastereomer), 5.4 (m, 1 H, CH-O), 3.52 (s, 3 H, OCH_3), 2.4 (s, 3 H, para CH_3), 2.3–1.1 (m, 9 H); HRMS calcd for $C_{25}H_{27}O_5F_3S$ 496.1524, found 496.1511.

[1(*R*),5(*S*),8(*S*)]-1-Methyl-8-(*p*-tolylthio)-*cis*-bicyclo-[3.3.0]octan-2-one (26c) and [1(*R*),5(*S*),8(*R*)]-1-Methyl-8-(*p*-tolylthio)-*cis*-bicyclo[3.3.0]-octan-2-one (26t). Sulfoxide **8d** was reduced by the zinc–acetic acid method as described above to give sulfide **8ds** in 95% yield: ^1H NMR ($CDCl_3$) δ 7.21 (d, J = 8 Hz, 2 H, meta H), 7.0 (d, J = 8 Hz, 2 H, ortho H), 6.13 (d, J = 15 Hz, 1 H, =CHS), 5.86 (dt, J = 15, 7.2 Hz, 1 H, =CHC), 2.32 (s, 3 H, para CH_3), 2.2–1.2 (m, 13 H); HRMS calcd for $C_{18}H_{22}O_2S$ 302.13347, found 302.13187.

To a solution of 1.0 g (3.31 mmol) of sulfide **8ds** in 55 mL of acetic acid was added a solution of 1 mL (9.1 mmol) of titanium(IV) chloride in 10 mL of acetic acid. The grayish yellow emulsion obtained was stirred for 20 min, then diluted with 0.3 mL (16.6 mmol) of water, stirred for additional 10 min, diluted with ether, filtered through Celite, and neutralized with aqueous $NaHCO_3$. The ether layer was separated, and the aqueous layer was extracted twice with ether. The combined extracts were washed with brine, dried ($MgSO_4$), concentrated, and column chromatographed to give 0.74 g (86% yield) of **26c** and **26t** in the ratio of 1:4.

For **26c**: ^1H NMR ($CDCl_3$) δ 7.32 (d, J = 8 Hz, 2 H, ortho H), 7.08 (d, J = 8 Hz, 2 H, meta H), 3.71 (t, J = 5.8 Hz, 1 H, CHS), 2.3 (s, 3 H, para CH_3), 1.18 (s, 3 H, CH_3), 2.5–1.3 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 220.5, 136.7, 132.9, 131.85, 129.5, 58.5, 58.2, 48.7, 39.05, 35.19, 31.18, 25.8, 22.5, 21.03; HRMS calcd for $C_{16}H_{20}OS$ 260.1230, found 260.1209. Anal. Calcd for $C_{16}H_{20}OS$: C, 73.80; H, 7.74; S, 12.31. Found: C, 73.49; H, 7.70; S, 12.55.

For **26t**: ^1H NMR ($CDCl_3$) δ 7.32 (d, J = 8 Hz, 2 H, ortho H), 7.08 (d, J = 8 Hz, 2 H, meta H), 3.19 (d, J = 6.8 Hz, 1 H, CHS), 2.3 (s, 3 H, para CH_3), 1.22 (s, 3 H, CH_3), 2.5–1.6 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 222.6, 136.4, 132.5, 131.2, 129.6, 60.1, 55.1, 47.1, 35.8, 33.8, 30.4, 24.9, 20.9, 18.3; HRMS calcd for $C_{16}H_{20}OS$ 260.1230, found 260.1215. Anal. Calcd for $c_{16}H_{20}OS$: C, 73.80; H, 7.74; S, 12.31. Found: C, 73.54; H, 7.62; S, 12.63.

The stereochemistry at C-1 and C-8 was proven by proton–proton NOE difference spectroscopy (irradiation at C-1 methyl group).

The following experiment serves as the general procedure for the hydrolytic ring closure reaction of enol thioether ketones.

***cis*-8-(Formyloxy)-5-methylbicyclo[3.3.0]octan-2-one (29c).** To 0.18 g (0.69 mmol) of sulfide **28c** in 70 mL of formic acid (88%) was added 0.1 mL of trifluoroacetic acid. The solution was stirred at 70 °C for 3 h, cooled, diluted with 200 mL of ether, and neutralized with 5 N NaOH. The organic layer was separated, and the aqueous layer was extracted twice with ether. The combined organic layers were washed with brine, dried ($MgSO_4$), concentrated, and column chromatographed to give 82 mg (65% yield) of **29c**, 10 mg (10% yield) of *cis*-8-hydroxy-5-methylbicyclo-[3.3.0]octan-2-one (**30c**), and 19 mg (7% yield) of 3-methyl-3-[3,3-bis-(*p*-tolylthio)propyl]cyclopentanone (**31c**).

For formate **29c**: ^1H NMR ($CDCl_3$) δ 8.04 (s, O=CH, area of 0.33), 8.01 (s, O=CH, area of 0.67), 5.52 (m, HCO, area of 0.67), 5.03 (m, HCO, area of 0.33), 2.7–1.1 (m, 9 H), 1.23 (s, CH_3, area of 0.67), 1.20 (s, CH_3, area of 0.33); ^{13}C NMR ($CDCl_3$) δ 216.6, 216.4, 160.18, 159.93, 76.29, 72.60, 61.54; 51.84, 49.93, 47.82, 41.37, 39.79, 37.70, 36.14, 34.48, 33.17, 29.52, 27.59, 26.19, 25.86. HRMS calcd for $C_{10}H_{14}O_3$ 182.0939, found 182.0927.

For alcohol **30c**: ^1H NMR ($CDCl_3$) δ 4.52 (m, 1 H, CHO), 2.7–1.1 (m, 10 H), 1.21 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 218.92, 75.04, 63.53, 47.46, 40.09, 37.60, 35.49, 34.98, 28.08; HRMS calcd for $C_9H_{14}O_2$ 154.099, found 154.0985.

For disulfide **31c**: ^1H NMR ($CDCl_3$) δ 7.35 (d, J = 8 Hz, 4 H, ortho H), 7.11 (d, J = 8 Hz, 4 H, meta H), 4.26 (t, J = 6 Hz, 1 H, CHS), 2.34 (s, 6 H, para CH_3), 2.3–1.7 (m, 10 H), 0.98 (s, 3 H, CH_3); ^{13}C NMR 218.98, 137.84, 133.10, 130.25, 129.56, 59.43, 51.90, 39.12, 38.33, 36.51, 35.00, 30.69, 24.75, 21.03; HRMS calcd for $C_{23}H_{28}OS_2$ 384.1575, found 384.1564.

***cis*-8-(Formyloxy)bicyclo[3.3.0]octan-2-one (29b)**: ^1H NMR ($CDCl_3$) δ 8.04 (s, CHO, area of 0.4), 7.98 (S, CHO, area of 0.6), 5.53 (m, CHO, area of 0.6), 5.05 (m, CHO, area of 0.4), 3.0–1.5 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 217.18, 216.72, 160.28, 160.08, 76.33, 72.84, 54.69, 49.87, 43.28, 40.94, 39.76, 35.05, 34.27, 31.12, 30.66, 29.01, 27.23, 25.14; HRMS calcd for $C_9H_{12}O_3$ 168.0783, found 168.0768.

3-[3,3-Bis(*p*-tolylthio)propyl]cyclopentanone (31b): ^1H NMR ($CDCl_3$) δ 7.35 (d, J = 8 Hz, 4 H, ortho H), 7.12 (d, J = 8 Hz, 4 H, meta H), 4.28 (t, J = 6 Hz, 1 H, CHS), 2.34 (s, 3 H, para CH_3), 2.3–1.4 (m, 11 H); ^{13}C NMR ($CDCl_3$) δ 219.18, 138.03, 133.32, 130.29, 129.66, 59.06, 44.96, 38.37, 36.71, 33.75, 32.71, 29.36, 21.12; HRMS calcd for $C_{22}H_{26}OS_2$ 370.1419, found 370.1398. Anal. Calcd for $C_{22}H_{26}OS_2$: C, 71.31; H, 7.07; S, 17.30. Found: C, 71.70; H, 7.08; S, 16.91.

(3aα,5aβ,6β,8aβ)-2,2-Dimethyl-6-(formyloxy)decahydrocyclopenta[*c*]pentalen-5-one (29d): ^1H NMR ($CDCl_3$) δ 7.98 (s, 1 H, CHO), 5.50 (m, 1 H, CHO), 2.68–1.2 (m, 12 H), 1.05 (s, 3 H, CH_3), 1.02 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 217.52, 160.01, 76.0, 64.10, 57.0, 50.78, 50.02, 46.21, 44.56, 40.08, 34.02, 29.87, 28.48, 26.0; HRMS $C_{14}H_{20}O_3$ 236.1407, found 236.1399. Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.07; H, 8.59.

(3aα,5aβ,6β,8aβ)-2,2-Dimethyl-6-hydroxy-1,2,3,3a,4,5,5a,-6,7,8-decahydrocyclopenta[*c*]pentalen-5-one (30d): ^1H NMR ($CDCl_3$) δ 4.50 (m, 1 H, CHO), 2.6–1.2 (m, 13 H), 1.05 (s, 3 H, CH_3), 1.035 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 220.21, 71.13, 63.79, 58.10, 57.15, 50.46, 45.73, 44.92, 40.74, 36.12 (2 C), 29.91, 28.96; HRMS calcd for $C_{13}H_{20}O_2$ 208.1458, found 208.1453.

(1β,5α,6β)-3,3-Dimethyl-7-(formyloxy)tricyclo[4.3.2.0^{1,5}]-undecan-11-one (31d): ^1H NMR ($CDCl_3$) δ 8.03 (s, 1 H, CHO), 5.08 (m, 1 H, CHO), 2.50–1.40 (m, 12 H), 1.14 (s, 3 H, CH_3), 1.09 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 217.49, 160.06, 72.90, 66.08, 58.81, 56.67, 52.0, 47.23, 46.12, 40.35, 40.07, 35.73, 33.0, 32.27; HRMS calcd for $C_{14}H_{20}O_3$ 236.1407, found 236.1411.

(1β,5α,6β)-3,3-Dimethyl-7-hydroxytricyclo[4.3.2.0^{1,5}]undecan-11-one (32d): ^1H NMR ($CDCl_3$) δ 3.87 (m, 1 H, CHO), 2.55 (d, J = 3.4 Hz, 1 H, CHC=O), 2.4–0.93 (m, 8 H), 1.14 (s, 3 H, CH_3), 1.08 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 219.39, 72.0, 61.25, 52.23, 50.36, 49.31, 47.57, 44.56, 40.15, 35.6, 32.76, 32.18, 29.94; HRMS calcd for $C_{13}H_{20}O_2$ 208.1458, found 208.1450.

(3aα,5aβ,6β,8β,8aβ)-6-(Formyloxy)-1,2,3,3a,4,5,5a,6,7,8-decahydro-2,2,8-trimethylcyclopenta[*c*]pentalen-5-one (29e): ^1H NMR ($CDCl_3$) δ 7.96 (s, 1 H, CHO), 5.58 (m, 1 H, CHO), 2.74–0.83 (m, 11 H), 1.06 (d, J = 6.9 Hz, 3 H, CH_3), 1.05 (s, 3 H, CH_3), 1.02 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 216.69, 160.08, 73.99, 64.93, 62.53, 49.02, 47.69, 45.56, 43.18, 41.91, 40.86, 39.5, 30.40, 29.13, 15.34; HRMS calcd for $C_{15}H_{22}O_3$ 250.1563, found 250.1558.

(3aα,5aβ,6β,8β,8aβ)-6-Hydroxy-1,2,3,3a,4,5,5a,6,7,8-decahydro-2,2,8-trimethylcyclopenta[*c*]pentalen-5-one (30e): ^1H NMR ($CDCl_3$) δ 4.27 (m, 1 H, CHO), 2.5–1.2 (m, 12 H), 1.11 (s, 3 H, CH_3), 1.02 (d, J = 8 Hz, 3 H, CH_3), 1.19 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 222.38, 71.77, 67.89, 61.53, 51.15, 49.32, 46.12, 44.50, 42.55, 41.02, 39.68, 30.92, 29.52, 13.97; HRMS calcd for $C_{14}H_{22}O_2$ 222.1614, found 222.1619.

(1β,5α,6β,7β,9β)-7-(Formyloxy)-3,3,9-trimethyltricyclo-[4.3.2.0^{1,5}]undecan-11-one (31e): ^1H NMR ($CDCl_3$) δ 8.02 (s, 1 H, CHO), 5.08 (ddd, J = 8.5, 4, 4 Hz, 1 H, CHO), 2.61 (d, J = 3.4 Hz, 1 H, CHC=O), 2.3–1.2 (m, 10 H), 1.14 (s, 3 H, CH_3), 1.09 (s, 3 H, CH_3), 0.89 (d, J = 6.7 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$)

δ 216.7, 160.30, 72.14, 55.70, 52.69, 52.18, 49.23, 44.16, 42.67, 39.46, 39.66, 34.03, 32.88, 32.12, 16.88; HRMS calcd for $C_{15}H_{22}O_3$ 250.1563, found 250.1569.

(1β,5α,6β,7β,9β)-7-Hydroxy-3,3,9-trimethyltricyclo[4.3.2.0^{1,5}]undecan-11-one (32e): ^{1}H NMR ($CDCl_3$) δ 3.90 (m, 1 H, CHO), 2.52 (d, J = 3.5 Hz, 1 H, CHC=O), 2.2–0.9 (m, 11 H), 1.13 (s, 3 H, CH_3), 1.08 (s, 3 H, CH_3), 0.86 (d, J = 6.7 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 219.58, 71.37, 59.40, 53.06, 52.51, 49.21, 44.40, 42.90, 39.66, 39.45, 38.37, 32.84, 32.18, 16.85; HRMS calcd for $C_{14}H_{22}O_2$ 222.1614, found 222.1606.

9-(Formyloxy)bicyclo[4.3.0]nonan-2-one (29f): ^{1}H NMR ($CDCl_3$) δ 8.02 (s, 1 H, CHO), 5.10 (m, 1 H, CHO), 2.75 (t, J = 3 Hz, 1 H, CHC=O), 2.4–1.5 (m, 11 H); ^{13}C NMR ($CDCl_3$) δ 160.03, 74.60, 51.88, 43.78, 29.64, 29.38, 27.99, 27.06, 24.07, 20.99; HRMS calcd for $C_{10}H_{14}O_3$ 182.0939, found 182.0933.

9-(*p*-Tolylthio)bicyclo[4.3.0]nonan-2-one (30f): ^{1}H NMR ($CDCl_3$) δ 7.27 (d, J = 8 Hz, 2 H, ortho H), 7.05 (d, J = 8 Hz, 2 H, meta H), 3.77 (t, J = 9 Hz, 1 H, CHS), 2.6–1.4 (m, 12 H), 2.31 (s, 3 H, para CH_3); ^{13}C NMR ($CDCl_3$) δ 211.62, 137.70, 133.40, 131.31, 129.65, 57.56, 51.33, 37.43, 36.11, 31.08, 30.84, 29.18, 26.08, 21.07; HRMS calcd for $C_{16}H_{20}OS$ 260.123, found 260.1222.

1(9)-Bicyclo[4.3.0]nonen-2-one (31f):[21] ^{1}H NMR ($CDCl_3$) δ 6.62 (s, 1 H, =CH), 2.86–1.22 (m, 11 H); ^{13}C NMR ($CDCl_3$) δ 199.51, 144.94, 138.38, 45.72, 40.27, 33.11, 31.75, 31.52, 24.02; HRMS calcd for $C_9H_{12}O$ 136.0885, found 136.0872.

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Addition Compounds of Alkali-Metal Hydrides. 30. Rapid Reaction of Trialkylboranes with Lithium Aluminum Hydride. A Novel and Quantitative Synthesis of Lithium Dialkylborohydrides

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For the first time, a wide variety of lithium dialkylborohydrides have been synthesized via a rapid, general, and quantitative reaction of trialkylboranes with lithium aluminum hydride in anhydrous ether at 25 °C. A new generation of lithium dialkylborohydrides such as the lithium dimethylborohydride ($LiMe_2BH_2$) and lithium diisopropylborohydride (Li-*i*-Pr_2BH_2) can now be routinely prepared in large quantities for studies on the reductions of organic functional groups. More importantly, since the dialkylborohydrides can also serve as masked intermediates for dialkylboranes, the present procedure provides easy access to a variety of dialkylboranes which cannot be obtained by direct hydroboration.

The importance of trialkylborohydrides as valuable selective reducing agents in organic synthesis is well-established.[1] In the past, several methods were reported for the synthesis of many hindered and even highly hindered trialkylborohydrides.[2] Surprisingly, very little is known about lithium borohydrides containing less than three alkyl groups on boron, a deficiency which can be primarily attributable to the instability of dialkylboranes and the lack of general procedures for their preparation.

Earlier, lithium dialkylborohydrides were prepared in a quantitative manner by the reduction of triethylenediamine–dialkylborane complexes with lithium aluminum hydride in anhydrous ether at 0 °C[3] (eq 1). Unfortunately,

$$R_2BH{\cdot}TED + LiAlH_4 \rightarrow LiR_2BH_2 + AlH_3{\cdot}TED\downarrow \quad (1)$$

this method is limited only to those dialkylboranes which can be prepared by direct hydroboration.[4] More recently, the synthesis of lithium dialkylborohydrides was achieved via a reduction of dialkylborinates with lithium monoethoxyaluminohydride in ether at 0 °C[5] (eq 2). Although

$$R_2BOMe + LiAlH_3(OEt) \rightarrow LiR_2BH_2 + AlH(OMe)(OEt)\downarrow \quad (2)$$

this procedure is general and efficient, it requires the prior preparation of the dialkylborinates[6] as well as lithium monoethoxyaluminohydride,[7] not always convenient because the dialkylborinates are not readily available in all cases.[8,9]

During a routine preparation of organoboranes for our isomerization studies,[10] we discovered that triisopropyl-

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