O_2 interference with the reductive mode of the detector, the mobile phase was purged overnight with N_2 and throughout analyses and was heated to 35 °C to reduce N_2 solubility. Sample transfer lines were sleeved with Tygon tubing filled with positive N_2 pressure to prevent O_2 diffusion into the mobile phase.

Esters. All esters were prepared as previously reported.[35] Esters **2**, **4**, **5**, **6**, and **7** were purified by chromatography on silica gel eluting with methylene chloride/hexane; **2** was further purified by distillation in vacuo and **7** by recrystallization (carbon tetrachloride/hexane). **1** was recrystallized from carbon tetrachloride and **3** from methylene chloride/hexane. The purity of all compounds was checked with TLC and ^1H NMR, which indicated a purity > 95%. Elemental analyses were done on the new esters **4** and **5**. Anal. Calcd for **4**, $C_6H_{10}N_2O_6$: C, 34.95; H, 4.89; N, 13.59. Found: C, 34.92; H, 4.92; N, 13.46. Calcd for **5**, $C_6H_9N_3O_8$: C, 28.69; H, 3.61; N, 16.73. Found: C, 28.94; H, 3.48; N, 16.92.

Solutions. For strong acid runs, the desired amount of 2.0 M $HClO_4$ solution was added to deionized, distilled water and enough 0.2 M $NaClO_4$ to give an ionic strength of 0.2 M. Titration of aliquots with standardized Na_2CO_3 gave the $[H^+]$ used in calculations.

For acetate-buffered runs, pH at 60 °C was calculated from pH at 23 °C by the equation $pH = pH_{23} + 0.056$, which can be derived from the equations $[H^+]_{23} = 1.753 \times 10^{-5}/r$ and $[H^+]_{60} = 1.542 \times 10^{-5}/r$ where the K_a were determined at 0.2 M ionic strength[45a] and r is the same at the two temperatures. Values of $[OH^-]$ were calculated from $[H^+]_{60}$ and $K_w^{60} = 9.614 \times 10^{-14}$.[45b] The salt effect on pH was first determined empirically at 23 °C by adding the desired amount of $NaClO_4$ to the buffer solution and the targeted pH achieved by mixing a $NaClO_4$ solution with standardized NaOAc and $HClO_4$ solutions taking this into account. The $[H^+]$ in the final solutions were determined by titrations in triplicate to an acetate end point with standardized NaOH.

Kinetic Procedure. Samples from stock solutions of the esters[35] (5.0 mM in acetonitrile) to give 30–50 μM concentrations were injected into the above solutions maintained at 60.0 ± 0.1 °C. Aliquots (2.0 mL, taken in triplicate) were removed two to three times per half-life, transferred to 2.0 mL polyethylene snap-cap centrifuge tubes, quenched in an acetone–dry ice bath and stored at −5 °C in the solid state until analysis. Reactions were followed to at least 88% conversion except for **4** which in buffered media was followed from 0.4 to 2 half-lives.

For HPLC analysis, liquified samples at 0 °C were purged with N_2 for 3 min and then to minimize O_2 contamination loaded into the injection loop by drawing the mixture through the waste line and out the syringe port. Plots of peak height vs concentration of authentic samples were linear with zero intercept, and so k_{obs} were calculated from ln (height) vs time curves.

Product Study. NMR spectra were taken of acetic acid, esters **1** and **2** and their corresponding alcohols, first in D_2O and then D_2O/OH^-. The spectra of esters in base gave information about the hydrolysis products, and those of alcohols about possible secondary products from alcohol breakdown in base.

For **2**, ester signals at 2.03, 2.18, an 4.94 ppm decreased in area when NaOH was added, and a new signal at 1.18 ppm due to OAc^- appeared. Other new signals at 2.44 and 4.72 ppm are due to a degradation product(s) of the initially formed alcohol, since signals at these same positions appeared when the alcohol was treated with NaOH. Similar results were found for **1**.

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Supplementary Material Available: Figures of k_{obs} vs $[H^+]$, k_{red} vs C, intercepts i vs $[OH^-]$, and log k_{OH} vs spectroscopic parameters and ^1H NMR spectra of all esters (12 pages). Ordering information is given on any current masthead page.

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Regio- and Stereochemistry in Electrophilic Reactions of 2-Propenyl-1,3-dithiane 1-Oxide

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The unsymmetrical allyllithium generated from 2-propenyl-1,3-dithiane 1-oxide (**2**) reacted at the α-site with halides and most of the carbonyl compounds tried. The α-addition reactions occurred predominantly on the face syn to the sulfinyl group. The α-syn addition reaction of **2** and an aldehyde usually yielded mixtures of the erythro and threo isomers, whose structures were determined by spectral methods. An X-ray diffraction analysis of the threo product **11t** obtained from the reaction with cinnamaldehyde indicated that in the crystal structure the 1,3-dithiane ring exists as a puckered chair conformation with an equatorial sulfinyl oxygen. However, the oxygen is axial in $CDCl_3$ solution as shown by its ^{13}C NMR spectrum.

Introduction

As a continuing study of 2-propenyl-1,3-dithiane (**1**), we herein report the reactions of its monosulfoxide (**2**). The electrophilic reactions of **2** are of interest for several reasons: (i) The anion of dithioacetal monosulfoxide or 1,3-dithiane 1-oxide has been explored as an equivalent for the carbonyl anion in alkylations and conjugate additions.[1] Thus, the anion of **2** can be potentially manipulated as an equivalent of the butenone anion. (ii) The regiochemistry in reactions of heteroatom-substituted unsymmetric allylic anion is a long-standing problem.[2] The present study may serve as an example to demonstrate controlling factors in regioselectivity. (iii) Allylic sulfoxides have been shown to be useful intermediates in organic synthesis.[3] The

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Scheme I

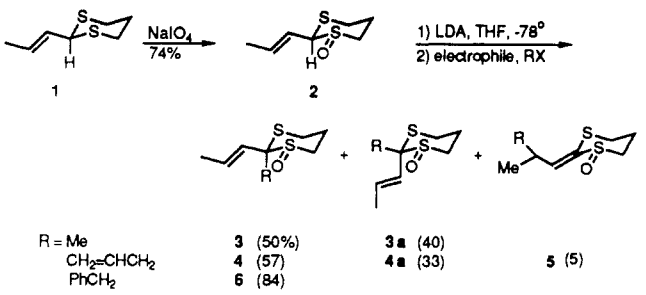


Table I. Reaction of 2Li with Various Aldehydes and Ketones

entry	carbonyl electrophile	products (% yield, isomer ratio)
1	propanal	**7e,t** (87, 70:30)
2	isobutyraldehyde	**8e** (89)
3	acrolein	**9e,t** (86, 43:57)
4	crotonaldehyde	**10e,t** (95, 45:55)
5	cinnamaldehyde	**11e,t** (85, 32:68)
6	benzaldehyde	**12e,t** (73, 56:44) + **13e,t** (15, 23:77)[a]
7	cyclopentanone	**14** (88)
8	cyclohexanone	**15** (91)
9	methyl vinyl ketone	**16e,t** (30, 14:86)
10	benzophenone	**17** (90)[a]
11	2-cyclopentenone	**18** (88)[b]
12	2-cyclohexenone	**19** (27, 62:38)[c] + **20** (34, 74:26)[d] + **21** (21, 81:19)[b]

[a] γ-Addition product. [b] γ-1,4-addition product. [c] α-1,2-Addition product. [d] γ-1,2-Addition product.

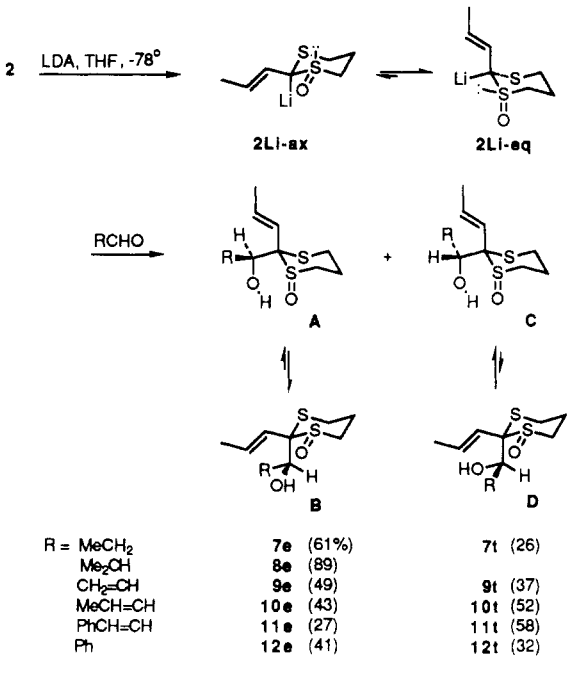
sulfoxide **2** can be anticipated to undergo similar transformation. (iv) The X-ray diffraction and NMR spectral methods are widely applied to study the conformations of dithiane monosulfoxides.[4] Investigation of the stereochemistry in reactions of **2** can further illustrate the conformational preference associated with the kinetic process. (v) If sulfoxide **2** can be prepared in an optically pure form,[4f,5] the subsequent reactions should proceed in asymmetric fashion.[6]

Results and Discussion

Oxidation of 2-propenyl-1,3-dithiane (**1**) with 1 equiv of sodium metaperiodate at 0 °C afforded monosulfoxide **2** in 74% yield and a small amount of its cis isomer **2a**. The H-2 and C-2 resonances in **2** appear at δ 4.03 and 66.7, while the corresponding signals in **2a** isomer are found at δ 4.36 and 58.6. Comparison of the NMR spectral data with values of known analogues indicates that **2** is the trans isomer having equatorial propenyl group and sulfinyl oxygen.[4f,5a,7] Treatment of **2** with lithium diisopropylamide (LDA) in THF at −78 °C resulted in a purple solution of the allyllithium, and the subsequent reactions with various electrophiles were carried out. Although the unsymmetric allyllithium of **2** may react at either the α- or γ-site with an electrophile, the reaction turned out to be highly α-regioselective with alkyl halides (Scheme I). Only with allyl bromide, the reaction at ambient temperature gave a small amount of side product **5** resulting from γ-substitution. The α-regioselectivity for reactions of **2** is in agreement with that observed in kinetically controlled alkylating reactions of allylic sulfoxides.[3a] The alkylating reactions of **2** showed a preference for attack at the face syn to the sulfinyl oxygen.[8] The syn methylated product **3** (having the trans configuration) shows a diagnostic carbon-13 chemical shift of δ 16.1 for an axial methyl group (C-1″),[4g,5b] while the anti methylated product **3a** has an equatorial methyl group appearing at the lower field (δ 24.8). The syn facial selectivity was increased to 100% in the reaction with benzyl bromide.

When aldehydes were used as the electrophile (Table I), the reactions also proceeded with complete α-regiose-

Scheme II



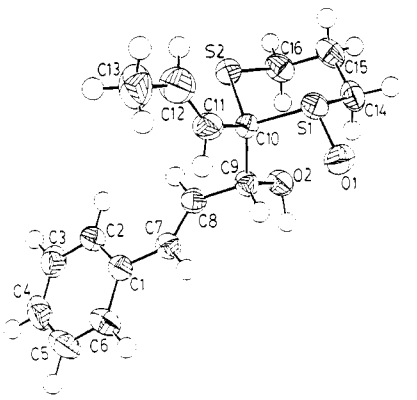


Figure 1. The ORTEP drawing of **11t**.

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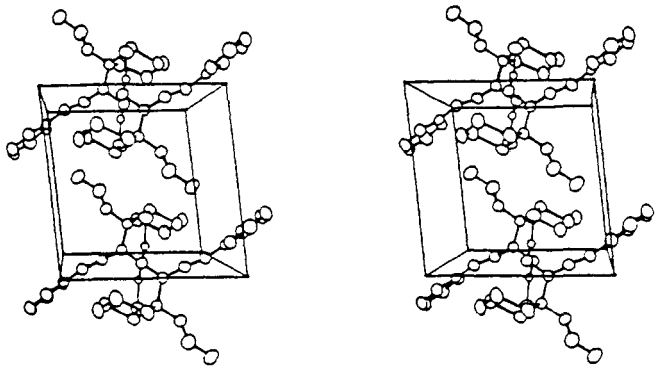
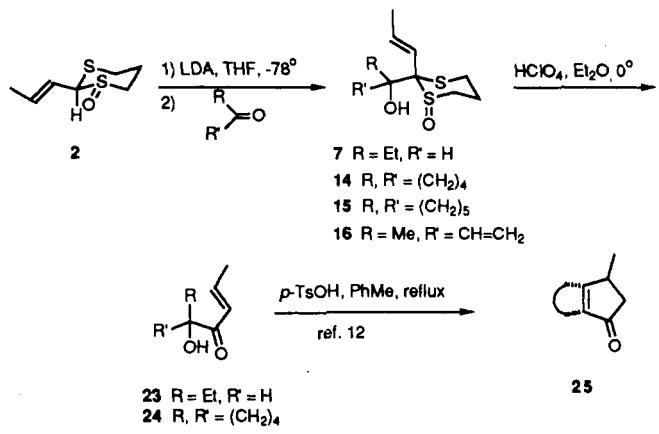


Figure 2. Crystal stereopacking diagram of **11t**.

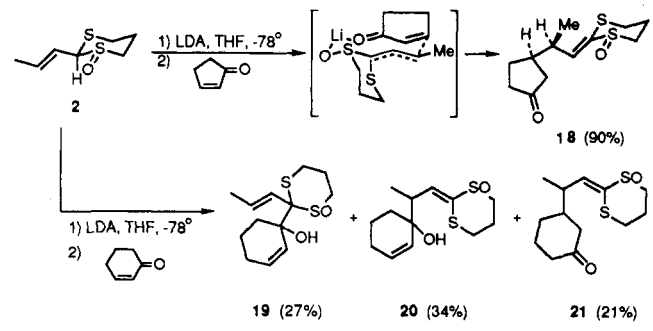
lectivity and syn facial selection (Scheme II). It is noted that the addition reactions with carbonyl compounds should be quenched at −78 °C by using acetic acid (3 equiv in THF); otherwise severe dissociation may occur when the reaction mixture is warmed over −30 °C. Of the two stereoisomers of α-syn adducts, the erythro product (**7e–12e**) was consistently more retained on a μ-Porasil column than the corresponding threo isomer (**7t–12t**). When an isomeric mixture of allylic alcohols (**10e/10t** = 45:55), obtained from the reaction of **2** and crotonaldehyde, was treated with MnO_2, it resulted in only oxidation product enone **22**. This experiment clearly indicates that **10e** and **10t** merely differ at the chirality of C-1″ (the carbon geminal to the hydroxyl group). The reaction of **2** with cinnamaldehye afforded two α-syn adducts **11e** (27%) and **11t** (58%). An X-ray diffraction analysis of the major product **11t** established its threo configuration. The crystal structure of **11t** showed a puckered chair conformation for the dithiane ring with equatorial oxygen and propenyl substituents (structure D). There is no intramolecular hydrogen bonding in the solid state, but the sulfinyl oxygen does exhibit strong hydrogen bonding with the hydroxyl group of another molecule to form a dimer.

Although the crystal structure of **11t** unambiguously indicates the equatorial sulfinyl oxygen, further ^{13}C NMR analysis reveals that the oxygen is axial in $CDCl_3$ solution. According to literature,[4g,5c] the C-5 resonance is shifted to higher field when the sulfinyl oxygen is in the axial orientation. In agreement with the reported values, the C-5 resonances in the threo products **7t–12t** all appear at rather high field (15.2–16.7 ppm) as a consequence of the shielding effect of axial sulfinyl oxygen atoms. On the other hand, the erythro products **7e–12e** showing the C-5 signals at normal positions of 19.8–25.1 ppm should have equatorial oxygen in solution. The NMR data listed in Table II show the vinyl protons (H-1′ and H-2′) in the threo series are more shielded than those in the erythro series, but the C-1″ resonances of the threo compounds are less shielded. This result further supports the assignment for axial propenyl substituent and equatorial hydroxylalkyl group in the threo compound. It is presumed that the threo compound existing as the intramolecular hydrogen bonded structure C with the oxygen axial is more stable than the one with oxygen equatorial (structure D), which is devoid of hydrogen bonding. On the other hand, structures A and B in the erythro series are both intramolecularly hydrogen bonded. Thus, B with an equatorial oxygen atom is more stable for the usual reasons. Lithiation of **2** may primarily generate an unstable allyllithium **2Li-ax**, which readily changes conformation to **2Li-eq** by flipping of the dithiane ring in order to release the anti-anomeric relationship (carbanion lone pair and sulfur atom lone pair) and to gain an extra carbanion–σ* (S–C) hyperconjugative interaction.[9] Based on this model, one can explain why a bulky electrophile such as benzyl bromide attacks **2Li-eq** exclusively from the equatorial direction to furnish the product **6**. The reaction of an aldehyde is considered to proceed via the chelating bicyclic transition state similar to the structure A or C. Therefore, the addition of an aldehyde on **2Li-eq** is anticipated to occur in excellent facial selection but in poor diastereoselectivity. We have previously reported that dithiane **1** reacts exclusively at the γ-site with aldehydes.[2c] The presence of a sulfinyl oxygen in **2** obviously causes a remarkable alteration of the reaction pathway (α-addition) with regard to the γ-addition in **1**.

Scheme III



Scheme IV



Dithiane oxide **2** reacted exclusively at the α-site with cyclopentanone and cyclohexanone to give **14** and **15** in 88% and 91% yields, respectively (Scheme III). Although the reaction with methyl vinyl ketone also resulted in low yields of α-addition products (4% of **16e** and 26% of **16t**), the reaction with benzophenone afforded a γ-addition product **17** (90% yield). The reaction with 2-cyclopentenone yielded a single γ-1,4-addition product **18**, whose stereochemistry is tentatively assigned by presuming a 10-membered transition state as that proposed for analogous reactions (Scheme IV).[10] The reaction with 2-cyclohexenone, however, gave a mixture of six isomers **19** (27%), **20** (34%), and **21** (21%) via α-1,2-, γ-1,2-, and γ-1,4-additions.[11]

Depending on the reaction mode, the anion of dithiane oxide **2** functions either as the equivalent of α,β-unsatu-

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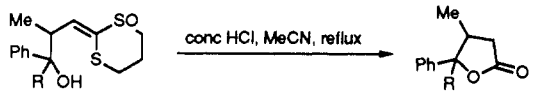
Table II. Some Characteristic ^1H and ^{13}C Signals (δ, $CDCl_3$) of Dithiane Oxide 2 and Its Reaction Products

compd	H-1′	H-2′	Me-2′	C-2	C-4	C-5	C-6	C-1′	C-2′	C-3′	C-1″
1	5.50	5.84	1.73	47.2	29.9	24.8	29.9	129.4	127.5	17.4	
2	5.65	5.93	1.71	66.7	29.7	28.6	53.2	135.8	121.7	18.1	
2a	5.72	6.06	1.86	58.6	29.3	24.8	45.6	134.4	120.9	18.1	
3	5.54	5.92	1.76	61.7	25.5	24.9	45.7	131.8	129.0	18.2	16.1
3a	5.83	6.06	1.84	62.5	26.0	29.1	47.2	132.0	122.5	18.2	24.8
4	5.49	5.92	1.74	64.8	24.8	21.6	44.4	132.6	126.7	18.2	35.0
4a	5.73	6.06	1.85	66.8	29.3	25.4	47.0	133.3	130.3	18.1	41.4
6	5.43	5.89	1.73	66.9	25.3	19.2	43.3	132.0	126.0	18.2	38.6
7e	5.84	6.08	1.79	67.5	24.9	21.4	44.5	134.2	123.9	18.5	73.7
7t	5.42	6.00	1.81	70.4	24.5	15.2	43.0	133.6	125.4	18.5	79.6
8e	(5.98–6.15)		1.80	66.8	25.4	22.7	45.5	126.0	133.2	18.7	74.7
9e	5.70	6.10	1.77	66.8	24.8	19.8	43.8	133.9	124.8	18.3	73.4
9t	5.32	6.01	1.74	68.9	24.6	16.7	43.5	133.9	123.1	18.3	77.7
10e	5.81	6.14	1.82	67.0	25.0	20.7	44.4	134.6	127.0	18.6	73.6
10t	5.37	6.04	1.82	69.8	24.5	15.5	43.1	134.0	126.7	18.5	78.4
11e	5.83	6.18	1.83	67.3	25.0	20.1	44.1	134.0	127.0	18.5	73.3
11t	5.45	6.05	1.80	69.7	24.7	16.2	43.4	134.0	127.7	18.5	78.0
12e	5.68	5.90	1.80	69.0	25.1	25.1	43.4	135.1	122.8	18.5	75.4
12t	5.23	5.88	1.73	71.1	24.4	14.9	43.1	134.3	124.5	18.3	80.3
14	5.31	6.19	1.85	73.6	24.6	14.0	42.5	134.7	124.0	18.6	88.3
15	5.4	6.2	1.8	75.5	24.7	14.4	42.1	134.4	124.6	18.6	78.4

Scheme V



13 R = H
17 R = Ph

26 R = H

rated acyl anion or as the equivalent of β-carbanion of butanoate ester. For instance, treatment of the α-addition product **14** with a catalytic amount of $HClO_4$ fforded an α'-hydroxy-α,β-unsaturated ketone **24** as an entry to the bicyclic enones **25** via the Nazarov reactions.[12] On the other hand, hydrolysis of the γ-addition products **13** with 10% HCl resulted in β-methyl-γ-phenyl γ-lactones **26** (Scheme V).[13] If the dithiane oxide **2** were obtained in an optically pure form, its stereospecific reaction with 2-cyclopentenones would serve as an entry to synthesis of various natural products such as steroids[14] and triquinanes.[9b] Our recent attempt on asymmetric oxidation of dithiane **1** by using a modified Sharpless reagent gave about 55% enantiomeric excess of sulfoxide **2**.[5]

Experimental Section

Melting points are not corrected. ^1H NMR spectra were recorded at 90, 200, or 300 MHz. Mass spectra were recorded at an ionizing voltage of 70 eV. Merck silica gel 60F sheets were used for analytical thin-layer chromatography. Merck silica gel 60 (230–400 mesh) was used for flash chromatography. High-pressure liquid chromatography was carried out on a liquid chromatograph, equipped with a refractive index detector. The samples were analyzed and/or separated on a μ-Porasil column (0.78 cm × 25 cm) by the indicated eluent with 5 mL/min flow rate.

2-Propenyl-1,3-dithiane 1-Oxide (2). (A) Using $NaIO_4$ as Oxidant. An aqueous solution (20 mL) of $NaIO_4$ (2.14 g, 10 mmol) was added to a methanolic solution (80 mL) of 2-propenyl-1,3-dithiane (1.6 g, 10 mmol) at 0 °C, and the mixture was stirred for 3 h. The mixture was filtered, the filtrate was concentrated in vacuo, and the residue was extracted three times with ethyl acetate. The combined extracts were washed with brine, dried (Na_2SO_4), and chromatographed on a SiO_2 column by elution with MeOH–EtOAc (3:97) to give sulfoxide **2** (1.30 g, 74%) and the cis isomer **2a** (0.11 g, 6%). **2**: colorless oily solid (hygroscopic); t_R 3.1 min (3% MeOH in EtOAc). Anal. C, H. **2a**: colorless oily solid; t_R 4.7 min.

(B) Asymmetric Oxidation. To a solution of titanium isopropoxide (2.98 mL, 10 mmol) and (+)-diethyl L-tartrate (3.42 mL, 20 mmol) in 30 mL of CH_2Cl_2 was added 0.18 mL of water (10 mmol) at 0 °C. The yellow solution was stirred for 15 min, and dithiane **1** (1.6 g, 10 mmol) was added. After 10 min, the solution was cooled to −20 °C, and *tert*-butyl hydroperoxide (1.38 mL, 85% purity, 11 mmol) was added dropwise. The mixture was kept stirring overnight in a refrigerator (−18 °C). After 1.8 mL of water was added, the mixture was warmed to room temperature with vigorous stirring, and a suitable amount of aluminum powder was added to make colloids for filtration. After being rinsed with portions of CH_2Cl_2, the filtrate was washed consecutively with 5% NaOH and brine. The sulfoxides **2** were obtained in 60% yield from the organic phase with recovery of dithiane **1**. By the ^1H NMR analysis with a chiral shift reagent, *N*-(1-phenylethyl)-3,5-dinitrobenzamide,[15] the trans sulfoxide **2**, $[\alpha]^{25}_D$ −31° (*c* 10.5, CH_2Cl_2), was shown to be 50% enantiomeric excess. Using (−)-diethyl D-tartrate as the chiral auxiliary, instead of its L-enantiomer, afforded **2** in 60% ee, $[\alpha]^{25}_D$ +37° (*c* 2.3, CH_2Cl_2). Pure **2** was calculated to have $[\alpha]$ ±62°.

General Procedure for Electrophilic Reactions of 2. Under an atmosphere of nitrogen, 0.75 mL (1.1 mmol) of *n*-BuLi (1.6 M solution in hexane) was added dropwise to a solution of diisopropylamine (0.18 mL, 1.2 mmol) in THF (2 mL) at −20 °C. The solution was stirred for 30 min and cooled to −78 °C, and a solution of 2-propenyl-1,3-dithiane 1-oxide (176 mg, 1.0 mmol) in THF (2 mL) was added dropwise. After 30 min, 1.0 mmol of an appropriate electrophile (halide or carbonyl compound) was added to the resulting purple solution. The yellow mixture was stirred for 30 min and quenched by addition of a THF solution of acetic acid (3 mmol) at −78 °C. The volatiles were removed in vacuo, and the residue was partitioned between ethyl acetate and water. The organic phase was separated, washed with brine, dried (Na_2SO_4), and concentrated to give crude products. Further separation or purification of the products (**3**–**21**) was carried out by means of chromatography and crystallization. Some pertinent data for **3**–**21** are reported and details are included in the supplementary material.

2-Methyl-2-propenyl-1,3-dithiane 1-Oxide. Trans isomer **3**: 50% yield; oil; t_R 6.1 min (EtOAc). Anal. C, H. Cis isomer **3a**: 40% yield; oil; t_R 5.2 min (EtOAc).

2-Allyl-2-propenyl-1,3-dithiane 1-Oxide. Trans isomer **4**: 57% yield; oil; t_R 10.4 min (EtOAc). Cis isomer **4a**: 33% yield; oil; t_R 8.0 min (EtOAc). Anal. C, H.

2-(2-Methyl-4-pentenylidene)-1,3-dithiane 1-oxide (5): 5% yield; oil; t_R 6.6 min (EtOAc).

***trans*-2-Benzyl-2-propenyl-1,3-dithiane 1-oxide (6)**: 84%

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yield; oil; t_R 5.3 min (EtOAc); IR (neat) 2917, 1630, 1038, 755, 700 cm^{-1}; MS m/z (rel intensity) 266 (27, M^+), 248 (8), 144 (100), 129 (100), 123 (40), 91 (42); ^1H NMR ($CDCl_3$) δ 1.73 (d, 3 H, J = 6.6 Hz), 1.87 (m, 1 H), 2.44–2.73 (m, 3 H), 2.81–2.88 (m, 2 H), 3.08 (d, 1 H, J = 13.7 Hz), 3.25 (d, 1 H, J = 13.7 Hz), 5.43 (d, 1 H, J = 15.6 Hz), 5.89 (dq, 1 H, J = 15.6, 6.6 Hz), 7.19–7.28 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 18.2 (q), 19.2 (t), 25.3 (t), 38.6 (t), 43.3 (t), 66.9 (s), 126.0 (d), 127.0 (d), 127.6 (d, 2 C), 131.0 (d, 2 C), 132.0 (d), 133.8 (s); exact mass for $C_{14}H_{18}OS_2$ requires 266.0799, found 266.0802.

***cis*-2-(1-Hydroxypropyl)-2-propenyl-1,3-dithiane 1-Oxide.** Erythro isomer **7e**: 61% yield; oil; t_R 6.6 min (10% hexane in EtOAc); IR (neat) 3264, 2959, 1654, 1431, 1113, 1032, 973 cm^{-1}; MS m/z (rel intensity) 234 (60, M^+), 159 (45), 123 (100), 112 (76); ^1H NMR ($CDCl_3$) δ 0.96 (t, 3 H, J = 7.4 Hz), 1.35 (m, 1 H), 1.67 (m, 1 H), 1.79 (d, 3 H, J = 6.5 Hz), 1.90 (m, 1 H), 2.34–2.57 (m, 3 H), 2.91–3.05 (m, 2 H), 4.18 (t, 1 H, J = 10.0 Hz), 4.43 (s, 1 H, OH), 5.84 (d, 1 H, J = 15.8 Hz), 6.08 (dq, 1 H, J = 15.8, 6.5 Hz); ^{13}C NMR ($CDCl_3$) δ 10.4 (q), 18.5 (q), 21.4 (t), 24.7 (t), 24.9 (t), 44.5 (t), 67.5 (s), 73.7 (d), 123.9 (d), 134.2 (d). Anal. Calcd for $C_{10}H_{18}O_2S_2$: C, 51.25; H, 7.74. Found: C, 51.10; H, 7.74. Threo isomer **7t**: 26% yield; oil; t_R 5.9 min (10% hexane in EtOAc); IR (neat) 3380, 2961, 1654, 1423, 1123, 1029, 985 cm^{-1}; MS m/z (rel intensity) 234 (2, M^+), 159 (30), 123 (79), 112 (100), 85 (32); ^1H NMR ($CDCl_3$) δ 0.93 (t, 3 H, J = 7.3 Hz), 1.32 (m, 1 H), 1.58–1.76 (m, 2 H), 1.81 (d, 3 H, J = 6.6 Hz), 2.44–2.56 (m, 2 H), 2.73–2.90 (m, 3 H), 4.04 (t, 1 H, J = 10.0 Hz), 4.10 (s, 1 H, OH), 5.42 (d, 1 H, J = 15.8 Hz), 6.00 (dq, 1 H, J = 15.8, 6.6 Hz); ^{13}C NMR ($CDCl_3$) δ 10.6 (q), 15.2 (t), 18.5 (q), 24.2 (t), 24.5 (t), 43.0 (t), 70.4 (s), 79.6 (d), 125.4 (d), 133.6 (d). Anal. Calcd for $C_{10}H_{18}O_2S_2$: C, 51.25; H, 7.74. Found: C, 51.47; H, 7.81.

***cis*-2-(1-Hydroxy-2-methylpropyl)-2-propenyl-1,3-dithiane 1-oxide (8e)**: 89% yield; colorless crystal; mp 142–143 °C (from EtOAc). Anal. C, H.

***cis*-2-(1-Hydroxyallyl)-2-propenyl-1,3-dithiane 1-oxide (9)**: mixture of erythro and threo isomers (57:43); 86% yield; t_R 6.0 min (EtOAc).

***cis*-2-(1-Hydroxycrotyl)-2-propenyl-1,3-dithiane 1-oxide.** Erythro isomer **10e**: 43% yield; oil; t_R 7.4 min (EtOAc). Anal. C, H. Threo isomer **10t**: 52% yield; oil; t_R 6.7 min (EtOAc). Anal. C, H.

***cis*-2-(1-Hydroxycinnamyl)-2-propenyl-1,3-dithiane 1-Oxide.** Erythro isomer **11e**: 27% yield; oily solid; t_R 10.5 min (10% hexane in EtOAc). Threo isomer **11t**: 58% yield; colorless plate crystal; mp 144–145 °C (from EtOAc); t_R 10.0 min (10% hexane in EtOAc). Crystal data for **11t**: $C_{16}H_{20}O_2S_2$, monoclinic, space group $P2_1/c$. Cell parameters: a = 9.010 (1), b = 19.989 (5), c = 8.813 (2) Å; β = 95.93 (1)°; D_c = 1.29 g/cm^3; z = 4. 2779 unique reflections were measured with CAD-4 Mo Kα radiation up to 2θ = 50°. 1422 reflections with $I > 2\sigma(I)$ were used in the refinement. The final refinement converged to R = 0.038 and R_W = 0.033 for 182 variables.

***cis*-2-(1-Hydroxybenzyl)-2-propenyl-1,3-dithiane 1-Oxide.** Erythro isomer **12e**: 41% yield; colorless plate crystal; mp 165–167 °C (from EtOAc); R_f 0.3 (EtOAc). Threo isomer **12t**: 32% yield; oil; R_f 0.3 (EtOAc).

2-(3-Hydroxy-2-methyl-3-phenylpropylidene)-1,3-dithiane 1-Oxide. Erythro isomer **13e**: 3% yield; oil; t_R 6.0 min (EtOAc). Threo isomer **13t**: 12% yield; oil; t_R 7.6 min (EtOAc).

***cis*-2-(1-Hydroxycyclopentyl)-2-propenyl-1,3-dithiane 1-oxide (14)**: 88% yield; colorless plate crystal; mp 142–144 °C (from EtOAc); R_f 0.3 (EtOAc); IR (KBr) 3254, 2952, 1637, 1446, 1431, 1027 cm^{-1}; MS m/z (rel intensity) 260 (100, M^+), 242 (70), 159 (49), 137 (88), 123 (53), 85 (52); ^1H NMR ($CDCl_3$) δ 1.36–2.00 (m, 8 H), 1.85 (d, 3 H, J = 6.0 Hz), 2.38–2.87 (m, 6 H), 4.27 (s, 1 H, OH), 5.31 (d, 1 H, J = 15.0 Hz), 6.19 (dq, 1 H, J = 15.0, 6.0 Hz); ^{13}C NMR ($CDCl_3$) δ 14.0 (t), 18.6 (q), 23.6 (t), 23.7 (t), 24.6 (t), 35.8 (t), 36.6 (t), 42.5 (t), 73.6 (s), 88.3 (s), 124.0 (d), 134.7 (d). Anal. Calcd for $C_{12}H_{20}O_2S_2$: C, 55.35; H, 7.74. Found: C, 55.29; H, 7.81.

***cis*-2-(1-Hydroxycyclohexyl)-2-propenyl-1,3-dithiane 1-oxide (15)**: 91% yield; colorless plate crystal; mp 128.5–130 °C (from EtOAc); R_f 0.28 (EtOAc). Anal. C, H.

***cis*-2-(1-Hydroxy-1-methylallyl)-2-propenyl-1,3-dithiane 1-Oxide.** Erythro isomer **16e**: 4% yield; oil; t_R 7.8 min (EtOAc). Threo isomer **16t**: 26% yield; oil; t_R 7.4 min (EtOAc).

2-(3-Hydroxy-2-methyl-3,3-diphenylpropylidene)-1,3-dithiane 1-oxide (17): 90% yield; colorless solid; mp 235–236 °C (from EtOAc); R_f 0.55 (EtOAc). Anal. C, H.

2-[2-(3-Oxocyclopentyl)propylidene]-1,3-dithiane 1-oxide (18): 90% yield; oil; t_R 10.8 min (1% MeOH in EtOAc); IR (neat) 2959, 1732, 1450, 1159, 1057, 906 cm^{-1}; MS m/z (rel intensity) 258 (2, M^+), 240 (43), 225 (48), 173 (36), 159 (18), 106 (48), 85 (100); ^1H NMR ($CDCl_3$) δ 0.79 (d, 3 H, J = 6.7 Hz), 1.50 (m, 1 H), 1.78–2.64 (m, 11 H), 2.90 (m, 1 H), 3.27 (m, 1 H), 6.42 (d, 1 H, J = 10.5 Hz). Anal. Calcd for $C_{12}H_{18}O_2S_2$: C, 55.77; H, 7.02. Found: C, 55.37; H, 7.00.

***cis*-2-(1-Hydroxycyclohex-2-en-1-yl)-2-propenyl-1,3-dithiane 1-Oxide. 19** (major isomer): 17% yield; oil; t_R 6.5 min (15% hexane in EtOAc). **19** (minor isomer): 10% yield; oil; t_R 8.0 min (15% hexane in EtOAc).

2-[2-(1-Hydroxycyclohex-2-en-1-yl)propylidene]-1,3-dithiane 1-Oxide. 20 (major isomer): 25% yield; oil; 9.1 min (15% hexane in EtOAc). **20** (minor isomer): 9% yield; oil; t_R 11.8 min (15% hexane in EtOAc).

2-[2-(3-Oxocyclohexyl)propylidene]-1,3-dithiane 1-Oxide. 21 (major isomer): 17% yield; oil; t_R 11.1 min (EtOAc). **21** (minor isomer): 4% yield; oil; t_R 11 min (EtOAc).

2-(1-Oxobut-2-enyl)-2-propenyl-1,3-dithiane 1-Oxide (22). A mixture of allyl alcohols **10** (246 mg, 1 mmol, erythro:threo = 45:55) and MnO_2 (435 mg, 5 mmol, Attenburrow active form) in CH_2Cl_2 (10 mL) was stirred at room temperature for 3 h. The mixture was filtered through a pad of Celite; the filtrate was concentrated and purified by HPLC to give a quantitative yield of enone **22** (242 mg, 99%); oil; t_R 5.2 min (EtOAc); IR (neat) 2900, 1686, 1628, 1445, 1295, 1055, 962 cm^{-1}; MS m/z (rel intensity) 244 (9, M^+), 159 (36), 153 (45), 122 (100); ^1H NMR ($CDCl_3$) δ 1.82 (d, 3 H, J = 6.9 Hz), 1.89 (d, 3 H, J = 6.9 Hz), 2.15 (m, 1 H), 2.30–2.55 (m, 2 H), 2.82 (m, 1 H), 2.98 (m, 1 H), 3.28 (m, 1 H), 5.78 (d, 1 H, J = 17.4 Hz), 6.04 (dq, 1 H, J = 17.4, 6.9 Hz), 6.49 (d, 1 H, J = 13.6 Hz), 7.08 (dq, 1 H, J = 13.6, 6.9 Hz); exact mass $C_{11}H_{16}O_2S_2$ requires 244.0592, found 244.0582.

5-Hydroxyhept-2-en-4-one (23). At 0 °C, a mixture of $HClO_4$ (catalytic amount, 70% aqueous solution) and Et_2O (5 mL) was added dropwise to an ethereal solution (20 mL) of α-addition product **7** (234 mg, 1 mmol). The hydrolysis was completed in 1 h as monitored by TLC analysis. Formation of reddish brown insoluble material was apparent. A 5% NaOH solution was added until the mixture solution became neutral. After ether was removed, the residue was chromatographed to give 67 mg (52%) of the desired product **23**: liquid; R_f 0.4 (20% EtOAc in hexane); IR (neat) 3459, 2967, 1686, 1626, 972 cm^{-1}; MS m/z (rel intensity) 129 (6, $M^+ + 1$), 111 (23), 69 (100); ^1H NMR ($CDCl_3$) δ 0.88 (t, 3 H, J = 7.3 Hz), 1.55 (m, 1 H), 1.85 (m, 1 H), 1.92 (d, 3 H, J = 6.7 Hz), 3.55 (d, 1 H, J = 5.4 Hz, OH), 4.29 (dt, 1 H, J = 7.3, 5.4 Hz), 6.23 (d, 1 H, J = 17.0 Hz), 7.02 (dq, 1 H, J = 17.0, 6.7 Hz); exact mass $C_7H_{12}O_2$ requires 128.0837, found 128.0841.

1-(1-Oxobut-2-enyl)cyclopentan-1-ol (24). The acid-catalyzed hydrolysis of **14**, according to the procedure for **7**, afforded a 72% yield of enone **24**: oil; t_R 4 min (25% EtOAc in hexane).

Tetrahydro-4-methyl-5-phenylfuran-2-one (26). A mixture of two isomers (77:23) of **13** (141 mg, 0.5 mmol), obtained as the γ-addition products (15%) from the reaction of **2** and benzaldehyde, in CH_2CN (10 mL) was refluxed with 1 mL of concentrated HCl (36% aqueous solution) for 3 h. The mixture was cooled, added to 7 mL of NaOH (5% aqueous solution), and extracted with EtOAc. The combined extracts were washed with brine, dried (Na_2SO_4), and concentrated to give 88% yield of γ-lactone products **26** containing the trans and cis isomers in a ratio of 77:23. The physical and spectral data for **26** have been described in ref 13.

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Supplementary Material Available: Full spectroscopic data for compounds **2–24** and X-ray data for compound **11t** including atomic coordinates, bond distances, and bond angles (14 pages). Ordering information is given on any current masthead page.