in 1.8 mL of THF was added in one portion. The ice bath was removed and the solution was stirred at room temperature for 12 h. The brown solution was poured into an equal volume of cold aqueous ammonium chloride and extracted with two equal volumes of ether. The extracts were backwashed with water, dried ($MgSO_4$), and concentrated by rotary evaporation to give 0.36 g of a brown semisolid. Column chromatography (silica gel/30% ether–cyclohexane) resulted in 0.11 g (42%) of a diastereomeric mixture of 1,2-bis(carbomethoxy)-3-chlorocyclopropane and 0.13 g (60%) of *N,N*-dimethylbenzenesulfinamide.

Reaction of 7 with 2-Propenal. The reaction was carried out in the manner described above. The extraction was done with pentane. Some product codistilled with pentane, but the residue after concentration and treatment with 2,4-dinitrophenylhydrazine yielded 40% of 2-chlorocyclopropanecarboxaldehyde as its 2,4-dinitrophenylhydrazone, mp 160–161 °C. In a separate run, *N,N*-dimethylbenzenesulfinamide was found to be produced in 81% yield.

Acknowledgment. This research was supported by the National Science Foundation.

Registry No.—**1**, 67069-79-8; **2a** isomer 1, 67069-67-4; **2a** isomer 2, 67069-68-5; **2b** isomer 1, 67069-69-6; **2b** isomer 2, 67069-70-9; **2c**, 67069-71-0; **2d** isomer, 67112-77-0; **2d** isomer 2, 67069-63-0; **3** isomer 1, 67112-78-1; **3** isomer 2, 67112-76-9; **3** isomer 3, 67069-62-9; **3** isomer 4, 67145-49-7; **4**, 67069-72-1; **6**, 67069-74-3; **7**, 67069-75-4; **8**, 5539-54-8; **9** isomer 1, 67069-76-5; **9** isomer 2, 67069-77-6; *cis*-6-*tert*-butyl-1-oxaspiro[2.5]octane, 7787-78-2; *trans*-6-*tert*-butyl-1-oxaspira[2.5]-octane, 18881-26-0; 1,2-bis(carbomethoxy)-3-chlorocyclopropane, 67069-78-7; 4-nitrobenzaldehyde, 555-16-8; 2-propenal, 107-02-8; dimethyl fumarate, 624-49-7.

Supplementary Material Available: Analytical and spectral data of the compounds discussed in this paper (3 pages). Ordering information is given on any current masthead page.

References and Notes

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Temperature-Dependent Rearrangement of 2-(2-Furyl)-2-lithio-1,3-dithiane

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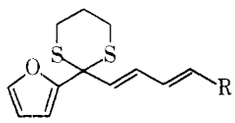
In the course of our work directed in the area of the Diels–Alder reaction, we required the preparation of compounds such as **1**. It was thought the use of 2-(2-furyl)-1,3-dithiane

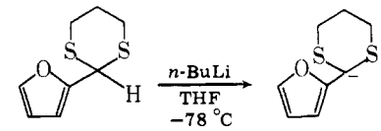


1

(**2**) as a nucleophilic acylating agent would provide an efficient entry into such a system. The use of lithiated 1,3-dithianes is well known and is the subject of two excellent reviews by Seebach.[1,2] Interestingly, the synthesis and use of compound **2** had not previously been recorded in the literature. We wish to report the preparation of **2** and the temperature dependent rearrangement of the anion produced from **2**.

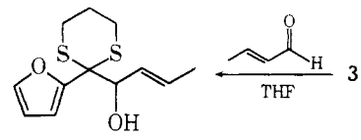
Results and Discussion

Preparation and Metalation of 2-(2-Furyl)-1,3-dithiane. The preparation of dithiane **2** was accomplished in



2 3

75% yield from furfural using the method of Corey and Seebach.[3] Metalation of **2** is complete within 10 min at −78 °C (method A). Reaction of anion **3** at −78 °C with crotonaldehyde and ethyl formate led to the isolation of alcohol **4** and aldehyde **5** in 95 and 60% yields, respectively.



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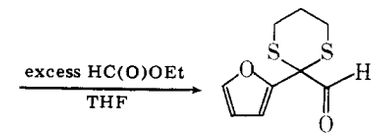

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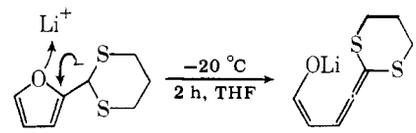
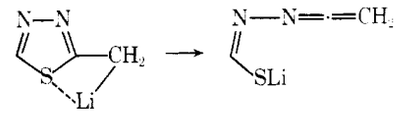
Temperature-Dependent Rearrangement of 3. When metalation was attempted using the method of Corey and Seebach[3] (method B), anion **3** underwent a novel rearrangement resulting in the formation of **6**. Analogy for such a re-

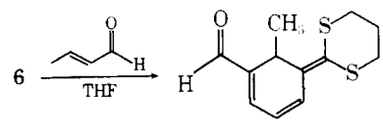


3 6

arrangement has previously been reported in the literature.[4] The rearrangement of 2-lithiomethylthiadiazoles reported by Meyers was also shown to be temperature dependent.[4a]



Compound **6** is postulated to account for the unexpected formation of ketene thioacetal **7**, the result of quenching the anion produced by method B with crotonaldehyde at −78 °C. Structural assignment **7** is based on the spectral characterization data (Experimental Section). The formation of **7** could be envisioned by one of two possible mechanisms. Compound **7** could arise from a 1,4 addition to crotonaldehyde at the γ



7

position of dienolate **6**, followed by cyclization and subsequent loss of H_2O. The other possibility is a Diels–Alder addition of **6** with crotonaldehyde followed by elimination of water after acidification.[5]

Further insight into the rearrangement was gained by quenching **6** with trimethylchlorosilane. Aqueous workup of the reaction furnished the cis unsaturated aldehyde **9** in quantitative yield. The structure is based on spectral data and the conversion of **9** to *n*-pentyl alcohol by successive treatment with $NaBH_4$ and Raney-Nickel.[6] The coupling constant of 7.5 Hz between H_2 and H_3 is indicative of a cis double bond when compared to *trans*-2-penten-4-ynal, a known trans-α,β-un-

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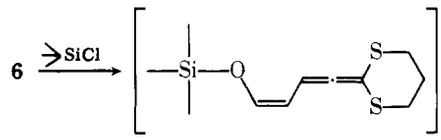
saturated aldehyde, which has a coupling constant of 16 Hz.[7] Nonaqueous workup led to an extremely unstable product. This product exhibited no absorptions indicative of an aldehyde in the IR or NMR. This is consistent with O-silylation rather than C-silylation and suggests the possible intermediacy of allene **8**. Although no direct evidence for **8** can be given, it seems to be most consistent with the results.



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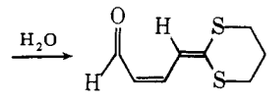

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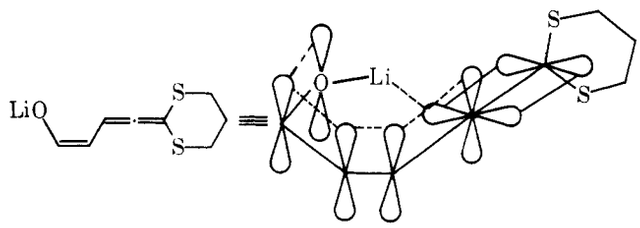
Reaction of **6** with D_2O led to the quantitative isolation of **9** with incorporation of deuterium in the γ position. In the NMR spectrum of the deuterated sample, a doublet at δ 6.63 in the spectrum of **9** was absent. Formation of the enol-OD followed by a 1,5-suprafacial shift of D would account for the position of the deuterium and the cis configuration about the double bond.[8] Anion **6** might best be depicted as shown below.



Attempts to quench **6** with other electrophiles (CH_3I, PhCOCl, and Ac_2O) led to unidentifiable products.

Experimental Section

All melting points were taken on a Fisher-Johns Mel-Temp apparatus and are uncorrected. IR spectra were obtained on a Beckman IR 4250 spectrometer. NMR spectra were recorded using a Varian A-60 spectrometer. All chemical shifts are reported in δ relative to tetramethylsilane as an internal standard. An AEI-MS902 mass spectrometer was used for mass spectral data. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Visible spectra were recorded on a Cary-14 spectrometer. All organic solutions were dried over sodium sulfate.

2-(2-Furyl)-1,3-dithiane (2). A solution of 50 mmol of 1,3-propanedithiol and 50 mmol of furfural in 50 mL of CH_2Cl_2 was stirred at 0 °C for 30 min under an atmosphere of N_2. Then 5 mmol of BF_3·Et_2O were added and the reaction was slowly warmed to room temperature. The solution was stirred overnight at room temperature. It was then washed with $NaHCO_3$ solution, dried, filtered, and concentrated. The residue was recrystallized from hexane/benzene solution yielding 7.0 g (75%) analytically pure **2** (mp 43 °C): NMR ($CDCl_3$) 2.1 (m, 2 H), 3.0 (m, 4 H), 5.31 (s, 1 H), 6.49 (m, 2 H), 7.5 (m, 1 H).

Anal. Calcd for $C_8H_{10}OS_2$: C, 51.57; H, 5.41. Found C, 51.7; H, 5.62.

Method A: General Procedure for Expected Adducts. A 0.10 M solution of dithiane **2** in THF was cooled to −78 °C. To this was added an equivalent amount of *n*-butyllithium. The reaction was stirred at −78 °C for 10 min. During this time the solution turns deep red. This was followed by addition of a 2 M THF solution of the appropriate electrophile. The reaction was stirred at −78 °C for 15 min. It was then slowly warmed to room temperature. The solution was poured into ether and washed with a buffered (pH 7) NH_4Cl/NH_4OH solution. The organic solution was dried, filtered, and concentrated. The residue was chromatographed on silica gel using ether/hexane.

2-(2-Furyl)-2-(1-hydroxy-2-butenyl)-1,3-dithiane (4): 95% yield; IR (film) 3435 cm^{-1}; NMR ($CDCl_3$) 1.70 (d, J = 4.0 Hz, 3 H), 2.00 (m, 2 H), 2.77 (m, 4 H), 4.37 (d, J = 4.0 Hz, 1 H), 5.55 (m, 2 H), 6.37 (m, 1 H), 6.60 (m, 1 H), 7.50 (m, 1 H). High resolution mass spectrum *m/e* 256.0600 ($C_{12}H_{16}O_2S_2$ requires 256.05918).

2-Formyl-2-(2-furyl)-1,3-dithiane (5). A fourfold excess of ethyl formate was used to quench the anion. The compound after chromatography was recrystallized from hexane/CH_2Cl_2: 60% yield; white crystals (mp 72 °C); IR ($CHCl_3$) 1730, 2705, and 2820 cm^{-1}; NMR ($CDCl_3$) 2.14 (m, 2 H), 3.05 (m, 4 H), 6.60 (m, 2 H), 7.10 (m, 1 H), 9.40 (s, 1 H). High resolution mass spectrum *m/e* 213.9939 ($C_9H_{10}O_2S_2$ requires 214.0122).

Method B: General Procedure for Rearrangement of 2-(2-Furyl)-1,3-dithiane. A solution of 40 mL of anhydrous THF and 10 mmol of dithiane **2** was cooled to −40 °C. To this solution was added 10 mmol of *n*-butyllithium. The reaction was warmed to −20 °C and stirred at this temperature for 2 h. The resulting dark red solution was cooled to −78 °C. This was followed by addition of 10 mmol of the appropriate electrophile. The reaction was slowly warmed to 0 °C, poured into ether, and washed with a buffered (pH 7) NH_4Cl/NH_4OH solution. The organic solution was dried, filtered, and concentrated. The residue was chromatographed on silica gel using ether/hexane.

2-(5-Formyl-6-methyl-2,4-cyclohexadien-1-ylidene)-1,3-dithiane (7): red oil; 15% yield; IR (film) 2800, 2709, 1650 cm^{-1}; NMR ($CDCl_3$) 1.0 (d, J = 4.0 Hz, 3 H), 2.28 (m, 2 H), 3.05 (m, 4 H), 4.20 (q, J = 4.0 Hz, 1 H), 6.14 (dd, J_{32} = 3.0 Hz, J_{34} = 4.8 Hz, 1 H), 6.98 (d, J_{23} = 3.0 Hz, 1 H), 7.19 (d, J_{43} = 4.8 Hz, 1 H), and 9.65 (s, 1 H). High-resolution mass spectrum *m/e* 238.0434 ($C_{12}H_{14}OS_2$ requires 238.0486). Visible spectra (CH_3OH) 441 nm.

2-(3-Formyl-(*Z*)-2-propen-1-ylidene)-1,3-dithiane (9): red oil; 100% yield; IR (film) 2800, 2710, 1655 cm^{-1}; NMR ($CDCl_3$) 2.28 (m, 2 H), 3.10 (m, 4 H), 6.10 (dd, J_{32} = 7.5 Hz, J_{34} = 4.2 Hz, 1 H), 6.63 (d, J_{12} = 6.0 Hz, 1 H), 7.68 (dd, J_{21} = 6.0 Hz, J_{23} = 7.5 Hz, 1 H), and 9.78 (d, J_{43} = 4.2 Hz, 1 H). High-resolution mass spectrum *m/e* 186.0154 ($C_6H_{10}OS_2$ requires 186.0173). Visible spectra (CH_3OH) 365 nm.

2-(4-Hydroxy-(*Z*)-2-buten-1-ylidene)-1,3-dithiane. To a solution of 4 mL of CH_3OH and 2 mmol of **9** was added 0.55 mmol of $NaBH_4$. The reaction was stirred at room temperature for 30 min. It was diluted with 30 mL of Et_2O and washed with saturated NaCl solution. The Et_2O was dried and concentrated: yield 0.30 g (8); IR (film) 3434 cm^{-1}; NMR ($CDCl_3$) 2.20 (m, 2 H), 3.10 (m, 4 H), 4.20 (d, J = 5.0 Hz, 2 H), 5.85 (m, 1 H), 6.50 (m, 2 H).

***n*-Pentyl Alcohol.** A solution of 0.53 mmol of 2-(4-hydroxy-(*Z*)-2-buten-1-ylidene)-1,3-dithiane and 1 g of W-4 Ra-Ni in 25 mL of EtOH was refluxed for 1 h. Analysis by GLC proved the product to be *n*-pentyl alcohol.

Registry No.—**2,** 67421-75-4; **4,** 67421-76-5; **5,** 67421-77-6; **7,** 67421-78-7; **9,** 67421-79-8; 1,3-propanedithiol, 109-80-8; furfural, 98-01-1; 2-(4-hydroxy-(*Z*)-2-buten-1-ylidene)-1,3-dithiane, 67421-80-1; pentanol, 71-41-0; 2-(2-furyl)-2-lithio-1,3-dithiane, 67421-81-2.

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Tri-*tert*-butylmethylsilane

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In connection with our studies of internal conformational dynamics in systems of the type t-Bu_3MX,[1] it became of interest to prepare tri-*tert*-butylmethylsilane (**1**, t-Bu_3SiCH_3). This compound had resisted a prior attempt at preparation by a copper-catalyzed methylene insertion into tri-*tert*-but-

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