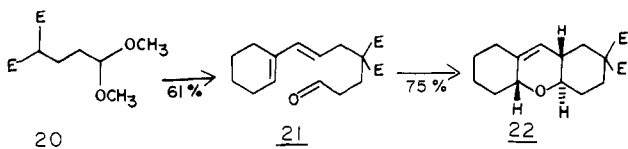
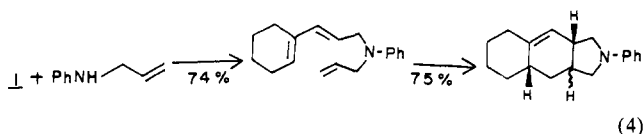


17<sup>5</sup> in a tungsten-catalyzed reaction [30 mol % (CH<sub>3</sub>CN)<sub>3</sub>W(CO)<sub>3</sub>, 30 mol % bpy, THF, reflux] (Scheme I). The trienyl acetate **13** serves as the best precursor for the Pd-catalyzed reaction to ensure formation of only the terminal  $\pi$ -allylpalladium intermediate. On the other hand, the better kinetics of internal acetates in tungsten-catalyzed reactions and the higher intrinsic chemo-selectivity in  $\pi$ -allyltungsten formation<sup>13b</sup> dictate **14** as the preferred precursor for the tungsten reaction. As a result of the complementarity in the regioselectivity of the alkylation, grossly different substitution patterns result in the tetrahydroindanes **18**<sup>5,14</sup> and **19**<sup>5,15</sup> that result from the subsequent Diels-Alder reaction (mesitylene, reflux).

Modified nucleophiles extend this sequence to a synthesis of heterocycles. For example, **1** reacts with the malonate **20** in a Mo-catalyzed reaction [20 mol % Mo(CO)<sub>6</sub>, BSA, toluene, reflux, 81%] to give **21**<sup>5,16</sup> after hydrolysis [PPTS, acetone, 75%]. Addition of a Lewis acid<sup>17</sup> to **21** [1 equiv of CH<sub>3</sub>AlCl<sub>2</sub>, 1 equiv of (CH<sub>3</sub>)<sub>2</sub>AlCl, methylene chloride, room temperature] effects a heteroatom Diels-Alder reaction to give a single adduct **22**.<sup>5,7,18</sup>



To our knowledge, this example is the first report of an aldehyde as the dienophile in an intramolecular Diels-Alder reaction.<sup>19</sup> Alternatively, a heteroatom can serve as the nucleophile<sup>20</sup> as shown in eq 4.<sup>21</sup> Only palladium catalysts [5 mol % (Ph<sub>3</sub>P)<sub>4</sub>Pd, (*i*-



C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>N C<sub>2</sub>H<sub>5</sub>, THF, reflux] succeed at present with heteroatom nucleophiles.

This convergent approach joins a masked conjugated diene with a potential dienophile in a metal-catalyzed alkylation reaction. Thus, each partner can be readily assembled individually and the sensitive substrate generated under very mild conditions immediately prior to intramolecular cycloaddition. The mildness of the conditions is emphasized by the successful utilization of the acrylates **2** and **6** (R = CO<sub>2</sub>CH<sub>3</sub>) since their anions are very unstable. The metal template provides a powerful steering mechanism in this cojoining. The regioselectivity of the alkylation dictates the nature of the Diels-Alder reaction. The types of skeletons that result from this rapid construction of polycyclic systems relate to such diverse natural products as the gibberellins<sup>11b</sup>

(14) A 2:1 mixture at the ring fusion with the *E* isomer dominating is assigned on the basis of the olefin region in the <sup>1</sup>H NMR and analogy.<sup>1</sup> Partial <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  6.34 (0.38 H, d, *J* = 16.4 Hz), 6.31 (0.62 H, d, *J* = 15.5 Hz), 6.11 (0.62 H, dd, *J* = 15.5, 7.5 Hz), 6.02 (0.38 H, dd, *J* = 16.4, 8 Hz).

(15) A 45:55 mixture of the *E* and *Z* ring-fusion isomers as determined by the methyl ester signals in the <sup>1</sup>H NMR spectrum (minor isomer at  $\delta$  3.72 and 3.69, major isomer at  $\delta$  3.69 and 3.65) is assigned by analogy.<sup>1</sup>

(16) Partial <sup>1</sup>H NMR  $\delta$  6.15 (1 H, dt, *J* = 15, 7 Hz), 5.85 (1 H, d, *J* = 15 Hz), 5.72 (1 H, ddt, *J* = 15, 8, 3 Hz), 5.05 (1 H, d, *J* = 15 Hz), 4.98 (1 H, d, *J* = 8 Hz), 4.60 (1 H, t, *J* = 3 Hz).

(17) Snider, B. B.; Phillips, G. B.; Cordova, R. *J. Org. Chem.* **1983**, *48*, 3003.

(18) <sup>1</sup>H NMR analysis allows assignment of the trans,anti stereochemistry. Partial <sup>1</sup>H NMR  $\delta$  4.03 (dm, *J* = 9.5 Hz), 3.14 (tm, *J* = 9.4 Hz).

(19) For a quasiintramolecular case, see ref 17. For intermolecular cases, see ref 17 and: Bednarski, M.; Danishefsky, S. *J. Am. Chem. Soc.* **1983**, *105*, 3716. Jurczak, J.; Bauer, T.; Filippek, S.; Tkacz, M.; Zygo, K. *J. Chem. Soc., Chem. Commun.* **1983**, 540 and references cited therein.

(20) Trost, B. M.; Keinan, E. *J. Org. Chem.* **1979**, *44*, 3451; *J. Am. Chem. Soc.* **1978**, *100*, 7779. Trost, B. M.; Genet, J. P. *Ibid.* **1976**, *98*, 8516.

(21) For related intramolecular Diels-Alder reactions, see: Babayam, A. T.; Melikyan, T. R.; Torosyan, G. H.; Mkrtchyan, R. S.; Tagmazyan, K. T. *Arm. Khim. Zh.* **1976**, *29*, 388; *Chem. Abstr.* **1976**, *85*, 143012.

(cf. **12**) and antibiotics represented by X-14547A<sup>22</sup> (cf. **18** and **19**).

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(22) Nicolaou, K. C.; Magolda, R. L. *J. Org. Chem.* **1981**, *46*, 1506. Roush, W. R.; Myers, A. G. *Ibid.* **1981**, *46*, 1509.

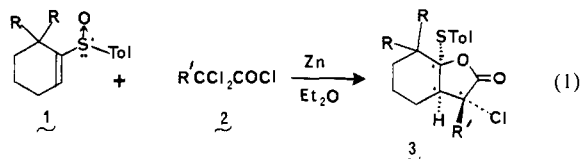
## Enantiospecific Lactonizations of Chiral 1-(Arylsulfinyl)cyclohexenes with Chloroketenes<sup>1</sup>

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The use of an enantiomerically pure sulfinyl group to activate a carbon-carbon double bond toward nucleophilic addition has only met with limited success to date due to the diminished Michael-reactivity of 1-alkenyl sulfoxides. Tsuchihashi was the first to add a carbon nucleophile to an optically pure styryl sulfoxide with significant asymmetric induction (60% ee).<sup>2</sup> More recently, Posner has shown that simple 1-alkenyl sulfoxides do not undergo conjugate additions with common organometallics.<sup>3</sup> However, when an additional activating group is present at the  $\alpha$  position of chiral 1-alkenyl sulfoxides, conjugate additions do indeed occur with a high degree of asymmetric induction.<sup>3,4</sup> Several years ago, we described a unique stereospecific cyclization of dichloroketene with simple 1-alkenyl sulfoxides.<sup>5</sup> At this time, we wish to report that this reaction, when applied to enantiomerically pure 1-(arylsulfinyl)cyclohexenes, leads to optically pure  $\gamma$ -butyrolactones **3** with complete enantiospecificity. We have, in fact, assembled as many as three contiguous chiral centers from a single chiral sulfur atom (eq 1).



When the pure *R* and *S* enantiomers<sup>6</sup> of 1-cyclohexenyl tolyl sulfoxide (**1**, R = R = L) were subjected to excess trichloroacetyl chloride (5 equiv) and zinc-copper couple in refluxing ether, high yields of the enantiomeric  $\gamma$ -butyrolactones **3** (R = R = H, R' = Cl) were obtained. While the crystalline products<sup>7</sup> rotated plane polarized light to an equal extent in opposite directions, we sought independent evidence for their enantiomeric purity. An attempt to analyze the 360-MHz <sup>1</sup>H NMR spectra of the products in the

(1) Taken in part from: Perez, A. D. Ph.D. Thesis University of Michigan, Ann Arbor, 1984; paper presented in part at the 11th International Symposium on the Organic Chemistry of Sulfur, Lindau, West Germany, Sept 10, 1984.

(2) Tsuchihashi, G.; Mitamura, S.; Inoue, S.; Ogura, K. *Tetrahedron Lett.* **1973**, 323.

(3) For an up-to-date review, see: Posner, G. In "Asymmetric Synthesis"; Morrison, J. D., Ed.; Academic Press: New York, 1983; Vol. 2, Part A, Chapter 8, p 225.

(4) (a) Posner, G. H.; Hulce, M.; Mallamo, J. P.; Drexler, S. A.; Clardy, J. *J. Org. Chem.* **1981**, *46*, 5244. (b) Posner, G. H.; Mallamo, J. P.; Hulce, M.; Frye, L. L. *J. Am. Chem. Soc.* **1982**, *104*, 4180.

(5) Marino, J. P.; Neisser, M. *J. Am. Chem. Soc.* **1981**, *103*, 7687.

(6) Prepared from the Grignard of 1-chlorocyclohexene and the menthol *p*-toluenesulfonates according to the Anderson method. Anderson, K. K. *J. Org. Chem.* **1964**, *29*, 1953.

(7) The enantiomeric lactones **3a** possessed a mp 111-112 °C. All rotations were taken in acetone with *c*  $\approx$  2.09 g/100 mL.

Scheme I

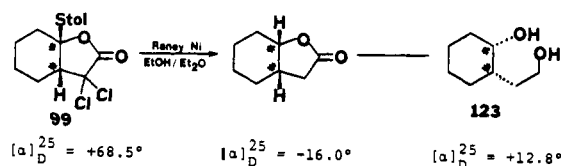


Table I

Sulfoxide	$[\alpha]_D^{25}$	Lactone <sup>1,2</sup>	Yield <sup>b</sup>	$[\alpha]_D^{25}$
	+5.9°		70	+68.5°
	-6.2°		68	-68.3°
	+166.5°		60	-91.1°
	+24.3°		25	+13.9°
	+5.9°		60	+50.7°

presence of a chiral shift reagent [Eu(tfc)<sub>3</sub>] did not lead to satisfactory resolution of the enantiomers. Therefore, we converted the lactones to the corresponding enantiomeric diols<sup>8</sup> **5** (Scheme I), which were then esterified with Mosher's acid<sup>9</sup> to the diastereomeric diesters **6**. The 360-MHz <sup>1</sup>H NMR spectra of the diesters **6** clearly indicated that each was pure within the limits of detection.<sup>10</sup>

In order to extend the generality of this reaction and test the asymmetric induction in more highly functionalized cyclohexenes, we examined the reactions of the *S* enantiomers of the known cyclohexenone derivative **3** (R,R = O) and its ketal (**3**, R,R = OCH<sub>2</sub>CH<sub>2</sub>O).<sup>11</sup> The results are summarized in Table I.

A particularly intriguing possibility arises when an unsymmetrical ketene is employed in the reaction, since an additional chiral center is generated. We found that addition of monochloroketene to 1-cyclohexenyl tolyl sulfoxide led to a single stereoisomer of the lactone **3d**. It would appear that the approach of the incipient carbanion to the double bond is such as to orient the larger chlorine atom away from the cyclohexane ring. Thus, steric factors have controlled the stereocenter  $\alpha$  to the lactone

(8) The optically active lactones **3a** were treated with excess Raney nickel at room temperature overnight. The 360-MHz <sup>1</sup>H NMR spectrum of **4** clearly indicated the *cis*-lactone. Further treatment of **4** with LiAlH<sub>4</sub> in ether yielded the optically active diols **5**.

(9) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.

(10) In the 360-MHz <sup>1</sup>H NMR spectra of the diastereomeric diesters **6**, the methoxyl hydrogens resonate at  $\delta$  3.41 and 3.53 with base-line separation. Thus, it was easily discernible that the product diesters were pure diastereomers.

(11) Posner, G. H.; Mallamo, J. P.; Miura, K. *J. Am. Chem. Soc.* **1981**, *103*, 2886.

(12) All new compounds gave correct elemental analyses for C, H, and Cl and possessed IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and MS spectral data consistent with the assigned structures.

carbonyl, and a third chiral center is set.

The ability to use either enantiomeric sulfoxide provides access to highly functionalized  $\gamma$ -butyrolactones of both configurations. The high enantiospecificity of this cyclization renders this process one of the best for chirality transfer from sulfur to carbon. Further studies are in progress to extend this enantiospecific lactonization to other types of ketenes and ketene equivalents.

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**Registry No.** (R)-(+)-**1a**, 93062-20-5; (S)-(-)-**1a**, 93062-21-6; (S)-(+)-**1b**, 86505-46-6; (S)-(+)-**1c**, 93062-22-7; **2** (R = Cl), 76-02-8; **2** (R = H), 79-36-7; (R,R)-**3a**, 93062-23-8; (S,S)-**3a**, 93062-24-9; **3b**, 93062-25-0; **3c**, 93062-26-1; **3d**, 93062-27-2; Cl<sub>2</sub>C=C=O, 4591-28-0; ClHC=C=O, 29804-89-5.

### Novel Structural Modulation in the First Ambient-Pressure Sulfur-Based Organic Superconductor (BEDT-TTF)<sub>2</sub>I<sub>3</sub>

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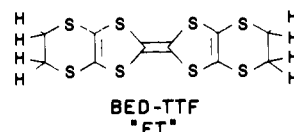
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Received August 6, 1984

The title compound [BEDT-TTF or "ET" herein bis(ethyl-



enedithio)tetrathiofulvalene, C<sub>10</sub>S<sub>8</sub>H<sub>8</sub>] is the first ambient-pressure sulfur-containing organic superconductor ( $T_c = 1.4$ – $1.5$  K).<sup>1,2</sup> This compound is further unique in having a displacively modulated structure below  $\sim 200$  K, the first to be observed in an organic superconductor, which persists to a temperature of at least 11 K.<sup>3</sup> Important features of the room-temperature structure are the existence of ribbons of I<sub>3</sub><sup>-</sup> anions and loose columnar stacks of ET molecules having *intrastack* S...S distances  $> 3.60$  Å, the sum of the van der Waals radii. The ET molecules are linked into infinite "corrugated" sheets by short *interstack* S...S distances less than 3.6 Å and which lay approximately perpendicular to the ET molecule column-packing axis.<sup>2</sup> These short interstack distances appear especially pertinent to the anisotropic (two-dimensional) electrical properties, which includes a relatively high conductivity in directions parallel to the sheets. Similarly short interstack, but long intrastack, S...S distances and anisotropic electrical conductivity were first observed in prototypical

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(1) Yagubskii, E. B.; Shchegolev, I. F.; Laukhin, V. N.; Kononovich, P. S.; Kartsovnik, A. K.; Zvarykina, A. V.; Buravov, L. I. *Zh. Eksp. Teor. Fiz., Pis'ma Red.* **1984**, *39*, 12; *JETP Lett. (Engl. Transl.)* **1984**, *39*, 12.

(2) (a) Crabtree, G. W.; Carlson, K. D.; Hall, L. N.; Copps, P. T.; Wang, H. H.; Emge, T. J.; Beno, M. A.; Williams, J. M. *Phys. Rev. B: Condens. Matter* **1984**, *30*, 2958. (b) Williams, J. M.; Emge, T. J.; Wang, H. H.; Beno, M. A.; Copps, P. T.; Hall, L. N.; Carlson, K. D.; Crabtree, G. W. *Inorg. Chem.* **1984**, *23*, 2558.

(3) Emge, T. J.; Leung, P. C. W.; Beno, M. A.; Schultz, A. J.; Wang, H. H.; Sowa, L. M.; Williams, J. M., unpublished results.