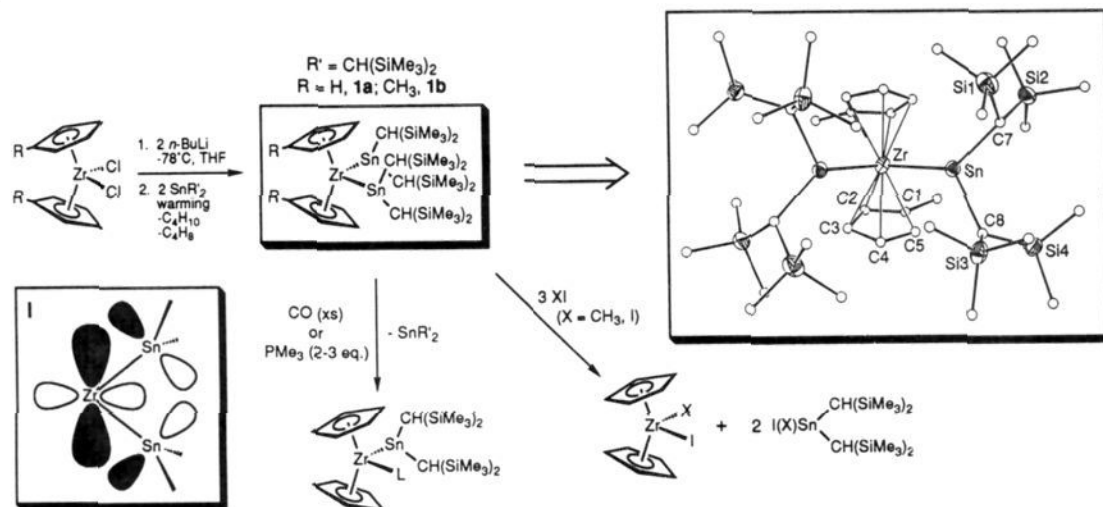
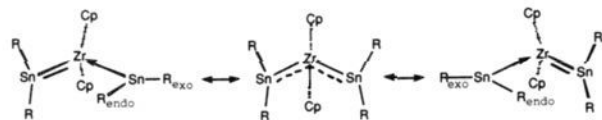


Scheme I



Scheme II



when compared to the sum of the covalent radii. This has been attributed in part to the absence of π back-bonding in these (mostly) d^0 derivatives. For **1b**, despite the steric requirements of the stannylene ligand, the Zr–Sn distance is only slightly greater than the sum of the covalent radii ($\approx 2.85 \text{ \AA}$)¹⁵ and is considerably shorter than the Zr–Sn distance of $3.086 (1) \text{ \AA}$ reported^{5a} for $[(\text{Ph}_3\text{Sn})_4\text{Zr}(\text{CO})_4]^{2-}$, a comparable 8-coordinate Zr(II) species. It is clear from both the orientation of the SnR_2 ligands and the short Zr–Sn distance that significant π donation from Zr to Sn is occurring in **1b**.¹⁶

Both **1a** and **1b** are fluxional in solution. At room temperature, an ^1H NMR spectrum consistent with the solid-state structure is observed. At -30°C the resonance for the SiMe_3 groups broadens and splits into three singlets at 0.44, 0.37, and 0.31 ppm in a 1:1:2 ratio, respectively. We interpret these observations in terms of a rotation of one stannylene ligand into the Sn–Zr–Sn' plane (Scheme II). In this limiting structure, π bonding is maximized between Zr and the perpendicular stannylene ligand, while the in-plane stannylene now functions as a datively bonded Lewis base. This structure is analogous to predicted¹⁷ and observed¹⁸ d^2 metallocene–carbene complexes stabilized by a Lewis base.

We have begun to explore the reactivity of these compounds (Scheme I). Reactions with other Lewis bases (PMe_3 , CO) proceed slowly to form composite zirconocene–Lewis base adducts. Qualitatively, the rates of these substitution reactions are comparable, suggesting a dissociative mechanism in which the rate-limiting step is loss of SnR_2 . Reactions with electrophiles (MeI , I_2) yield the oxidative addition products expected upon reaction of these reagents with free SnR_2 ¹⁹ and “zirconocene”.²⁰ Since

(15) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(16) A short Cr–Sn distance of 2.562 \AA was rationalized by invoking π bonding to Sn: Cotton, J. D.; Davison, P. J.; Goldberg, D. E.; Lappert, M. L.; Thomas, K. M. *J. Chem. Soc., Chem. Commun.* **1974**, 893.

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(19) Cotton, J. D.; Davidson, P. J.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2275.

(20) $\text{Cp}_2\text{ZrMe}_1^{20a}$ and $\text{Cp}_2\text{ZrI}_2^{20b}$ identified by comparison to authentic samples. (a) Demerseman, B.; Bouquet, G.; Bigogne, M. *J. Organomet. Chem.* **1977**, *132*, 223. (b) Druce, P. M.; Kingston, B. M.; Lappert, M. F.; Spalding, T. R.; Srivastava, R. *J. Chem. Soc. A* **1969**, 2106.

we are most interested in reactions which preserve the Zr–Sn linkage, we are currently exploring the reactivity of **1a** and **1b** with oxidizing agents. This approach appears promising and results will be reported in due course.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Guelph for financial support of this work.

Supplementary Material Available: Experimental details, spectroscopic and analytical data for **1a** and **1b**, and tables of crystal, collection, and refinement data, atomic coordinates and isotropic thermal parameters, bond lengths and angles, H atom coordinates, and anisotropic thermal parameters for **1b** (9 pages); listing of observed and calculated structure factors for **1b** (19 pages). Ordering information is given on any current masthead page.

Diastereoselective Additions of Chiral (*E*)-Crotlylsilanes to α -Alkoxy and β -Alkoxy Aldehydes. A One-Step, Silicon-Directed Tetrahydrofuran Synthesis

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Substituted furans occur frequently as subunits of many biologically important natural products including the structurally complex polyether¹ and nucleoside² antibiotics. Within the context of natural product synthesis, the construction of furans having well-defined stereochemistry remains a current challenge in organic synthesis.³ Here we describe an operationally simple method for the assemblage of highly functionalized tetrahydrofurans from simple achiral aldehydes and chiral (*E*)-crotlylsilanes, under mild

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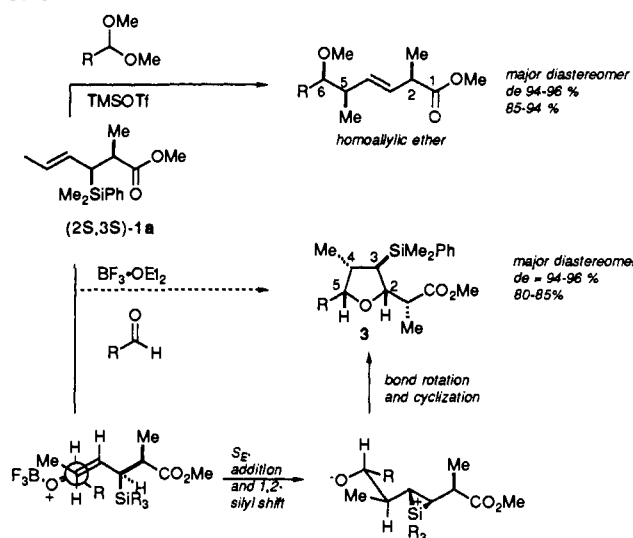
(3) (a) For a review on electrophile-promoted cyclizations to form tetrahydrofurans see: Bartlett, P. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984, Vol. 3, Chapter 6. (b) β -Hydroxy-sulfides: Williams, W. R.; Phillips, J. G. *Tetrahedron* **1985**, *42*, 3013–3019.

Table I. Asymmetric Synthesis of Substituted Tetrahydrofurans

entry	aldehydes	(E)-crotylsilane	reaction cond't. ^a Temp/hour	major diastereomer ^b	yield ^c %	ratio 4,5-syn/anti ^d	%de ^e	%yield of 4
1			-78 °C/15h		85	30:1	96	
2			-78 °C/15h		85	30:1	96	
3			-78 °C/15h		80	30:1	96	
4 ^f			-78 °C/15h		68	30:1	96	
5			-30 °C/15h		65	30:1	96	
6			-30 °C/15h		50	20:1	96	

^a All reactions were run in CH_2Cl_2 (0.2–0.5 M) with $\text{BF}_3\cdot\text{OEt}_2$ (1.0 equiv) as the Lewis acid and 1.2 equiv of the aldehyde. ^b Assignment of stereochemistry is based on 2D-NOE and multiple difference NOE experiments. ^c All yields are based on pure materials isolated by chromatography on SiO_2 . ^d Ratio of products was determined by ^1H NMR (400 MHz), operating at an S/N ratio of $>200:1$. ^e Optical purities refer to the de for the 4,5-syn stereocenters derived from anti- S_{E} and syn- S_{E} modes of addition and were determined by ^1H NMR (400 MHz) analysis of the addition products after chromatography on SiO_2 (plug). ^f Reaction was run using SbCl_5 (1.0 equiv) as the Lewis acid.

Scheme I



reaction conditions ($\text{BF}_3\cdot\text{OEt}_2$, CH_2Cl_2 , -78 to -30 °C). This method for furan construction is an extension of related studies from our laboratories and is based on the utility of the α -substituted β -silyl-(*E*)-crotylsilanes **1**,⁴ in highly diastereo- and en-

antioselective addition reactions to activated acetals.⁵ Those reactions resulted in the formation of highly functionalized homoallylic ethers, wherein 1,4- and 1,5-remote stereogenic centers were established with equally high levels of diastereoselectivity (Scheme I). In order to further probe the utility of these reagents in asymmetric allylsilane based bond construction methodology, we sought the use of an aldehyde as the electrophilic component with the expectation that similar levels of diastereoselection could be achieved to deliver the complementary homoallylic alcohols.⁶ Although allenylsilanes have been employed as carbon nu-

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(5) (a) Aryl acetals: Panek, J. S.; Yang, M. *J. Am. Chem. Soc.* **1991**, *113*, 6594–6600. (b) Hetero-substituted acetals: Panek, J. S.; Yang, M. *J. Org. Chem.* **1991**, *56*, 5755–5758.

(6) Homoallylic alcohols from chiral allyl and crotylboronates see: (a) Roush, W. R.; Hoong, L. K.; Palmer, M. A. J.; Park, J. C. *J. Org. Chem.* **1990**, *55*, 4109–4117. (b) Roush, W. R.; Hoong, L. K.; Palmer, M. A. J.; Straub, J. A.; Palkowitz, A. D. *J. Org. Chem.* **1990**, *55*, 4117–4126. (c) Roush, W. R.; Ando, K.; Powers, D. B.; Palkowitz, A. D.; Halterman, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 6339–6348. (d) Roush, W. R.; Palkowitz, A. D.; Ando, K. *J. Am. Chem. Soc.* **1990**, *112*, 6348–6359 and references cited therein. For other recent reports on enantioselective allylations see: (e) Corey, E. J.; Yu, C.-M.; Kim, S. S. *J. Am. Chem. Soc.* **1989**, *111*, 5495–5496. (f) Short, R. P.; Masamune, S. *J. Am. Chem. Soc.* **1989**, *111*, 1892–1894. (g) Hoppe, D.; Zschage, O. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 69–71. (h) Reetz, M. T.; Zierke, T. *Chem. Ind. (London)* **1988**, 663–664. (i) Faller, J. W.; Linebarrier, D. L. *J. Am. Chem. Soc.* **1989**, *111*, 1937–1939.

cleophiles in approaches to oxygen and nitrogen heterocycles,⁷ the present furan synthesis considerably extends those original observations, as it documents the participation of (*E*)-crotylsilanes in the asymmetric addition to aldehydes promoting a silicon-directed heterocyclization which results in the formation of tetrahydrofurans.⁸ The formation of the isolated 2,5-cis-substituted furans is consistent with the well-precedented stereochemical course of Lewis acid-promoted additions of chiral crotylsilanes and stannanes to aldehydes and activated acetals and the fact that the heterocyclization proceeds with inversion of configuration at the C2 center.^{3,5,9} An intriguing aspect of the furan synthesis is that the 1,2-silyl migration competes favorably with elimination of the dimethylphenylsilyl (DMPS) group after condensation with the aldehyde. As illustrated in Scheme I with the (2*S*,3*S*)-diastereomer **1a**, a diastereoface selective addition to the *si* face of the aldehyde simultaneously generates two new stereocenters and a β -silyl carbocation stabilized through the $\sigma \rightarrow \pi$ conjugation of the adjacent C-Si bond. A 1,2-cationic migration of the DMPS group¹⁰ is followed by heterocyclization producing the 2,5-cis tetrahydrofuran **3**. The process is further enhanced by the fact that the tetrahydrofurans are equipped with a DMPS group, a known hydroxyl group synthon, and functionalized at C2 and C5 for further synthetic transformations.¹¹

The results of the asymmetric furan synthesis are summarized in Table I. For these examples, $\text{BF}_3 \cdot \text{OEt}_2$ was determined to be the most effective Lewis acid for efficient conversion to the tetrahydrofuran. In the reactions with α -benzyloxy acetaldehyde (**2a**) both syn and anti α -methyl (*E*)-crotylsilanes **1a** and **1c** exhibited excellent levels of diastereoselection producing the tetrahydrofurans **3a** and **3c** with *de*'s reaching 96% as determined by NMR analysis. The condensation reactions with the β -benzyloxy aldehyde **2b** showed similar levels of selectivity; however, the reaction temperature was necessarily increased to -30°C to ensure the efficient conversion to the furan product. The tetrahydrofurans **3b-e** were subjected to a Hg^{II} oxidation [$\text{Hg}(\text{OAc})_2/32\% \text{AcOOH}/\text{AcOH}/\text{cat. H}_2\text{SO}_4/\text{RT}$]¹¹ to give the diastereomerically pure alcohols **4b-e**, thus establishing the synthon equivalency of the DMPS group.

In conclusion, the asymmetric additions of chiral (*E*)-crotylsilanes to α - and β -benzyloxy aldehydes constitute a remarkably simple procedure for the construction of nearly optically pure tetrahydrofurans. The distinguishing features of this Lewis acid-mediated tetrahydrofuran synthesis are the high levels of diastereoface selection and the facility of the 1,2-silyl migration allowing heterocyclization. Further studies of these organosilane reagents in asymmetric transformations are in progress.

Acknowledgment. This work has been financially supported by the National Institutes of Health (CA47249).

Supplementary Material Available: Experimental procedures and spectral data for all reaction products (5 pages). Ordering information is given on any current masthead page.

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Use of Sterically Hindered Sensitizers for Improved Photoinduced Electron-Transfer Reactions

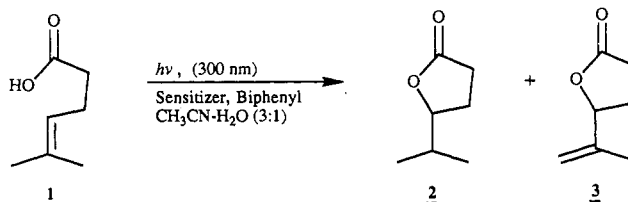
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Photoinduced single-electron-transfer (SET) reactions are potentially of great value to synthetic organic chemists.¹ Unfortunately, low quantum yields and/or poor product yields often prevent these photoinduced SET reactions from being widely used in organic synthesis. Both strained and unsaturated organic molecules are known to form cation radicals as a result of electron transfer to photoexcited sensitizers (excited-state oxidants).¹ The resulting cation radical-anion radical pairs can undergo a variety of reactions including back electron transfer, nucleophilic attack on the cation radical, electrophilic attack on the anion radical, reduction of the anion radical, and addition of the anion radical to the cation radical. Because of our interest in the use of photoinduced SET reactions to achieve anti-Markovnikov addition of nucleophiles to carbon-carbon multiple bonds,^{2,3} we sought to minimize side reactions and to maximize quantum yields. We felt that sterically hindering the photosensitizer might accomplish these goals. In particular, we desired to minimize coupling reactions between the cation radical and the anion radical, which can be a major side reaction.^{4,5} We now report that our overall goals of increasing both product yields and quantum yields can be accomplished through the use of sterically encumbered photosensitizers.

The anti-Markovnikov lactonization of 5-methyl-4-hexenoic acid (**1**) to **2** and **3**, a photoinduced SET reaction which has been studied in detail,² was chosen as the model reaction for the evaluation of a series of sensitizers. The sensitizers studied were



1,4-dicyanobenzene (**4**),⁵ 4,4'-dicyanobiphenyl (**5**),⁶ 4,4'-dicyano-3,3',5,5'-tetramethylbiphenyl (**6**),^{7,8} 1-cyanonaphthalene (**7**),⁹ 1,4-dicyano-2,3,5,6-tetramethylbenzene (dicyanodurene) (**8**),¹⁰ 9,10-dicyano-1,2,3,4,5,6,7,8-octahydroanthracene (**9**),^{7,8} and 1,4-dicyano-2,3,5,6-tetraethylbenzene (**10**).^{7,8} Table I lists the

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(7) Satisfactory elemental analyses and/or exact mass molecular weights were obtained for all new compounds. All compounds gave spectral data consistent with the assigned structures.

(8) 4,4'-Dicyano-3,3',5,5'-tetramethylbiphenyl was prepared through an Ullmann coupling¹¹ of 4-bromo-2,6-dimethylbenzotrile. 9,10-Dicyano-1,2,3,4,5,6,7,8-octahydroanthracene and 1,4-dicyano-2,3,5,6-tetraethylbenzene were prepared by iodination¹⁰ of the appropriate alkylated benzene followed by replacement of the iodide by cyanide using copper cyanide.¹⁰

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