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) d⁰ 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 ($\approx 2.85 \text{ Å}$)¹⁵ and is considerably shorter than the Zr–Sn distance of 3.086 (1) Å reported^{5a} for [(Ph₃Sn)₄Zr(CO)₄]^{2–}, a comparable 8-coordinate Zr(II) species. It is clear from both the orientation of the SnR₂ 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 SiMe₃ 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 d² 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 (PMe₃, 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 SnR₂. Reactions with electrophiles (MeI, I₂) yield the oxidative addition products expected upon reaction of these reagents with free SnR₂¹⁹ and "zirconocene".²⁰ Since

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.

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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*)-Crotylsilanes 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*)-crotylsilanes, under mild

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

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

^{(17) (}a) Frankl, M. M.; Pietro, W. J.; Hout, R. F., Jr.; Hehre, W. J. Organometallics 1983, 2, 281. (b) Frankl, M. M.; Hehre, W. J. Organometallics 1983, 2, 457.

⁽¹⁸⁾ Schrock, R. R. Science 1983, 219, 13.

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

⁽²⁰⁾ Cp₂ZrMeI^{20a} and Cp₂ZrI₂^{20b} identified by comparison to authentic samples. (a) Demerseman, B.; Bouquet, G.; Bigorgne, 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.

Polyether Antibiotics; Westley, J. W., Ed.; Marcel Decker: New York, 1982, Vol. 1–2.

⁽²⁾ Nucleoside Antibiotics; Garner, P. In Studies in Natural Product Chem., Vol. I Part A; Atta-Yr-Rhaman Ed.; Elsevier: Amsterdam, 1988, pp 397-434.

^{(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 -Hydroxysulfides: Williams, W. R.; Phillips, J. G. *Tetrahedron* **1985**, *42*, 3013–3019.

Table I. Asymmetric Synthesis of Substituted Tetrahydrofurans



^{*a*}All reactions were run in CH₂Cl₂ (0.2–0.5 M) with BF₃·OEt₂ (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 SiO₂. ^{*d*}Ratio of products was determined by ¹H NMR (400 MHz), operating at an S/N ratio of >200:1. ^{*c*}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 SiO₂ (plug). ^{*f*}Reaction was run using SbCl₅ (1.0 equiv) as the Lewis acid.

Scheme I



reaction conditions (BF₃·OEt₂, CH₂Cl₂, -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-

attribugh anonyishanes have been employed as carbon nu-

^{(4) (}a) Sparks, M. A.; Panek, J. S. J. Org. Chem. 1991, 56, 3431-3438.
(b) Sparks, M. A.; Panek, J. S. Tetrahedron Lett. 1991, 32, 4085-4088. (c) Panek, J. S.; Beresis, R.; Xu, F.; Yang, M. J. Org. Chem., in press. (5) (a) Aryl acetals: Panek, J. S.; Yang, M. J. Am. Chem. Soc. 1991, 113,

^{(5) (}a) Aryl acetais: 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 (2S,3S)-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, BF₃ OEt₂ 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 [Hg-(OAc)₂/32% AcOOH/AcOH/cat. H₂SO₄/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.

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

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

(2) Gassman, P. G.; Bottorff, K. J. J. Am. Chem. Soc. 1987, 109, 7547. (3) Gassman, P. G.; Bottorff, K. J. Tetrahedron Lett. 1987, 28, 5449.

(4) For selected examples of cation radical-anion radical coupling reactions, see: McCullough, J. J.; Miller, R. C.; Wu, W.-S. Can. J. Chem. 1977, 55, 2909. Borg, R. M.; Arnold, D. R.; Cameron, T. S. Can. J. Chem. 1984, 62, 1785. Lewis, F. D.; DeVoe, R. J.; MacBlane, D. B. J. Org. Chem. 1982, Kojima, M.; Sakuragi, H.; Tokumaru, K. Tetrahedron Lett. 1981,
 22, 2889. Albini, A.; Fasani, E.; Sulpizio, A. J. Am. Chem. Soc. 1984, 106, 22, 2005. Alohi, A., Fasahi, E., Suprizio, A., A. A. M. Chem. Soc. 1977, 99, 5806, 3562. Pac, C.; Nakasone, A.; Sakuri, H. J. Am. Chem. Soc. 1977, 99, 5806, Mizuno, K.; Ogawa, J.; Otsuji, Y. Chem. Lett. 1981, 741. Yamada, S.; Nakagawa, Y.; Watabiki, O.; Suzuki, S.; Ohashi, M. Chem. Lett. 1986, 361. Gassman, P. G.; Carroll, G. T. Tetrahedron 1986, 42, 6201.

(5) Arnold, D. R.; Wong, P. C.; Maroulis, A. J.; Cameron, T. S. Pure Appl. Chem. 1980, 52, 2609.

(6) Gassman, P. G.; Burns, S. J. J. Org. Chem. 1988, 53, 5576.
(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-dimethylbenzonitrile. 9,10-Dicyano-Chimann couping.¹⁷ of 4-brondo-2,0-dimethylbenzontrine. 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
(9) Maroulis, A. J.; Arnold, D. R. J. Am. Chem. Soc. 1976, 98, 5931.
(10) Suzuki, H.; Nakamura, K.; Goto, R. Bull. Chem. Soc. Jpn. 1966, 39, 128.
Suzuki, H.; Hanafusa, T. Synthesis 1974, 1, 53.
(11) Chem. D. K. J. Chem. Chem. 1986, 51, 2627.

(11) Colon, I.; Kelsey, D. R. J. Org. Chem. 1986, 51, 2627.

^{(7) (}a) Danheiser, R. L.; Kwasigroch, C. A.; Tasi, Y.-M. J. Am. Chem. Soc. 1985, 107, 7233-7235. (b) Related allenylsilane additions see: Dan-heiser, R. L.; Carini, D. J., Basak, A. J. Am. Chem. Soc. 1981, 103, 1604-1606. (c) Allyltrimethylsilane addition to a chiral aldehyde with furan formation see: Sugimura, H. Tetrahedron Lett. 1990, 31, 5909-5912.

⁽⁸⁾ All new compounds were isolated as chromatographically pure mate-rials and exhibited acceptable ¹H NMR, ¹³C NMR, IR, MS, and HRMS spectral data

 ⁽⁹⁾ S_E additions: (a) Hayashi, T.; Konishi, M.; Ito, H.; Kumada, M. J. Am. Chem. Soc. 1982, 104, 4962-4963. For Lewis acid catalyzed intramolecular additions of certain allylsilanes and stannanes to aldehydes, a synclinal arrangement of the reacting olefins has been postulated, [cf. Denmark, S. E.; Weber, E. J. Helv. Chim. Acta 1983, 66, 1655–1560]. (b) These findings are consistent with a stereospecific anti $S_{E'}$ process as previously reported for cases involving intermolecular additions of chiral allyl- and crotylsilanes, allylstannanes, and recently chiral allenylstannanes [cf. Marshall, J. A., Wang,

<sup>X. J. Org. Chem. 1991, 56, 3211-3213].
(10) Brook, A. G.; Bassindale, A. R. In "Rearrangements in the Ground</sup> and Excited States"; de Mayo, P., Ed.; Academic Press; New York, 1980, (11) Fleming, I.; Sanderson, P. E. J. Tetrahedron Lett. 1987, 28,

^{4229-4232.}

⁽¹⁾ For leading references to photoinduced SET reactions, see: Photoinduced Electron Transfer; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part C.