solution. Further study is necessary to clarify the exact nature of this effect.

Analogous NOE and T_1 studies indicate that disaccharides **4** and **5** (**6**) exist in essentially the same preferred conformation, i.e., B in Figure 1, as do **7** and **8**, i.e., C in Figure 1.[4] Furthermore, the experimentally determined preferred conformation in each of these systems[1e] is close to the one predicted by diamond lattice analysis.

In summary, we have shown that *C*-disaccharides **2a,b**, **5a,b**, and **8a,b** and the corresponding parent disaccharides **1a,b**, **4a,b**, and **7a,b** are conformationally similar. In addition, we have demonstrated that analysis of steric interactions primarily around the nonglycosidic bond in the *C*- and *O*-disaccharides, using a diamond lattice, provides a useful model for predicting the preferred conformation in these systems. In all the cases examined, the experimentally determined preferred conformation was found to correspond well, at least to the first approximation, with the predicted conformation.

Acknowledgment. We are deeply indebted to Professor Singel and Dr. Huang of Harvard University for helpful discussions on NMR studies. Financial support from the National Institutes of Health (NS 12108) is gratefully acknowledged. W.H.M. thanks the National Institutes of Health for the support of a Postdoctoral Fellowship (1 F32 GM 11547).

Supplementary Material Available: Schemes for the synthesis of **1a,b**, **4a,b**, and **7a,b** (3 pages). Ordering information is given on any current masthead page.

(4) The dideuteriated analogues of **8a,b** are not available at this time. However, based on the other two cases reported here, we anticipate that the dideuterated substrates of **8a,b** will yield data which compares even better with that observed for **6a,b**.

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Regioselective Silylolefination of Allylic Dithioacetals. Stereoselective Synthesis of 1-(Trimethylsilyl)butadienes[1]

Summary: 1-(Trimethylsilyl)butadienes are regioselectively and stereoselectively synthesized in good to excellent yields from the reactions of allylic dithioacetals and [(trimethylsilyl)methyl]magnesium chloride in the presence of 5 mol % of $NiCl_2(PPh_3)_2$ in refluxing ether–benzene. Alkyl or aryl substituents at C-2 and/or C-3 positions in the starting dithioacetals do not affect the regiochemistry of the reactions. The regioselectivity of this reaction may arise from the interaction of the sulfur moiety in dithioacetals with nickel during the course of the reaction.

Sir: 1-(Trimethylsilyl)butadienes (**1**) are apparently valuable building blocks in organic syntheses but have only briefly been explored.[2-5] Most of literature methods for the preparation of **1** require multistep synthesis, and sometimes starting materials are not readily accessible.[2-5] The transition metal catalyzed coupling reaction of organosulfur compounds with Grignard reagents is well-documented.[6] We recently reported that benzylic dithioacetals can couple with Grignard reagents to give alkylated olefins.[7] (*E*)-β-silylstyrenes were conveniently prepared according to this procedure.[7b] Allylic dithioacetals (**2**) have two possible sites for coupling, and it is noted that reactions with allylic acetals[8] and geminal diacetates[9] are generally nonselective. However, the sulfur moiety in **2** might have directive effect to stabilize the intermediate such that the regiochemistry of the coupling reaction could be controlled. We have tested this viewpoint and now describe the nickel-catalyzed coupling reaction of **2** with Me_3SiCH_2MgCl (**3**).

In a typical procedure a mixture of **2**[10] and 4 equiv of **3** in the presence of 5 mol % of $NiCl_2(PPh_3)_2$ in ether–benzene was heated under reflux overnight. After usual workup and chromatographic purification, the silylated dienes **1a–j** were obtained in good to excellent yields.[11] The results are tabulated in Table I.

As can be seen from Table I, the reaction provides a very efficient synthesis of **1** and, more importantly, the reaction is regiospecific. Alkyl or aryl substituents at C-2 and C-3 positions in **2** do not affect the selectivity. The nature of the dithioacetal functionality has essentially no effect on the reaction. Either open chain (entry 10) or six-membered ring (entry 11) dithioacetals afforded **1a** in 82 and 76% yields, respectively. It is interesting to note that conjugative preference[12] is not essential in these reactions, e.g., crotonaldehyde derivative giving **1f** in 65% yield (entry 6). A similar observation was made in the reaction of **2g** (entry 7).

(1) Transition Metal Promoted Reactions. 25.

(2) (a) Carter, M. J.; Fleming, I.; Percival, A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2415 and references therein. (b) Jung, M. E.; Gaede, B. *Tetrahedron* **1979**, *35*, 621. (c) Koreeda, M.; Ciufolini, M. A. *J. Am. Chem. Soc.* **1982**, *104*, 2308. (d) Chou, T.-s.; Tso, H.-H.; Tao, Y.-T.; Lin, L. C. *J. Org. Chem.* **1987**, *52*, 244.

(3) (a) Corriu, R.; Escudie, N.; Guerin, C. *J. Organomet. Chem.* **1984**, *264*, 207. (b) Zubritsku, L. M.; Romashchenkova, N. D.; Petrov, A. A. *Zh. Org. Khim.* **1983**, *19*, 2465.

(4) (a) Chan, T.-H.; Li, J.-S. *J. Chem. Soc., Chem. Commun.* **1982**, 969. (b) Miller, J. A.; Zweifel, G. *J. Am. Chem. Soc.* **1983**, *105*, 1383. (c) Bloch, R.; Abecassis, J. *Tetrahedron Lett.* **1983**, *24*, 1247. (d) Block, E.; Aslam, M.; Eswarakrishnan, V.; Wall, A. *J. Am. Chem. Soc.* **1983**, *105*, 6165. (e) Block, E.; Aslam, M.; Eswarakrishnan, V.; Gebreyes, K.; Hutchinson, J.; Iyer, R.; Laffitte, J.-A.; Wall, A. *J. Am. Chem. Soc.* **1986**, *108*, 4568. (f) Boo, B. H.; Gaspar, P. P. *Organometallics* **1986**, *5*, 698.

(5) Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1988**, *53*, 918.

(6) (a) Wenkert, E.; Ferreira, T. W.; Michelotti, E. L. *J. Chem. Soc., Chem. Commun.* **1979**, 637. (b) Okamura, H.; Miura, M.; Takei, H. *Tetrahedron Lett.* **1979**, 43. (c) Tiecco, M.; Testaferri, L.; Tingoli, M.; Chianelli, D.; Wenkert, E. *Tetrahedron Lett.* **1982**, *23*, 4629. (d) Wenkert, E.; Ferreira, T. W. *J. Chem. Soc., Chem. Commun.* **1982**, 840. (e) Fiandanese, V.; Marchese, G.; Naso, F.; Ronzini, L. *J. Chem. Soc., Chem. Commun.* **1982**, 647. (f) Wenkert, E.; Fernandes, J. B.; Michelotti, E. L.; Swindell, C. S. *Synthesis* **1983**, 701. (g) Wenkert, E.; Leftin, M. H.; Michelotti, E. L. *J. Chem. Soc., Chem. Commun.* **1984**, 617. (h) Sugimura, H.; Takei, H. *Chem. Lett.* **1985**, 351.

(7) (a) Ni, Z.-J.; Luh, T.-Y. *J. Chem. Soc., Chem. Commun.* **1987**, 1515. (b) Ni, Z.-J.; Luh, T.-Y. *J. Org. Chem.* **1988**, *53*, 2129. (c) Ni, Z.-J.; Luh, T.-Y. *J. Chem. Soc., Chem. Commun.* **1988**, 1011.

(8) Wenkert, E.; Ferreira, T. W. *Organometallics* **1982**, *1*, 1670.

(9) (a) Lu, X.; Huang, Y. *J. Organomet. Chem.* **1984**, *268*, 185. (b) Trost, B. M.; Vercauteren, J. *Tetrahedron Lett.* **1985**, *26*, 131.

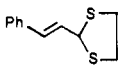
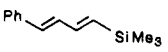
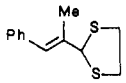
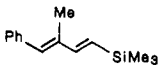
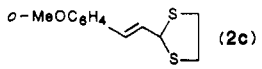
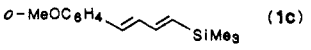
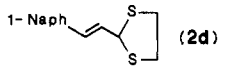
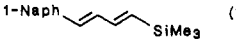
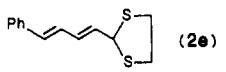
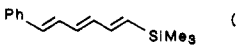
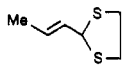
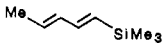
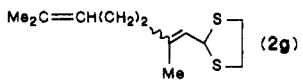
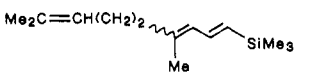
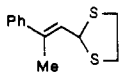
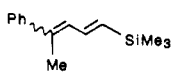
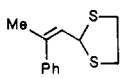
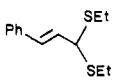
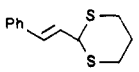
(10) Dithioacetals **2** were prepared according to standard procedure by treating the aldehyde with 1,2-ethanedithiol in the presence of a catalytic amount of $BF_3{\cdot}OEt_2$. Cf. Fieser, L. F. *J. Am. Chem. Soc.* **1954**, *76*, 1945.

(11) All new compounds gave satisfactory spectroscopic data and accurate mass measurements. The ^1H NMR and ^{13}C NMR data are outlined in the supplementary material.

(12) (a) Felkin, H.; Swierczewski, G. *Tetrahedron* **1975**, *31*, 2735. Chuit, C.; Felkin, H.; Roussi, G.; Swierczewski, G. *J. Organomet. Chem.* **1977**, *127*, 371. (b) Buchwalter, B. L.; Burfitt, I. R.; Felkin, H.; Joly-Goudet, M.; Naemura, K.; Salomon, M. F.; Wenkert, E.; Woukulich, P. M. *J. Am. Chem. Soc.* **1978**, *100*, 6445.

0022-3263/88/1953-5582$01.50/0

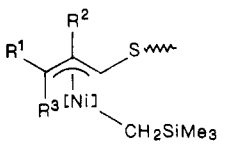
Table I. Nickel-Catalyzed Silylolefination of Allylic Dithioacetals

entry	substrate	product	% yield[a]
1	 (2a)	 (1a)	91
2	 (2b)	 (1b)	80
3	 (2c)	 (1c)	79
4	 (2d)	 (1d)	91
5	 (2e)	 (1e)	88
6	 (2f)	 (1f)	65[b]
7	 (2g)	 (1g)	93[c] 92[d]
8	 (2h)	 (1h)	88[e]
9	 (2i)	1h	88[f]
10		1a	82
11		1a	76

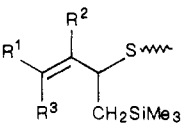
[a] Isolated yield unless otherwise specified. [b] GC yield. [c] **2g**, E/Z = 21/79; **1g**, E/Z = 21/79. [d] **2g**, E/Z = 64/36; **1g**, E/Z = 68/32. [e] E/Z = 92/8. [f] E/Z = 94/6.

The reaction can be extended to dienyl dithioacetal derivatives. To illustrate this, **2e** was converted into silatriene **1e** in 88% yield (entry 5). It is noted that vinylsilanes can be transformed into enals,[13] which could in turn serve as precursors for higher homologues of vinylsilanes. Accordingly, by combining our reaction with this latter procedure, homologation of enals could be achieved.

The mechanism of reaction has not been established, but the reaction may follow a pathway similar to that suggested of the benzylic case.[7] The two caron–sulfur bonds in **2** are cleaved consecutively,[7] allylic intermediate **4** being involved. Several factors may affect the regioselectivity of π-allyl system[14,15] (allyl sulfides being generally nonselective[16]). However, the second sulfur atom in **4** may have a tendency to interact with the metal center causing reductive elimination of **4** to proceed regioselectively. Oxidative addition[17] of intermediate **5** with nickel catalyst, followed by β-elimination,[18] would give **1**.



4



5

It is particularly noteworthy that the reactions are highly stereoselective. The configuration of the silyl-substituted double bond is always trans. These results are understandable within the framework of the steric requirement of the reaction.[7] Retention of configuration at the olefinic carbon(s) has been found in most examples in Table I. It is noted that a mixture of E/Z isomers of the dithioacetal **2g** afforded a mixture of dienes. The E/Z ratio of the product **1g** was found to be the same as the ratio of the starting material **2g** (entry 7). However, exceptional cases have been found in the reactions of the geometrical isomers **2h** and **2i** (entries 8 and 9). In these substrates, the same product distribution was obtained. Presumably, equilibration of the intermediate (eq 1) may occur to give the more stable E isomer as the major product.

(13) (a) Chan, T. H.; Lau, P. W. K.; Mychajlowskij, W. *Tetrahedron Lett.* **1977**, 3317. (b) Pilot, J. P.; Dunogues, J.; Calas, R. *Bull. Soc. Chim. Fr.* **1975**, 2143. (c) Yamamoto, K.; Nunokawa, O.; Tsuji, J. *Synthesis* **1977**, 721. (d) Yamamoto, K.; Yoshitake, J.; Qui, N. T.; Tsuji, J. *Chem. Lett.* **1978**, 859. (e) Yamamoto, K.; Ohta, M.; Tsuji, J. *Chem. Lett.* **1979**, 713.

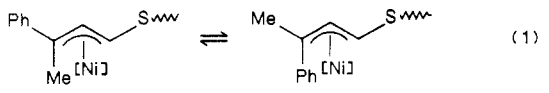
(14) Trost, B. M.; Hung, M. H. *J. Am. Chem. Soc.* **1983**, *105*, 7757.

(15) For recent reviews see: (a) Trost, B. M. *Acc. Chem. Res.* **1980**, *11*, 385. (b) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1. (c) Tsuji, J. *Tetrahedron* **1986**, *42*, 4361. (d) Trost, B. M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 107.

(16) Okamura, H.; Takei, H. *Tetrahedron Lett.* **1979**, 3245. In the presence of conjugative effect, the reaction shows selectivity. Cf. Wenkert, E.; Fernandes, J. B.; Michelotti, E. L.; Smindell, C. S. *Synthesis* **1983**, 701.

(17) (a) Wenkert, E.; Shepard, M. E.; McPhail, A. T. *J. Chem. Soc., Chem. Commun.* **1986**, 1390. (b) Osakada, K.; Maeda, M.; Nakamura, Y.; Yamamoto, T.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* **1986**, 442.

(18) Trost, B. M.; Schmidt, T. *J. Am. Chem. Soc.* **1988**, *110*, 2301.



(1)

In summary, we have demonstrated the first regioselective reactions of allylic dithioacetals and its application to facile stereoselective synthesis of silylated dienes. Further extension to other dienes and exploration of **1** is in progress.

Acknowledgment. We thank the Croucher Foundation for generous support. Z.J.N. thanks the Lee Hysan Foundation for a fellowship.

Registry No. **1a**, 70960-88-2; **1b**, 116973-01-4; **1c**, 116973-02-5; **1d**, 116973-03-6; **1e**, 116973-04-7; **1f**, 80400-46-0; (*E*,*E*)-**1g**, 116973-05-8; (*E*,*Z*)-**1g**, 116973-06-9; (*E*,*E*)-**1h**, 116973-07-0; (*E*,*Z*)-**1h**, 116973-08-1; **2a**, 87094-78-8; **2b**, 116972-94-2; **2c**, 116972-95-3; **2d**, 116972-96-4; **2e**, 116972-97-5; **2f**, 116972-98-6; (*E*)-**2g**, 77085-93-9; (*Z*)-**2g**, 77086-06-7; **2h**, 116972-99-7; **2i**, 116973-00-3; **3**, 13170-43-9; (*E*)-$PhCH{=}CHCH(SEt)_2$, 53963-34-1; (*E*)-$PhCH{=}CHCHS\overline{(CH_2)_3}S$, 69178-10-5; $NiCl_2(PPh_3)_2$, 14264-16-5.

Supplementary Material Available: Physical (IR, accurate mass, ^1H and ^{13}C NMR) data for **1a-h** are available (3 pages). Ordering information is given on any current masthead page.

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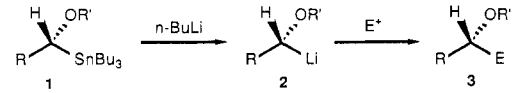
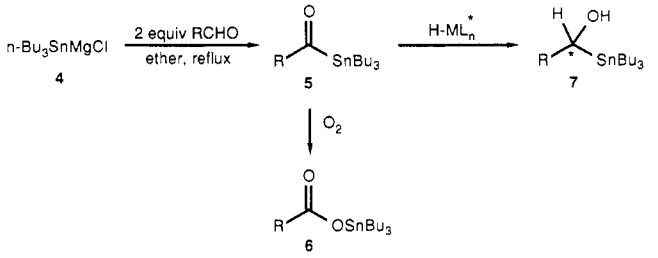
Asymmetric Reduction of Acylstannanes. Preparation of Enantiomerically Enriched α-Alkoxystannanes

Summary: Reduction of acylstannanes (**5**) with BINAL-H reagents affords α-hydroxystannanes in reasonable chemical (45-69%) and consistently good optical (up to 96% ee) yields with predictable stereochemistry.

Sir: α-Alkoxystannanes (**1**) have received considerable recent attention as precursors to α-alkoxyorganolithium reagents (**2**)[1-6] and the corresponding organocopper reagents.[7,8] Tin-lithium exchange occurs readily at low temperatures with retention of configuration to afford configurationally stable α-alkoxyorganolithium reagents.[2] Thus a preparation of enantiomerically pure α-alkoxystannanes would be very desirable as it would constitute an entry into homochiral α-alkoxyorganolithium reagents, species which should be useful as asymmetric building blocks. Previous reports of homochiral α-alkoxystannanes involve chromatographic resolution of diastereomeric derivatives[2,9] and an example of a compound prepared from an α-chloro boronic ester.[10] We report herein that α-alkoxystannanes are readily accessible in good enantiomeric purity by asymmetric reduction of acylstannanes.



Scheme I



As a large number of asymmetric reducing agents have been developed,[11] asymmetric reduction of acylstannanes is a rather obvious approach to homochiral α-alkoxystannanes. However, acylstannanes have been relatively obscure compounds until recently,[12] and little is known about their chemistry other than that they are relatively labile compounds. They were prepared by the reaction of (tributylstannyl)magnesium chloride (1 equiv) with aldehydes (>2 equiv, ether, reflux, Scheme I).[12] Although acyltributylstannanes are sensitive to oxygen (being quantitatively converted to the corresponding crystalline tributyltin carboxylates (**6**) within minutes at room temperature),[13] they may be purified by vacuum distillation and stored under argon in a freezer unchanged for months.

While it had been shown some 20 years ago that $LiAlH_4$ reduction of acetyltriphenylstannane affords 1-(triphenylstannyl)ethanol (unspecified conditions, yield),[14] other reports of the reduction of acylstannanes have not appeared.[15] Preliminary investigations into the feasibility of preparing homochiral α-hydroxystannanes from acylstannanes suggested that the latter compounds are extremely susceptible to reduction. For example, exposure of propanoyltributylstannane to $LiAlH_4$ (1 equiv, ether) or BH_3·THF (1 equiv, THF) at -78 °C for 5 min followed by an aqueous workup gave the expected (racemic) α-hydroxystannane in >95% yield. Hence, we were encouraged

(1) Still, W. C. *J. Am. Chem. Soc.* **1979**, *100*, 1481.
(2) Still, W. C.; Sreekumar, C. *J. Am. Chem. Soc.* **1980**, *102*, 1201.
(3) Sawyer, J. S.; Macdonald, T. L.; McGarvey, G. J. *J. Am. Chem. Soc.* **1984**, *106*, 3376. Sawyer, J. S.; Kucerovy, A.; Macdonald, T. L.; McGarvey, G. J. *J. Am. Chem. Soc.* **1988**, *110*, 842.
(4) McGarvey, G. J.; Kimura, M. *J. Org. Chem.* **1985**, *50*, 4655.
(5) Lesimple, P.; Beau, J.-M.; Sinay, P. *J. Chem. Soc., Chem. Commun.* **1985**, 894.
(6) Duchene, A.; Quintard, J.-P. *J. Chem. Soc., Chem. Commun.* **1987**, 29.
(7) Linderman, R. J.; Godfrey, A. *Tetrahedron Lett.* **1986**, *27*, 4553. Linderman, R. J.; Godfrey, A.; Horne, K. *Tetrahedron Lett.* **1987**, *28*, 3911.
(8) Hutchinson, D. K.; Fuchs, P. L. *J. Am. Chem. Soc.* **1987**, *109*, 4930.
(9) Jephcote, V. J.; Pratt, A. J.; Thomas, E. J. *J. Chem. Soc., Chem. Commun.* **1984**, 800.
(10) Matteson, D. S.; Sarkar, A.; Sadhu, K. M. Poster PS2-36 presented at the 4th IUPAC Symposium on Organometallic Chemistry Directed toward Organic Synthesis, July 26-30, 1987, Vancouver, B.C., Canada.
(11) For recent comparisons of some asymmetric reducing agents, see: Imai, T.; Tamura, T.; Yamamuro, A.; Sato, T.; Wollman, T. A.; Kennedy, R. M.; Masamune, S. *J. Am. Chem. Soc.* **1986**, *108*, 7402. Brown, H. C.; Park, W. S.; Cho, B. T.; Ramachandran, P. V. *J. Org. Chem.* **1987**, *52*, 5406.
(12) Quintard, J.-P.; Elissondo, B.; Mouko Mpegna, D. *J. Organomet. Chem.* **1983**, *251*, 175. Verlhac, J.-B.; Chanson, E.; Jousseaume, B.; Quintard, J.-P. *Tetrahedron Lett.* **1985**, *26*, 6075.
(13) While this work was in progress, similar observations were reported: Kosugi, M.; Naka, H.; Harada, S.; Sano, H.; Migita, T. *Chem. Lett.* **1987**, 1371. Kosugi, M.; Naka, H.; Sano, H.; Migita, T. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3462.
(14) Peddle, G. J. D. *J. Organomet. Chem.* **1966**, *5*, 486.
(15) Very recently, the asymmetric reduction of an acylstannane with (*R*)-BINAL-H was reported: Marshall, J. A.; Gung, W. Y. *Tetrahedron Lett.* **1988**, *29*, 1657. The *S* alcohol was obtained with high enantioselectivity (in agreement with Scheme III).

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