chemistry offers a novel and effective method for the synthesis of 5- and 6-membered ring ketones. Continued exploration of the scope of the reaction and its applications are in progress. Some subsequential carbon–carbon bond formation reactions using the β-triphenylgermyl functionality produced in these reactions are being developed.

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Supplementary Material Available: Spectral data for products (**2a,b,d,f–k**) (4 pages). Ordering information is given on any current masthead page.

Allylic Transpositions of Enantiomerically Pure C1-Acyloxy (*E*)-Crotylsilanes: Stereospecific Synthesis of (*E*)-Vinylsilanes†

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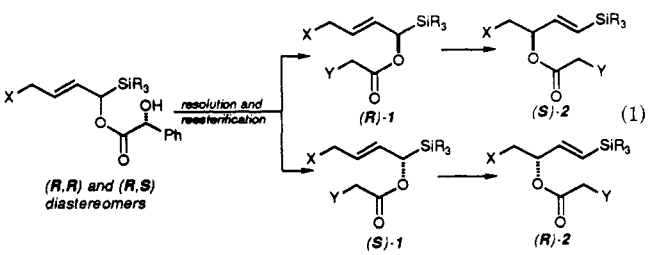
Summary: Treatment of (*R*)- or (*S*)-C1-acylated (*E*)-crotylsilanes **1** with catalytic amounts of boron trifluoride etherate or dichloropalladium bisacetonitrile [$PdCl_2(CH_3CN)_2$] in methylene chloride at room temperature resulted in an allylic transposition of the ester group with generation of optically active C3-oxygenated (*E*)-vinylsilanes.

The flexibility and skillful utilization of vinylsilanes in organic synthesis has rendered these molecules among the most versatile in modern organic chemistry.[2] Consequently, the development of new methodology which provides an expedient approach to the synthesis of this important class of organometallic compounds may have considerable potential. The inclusion of an oxygen functionality adjacent to the double bond and the ability to carry out the process in an asymmetric sense would further broaden its utility and scope. In addition to serving as precursors to carbonyl compounds[3] vinylsilanes function as effective vinyl anion equivalents that participate in a variety of carbon–carbon bond-forming processes including substitution[4] and cation π-cyclization reactions.[5] They have been employed in [4 + 2] cycloaddition strategies,[6] in Claisen rearrangements,[7] and more recently as precursors to alkylidene carbenes.[8] In conjunction with studies directed at the development of new methods for the asymmetric synthesis of biologically important hexoses from non-carbohydrate precursors we have had the opportunity to examine new methods for the preparation and utilization of homochiral C3-oxygenated (*E*)-vinylsilanes.[9] An attractive approach was the possibility of establishing a direct and stereospecific synthesis of an (*E*)-vinylsilane through a [3,3] sigmatropic rearrangement (*allylic transposition*) of an allylic silane system. The use of 1,2-disubstituted olefins adjacent to a geminally substituted (acyloxy)trialkylsilane center represented an intriguing possibility if an effective catalyst could be found to affect the desired rearrangement (eq 1). Herein we report our efforts to develop suitable reaction conditions that catalyze the suprafacial interchange of an ester functionality on homochiral C1-oxygenated (*E*)-crotylsilanes into optically active (*E*)-3-acyl-1-(trialkylsilyl)-1-butenoate derivatives.[10]



(1)

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(1) Recipient of a graduate fellowship from the Organic Chemistry Division of the American Chemical Society sponsored by Merck Sharp and Dohme, 1989–1990.

(2) For recent reviews on the chemistry of vinylsilanes, see: (a) Fleming, I. *Org. React.* **1989**, *37*, 57. (b) Overman, L. E.; Blumenkopf, T. A. *Chem. Rev.* **1986**, *86*, 1303. (c) Birkofer, L.; Stuhl, O. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley and Sons Ltd.: New York, 1989; Chapter 10.

(3) (a) Stork, G.; Jung, M. E. *J. Am. Chem. Soc.* **1974**, *96*, 3682. (b) Stork, G.; Colvin, E. *J. Am. Chem. Soc.* **1971**, *93*, 2080.

(4) Hudrlik, P. F.; Peterson, D.; Rona, R. J. *J. Org. Chem.* **1975**, *40*, 2236.

(5) (a) Blumenkopf, T. A.; Bratz, M.; Castaneda, A.; Look, G. C.; Overman, L. E.; Rodriguez, D.; Thompson, A. S. *J. Am. Chem. Soc.* **1990**, *112*, 4386. (b) Blumenkopf, T. A.; Look, G. C.; Overman, L. E. *J. Am. Chem. Soc.* **1990**, *112*, 4399. (c) Overman, L. E.; Castaneda, A.; Blumenkopf, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 1303.

(6) Fleming, I.; Sarkar, A. K.; Doyle, M. J.; Raithby, P. R. *J. Chem. Soc., Perkin Trans. 1* **1989**, 2023.

(7) (a) Russell, A. T.; Proctor, G. *Tetrahedron Lett.* **1987**, *28*, 2041 and 2045. (b) Sato, T.; Tsunekawa, H.; Kohama, H. Fujasawa, T. *Chem. Lett.* **1986**, 1556. (c) For Claisen rearrangements of the corresponding tributylstannane derivatives in racemic form, see: Ritter, K. *Tetrahedron Lett.* **1990**, *31*, 627. (d) Panek, J. S.; Sparks, M. A., unpublished results.

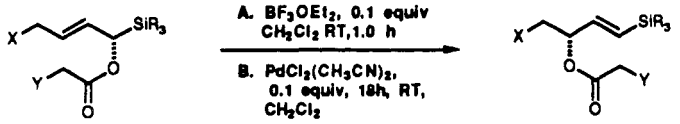
(8) Ochiai, M.; Takaoka, Y.; Nagao, Y. *J. Am. Chem. Soc.* **1988**, *110*, 6565.

(9) (a) The racemic 1-(trimethylsilyl)-2-buten-1-ol, precursor to (*S*)-**1a** and **1b**, was prepared from (*E*)-crotyl alcohol in 90% yield, via a reverse Brook rearrangement as reported by Danheiser: Danheiser, R. L.; Fink, D. M.; Okano, K.; Tsai, Y.-H.; Szczepanski, S. W. *Org. Synth.* **1987**, *66*, 14. Danheiser, R. L.; Fink, D. M.; Okano, K.; Tsai, Y.-H.; Szczepanski, S. W. *J. Org. Chem.* **1985**, *50*, 5393. The dimethylphenylsilyl derivatives, precursors to (*R*)-**1c–e** were prepared by the addition of lithium dimethylphenylsilane to crotonaldehyde to afford the desired racemic silane alcohols in good yield (70–80%) after purification on SiO_2 (see: Burke, S. D.; Saunders, J. O.; Oplinger, J. A.; Murtiashaw, C. W. *Tetrahedron Lett.* **1985**, *26*, 1131. Ager, D. J.; Fleming, I.; Patel, S. K. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2520). Similarly, addition of (dimethylphenylsilyl)lithium to 4-(benzyloxy)-2-butenal gave the racemic alcohols that were used as precursors to (*R*)-**1f** and **1g**. The starting *E* aldehyde (Danishefsky, S. J.; Regan, J. *Tetrahedron Lett.* **1981**, *22*, 3919) was prepared by oxidation of the corresponding *Z* alcohol with PCC on silica gel (1:2 w/w) in CH_2Cl_2 (64% yield, see: Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, *16*, 2647) or by Swern oxidation (99% yield, see: Swern, D.; Omura, K. *Tetrahedron* **1978**, *34*, 1651) to afford the 1-(dimethylphenylsilyl)-4-(benzyloxy)-2-buten-1-ol (**1d**) in 60% isolated yield. (b) The homochiral allyl silanes (*R*)- and (*S*)-**1** were obtained by resolution with (*R*)-*O*-acetylmandelic acid: Panek, J. S.; Sparks, M. A. *J. Org. Chem.*, submitted for publication. The absolute stereochemistry of the C1-hydroxy allylic silane precursors to (*R*)- and (*S*)-**1** was assigned from inspection of the ^1H NMR chemical shifts of the vinyl methyl and the silicon methyl groups of the derived (*R*)-*O*-acetyl mandelate esters by the method of Trost: Trost, B. M.; Belletire, J. L.; Godleski, S.; McDougal, P. G.; Balkovek, J. M.; Baldwin, J. J.; Christy, M. E.; Ponticello, G. S.; Varga, S.; Springer, J. P. *J. Org. Chem.* **1986**, *51*, 2370.

(10) All new compounds were isolated as chromatographically homogeneous materials and exhibited acceptable ^1H NMR, ^{13}C NMR, IR, and HRMS spectral data. All compounds were determined to be greater than 98% pure by ^1H NMR (400 MHz, 93.94 kG, operating at a S/N of 200:1).

0022-3263/90/1955-5564$02.50/0

Table I. Stereospecific Allylic Transpositions of (*S*)-(*E*)-Crotylsilanes[a]



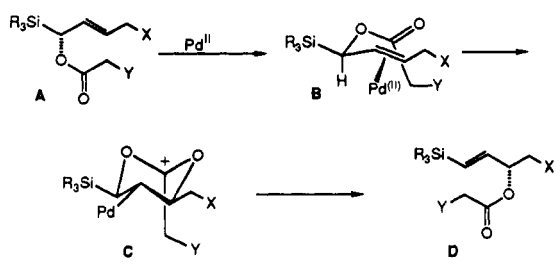
entry	(*E*)-crotylsilane	SiR_3	X	Y	reaction conditions[b]	(*E*)-vinylsilane product (% yield)[c]	(*E*)-vinylsilane ester ratio (*RR*:*SR*)[d]
1	**1a**	$SiMe_3$	H	H	B	**2a** (71)	1.0:0
2	**1a**	$SiMe_3$	H	H	A	**2a** (85)	1.7:1
3	**1c**	$SiMe_2Ph$	H	H	A	**2c** (80)	1.9:1
4	**1d**	$SiMe_2Ph$	H	OCH_3	B	**2d** (75)	1.0:0
5	**1d**	$SiMe_2Ph$	H	OCH_3	A	**2d** (95)	1.3:1
6	**1e**	$SiMe_2Ph$	H	Cl	B	**2e** (76)	1.0:0
7	**1f**	$SiMe_2Ph$	H	N_3	B	**2f** (60)	1.0:0

[a] The homochiral allylic silanes were obtained from a classical resolution using (*R*)-*O*-acetylmandelic acid, see ref 9b. [b] The transposition reactions were run in freshly distilled methylene chloride [CaH_2], at 0.2 M in substrate; palladium dichloride bisacetonitrile was purchased from Aldrich Chemical Co. [c] All yields are based on pure materials isolated by chromatography on SiO_2. [d] Ratio of esters indicates the ratio of mandelic esters (*RR*:*SR*) after hydrolysis [LiOH/aqueous THF] of the allylic ester and reesterification [DCC/cat. DMAP] of the resulting allylic alcohol with (*R*)-*O*-acetylmandelic acid.[27] The ratios were determined by ^1H NMR (400 MHz), operating at S/N ratio of >200:1.

Hitherto, systems of this structural type bearing vinyltrimethylsilanes have been prepared in optically active form through a kinetic resolution using the Sharpless asymmetric epoxidation.[11]

Earlier reports from our laboratory have established the utility of *racemic heterosubstituted allylic silanes* as useful homoenolate equivalents[12] in diastereoselective C-glycosidation reactions and as reagents that are capable of providing high levels of π-facial selectivity in catalytic osmylation reactions.[13] In the context of asymmetric synthesis methodology, the successful implementation of the allylic ester transposition was based on the availability of optically pure allylic silanes. From a mechanistic and synthetic vantage point systems of this type possess several desirable features. First, the starting materials, allylic silanes, are obtainable in optically pure form as their alcohol derivatives from a resolution with mandelic acid. Second, the derived acyloxy allylic silanes (*R*)- and (*S*)-**1** undergo a stereospecific sigmatropic rearrangement[14] to yield only vinylsilanes with the *E* configuration. Third, the reagents and reaction conditions used for successful transposition tolerate a range of functionality including different silicon groups and heteroatoms α to the ester carbonyl (Y = Cl, N_3, OMe).[15] Finally, the allylic silanes

Scheme I

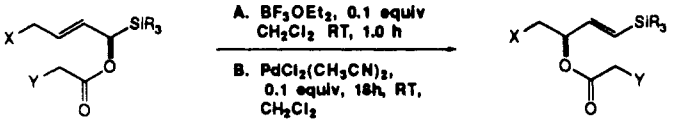


behave like esters of allylic alcohols in the palladium dichloride catalyzed reactions providing direct access to vinyl silanes, (*R*)- and (*S*)-**2**, with useful levels of optical purity.

Palladium-Catalyzed Allylic Transpositions. Mercury(II) and palladium(II) salts have found broad applications as catalysts for low-temperature sigmatropic rearrangements.[16] Recent studies by Overman, Bosnich, and others have defined the structural requirements and mechanistic features of Pd(II)-catalyzed allylic ester transpositions[17] and Cope rearrangements[18] and have demonstrated that these reactions proceed at an accelerated rate relative to the thermal variants. The important results of our study are summarized in Tables I and II. They clearly indicate that the choice of catalyst [Lewis acid or $PdCl_2(MeCN)_2$] has a large influence on the degree of syn selectivity in the product. The use of a catalytic amount of palladium dichloride bisacetonitrile [0.1 equiv of $PdCl_2(MeCN)_2$, CH_2Cl_2, room temperature] resulted in the efficient interchange of ester functionality with the formation the (*E*)-vinylsilanes with complete preservation of chirality (see entries 1, 4, 6, and 7 in Table I and entries 1, 3, and 5–8 in Table II).[19] Surprisingly, the reactions of the C4-(benzyloxy) derivatives (entries 6–8, Table II)

(11) Kitano, Y.; Matsumoto, T.; Sato, F. D. *Tetrahedron* **1988**, *44*, 4073 and references cited therein.
(12) Panek, J. S.; Sparks, M. A. *J. Org. Chem.* **1989**, *54*, 2034.
(13) Panek, J. S.; Cirillo, P. F. *J. Am. Chem. Soc.* **1990**, *112*, 4873.
(14) We would like to emphasize that the use of the term *sigmatropic rearrangement* is not intended as a mechanistic interpretation but is meant to refer to the overall bonding changes which occur in the allylic ester transposition of the C1-(acyloxy) allylic silane. As pointed out by Professor Overman,[16] the sigmatropic rearrangement nomenclature was originally used by Woodward and Hoffmann for "uncatalyzed intramolecular processes" [cf. Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1970; Chapter 7] and has been widely employed in recent years to characterize reactions which are not of this mechanistic type.
(15) Following resolution, the mandelate esters were reduced with $LiAlH_4$ to afford optically pure alcohols. The crotyl alcohols were reesterified under standard conditions: **1a**, **1c**, and **1g** were prepared by acylation of the appropriate crotyl alcohols (Ac_2O, Et_2N, cat. DMAP) in CH_2Cl_2 at ambient temperature. Yields after chromatography were >70%. Compounds **1b**, **1d**, and **1h** were prepared by DCC coupling of the starting crotyl alcohols with methoxyacetic acid (1.1 equiv of methoxyacetic acid, 1.1 equiv of DCC, catalytic DMAP, CH_2Cl_2, room temperature). Yields of the 2-methoxyacetates ranged from 80 to 98%. Compound **1e** was prepared by acylation of the crotyl alcohol with α-chloroacetyl chloride (1.1 equiv of pyridine, catalytic DMAP, CH_2Cl_2; 90% yield after SiO_2). To form compound **1f**, the α-chloro ester **1e** was dissolved in dry DMF and treated with 1.5 equiv of sodium azide (ambient temperature, 16 h, purified yield 85%).
(16) (a) For transition metal catalyzed sigmatropic rearrangements, see: Lutz, R. P. *Chem. Rev.* **1984**, *84*, 205. (b) Overman, L. E.; Campbell, C. B. *J. Am. Chem. Soc.* **1978**, *100*, 4822. (c) Overman, L. E.; Campbell, C. B. *J. Org. Chem.* **1976**, *41*, 3338.
(17) Overman, L. E. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 579.
(18) For mechanistic studies of transition metal catalyzed Claisen rearrangements, see: (a) Overman, L. E.; Renaldo, A. F. *J. Am. Chem. Soc.* **1990**, *112*, 3945. (b) Auburn, P. R.; Whelan, J.; Bosnich, B. *Organometallics* **1986**, *5*, 1533. (c) Schenck, T. G.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2058. (d) Overman, L. E.; Jacobsen, E. J. *J. Am. Chem. Soc.* **1982**, *104*, 7225. (e) Henry, P. M. *J. Am. Chem. Soc.* **1972**, *94*, 5200.
(19) The use of anhydrous mercury(II) trifluoroacetate failed to catalyze the allylic transposition, resulting in the recovery of starting material.

Table II. Stereospecific Allylic Transpositions of (*R*)-(*E*)-Crotylsilanes[a]



entry	(*E*)-crotylsilane	SiR_3	X	Y	reaction conditions[b]	(*E*)-vinylsilane product (% yield)[c]	(*E*)-vinylsilane ester ratio (*SR*:*RR*)[d]
1	**1b**	$SiMe_3$	H	OCH_3	B	**2b** (85)	1.0:0
2	**1c**	$SiMe_2Ph$	H	H	A	**2c** (97)	1.7:1
3	**1d**	$SiMe_2Ph$	H	OCH_3	B	**2d** (80)	1.0:0
4	**1f**	$SiME_2Ph$	H	N_3	A	**2f** (98)	2.4:1
5	**1c**	$SiMe_2Ph$	H	H	B	**2c** (70)	1.0:0
6	**1g**	$SiMe_2Ph$	OBn	H	B	**2g** (80)[e]	1.0:0
7	**1h**	$SiMe_2Ph$	OBn	OCH_3	B	**2h** (30)[e,f]	-
8	**1i**	$SiMe_2Ph$	OBn	CH_3	B	**2i** (60)[e,f]	-

[a] The homochiral allylic silanes were obtained from a classical resolution using (*R*)-*O*-acetylmandelic acid, see ref 9. [b] The transposition reactions were fun in freshly distilled methylene chloride [CaH_2], at 0.2 M in substrate; palladium dichloride bisacetonitrile was purchased from Aldrich Chemical Co. [c] All yields are based on pure materials isolated by chromatography on SiO_2. [d] Ratio of esters indicates the ratio of mandelic esters (*SR*:*RR*) after hydrolysis [LiOH/aqueous THF] of the allylic ester and reesterification [DCC/cat. DMAP] of the resulting allylic alcohol with (*R*)-*O*-acetylmandelic acid.[27] The ratios were determined by ^1H NMR (400 MHz), operating at S/N ratio of >200:1. [e] Based on recovered starting material. [f] Run on racemic material.

were less efficient, giving only modest yields of **2**.[20]

Our experimental results concerning the Pd(II)-catalyzed allylic transposition reactions are in accord with a mechanism which has been previously proposed for allylic esters.[17,18,21] Scheme I illustrates this mechanism by which a Pd(II) species catalyzes the allylic transposition A → D. The syn (suprafacial) stereochemistry is established from preferential addition of the palladium(II) species to the diastereotopic face of the olefin, anti to the ester group (B). Presumably this intermediate forms the palladium-bound species (C) which rearranges to give the desired product and regenerate the catalyst. The steric requirements of the six-membered intermediate allow for the formation of the vinylsilane D with preservation of chirality.[18,21]

Lewis Acid Catalyzed Allylic Transpositions. Although thermal and Lewis acid catalyzed [3,3] sigmatropic rearrangements of allylic esters[22] have been known for several years, examples involving allylic metals have not been reported.[23] Our studies in this area have shown that a number of different Lewis acids in catalytic amounts (0.05–0.1 equiv) rapidly and cleanly catalyze the stereospecific transposition of an ester group of an C1-(acyloxy) allylic silane into an (*E*)-vinylsilane at room temperature.[24] In contrast to the palladium dichloride catalyzed reactions, lower levels of syn selectivity were obtained for these cases. Important points which are raised from these experiments include the wide range of structural types that undergo reaction with a large rate acceleration when the reaction was run at room temperature. Although reaction rates were comparable at room temperature, and generally complete after 1 h, low-temperature experiments (−78 to −10 °C) revealed that the size of the silicon group had an effect on the overall rate of reaction. The yields were uniformly better for the BF_3·OEt_2-catalyzed reactions by an average of 20% (compare entries 4 and 5 in Table I).[25] As the size of the silicon group increased from trimethylsilyl to dimethylphenylsilyl the level of syn selectivity increased (compare entries 2 and 3 in Table I). These stereochemical results provide support for the involvement of the Lewis acid through coordination with the oxygen atoms of the ester directing it to a cyclic six-membered transition state. Unfortunately, the C4-(benzyloxy) derivatives failed to undergo successful transposition of the ester under Lewis acid catalysis.[26]

In conclusion, the palladium dichloride catalyzed allylic transpositions of homochiral C1-oxygenated allylic silanes (*R*)- and (*S*)-**1** provide a new and effective method for the synthesis of (*E*)-vinylsilanes **2** in optically active form. The diminished levels of syn selectivity in the Lewis acid catalyzed reactions most likely reflect the loss of a stereocontrolling element in the transition state. Further studies on the scope of the allylic ester transposition reactions including the Lewis acid catalyzed process, and their applications toward the synthesis of carbohydrate-based natural products are currently underway and will be reported in due course.

Acknowledgment. This work has been financially supported by the National Institutes of Health (CA47249). We are grateful to Ms. Heather L. Nimmons and Mr. Michael Creech for performing mass spectral measurements.

Supplementary Material Available: General experimental procedures for the allylic transposition reactions, along with spectroscopic data (7 pages). Ordering information is given on any current masthead page.

(20) Efforts to increase the efficiency of this reaction by changing the reaction solvent [CH_3CN, THF, or 1,2-dichloroethane] and increasing the amount of catalyst resulted in decomposition of the starting allylic silane.

(21) For earlier reports of chirality preservation in palladium-catalyzed allylic transpositions, see: (a) Danishefsky, S. J.; Cabel, M. P.; Chow, K. *J. Am. Chem. Soc.* **1989**, *111*, 3456. (b) Saito, S.; Hamano, S.; Moriyama, H.; Okada, H.; Moriwake, T. *Tetrahedron Lett.* **1988**, *29*, 1157. (c) Grieco, P. A.; Takigawa, S. L.; Bongers, S. L.; Tanaka, H. *J. Am. Chem. Soc.* **1980**, *102*, 80.

(22) Hill, R. K. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, p. 503.

(23) For an interesting report on the BF_3·OEt_2-catalyzed 1,3-isomerization of optically active C1-alkoxy allylic stannanes, see: Marshall, J. A.; Gung, W. Y. *Tetrahedron Lett.* **1989**, *30*, 7349.

(24) Other Lewis acids that were screened and which successfully catalyzed the allylic transposition include $TiCl_4$, TMSOTf, TBSOTf, and $SnCl_4$.

(25) With the exception of the C4-(benzyloxy) derivatives (see ref 26) **1g** and **1h**, no signs of competing protiodesilylatyion were observed.

(26) Several different Lewis acids were examined [$TiCl_4$, TMSOTf, TBSOTf, and $SnCl_4$] under a variety of conditions; however, only products from decomposition and protiodesilylation (4-(benzyloxy)-2-butenal) could be detected by spectroscopic and chromatographic methods.

(27) Whitesell, J. K.; Reynolds, D. *J. Org. Chem.* **1983**, *48*, 3548.