siderably improved three selectivity is obtained<sup>16</sup> in comparison to (E)-1b, as readily predicted by an enhanced 1,3 interaction of R  $\leftrightarrow$  Me<sub>3</sub>Si in T<sub>2</sub> relative to that of R  $\leftrightarrow$  H<sub> $\beta$ </sub> for (E)-1b.

Further efforts are in progress to establish more variations with higher diastereoselectivities on the basis of this transition-state model. Finally, it should be noted that this model cannot, of course, explain the whole story of diastereoselection in the [2,3] Wittig rearrangement in general. Recently we have found a few variations<sup>16</sup> that exhibit the opposite sense of stereoselection to that generally observed in this study.

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**Registry No.** (E)-1b, 79704-95-3; (Z)-1b, 79704-96-4; (E)-1c, 84118-82-1; (E)-1d, 79705-05-8; (Z)-1d, 79705-06-9; (E)-1e, 27299-30-5; (Z)-1e, 27299-31-6; (E)-1f, 84118-83-2; (Z)-1f, 84118-84-3; (E,E)-1g, 84118-85-4; (Z,E)-1g, 84118-86-5; threo-2a, 79705-03-6; erythro-2a, 79705-02-5; threo-2h, 79704-97-5; erythro-2b, 79704-93-1; threo-2c, 84118-87-6; erythro-2c, 84118-88-7; threo-2d, 79705-08-1; erythro-2d, 79705-07-0; threo-2e, 52922-10-8; erythro-2e, 52922-19-7; threo-2f, 83173-78-8; erythro-2f, 84118-89-8; threo-2g, 84118-90-1; erythro-2g, 84118-91-2.

(16) Such variations include (crotyloxy)acetic acids (ref 2c), 2-[(crotyloxy)methyl]-4,4-dimethyl-2-oxazolines (*Tetrahedron Lett.*, in press), and crotyl benzyl sulfides (unpubliched), which all exhibit only low-tomoderate degrees of stereoselection. To explain the opposite sense of diastereoselection, an entirely different transition-state model should be considered.

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## Enantioselective Allylation of Aldehydes with an Optically Active Allylsilane<sup>1</sup>

Summary: Reaction of aldehydes with an optically active allylsilane, (R)-3-phenyl-3-(trimethylsilyl)propene, in the presence of titanium chloride has been found to proceed with high enantioselectivity to produce optically active homoallylic alcohols of up to 91% ee.

Sir: There has been intense interest and activity in enantioselective addition of organometallics to prochiral carbonyl compounds.<sup>2</sup> Enantioselective allylation must be especially promising because the produced optically

Scheme I



active homoallylic alcohols can be converted into various useful compounds such as  $\beta$ -hydroxy acids.<sup>3</sup> We report here highly stereoselective allylation using an optically active allylsilane.

(R)-3-Phenyl-3-(trimethylsilyl)propene (1), which was prepared by an asymmetric Grignard cross-coupling with a chiral (ferrocenylphosphine)palladium catalyst,<sup>4</sup> was allowed to react with pivalaldehyde (2a), isobutyraldehyde (2b), and acetaldehyde (2c) in the presence of titanium tetrachloride in dichloromethane.<sup>5</sup> Optically active homoallylic alcohols 3a-c with the carbon-carbon double bond of E configuration<sup>6</sup> were produced in good yields (Scheme I). The reaction conditions and results are summarized in Table I, which also contains methods of determining the absolute configuration and enantiomeric purity of the alcohols 3. The following significant features are noteworthy. (1) The present allylation proceeded with high enantioselectivity (>95%) in the reaction with aldehydes **2a** and **2b** containing larger alkyl groups ( $\mathbf{R} = t$ -Bu and *i*-Pr), and hence the homoallylic alcohols of very high enantiomeric purity could be obtained (entries 1, 3, and 4). (2) The enantioselectivity decreased to 70% in the reaction with acetaldehyde (2c, R = Me; entry 5). (3) Higher reaction temperature lowered the selectivity (entry 2). (4) The aldehydes 2a-c were all attacked on their re face preferentially by the allylsilane (R)-1, giving rise to 3 over their enantiomers 4.

The stereochemistry of  $S_E'$  reaction of allylsilanes has been established to be anti (electrophiles enter the double bond from the side opposite to the leaving silyl group),<sup>4,7</sup>

<sup>(15)</sup> In this rearrangement, lithium dicyclohexylamide was used in place of *n*-BuLi because the use of *n*-BuLi produced a considerable amount of byproducts. The threo/erythro ratio was determined by GLC analysis (PEG 20M, 150 °C),  $t_{\rm R}$  12.2 min (erythro-4) and 9.5 min (threo-4); cf. Felkin, H.; Gault, Y.; Roussi, G. Tetrahedron 1970, 26, 3761. The ratio was further confirmed by NMR analysis with the aid of Eu(fod)<sub>3</sub>.

Optically Active Allylsilanes. 4. For part 3, see Hayashi, T.; Ito,
 H.; Kumada, M. Tetrahedron Lett. 1982, 23, 4605.
 (2) For example, see (a) Seebach, D.; Crass, G.; Wilka, E.-M.; Hilvert,

<sup>(2)</sup> For example, see (a) Seebach, D.; Crass, G.; Wilka, E.-M.; Hilvert, D.; Brunner, E. Helv. Chim. Acta 1979, 62, 2695. (b) Mukaiyama, T. In "Asymmetric Reactions and Processes in Chemistry"; Eliel, E. L., Otsuka, S., Ed.; American Chemical Society: Washington, DC, 1982; ACS Symp. Ser. No. 185, Chapter 2.

<sup>(3)</sup> Enantioselective allylation by use of chiral allylborane derivatives has been reported: (a) Herold, T.; Schrott, U.; Hoffmann, R. W. Chem. Ber. 1981, 114, 359. (b) Hoffmann, R. W.; Herold, T. Chem. Ber. 1981, 114, 375. (c) Midland, M. M.; Preston, S. B. J. Am. Chem. Soc. 1982, 104, 2330.

<sup>(4)</sup> Hayashi, T.; Konishi, M.; Ito, H.; Kumada, M. J. Am. Chem. Soc.
1982, 104, 4962.
(5) The reaction was carried out according to the reported procedure:

<sup>(5)</sup> The reaction was carried out according to the reported procedure:
(a) Hosomi, A.; Sakurai, H. Tetrahedron Lett. 1976, 1295. (b) Fleming,
I.; Paterson, I. Synthesis 1979, 446.

<sup>(6)</sup> Uncontaminated with Z olefin within the limits of detection.

<sup>(7)</sup> Hayashi, T.; Konishi, M.; Kumada, M. J. Am. Chem. Soc. 1982, 104, 4963.

Table I. Reaction of Allylsilane (R)-1 with Aldehydes 2 in the Presence of Titanium Chloride in Dichloromethane<sup>a</sup>

entry	% ee of ( <i>R</i> )-1	aldehyde 2	yield, <sup>b</sup> %	$[\alpha]^{20}$ D of 3, deg (c in CCl <sub>4</sub> )	% ee of 3 (confign)
 1	95	t-BuCHO (2a)	71	+44.7(0.5)	$91^{c} (R)^{d}$
2	90	t-BuCHO (2a)	67 <i>°</i>	+35.8(0.5)	$73^c (R)^d$
3	95	<i>i</i> -PrCHO (2b)	66	+24.7(0.4)	$91^{c} (R)^{f}$
4	85	<i>i</i> -PrCHO (2b)	63	+23.7(2.8)	$84^{g,h} (R)^{f}$
5	91	MeCHO (2c)	83	+14.2(1.6)	$64^{g,i}(S)^{f}$

<sup>a</sup> Titanium chloride (1.1 equiv) was added at -78 °C to a mixture of 1 (1.0 equiv) and 2 (1.1 equiv) in dichloromethane. The mixture was stirred at -78 °C for 2 min, unless otherwise noted, and quenched with water. <sup>b</sup> Isolated yields by preparative TLC (silica gel-chloroform). Yields are based on 1 and not optimized. <sup>c</sup> Determined by <sup>1</sup>H NMR spectra of the alcohol 3 with Eu(dcm)<sub>3</sub>. The signals *tert*-butyl of (*R*)-3a and isopropyl methyl of (*R*)-3b appeared at higher field than those of their enantiomers. <sup>d</sup> Determined by <sup>1</sup>H NMR of the diastereomeric esters of (*R*)-O-methylmandelic acid. The *tert*-butyl signal of (*R*)-3a appeared at higher field than that of (*S*)-4a (Dale, J. A.; Mosher, H. S. J. Am. Chem. Soc. 1973, 95, 512). <sup>e</sup> Reaction at room temperature for 2 min. <sup>f</sup> The configuration was determined by the optical rotation of the  $\beta$ -hydroxy ester 6b or 6c whose configuration is known. (+)-(*R*)-6b (Nakazaki, M.; Arakawa, H. Bull. Chem. Soc. Jpn. 1961, 34, 453), (+)-(*S*)-6c (Lemieux, R. U.; Giguere, J. Can. J. Chem. 1951, 29, 678). <sup>g</sup> The enantiomeric excess was determined by <sup>1</sup>H NMR spectra of the  $\beta$ -hydroxy ester 6b or 6c, using Eu(dcm)<sub>3</sub>. The CH<sub>3</sub>O signal of (*R*)-6b and (*S*)-6c appeared at lower field than that of their enantiomers. <sup>h</sup> The alcohol (+)-3b was converted into  $\beta$ -hydroxy ester 6b with [ $\alpha$ ]<sup>26</sup><sub>D</sub> + 18.1° (c 0.9, ethanol). <sup>i</sup> The alcohol (+)-3c was converted into  $\beta$ -hydroxy ester 6c with [ $\alpha$ ]<sup>25</sup><sub>D</sub> + 15.0° (c 0.9, chloroform).

and therefore the present asymmetric reaction must proceed via an acyclic linear transition state,<sup>8,9</sup> not via a cyclic six-membered transition state analogous to that proposed for the reaction of allylic organometallics<sup>10</sup> such as allylboranes.<sup>3</sup> The enantioselectivity observed here can be visualized by the mechanism shown in Scheme II.<sup>11</sup> The transition state A where the aldehyde is attacked on its *re* face leading to the alcohol **3** is sterically favored over the diastereomeric transition state B, which suffers steric repulsion between the alkyl group R on the aldehyde and the phenyl group on the allylsilane 1. The steric repulsion is less effective when R is Me than when R is larger *i*-Pr or *t*-Bu.<sup>12</sup>

The allylsilane (R)-1 was found also effective for the reaction with methyl benzoylformate (7) to give tertiary alcohol 8 in >95% optical yield.<sup>13</sup> Investigations on the



(8) Titanium chloride is omitted for simplicity, which may activate aldehydes by coordinating to the carbonyl oxygen.

(10) For a review, see Courtois, G.; Miginiac, L. J. Organomet. Chem. 1974, 69, 1.

enantioselective allylation of other prochiral substrates are currently under way.

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(12) One referee suggested an alternative mechanism involving synclinal geometries C and D to account for the high enantioselectivity: C is much more sterically favorable than D.



(13) Reaction at -78 °C for 1 h gave 85% yield of 8:  $[\alpha]^{20}_{D} + 12.7^{\circ}$  (c 1.1, ethanol). Enantiomeric purity was determined to be 92% by <sup>1</sup>H NMR, using Eu(dcm)<sub>3</sub>.

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<sup>(9)</sup> A linear transition state has been proposed for aldol-type condensation of enol silyl ethers and acetals catalyzed by trimethylsilyl trifluoromethanesulfonate (Murata, S.; Suzuki, M.; Noyori, R. J. Am. Chem. Soc. 1980, 102, 3248), to which the present allylation is quite analogous in that only the electrophile is activated. The erythro selectivity of  $\gamma$ -substituted allylsilanes may also support the linear transition state.<sup>7</sup>

<sup>(11)</sup> Concerning the conformation of allylsilane 1 at the reaction, see ref 4.