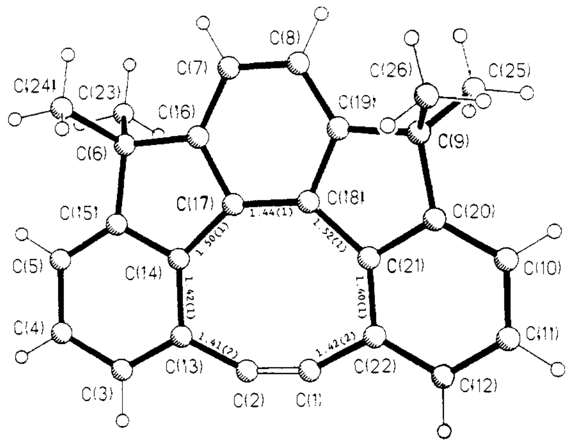

Figure 1. Perspective view of compound **2**. The bond lengths listed are the averages of the corresponding values from three crystallographically independent molecules.

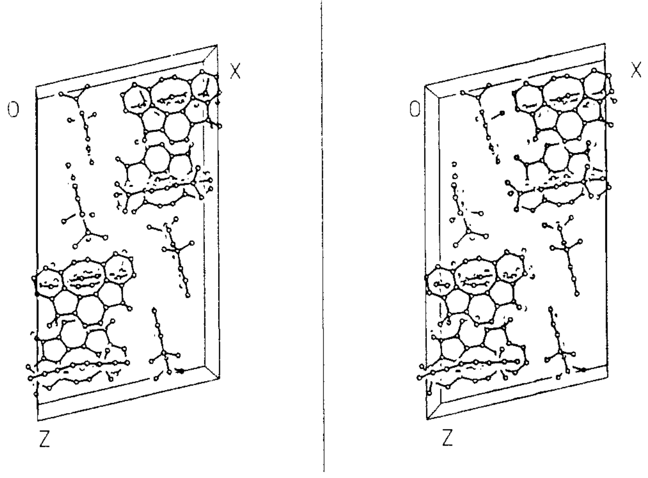

Figure 2. Stereoview of the crystal structure of compound **2**. The origin of the unit cell lies at the upper left corner, with *a* pointing from left to right at a slant, *b* toward the reader, and *c* downwards.

A single-crystal X-ray diffraction study[9,10] confirmed the planar structure of **2**. The structural determination also revealed that there are three crystallographically independent molecules (designated I-III) in the asymmetric unit. The structures of these three independent molecules are similar to each other and, as an example, Figure 1 shows a perspective view of molecule I. Comparing with the standard triple bond [1.18 (1) Å],[11] the C≡C triple bonds [1.19 (2) Å] in molecules I and III are exactly equal to it, but the one in molecule II [1.23 (2) Å] appears to be marginally longer, which correlates with the fact that the planarity of the eight-membered ring and the coplanarity of this ring with the three benzo groups in II are distinctly worse than those in I and III. Also of structural interest is the bent acetylenic angle of **2**. As expected, these angles in molecules I and III are similar to those of other cyclooctynes,[2] showing an average value of 153.3°. Interestingly, the average value of the corresponding angles in molecule II is only 146.5°. The mean deviations of the carbon atoms comprising the eight-membered ring from their respective least-squares plane are 0.02 (2) Å for I, 0.07 (2) Å for II, and 0.01 (2) Å for III; the dihedral angles between the eight-membered ring and the three annelated benzene rings are 3 (1)°, 2 (1)°, and 3 (1)° for I, 6 (1)°, 3 (1)°, and 8 (1)° for II, and 3 (1)°, 1 (1)°, and 3 (1)° for III, respectively. Except for the triple bond, the other corresponding C-C bond lengths of the eight-membered ring in I-III are very close to one another, and the averages for the three molecules are shown in Figure 1. The crystal structure of **2** consists of a packing of discrete molecules with normal van der Waals contacts, and the three independent molecules are almost perpendicular to each other (Figure 2); values of the dihedral angle between pairs of least-squares molecular planes are as follows: I-II 93.0 (9)°, II-III 77.8 (9)°, and I-III 81.4 (9)°.

In conclusion, we have synthesized a stable planar derivative of 13,14-didehydrotribenzo[*a*,*c*,*e*]cyclooctene (**1**), the only elusive member in the family of benzene-annelated cyclooctatrienyne.

Acknowledgment. We thank Yu-Xin Cui for measuring the proton and carbon-13 NMR spectra for all new compounds.

Registry No. 2, 129000-06-2; **3**, 106865-81-0.

Supplementary Material Available: Electronic spectrum, proton NMR spectrum, carbon-13 NMR spectrum, and a listing of crystallographic data, atomic coordinates, bond lengths, bond angles, anisotropic temperature factors, and hydrogen coordinates for **2** (17 pages); tables of observed and calculated structure factors for **2** (26 pages). Ordering information is given on any current masthead page.

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[9] Compound **2** crystallizes in the monoclinic space group $P2_1/n$ with a = 15.809 (7), b = 12.799 (2), c = 28.297 (3) Å; β = 102.99 (2)°; V = 5579 (3) Å^3; Z = 12; and ρ_{calcd} = 1.187 g/cm^3. A crystal having approximately dimensions of 0.22 × 0.34 × 0.38 mm was mounted on a Nicolet R3m/V diffractometer. Intensity data of 7285 independent reflections collected with Mo Kα radiation (λ = 0.71073 Å) at room temperature (21 °C) by ω scan mode in the range of 3° $\leq 2\theta \leq$ 45° were processed with the profile-fitting procedure and corrected for absorption by using ψ scan data. The structure was solved by direct-phase determination and refined with anisotropic temperature factors for all non-hydrogen atoms. The hydrogen atoms were generated geometrically (C-H bonds fixed at 0.96 Å) and assigned the same isotropic temperature factor of U = 0.08 Å^2. The structure was refined to the current residual values of R = 0.098 and R_w = 0.060 with 704 variables and weighting scheme of $w = [\sigma^2(F_o) = 0.00005|F_o|^2]^{-1}$ for 3327 observed reflections $[|F_o| \geq 5\sigma(|F_o|)]$.

[10] Supplementary material.

[11] Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1-S19.

Asymmetric Claisen Rearrangement Catalyzed by Chiral Organoaluminum Reagent

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Received May 29, 1990

Reported herein is the first successful example of the asymmetric Claisen rearrangement of allyl vinyl ethers catalyzed by a chiral organoaluminum reagent, (*R*)-**1** or (*S*)-**1**.

The Claisen rearrangement of allyl vinyl ethers takes place by a concerted mechanism through a cyclic six-membered chairlike transition state.[1,2] For the asymmetric rearrangement, two possible chairlike transition states, A and B, must be considered, each of which is readily interconvertible and produces enantiomers **3** and **4**, respectively (Scheme I). Our interest is in the ability of chiral organoaluminum reagents of type **1** to discriminate between these two possible chairlike structures.[3]

The reaction of cinnamyl vinyl ether **2** (R = Ph, X = H) with (*R*)-**1** (Ar = Ph)[4] resulted only in C-O bond cleavage without any rearrangement. Introduction of the methyl substituent into substrate **2** (i.e., R = Ph, X = Me) yielded the desired rearranged ketone in 43% yield, but the optical yield was quite low (13% ee).

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[1] Reviews: (a) Rhoads, S. J.; Raulins, N. R. *Org. React.* (*N.Y.*) **1975**, *22*, 1. (b) Bennett, G. B. *Synthesis* **1977**, 589. (c) Ziegler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227. (d) Bartlett, P. A. *Tetrahedron* **1980**, *36*, 2. (e) Hill, R. K. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3B, p 503. (f) Carruthers, W. *Some Modern Methods of Organic Synthesis*, 3rd ed.; Cambridge University Press: Cambridge, 1986; p 167. (g) Blechert, S. *Synthesis* **1989**, 71.

[2] Maruoka, K.; Nonoshita, K.; Banno, H.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 7922; **1990**, *112*, 316.

[3] For asymmetric ortho Claisen rearrangement in a chiral solvent, see: Saeva, F. D.; Sharpe, P. E.; Olin, G. R. *J. Am. Chem. Soc.* **1975**, *97*, 204. The optical yield and absolute configuration has not been reported, however.

[4] Maruoka, K.; Itoh, T.; Shirasaka, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 310.

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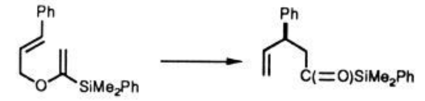
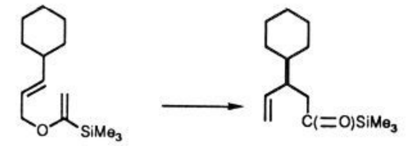
Table I. Asymmetric Claisen Rearrangement[a]

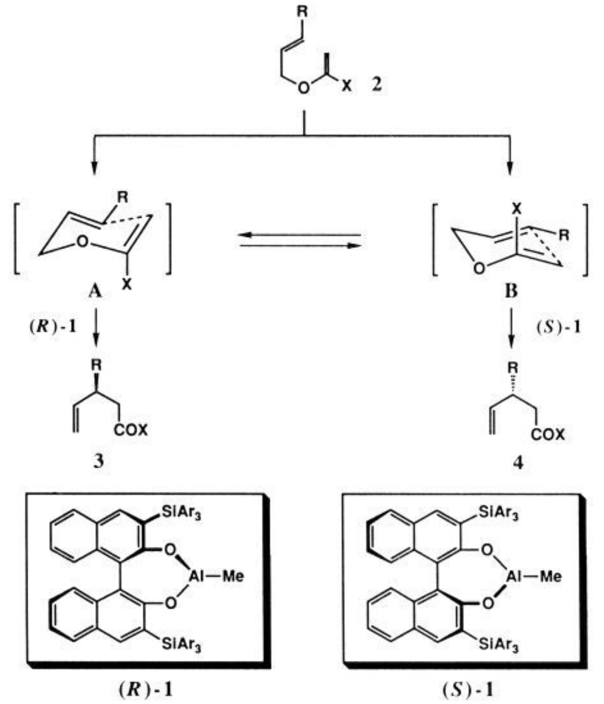
entry	catalyst (*R*)-**1**	conditions (°C, h)	yield[b] (%)	$[\alpha]_D$[c] (deg)	% ee[d] (config)
					
1	$Ar_3 = Bu^tMe_2$	-20, 24	22		14 (*S*)[f]
2	Ar = Ph	-20, 8	86	-32.6	80 (*S*)[f]
3	$Ar_3 = Bu^tPh_2$	-20, 3	99	-38.5	88 (*S*)[f]
4	Ar = Ph[e]	-20, 5	85	+34.6	80 (*R*)[f]
					
5	Ar = Ph	-40, 16	65	-19.4	85 (*S*)[f]
6	$Ar_3 = Bu^tPh_2$	-40, 8	76	-20.6	90 (*S*)[f]
					
7	Ar = Ph	-20, 4	79	+3.4	61 (*S*)[g]
8	$Ar_3 = Bu^tPh_2$	-20, 4	84	+4.0	71 (*S*)[g]
					
9	Ar = Ph	-40, 15	73	-23.7	91 (*S*)[h]
10	$Ar_3 = Bu^tPh_2$	-40, 16	68		93 (*S*)[h]

[a] Unless otherwise noted, the rearrangement of **2** was carried out with 1.1–2 equiv of (*R*)-**1**. [b] Isolated yield. [c] In $CHCl_3$ (*c* 0.5). [d] Determined by GLC analysis after conversion to the ketals of (2*R*,3*R*)-butanediol with $HC(OEt)_3$ (2 equiv) and catalytic *p*-TsOH in benzene. [e] Use of (*S*)-**1** as catalyst. [f] Correlated to the known (*S*)-3-phenyl-4-pentenal (Berlan, J.; Besace, Y.; Pourcelot, G.; Cresson, P. *Tetrahedron* **1986**, *42*, 4757) by desilylation of **3** or **4** (R = Ph; X = $SiMe_3$) with py·HF. [g] Determined by conversion to (*S*)-3-cyclohexylpentanal by (i) catalytic hydrogenation with Raney Ni/H_2, (ii) desilylation with py·HF, and (iii) the Swern oxidation (Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165). The authentic aldehyde was independently prepared according to the reference: Fujiwara, J.; Fukutani, Y.; Hasegawa, M.; Maruoka, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1984**, *106*, 5004. [h] The authentic (*S*)-3-phenyl-1-(trimethylgermyl)-1-pentanone was synthesized from (*S*)-3-phenylpentanal (see footnote *g*) by reaction with Me_3GeLi (Bulten, E. J.; Noltes, J. G. *J. Organomet. Chem.* **1971**, *29*, 397.) followed by the Swern oxidation.

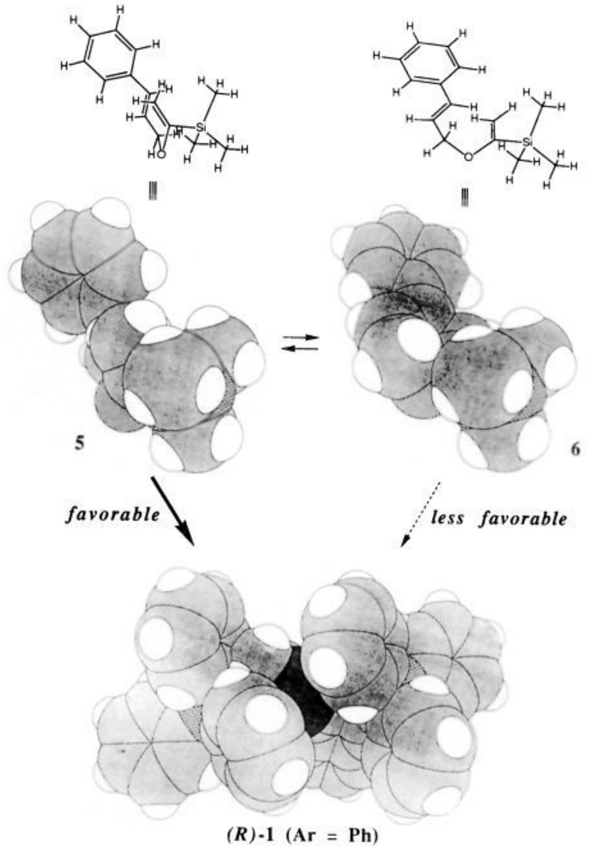
In marked contrast, the trimethylsilyl and trimethylgermyl derivatives **2** (R = Ph; X = $SiMe_3$, $GeMe_3$) were successfully transformed under the influence of (*R*)-**1** (Ar = Ph) to the corresponding acylsilane and acylgermane **3** (R = Ph; X = $SiMe_3$, $GeMe_3$), respectively, with high optical purity (80–90% ee).[5] Other selected examples are listed in Table I.

The ligand effect of various chiral organoaluminum reagents was studied in the rearrangement of **2** (R = Ph; X = $SiMe_3$). No rearrangement was observed with 3,3′-diphenylbinaphthol as ligand. Among various trialkylsilyl substituents in (*R*)-**1**, use of the more bulky *tert*-butyldiphenylsilyl group exhibited the highest enantioselectivity (entry 3 vs 1 and 2).[6] However, introduction of alkyl substituents at the remote para position of the triphenylsilyl groups lowered the selectivity.[7] Use of other solvents such as toluene, ether, and THF significantly retarded the rate of the rearrangement.[8] The present method is chirally flexible and allows the synthesis of both antipodal products by choosing the handedness of the chiral aluminum reagents (entry 4 vs 2).

Scheme I



Scheme II



(*R*)-**1** (Ar = Ph)

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[5] The starting allyl vinyl ethers **2** (R = Ph; X = $SiMe_3$, $GeMe_3$) were prepared by treatment of cinnamyl alcohol with ethyl α-(trimethylsilyl)vinyl ether (Soderquist, J. A. *Org. Synth.* **1989**, *68*, 25) or ethyl α-(trimethylgermyl)vinyl ether in the presence of catalytic mercuric acetate.

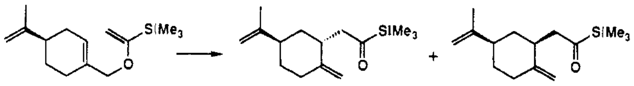
[6] Maruoka, K.; Itoh, T.; Araki, Y.; Shirasaka, T.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2975.

[7] Rearrangement of **2** (R = Ph; X = $SiMe_3$) with (*R*)-**1** (Ar = *p*-tolyl and *p*-$(C_6H_4)Bu^t$) in CH_2Cl_2 at -25 to +25 °C gave rise to **3** (R = Ph; X = $SiMe_3$) in 62% and 48% ee, respectively, with the *S* configuration.

[8] Attempted reaction of **2** (R = Ph; X = $SiMe_3$) with (*R*)-**1** (Ar = Ph) in these solvents at -40 to 0 °C resulted in most recovery of the starting **2**.

Based on these experimental findings, the transition state in the asymmetric Claisen rearrangement can be visualized as shown in Scheme II. The space-filling models **5** and **6** of cinnamyl vinyl ether **2** (R = Ph; X = $SiMe_3$) are derived by appropriate rotation of the two possible chairlike structures A and B (R = Ph; X = $SiMe_3$), respectively. In this rearrangement, the orientation of the α-methylene groups of **2** (R = Ph; X = $SiMe_3$) is of the utmost importance for high enantioselection, and the chiral aluminum reagent (*R*)-**1** (Ar = Ph) can discriminate between these two conformations only by a difference in orientation of the α-methylene groups. The conformation **5** makes a good match for the molecular cleft of the chiral aluminum reagent, producing the *S* isomer **3** (R = Ph; X = $SiMe_3$). In contrast, the conformation **6**, because of the projecting α-methylene substituent, is prevented from approaching the cleft of the aluminum reagent.

The importance of acylsilanes and acylgermanes in organic synthesis has already been demonstrated.[9] The present method, in addition to its asymmetric character, should provide a facile route to the general synthesis of acylsilanes and germanes as illustrated:



trans isomer *cis isomer*

Heat (200 °C) : 91 % (85:15)
(±)-1 at -20 °C : 75 % (97: 3)

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[9] (a) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981. (b) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: New York, 1983. (c) Ricci, A.; Degl'Innocenti, A. *Synthesis* **1989**, 647. (d) Kiyooka, S.; Hamada, M.; Matsue, H.; Fujiyama, R. *Chem. Lett.* **1989**, 1385.

Stereochemistry of the Cross-Coupling Reaction of Chiral Alkylsilanes with Aryl Triflates: A Novel Approach to Optically Active Compounds

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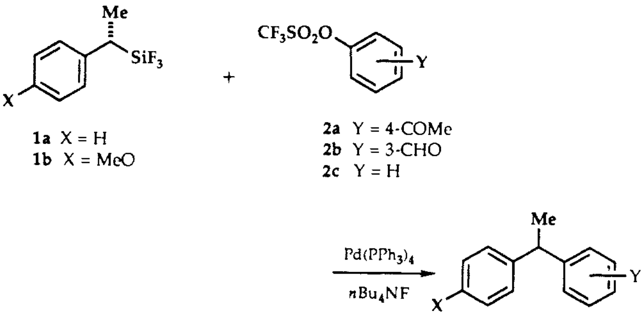
Received May 22, 1990

Organosilicon compounds smoothly couple with organic triflates with the aid of fluoride ion and a palladium catalyst.[1] The striking feature of this reaction is that, in addition to alkenyl- and arylfluorosilanes, alkyltrifluorosilanes undergo the carbon–carbon bond formation. We have studied the stereochemistry of the cross-coupling reaction of the chiral silanes available by asymmetric hydrosilylation[2] to disclose that the reaction proceeds with almost complete retention of the configuration at the lowest possible temperatures. Furthermore, the stereochemical outcome was found to reverse at higher temperatures or in the presence of hexamethylphosphoric triamide (HMPA).

The reaction of 2.0 equiv of (*S*)-1-phenyl-1-(trifluorosilyl)ethane (34% ee) (**1a**)[3] with 1.0 equiv of 4-acetylphenyl triflate (**2a**) took place smoothly in the presence of 5 mol % of $Pd(PPh_3)_4$ and 2.0 equiv of tetrabutylammonium fluoride (TBAF) in tetrahydrofuran (THF) to afford optically active 1-phenyl-1-(4-acetylphenyl)ethane (**3a**)[4] in 51–31% yields along with acetophenone (4–52% yield).[5] To our surprise, the optical purity and the absolute configuration of **3a** varied, depending on the reaction temperature. At low temperatures the cross-coupling reaction proceeded predominantly with retention of the configuration of the carbon atom bonded to the silicon: the reaction of (*S*)-**1a** (34% ee) with **2a** proceeded with nearly complete retention at 50 °C to give **3a** (32–34% ee). At higher temperatures the optical purity of **3a** decreased linearly, and above 75 °C inversion of the configuration predominated. The % ee of **3a** vs reaction temperature is shown in Figure 1.[6]



1a X = H
1b X = MeO

2a Y = 4-COMe
2b Y = 3-CHO
2c Y = H

3a X = H
Y = 4-COMe
3b X = H
Y = 3-CHO
3c X = MeO
Y = H

Similar temperature dependence of the stereochemistry was also observed in the reaction of **1a** (34% ee) with 3-formylphenyl triflate (**2b**). At 60 °C (*S*)-1-phenyl-1-(4-formylphenyl)ethane (**3b**) (32% ee) was isolated in 46% yield. The % ee of **3b** also decreased linearly when the reaction was carried out at higher temperatures and reached 0 at roughly 80 °C (Figure 1). Above 80 °C inversion of the configuration resulted, and (*R*)-**3b** of 28% ee was produced at 100 °C.

To evaluate the solvent effect on the stereochemistry, the reaction of 2.3 equiv of (*S*)-**1a** (38% ee) with 1.0 equiv of **2a** was conducted in the presence of $Pd(PPh_3)_4$ (5 mol %) and 2.3 equiv of TBAF in various solvents at 60 °C.[7] Solvent, absolute configuration of coupled product **3a**, and its optical purity were as follows: HMPA–THF (1:10), *R*, 8% ee; *N*,*N*-dimethylformamide–THF (DMF–THF) (1:10), *S*, 16% ee; dimethyl sulfoxide–THF (DMSO–THF) (1:10), *S*, 16% ee. Apparently, in the presence of such a polar solvent as HMPA, inversion of the configuration predominated, whereas retention was still preferred in DMF and DMSO.

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[1] Hatanaka, Y.; Hiyama, T. *Tetrahedron Lett.* **1990**, *31*, 2719 and the references cited therein.

[2] (a) Hayashi, T.; Kabeta, K. *Tetrahedron Lett.* **1985**, *26*, 3023. (b) Hayashi, T.; Matsumoto, T.; Itoh, Y. *J. Am. Chem. Soc.* **1988**, *110*, 5579. (c) Hayashi, T.; Tamao, K.; Katsuro, Y.; Nakae, I.; Kumada, M. *Tetrahedron Lett.* **1980**, *21*, 1871. Alternative methods: (d) Cullen, W. R.; Han, N. F. *J. Organomet. Chem.* **1987**, *269*, 333. (e) Fleming, I.; Kindon, N. D. *J. Chem. Soc., Chem. Commun.* **1987**, 1177. (f) Chan, T. H.; Pellon, P. *J. Am. Chem. Soc.* **1989**, *111*, 8737.

[3] The optically active silanes used in this work were prepared by fluorination of the corresponding chlorosilanes, which were synthesized by the asymmetric hydrosilylation of the corresponding styrenes. See ref 2c.

[4] The coupled product **3a** was transformed to 1-(4-hydroxyphenyl)-1-phenylethane by the Baeyer–Villiger oxidation followed by alkaline hydrolysis. The optical purity of the final product was estimated by HPLC analysis using a chiral column (CHIRALCEL OB, hexane–2-propanol, 80:1). The absolute configuration was determined according to the literature: Okamoto, K.; Yamada, H.; Nitta, I.; Shingu, H. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 299.

[5] The following procedure is representative: To a THF solution of **2a** (45 mg, 0.20 mmol) and freshly prepared tetrakis(triphenylphosphine)palladium (12 mg, 0.010 mmol, 5 mol %) were added (*S*)-**1a** (76 mg, 0.40 mmol, 34% ee) and then a THF solution of TBAF (1.0 M, 0.40 mL, 0.40 mmol) under an argon atmosphere, and the resulting mixture was heated at 50 °C for 6 h. Concentration and purification by column chromatography (silica gel) using hexane–ethyl acetate (10:1) gave (*S*)-**3a** (18 mg, 41% yield) as a colorless oil: $[\alpha]^{20}_D$ +3.28° (*c* 2.0, $CHCl_3$); HPLC 32% ee (column, CHIRALCEL OB; eluent, hexane–2-propanol, 80:1); ^1H NMR ($CDCl_3$, 90 MHz) δ 1.65 (d, *J* = 7.0 Hz, 3 H), 2.52 (s, 3 H), 4.22 (q, *J* = 7.0 Hz, 1 H), 6.98–7.51 (m, 7 H), 7.90 (d, *J* = 8.5 Hz, 2 H); IR (neat) 3000, 2900, 1690, 1615, 850, 770, 705 cm^{-1}. Reactions above 70 °C were carried out in a sealed tube. The temperature indicated in Figure 1 is that of the heating bath. Because the coupling reaction required an induction period (30–120 min at 70 °C, 10–15 min at 100 °C), we may well assume that the reaction has started at the temperature shown.

[6] The % ee's shown in Figure 1 are the mean values of three independent experiments. The % ee's of **3a** observed in the reaction at 100 °C were variable, and thus the data shown in Figure 1 involve relatively large deviations.

[7] Racemization of **1a** under the reaction conditions can safely be ignored, since heating the (*S*)-**1a** (38% ee) in the presence of $Pd(PPh_3)_4$ and TBAF in HMPA or DMF at 60 °C for 6 h did not cause any loss of the optical activity.

0002-7863/90/1512-7793$02.50/0