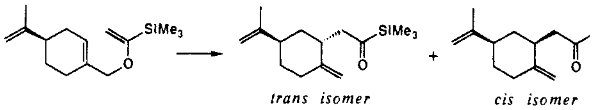
Based on these experimental findings, the transition state in the asymmetric Claisen rearrangement can be visualized as shown in Scheme II. The space-filling models **5** and **6** of cinnamyl vinyl ether **2** (R = Ph; X = $SiMe_3$) are derived by appropriate rotation of the two possible chairlike structures 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:



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

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

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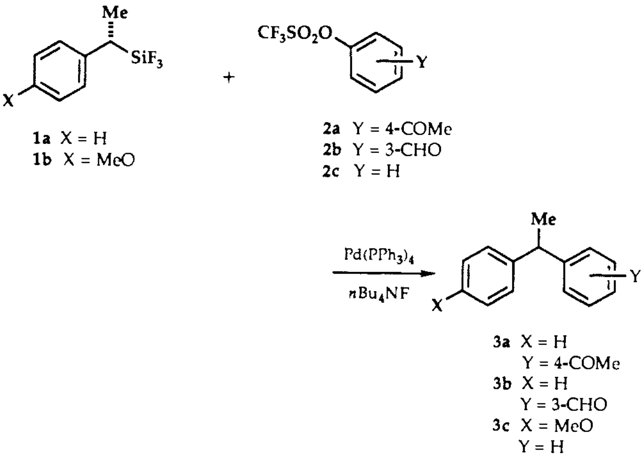
Organosilicon compounds smoothly couple with organic triflates with the aid of fluoride ion and a palladium catalyst.[1] The striking feature of this reaction is that, in addition to alkenyl- and arylfluorosilanes, alkyltrifluorosilanes undergo the carbon–carbon bond formation. We have studied the stereochemistry 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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(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); ^{1}H 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.

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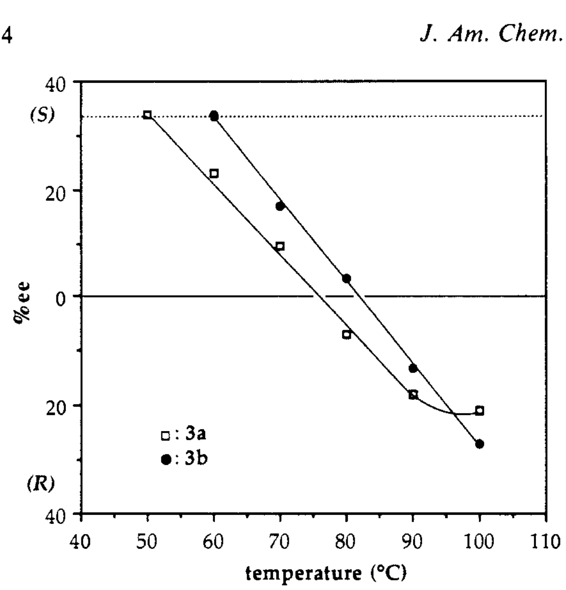

Figure 1. Temperature dependence of the stereochemistry of the cross-coupling products **3a** and **3b** derived from **1a** (34% ee).

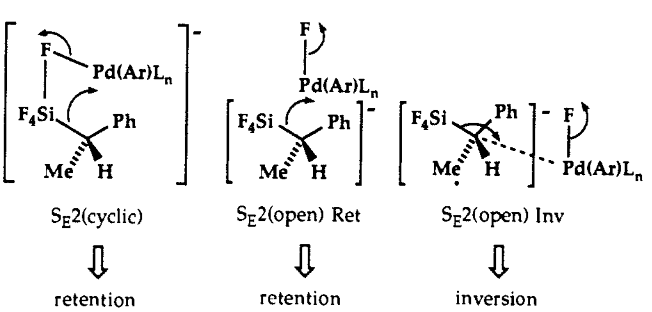

Figure 2. Proposed transition-state models for transmetalation.

When (*S*)-1-(4-methoxyphenyl)-1-(trifluorosilyl)ethane (**1b**) (18% ee) was allowed to react with phenyl triflate (**2c**) in THF at 60 °C, (*R*)-1-(4-methoxyphenyl)-1-phenylethane (**3c**) of 9% ee was obtained in 35% yield. Thus, the total stereochemistry was still retention, but an electron-donating group X of **1** was found to sharply diminish the % ee of the coupled product.

The palladium-catalyzed cross-coupling of an organosilane with a triflate is assumed to involve a pentacoordinate silicate which can be generated by the nucleophilic attack of fluoride ion to an organosilicon compound.[8] The transmetalation reaction between the silicate and an arylpalladium complex gives an intermediate (1-phenylethyl)(aryl)palladium species, whose reductive elimination affords a coupled product. Since the reductive elimination of a diorganopalladium complex takes place with retention of the configuration of the alkyl ligand,[9] the observed stereochemical outcome of the silicon-based coupling reaction should reflect that of the transmetalation step in a catalytic cycle. Although transmetalation is one of the important basic reactions of transition metal catalyzed transformations, its mechanistic aspect remained relatively unexplored. The stereochemistry reported for alkyl transfer from mercury to palladium[10] is retention of configuration, and that for the transmetalation in HMPA of a chiral benzyltin compound with an acylpalladium complex is inversion.[11] Our results clearly show for the first time that the stereochemistry of transmetalation is decisively influenced by the reaction temperature and the solvent used. To explain the above observations we consider three transition-state models for the transmetalation as illustrated in Figure 2. The retention of configuration in THF at low temperatures may be ascribed to a cyclic four-centered transition state (S$_E$2 (cyclic))[12] which should be promoted by a fluoride bridge. Hereby coordinative unsaturation of a pentacoordinate silicate[13] is essential for the smooth coupling reaction. Since a large excess of TBAF (6 equiv), which leads to coordinatively saturated hexacoordinate silicates,[14] completely suppressed the reaction of **1a** with **2b** at 60 °C, an alternative model (S$_E$2 (open) Ret)[15] seems unlikely, wherein the coordinative unsaturation of silicon species is dispensable. At higher temperatures or in HMPA-THF solvent, the fluoride bridge is cleaved to induce a back-side attack of the palladium complex, leading to the inversion of configuration (S$_E$2 (open) Inv).[16] The inversion observed for the reaction in HMPA-THF is fully consistent with the stereochemistry reported by Stille and Labadie for the reaction of the chiral benzyltin compound.[11]

In summary, we have found that the stereochemistry of the cross-coupling reaction using organosilicon compounds could be controlled from almost complete retention to inversion by tuning the reaction temperature and the solvent. The method described herein allows us to synthesize a wide range of optically active molecules. Studies on its synthetic application as well as mechanistic details are currently in progress in our laboratory.

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(8) We have observed that [18-crown-6-K]$^+$,[Ph$_n$SiF$_{5-n}$]$^-$ (*n* = 1–3) (Damrauer, R.; Danahey, S. E. *Organometallics* **1986**, *5*, 1490) underwent the cross-coupling reaction and reactivity order was parallel to that of Ph$_n$SiF$_{4-n}$. This strongly suggests the participation of a pentacoordinate silicate as an active species in the silicon-based cross-coupling reaction: Hatanaka, Y.; Hiyama, T., to be published.

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The Equilibrium Constant for the Interconversion of Homocub-1(9)-ene and Homocuban-9-ylidene[1]

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Insertions of singlet carbenes into adjacent carbon-hydrogen and carbon-carbon bonds are normally irreversible.[3] Recently, highly strained alkenes have been found for which the reversion to the divalent state is energetically possible.[4] A spectacular example is the work of Eaton and Hoffmann in which 9-phenyl-1(9)-homocubene was shown to revert to the related carbene.[5] We have previously demonstrated that the parent carbene (**1**) and bridgehead alkene (**2**) interconvert using **3** and **4** as precursors.[6] In this communication we use a combination

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[†] The Ohio State University.

[‡] Princeton University.

(1) It gives us the greatest pleasure to dedicate this paper to Prof. Dr. Wolfgang Kirmse on the occasion of his 60th birthday. This work was supported both at Ohio State (Grant CHE-8814950) and Princeton (Grant CHE-8800448) by the National Science Foundation.

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