Stereochemical Control of the Reaction of Chlorosilane with Methyllithium by the Addition of Metal Cyanide: Inversion by Potassium Cyanide and Retention by Copper(I) Cyanide

Kohei Tamao,* Hayato Tsuji, Akio Toshimitsu
Institute for Chemical Research, Kyoto University, Uji, Kyoto, 611-0011, Japan
Fax +81 774 383186; E-mail: tamao@scl.kyoto-u.ac.jp
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Dedicated with admiration and respect to Professor Ryoji Noyori in honor of his scientific achievements.

Abstract: In the 1,4-dichlorotetrasilane derivative composed of disilane units bearing two pentamethylene tethers, the substitution of a chlorine atom on the silicon atom by the methyl group during the reaction with methyllithium mainly proceeds with inversion of configuration of the silicon atoms, (1) the yield being dramatically improved by the addition of potassium cyanide, and (2) the stereochemistry being changed to retention of configuration by the addition of copper(I) cyanide.

Key words: bicyclic compounds, copper(I) cyanide, organosilicon compounds, potassium cyanide, stereoselectivity

In our recent study on the photophysical properties of conformationally controlled oligosilanes using disilane units configurationally constrained into syn or anti by two pentamethylene tethers (Figure), we reported the synthesis of the tetrasilane compound anti,anti-dimer 2 (shown in Scheme) by the reaction of syn,syn-1,4-dichlorotetrasilane 1 with methyllithium with inversion of configuration at both silicon centers. Since the yield of this reaction was not satisfactory (30%), we have been trying to optimize the reaction conditions and found the following unprecedented effect by metal cyanides: (1) the yield and the selectivity for 2 are dramatically increased by the addition of potassium cyanide to the reaction mixture, and (2) the stereoselectivity is completely changed from inversion to retention by the change in the counteranion of the cyanide salt added, namely from potassium to copper(I). These results are reported in this paper.

Scheme

Table Yields of 2, 3 and 4 in the reaction of 1 with methyllithium

<table>
<thead>
<tr>
<th>entry</th>
<th>additive</th>
<th>amount (molar amount)</th>
<th>isolated yields (%)b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>total 2 3 4</td>
</tr>
<tr>
<td>1</td>
<td>none</td>
<td>---</td>
<td>45 30 15 trace</td>
</tr>
<tr>
<td>2</td>
<td>KCN</td>
<td>0.4</td>
<td>62 49 10 3</td>
</tr>
<tr>
<td>3</td>
<td>KCN</td>
<td>2</td>
<td>90 67 15 8</td>
</tr>
<tr>
<td>4</td>
<td>CuCN</td>
<td>0.4</td>
<td>68 trace 18 50</td>
</tr>
<tr>
<td>5</td>
<td>CuCN</td>
<td>2</td>
<td>51 trace 17 34</td>
</tr>
</tbody>
</table>

aCarried out using 1 and MeLi (4 molar amount) in THF-Et2O (ca. 5:1) at 0 °C - r.t. for 10 h. bIsolated by GPC.

In contrast, in the presence of a catalytic amount of copper(I) cyanide (0.4 molar amount), the syn,syn-dimer 4 was found to be the major product (50% yield) accompanied by the formation of the anti,syn-dimer 3 (18% yield) (entry 4). The structure of 4 was unambiguously confirmed by X-ray crystallographic analysis as shown in

Careful analysis of the reaction of the syn,syn-dichloride 1 with methyllithium (4 molar amount in THF-ether ca. 6:1, 0 °C – r.t., 12 h) revealed that, in addition to the anti,anti-dimer 2 in 30% yield, the anti,syn-dimer 3 arising from the substitution reaction with retention of configuration at one silicon center was also formed in 15% yield (Scheme and Table, entry 1). With the addition of potassium cyanide to this reaction mixture, the yields of 2 were dramatically increased (entries 2 and 3) accompanied by the formation of a small amount of syn,syn-dimer 4, the yields of the anti,syn-dimer 3 remaining nearly the same. Thus, the total number of reactions with inversion of configuration N(inv) and that with retention N(ret) at each silicon center were only slightly changed, keeping the N(inv)/N(ret) at 4.8: 1 ~ 6.8: 1 (Figure 1, none and KCN).

Figure

In the 1,4-dichlorotetrasilane derivative composed of disilane units bearing two pentamethylene tethers, the substitution of a chlorine atom on the silicon atom by the methyl group during the reaction with methyllithium mainly proceeds with inversion of configuration of the silicon atoms, (1) the yield being dramatically improved by the addition of potassium cyanide, and (2) the stereochemistry being changed to retention of configuration by the addition of copper(I) cyanide.

Key words: bicyclic compounds, copper(I) cyanide, organosilicon compounds, potassium cyanide, stereoselectivity
change in the stereochemical course from inversion to retention in the hydrolysis or alcoholysis of halosilanes by the addition of coordinating HMPA, DMSO or DMF, and (2) an increase in the yield of the reaction of chlorosilanes with Grignard reagents by the addition of catalytic quantities of copper(I) cyanide or thiocyanate. The key roles of the penta- or hexa-coordinate silicon compounds have been suggested in both cases. Further studies on the metal cyanide effect on other reactions are currently in progress in our laboratory.

Typical Experimental Procedure: syn,syn-1,4-Dichlorotetrasilane 1 was prepared by the reaction of the corresponding anti,anti-1,4-diphenyltetrasilane 2 (104 mg, 0.19 mmol) with HCl gas in benzene (1.5 mL) and in the presence of AlCl3 (1.1 mg, 0.008 mmol) at 15 °C for 3 h, followed by the addition of dry acetone and hexane, filtration, and concentration. To a mixture of 1 and potassium cyanide (25 mg, 0.38 mmol) in THF (3.5 mL) was added methyl lithium (1.1 M in ether, 0.66 mL, 0.73 mmol) at 0 °C and the reaction mixture was stirred at room temperature for 10 h. After the addition of 10% NH4Cl aq. solution (10 mL), the products were extracted with ether (10 mL × 3). The organic layer was washed with brine, dried (MgSO4), and concentrated in vacuo to leave a pale yellow oil. After the purification by column chromatography (silica gel; hexane as eluant), the product was obtained with 30% yield. For a mixture of the products, the ratio of the number of 

\[ \text{inv} / \text{ret} \] is defined by

\[ \left( \frac{\text{yield of } \text{inv}}{\text{yield of } \text{ret}} \right) \times \left( \frac{\text{yield of } \text{ret}}{\text{yield of } \text{inv}} \right) \]

Figure 2.4 As shown in Figure 1, \( N(\text{inv})/N(\text{ret}) = 1: 6.6 \) was just the opposite to those observed with KCN as the additive. It should be noted that copper(I) cyanide contributes not only to a dramatic change in the major course of the reaction to retention but also to the improvement in the total yield of the methylation products. The yield of 4, however, was not improved by the increase in the amount of copper(I) cyanide to two molar amount (entry 5), presumably due to the conversion of a significant amount of the methylolithium to the so-called higher order cuprate which does not react with chlorosilanes.5


Figure 1 Total yields of 2, 3, and 4, and ratios of the number of reactions with inversion \( N(\text{inv}) \) (white) and retention \( N(\text{ret}) \) (black) of configuration.

Figure 2 X-ray structure of 4 drawn at 30% probability level (all hydrogen atoms are omitted for clarity). The crystals contain two independent molecules, one of which is shown here. Selected distances [Å] and angles [°]: Si1–Si2 2.3657(7), Si2–Si2* 2.3526(9), Si2*–Si2–Si1–C1 1.51(9), Si3–Si4 2.3588(7), Si4–Si4* 2.3419(9), Si4*–Si4–Si3–C12 16.05(10).

Although the details are not yet clear, the improvements in the yields of the methylated products and the change in the stereochemical pathways by the addition of metal cyanide described herein may be related to the following previous observations: (1) the rate enhancement and the

References and Notes

(3) The ratio \( N(\text{inv})/N(\text{ret}) \) is defined by \( \left( \text{yield of } \text{inv} \right) \times \left( \text{yield of } \text{ret} \right) \).
Crystal data for C_{22}H_{46}Si_{4}:

\[M = 422.95, \text{triclinic, }\]
\[a = 10.6644(8), b = 13.888(1), c = 8.6630(6) \text{ Å, }\]
\[\alpha = 91.037(5), \beta = 102.920(4), \gamma = 85.797(4)^\circ, V = 1247.1801 \text{ Å}^3, T = 173 \text{ K, space group P-1 (no. 2), } Z = 2,\]
\[\mu(\text{MoK}α) = 2.44 \text{ cm}^{-1}.\]
A total of 4782 reflections was collected. The final cycle of the full-matrix least-squares refinement was based on 4191 observed reflections (3σ(I)) and 236 variable parameters. The structure was refined to a goodness of fit (GOF) of 1.26 and the final residuals of R = 0.052 and wR = 0.070. Crystallographic data of 4 have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-156100. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB1 1EZ, UK (fax:+44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

It has been proposed that chlorotrimethylsilane activates, but would not react with Me_{2}CuLi. Lipshutz, B. H.; Dimock, S. H.; James, B. J. Am. Chem. Soc. 1993, 115, 9283, and references cited therein.


In our previous paper, this compound has been postulated to be the syn,syn-dimer. Recently, an X-ray crystallographic analysis confirmed the anti,anti-structure of this compound.

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