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Silyl-cupration of a propargylsilane as a test for the reversibility of a metallo-metallation

Maria Angeles Cubillo de Dios, Ian Fleming *, Wibke Friedhoff, Philip D.W. Woode

Department of Chemistry, Lensfield Road, Cambridge CB2 1EW, UK

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Abstract

Silyl-cupration of propargylsilanes is normal in giving mainly the product with a silyl group at the terminus and the copper atom in the centre. There is no evidence of the copper atom and the originally-resident silyl group undergoing a retro silyl-cupration to give an allenylsilane. © 2001 Elsevier Science B.V. All rights reserved.

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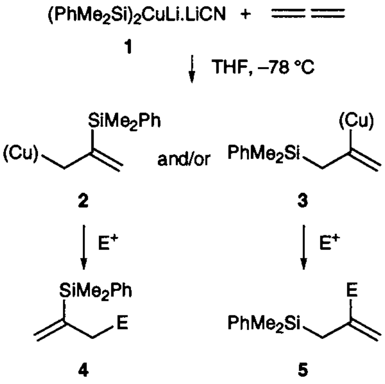
1. Introduction

We showed some years ago that the silyl-cuprate reagent **1** reacted with allene to give the intermediate **2**, in which the silyl group was attached to the central atom and the copper to the terminus [1], as shown by its reaction with almost all electrophiles, including chlorine, to give vinylsilanes **4**. There were however two extraordinary exceptions. When the electrophile was bromine, the product was a mixture of the vinylsilane **4** (E = Br) and the allylsilane **5** (E = Br), and when the electrophile was iodine the product was exclusively the allylsilane **5** (E = I). The simplest explanation for these results was that the intermediates **2** and **3** were in rapid equilibrium, and that the silyl-cupration, an example of a metallo-metallation, was easily reversible, as some other metallo-metallations are. Our efforts to prove this at that time were unsuccessful. In particular, although we were able to reassemble separately cuprates with the stoichiometry of each of the intermediates **2** and **3**, starting with the iodides **4** (E = I) and **5** (E = I), they did not react in the same way as the intermediate(s) produced directly from the silylcuprate and allene. Even if reversibility is the explanation, it still remains a puzzle why iodine, surely a powerful electrophile, would select the regioisomer **3** to react with, when almost all other electrophiles, including quite weak ones like epoxides, reacted cleanly with the isomer **2**. In this paper we report our efforts to examine a system that might be expected to show the reverse step **3** → **1** + allene, if it is a feasible pathway (Scheme 1).

We already knew that silyl-cupration of terminal acetylenes was highly regioselective, placing the silyl group cleanly at the terminus and the copper atom on the inside [2]. We reasoned that if we were to carry out this reaction on the propargylsilane **6**, we would obtain the intermediate **7** (Scheme 2). This intermediate has critically the same feature as the intermediate **3**, namely a silyl group at the tetrahedral terminus and a copper atom on the central carbon atom (**7**, lasso). If it were to



Scheme 1.

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* Corresponding author.

E-mail address: if10000@cam.ac.uk (I. Fleming).

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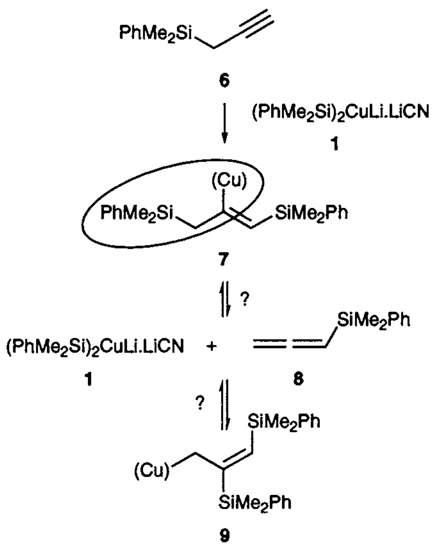
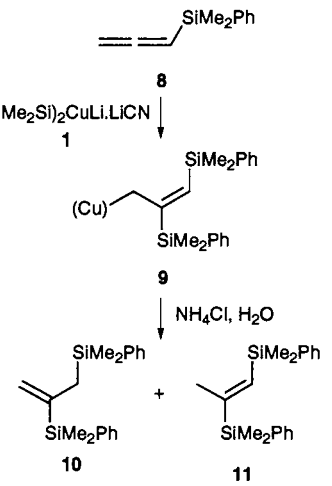


Scheme 2.

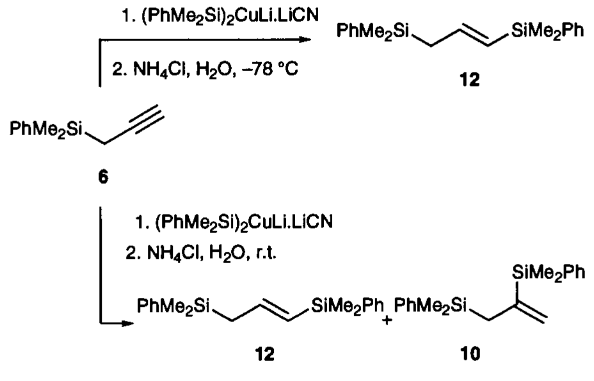


Scheme 3.

undergo a retro metallo-metallation it would give the allene **8** and the silylcuprate, and these might then combine in the opposite sense to give the regioisomer **9**.

2. Results and discussion

First we checked what would happen if the allene **8** and the silylcuprate were to react with each other. We have just suggested that it would give the intermediate **9**, and this is indeed what happened — the product from an aqueous work-up was a mixture of the two vinylsilanes **10** and **11**, in ratios that varied with the temperature of the quench, but both were always present (Scheme 3).



Scheme 4.

We then carried out the critical silyl-cupration of the propargylsilane **6**, and obtained, after quenching the reaction mixture at −78°C with aqueous ammonium chloride solution, cleanly the allylsilane **12**. However, when we allowed the reaction mixture to warm to room temperature before quenching, the allylsilane **12** was accompanied by its regioisomer **10** (Scheme 4). This isomer might have been produced by either of two pathways. One is the simple reversal of the first step, and readdition to the acetylene group with the opposite regiochemistry, the other is that it might have been the reaction we were looking for, a retro metallo-metallation in the direction **7**→**8**, followed by readdition, although we would have to accept, since there was no sign of the vinylsilane **11**, that the protonation step had been more highly regioselective than it had been when we had made the intermediate **9** deliberately. The reversibility in the reaction with the acetylene was not something that had been noticed before, and indeed a simple acetylene, oct-1-yne, gave only the terminal vinylsilane no matter what temperature the mixture was quenched at. This made it seem a little more possible that the product **10** was not produced by the first pathway. Accordingly, we carried out an experiment that would distinguish between the two pathways.

Silyl-cupration of propargyltrimethylsilane **13** similarly gave only the allylsilane **14** when the mixture was quenched at −78°C, and a mixture of the allylsilane **14** and its regioisomer **15** when it was quenched at room temperature. The critical detail is that the product **15** has the trimethylsilyl group in the allylic position and the phenyldimethylsilyl group on the central atom, as shown by protodesilylation **15**→**16**, which cleanly removed the trimethylsilyl group. If the allene had been formed, the by-product analogous to **15** would have had the silyl groups interchanged. This product was therefore the result of reversibility in the addition to the acetylene, and the allene was not being formed (Scheme 5).

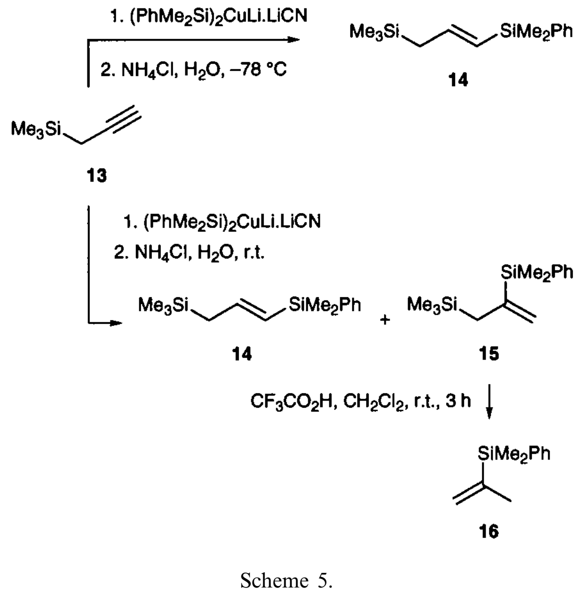
In conclusion, we have shown once again that the unusual regioselectivity when iodine is used to quench the product from the silyl-cupration of allene is probably not explained simply by the reversibility of the silyl-cupration step. It remains something of a mystery, to which we now add the mystery that whereas the silyl-cupration of terminal acetylenes is highly regioselective at any temperature between −78°C and room temperature, the corresponding reaction with propargylsilanes is evidently not.

3. Experimental

NMR spectra were recorded on Bruker AM400 and AC250 instruments with chemical shifts measured relative to chloroform δ7.25. Coupling constants are expressed in Hertz. The IR spectrum was recorded on a Perkin–Elmer FT-IR 1620 machine using sodium chloride plates. Column chromatography was carried out using Merck Kieselgel 60 (230–400 mesh ASTM) and TLC using glass plates coated to 1 mm with Kieselgel 60 PF_{254}. Tetrahydrofuran (THF) and ether were freshly distilled from lithium aluminium hydride under argon.

*3.1. Preparation of propargyldimethyl(phenyl)silane (**6**) and allenyldimethyl(phenyl)silane (**8**)*

Magnesium turnings (1.2 g, 41 mmol) were covered with dry ether (5 ml) under argon, and mercury(II) chloride (0.02 g) was added followed by propargyl bromide (0.5 g, 4.2 mmol) in a single portion. After 1.3 h, the reaction started (the mixture became dark and started to boil). The flask was cooled with water at room temperature (r.t.) and propargyl bromide (4.5 g, 46 mmol) in dry ether (35 ml) was added via cannula at a rate to maintain the internal temperature at r.t. The mixture was then stirred at r.t. for 12 h, cooled to 0°C and chlorodimethyl(phenyl)silane (8 ml) added slowly by syringe. The mixture was stirred overnight at r.t. A saturated solution of ammonium chloride was added at 0°C, followed by diethyl ether. The ether layer was dried ($MgSO_4$), evaporated off, and the residue chromatographed [SiO_2, light petroleum (bp 40–60°C)] to give propargyldimethyl(phenyl)silane [3] (8.0 g, 82%); δ_H(250 MHz; $CDCl_3$) 7.65–7.55 (2 H, m, Ph), 7.46–7.32 (3 H, m, Ph), 1.87 (1 H, t, *J* 2.9, C≡CH), 1.74 (2 H, d, *J* 2.9, CH_2Si) and 0.42 (6 H, s, $SiMe_2$) and allenyldimethyl(phenyl)silane [3] (1.2 g, 12%); δ_H(250 MHz; $CDCl_3$) 7.6–7.5 (2 H, m, Ph), 7.45–7.15 (3 H, m, Ph), 5.06 (1 H, t, *J* 7, C=CHSi), 4.40 (2 H, d, *J* 7, $=CH_2$) and 0.40 (6 H, s, $SiMe_2$).



Scheme 5.

3.2. Silyl-cuprations (general procedure)

Typically, the alkyne or allene (1 mmol) in THF (3 ml) was injected into a stirred solution of the silyl-cuprate reagent [4] (1.1 mmol) in THF under argon at −78°C and the mixture stirred for 1 h. The mixture was quenched at −78°C with saturated aqueous ammonium chloride solution (10 ml) and allowed to warm to r.t. After 2 h the solution was extracted with diethyl ether (3 × 10 ml). The combined organic layers were washed with distilled water (3 × 10 ml), and brine (2 × 10 ml), dried ($MgSO_4$), and evaporated under reduced pressure. Chromatography [SiO_2, light petroleum (bp 30–40°C)] gave the products.

*3.3. Silyl-cupration of the allenylsilane **8***

Silyl-cupration of allenyldimethyl(phenyl)silane (0.2 g, 1.15 mmol) gave a 1:1 mixture (0.163 g, 46%) of 2,3-bis[dimethyl(phenyl)silyl]-1-propene (**10**), showing the signals (^{1}H-NMR) identical to those of the pure sample prepared below, and *E*-1,2-bis[dimethyl(phenyl)silyl]-1-propene (**11**) with diagnostic signals at δ_H(250 MHz; $CDCl_3$) 6.31 (1 H, q, *J* 1, =CHSi), 1.84 (3 H, d, *J* 1, =CMe) and 0.45–0.20 (12 H, 4 × s, 2 × Si*Me*$_2$Ph).

*3.4. E-1,3-Bis[dimethyl(phenyl)silyl]-1-propene (**12**)*

Silyl-cupration of propargyldimethyl(phenyl)silane (0.2 g, 1.15 mmol) gave the silane **12** (0.25 g, 69%); δ_H(250 MHz, $CDCl_3$) 7.58–7.26 (10 H, m, 2 × Ph), 6.08 (1 H, dt, *J* 18.4. and 7.76, CH_A=CH_BSi), 5.56 (1 H, dt, *J* 18.4 and 1.2, CH_A=CH_BSi), 1.91 (2 H, dd, *J* 7.76 and 1.2, CH_2Si) and 0.33 (12 H, s, 2 × Si*Me*$_2$Ph); δ_C(100 MHz, $CDCl_3$) 145.3+, 139.6+, 138.5−, 133.9+, 133.7+, 129.1+, 128.8+, 127.8+, 127.7+, 126.6+, 27.8−, −2.22+ and −3.34+ (+ =CH or CH_3, − =C or CH_2); *m*/*z* (EI) 310 (29%, M^+), 295 (13, M − Me), 175 (8, M − $SiMe_2Ph$), 160 (74, M − Me −

$SiMe_2Ph$) and 135 (100) $SiMe_2Ph$) (Found: M^+, 310.1572. $C_{19}H_{26}Si_2$ requires M, 310.1573).

*3.5. Silyl-cupration of the propargylsilane **6** with warming to room temperature before quenching*

The experiment was repeated, but the mixture was allowed to warm to r.t. and stirred for 1 h before being quenched with aqueous saturated ammonium chloride solution. The standard work-up gave the silanes **12** (48%) and 2,3-bis[dimethyl(phenyl)silyl]-1-propene (**10**) (32%); δ_H(400 MHz; $CDCl_3$) 7.57–7.25 (10 H, m, Ph), 5.53 (1 H, d, *J* 2.6, $=CH_ACH_B$), 5.34 (1 H, d, *J* 2.6, $=CH_ACH_B$), 1.86 (2 H, s, CH_2) and 0.33–0.20 (12 H, 4 × s, 2 × $SiMe_2Ph$); δ_C(100 MHz, $CDCl_3$) 146.8 −, 139.4 −, 138.3 −, 134.1 +, 133.7 +, 129.7 +, 129.5 +, 128.1 +, 127.9 +, 125.7 −, 23.85 −, −2.64 + and −3.02 + (+ =CH or CH_3, − =C or CH_2).

*3.6. E-1-[Dimethyl(phenyl)silyl]-3-(trimethylsilyl)-1-propene (**14**)*

Silyl-cupration of propargyltrimethylsilane (0.07 ml, 0.5 mmol) gave the silane **14**; R_f [light petroleum (b.p. 30–40°C)] 0.47; ν_{max}(film)/cm^{-1} 1950 (Ph), 1877 (Ph), 1813 (Ph), 1603 (C=C), 1426 ($SiMe_2$), 1250 ($SiMe_3$) and 1113 (SiPh); δ_H(400 MHz; $CDCl_3$) 7.58–7.48 (2 H, m, Ph), 7.43–7.26 (3 H, m, Ph), 6.16 (1 H, dt, *J* 18.4 and 7.8, $CH_A=CH_BSi$), 5.56 (1 H, dt, *J* 18.4 and 1.2, $CH_A=CH_BSi$), 1.69 (2 H, dd, *J* 7.8 and 1.2, CH_2Si), 0.33 (6 H, s, $SiCMe_2Ph$) and 0.03 (9 H, s, $SiMe_3$); δ_C(100 MHz; $CDCl_3$) 146 +, 139.8 −, 133.9 +, 128.8 +, 127.8 +, 125.5 +, 28.8 −, −2.1 + and −3.9 + (+ =CH or CH_3, − =C or CH_2), identical (^{1}H-NMR) with the known compound [5].

*3.7. Silyl-cupration of the propargylsilane **13** with warming to room temperature before quenching*

The experiment was repeated, but the mixture was allowed to warm to r.t. and stirred for 1 h before being quenched with aqueous saturated ammonium chloride solution. After 2 h, the solution was worked up as before to give a mixture (3:1) of the silanes **14** and **15**; δ_H(400 MHz; $CDCl_3$) showed the signals of the allylsilane **14** together with the following diagnostic signals for 2-dimethyl(phenyl)silyl-3-trimethylsilyl-1-propene (**15**) [6]: δ_H(250 MHz; $CDCl_3$) 5.55 (1 H, br d, *J* 2.8, $=CH_AH_B$), 5.31 (1 H,br d, *J* 2.8, $=CH_ACH_B$), 1.64 (2 H, d, *J* 1 CH_2Si) and −0.1 (9 H, s, $SiMe_3$).

*3.8. 2-Dimethyl(phenyl)silylpropene (**16**)*

The mixture of silyl-cupration products **14** and **15** was stirred with trifluoroacetic acid (three equivalents) in dichloromethane (2 ml) at r.t. for 3 h, conditions that completely protodesilylated the isomer **14**. The mixture was washed with sodium carbonate solution (2 N, 10 ml), dried ($MgSO_4$) and evaporated under reduced pressure to give only the vinylsilane **16**; δ_H(250 MHz; $CDCl_3$) 7.67–7.48 (2 H, m, Ph), 7.43–7.28 (3 H, m, Ph), 5.69 (1 H, q, *J* 1.3, $CH_AH_B=CSi$), 5.35 (1H, q, *J* 1.3, $CH_AH_B=CSi$), 1.84 (3 H, t, *J* 1.3, CMe) and 0.42 (6 H, s, $SiMe_2Ph$) identical (^{1}H-NMR) with the known compound [1].

3.9. E-1-Dimethyl(phenyl)silyloctene

1-Octyne (0.11 ml, 0.8 mmol) was injected over a stirred solution of the silyl-cuprate reagent (0.8 mmol) under argon at −78°C and the mixture stirred for 1 h. The mixture was allowed to warm to r.t. and stirred for 1 h before being quenched with aqueous saturated ammonium chloride solution (10 ml). The standard aqueous work-up gave only the 1-silyloctene; R_f [light petroleum (bp 30–40°C)] 0.51; δ_H(250 MHz; $CDCl_3$) 7.55–7.25 (5 H, m, Ph); 6.11 (1 H, dt, *J* 18 and 6, $CH=CHSi$), 5.74 (1 H, dt, *J* 18 and 1.6, $CH=CHSi$), 2.15 (2 H, m, $CH_2CH=CHSi$), 1.43–1.20 (8 H, m, 4 × CH_2), 0.88 (3 H, t, J 7, CH_2Me) and 0.3 (6 H, s, $SiMe_2$), closely similar to the lower homologue (*E*)-1-dimethyl(phenyl)silylhexene [2] and the higher homologue (*E*)-1-dimethyl(phenyl)silyltridecene [7].

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