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New Findings on the Regiochemistry of the Silylcupration of Allene

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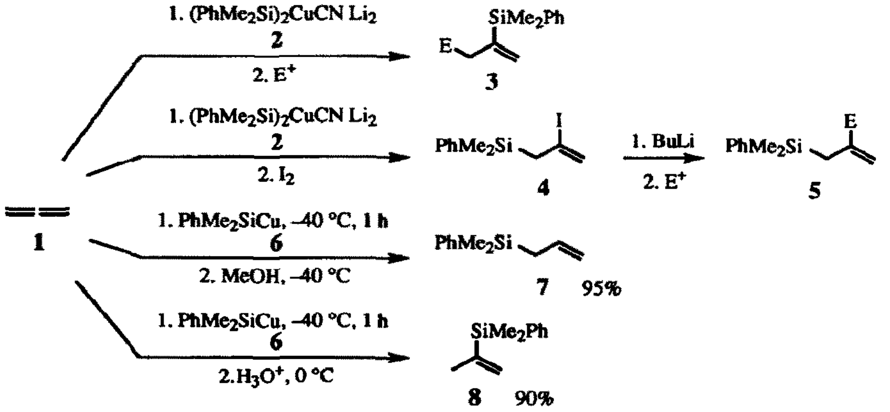
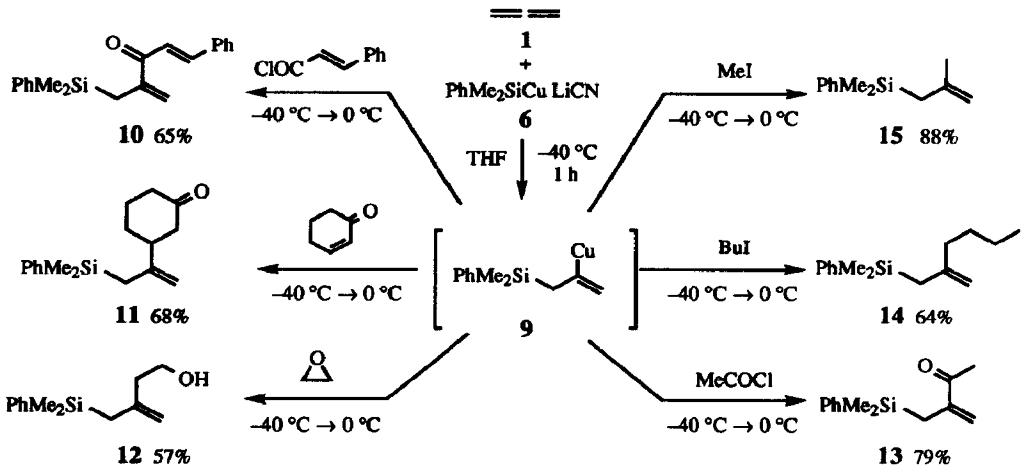
Abstract Allene **1** reacts at –40 °C with the phenyldimethylsilylcopper reagent **6**, with the opposite regioselectivity to that shown by the corresponding silylcuprate reagent **2**, to give allylsilanes **7** and **10-15** rather than vinylsilanes.

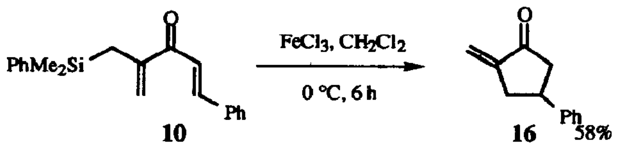
We reported earlier,[1,2] that lithium bis(phenyldimethylsilyl)cuprate **2** reacts stereospecifically with allenes by *syn* addition of the silyl and copper groups to one of the double bonds to give, after the addition of an electrophile, allyl- or vinylsilanes. The addition is usually regioselective, with the formation of allyl- or vinyl-silanes determined by the substitution pattern of the allene[1] but not by the temperature. The reaction of the silylcuprate reagent **2** with allene itself **1** almost invariably gives vinylsilanes **3** both at low (–78 °C) and at high (0 °C) temperatures. The only exception to this general rule is the reaction with iodine as the electrophile, when the product is the allylsilane **4**, instead of the vinylsilane **3** (E=I). The reversibility of the reaction may or may not be the reason for this striking anomaly.[1] The iodine in the allylsilane **4** can be exchanged for lithium, which can be replaced by an electrophile, thereby allowing the synthesis of a limited range of allylsilanes **5**, regioisomeric with the vinylsilanes **3**. Hitherto, this multistep sequence had been the best method[3] for controlling regiochemistry.

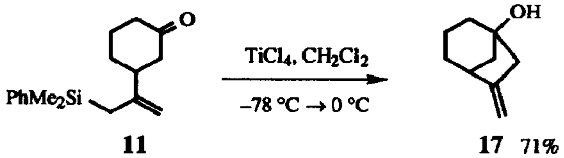


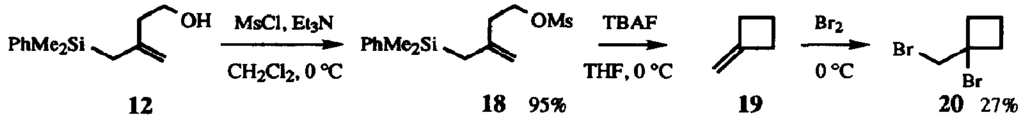
We now report a better solution to this problem: the phenyldimethylsilyl-copper reagent **6**, prepared by mixing one equivalent of phenyldimethylsilyl-lithium and one equivalent of copper(I) cyanide at 0 °C in THF, although less reactive, requiring a temperature of –40 °C for the silyl-cupration step, shows the opposite regiochemistry at this temperature to that of the corresponding cuprate reagent. It also shows a temperature dependence, giving the allylsilane **7** after protonation with methanol at –40 °C, but the vinylsilane **8** at 0 °C.

In addition to the proton, several of the more common carbon electrophiles react between –40 °C and 0 °C with the allylsilane-vinylcopper intermediate **9** to give goods yields of the allylsilanes **10-15**. The allylsilane unit is in many ways a more useful carbon nucleophile than the vinylsilanes that we were able to make so easily before. We exemplify this point with three examples of allylsilane-terminated cyclisations using the allylsilanes **10-12**, two Lewis acid-catalysed, giving the ketone **16** and the alcohol **17**, each based on known types of allylsilane reaction,[4] and one unprecedented fluoride ion-catalysed alkylation, giving the cyclobutane **19**, which we isolated as its dibromide **20**.









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3 The corresponding reactions with the bis(t-butyldiphenylsilyl)cuprate provide another method for regiocontrol.[5] They allow control of regiochemistry by appropriate choice of temperature at which the electrophile is added. Allylsilanes are the major products at low temperatures and vinylsilanes at higher temperatures. Unfortunately, the synthetic usefulness of these allylsilanes and vinylsilanes is severly compromised by the poor nucleofugal properties of the hindered silyl group.

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