Reaction of a Silyl–Copper Reagent with Acetylenes: a New Synthesis of Vinylsilanes†

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Summary A silyl-cuprate reagent adds regioselectively to terminal acetylenes and the intermediate (**3**) reacts with electrophiles to give 2,2-disubstituted vinylsilanes.

We reported earlier that a silyl-copper reagent prepared by mixing dimethylphenylsilyl-lithium and copper(I) iodide reacted with enones to produce, after work-up, β-silyl carbonyl compounds.[1] We now report that silyl-copper reagents react with terminal acetylenes. The silyl-copper reagent, prepared by mixing one equivalent of dimethylphenylsilyl-lithium with one equivalent of copper(I) cyanide, reacted with hex-1-yne (**1**) in 20 min at 0 °C in tetrahydrofuran (THF). Aqueous work-up then gave a 1:2 mixture of the vinylsilanes, (**2**) and (**4**). However, the silyl-copper reagent, prepared by mixing two equivalents of dimethylphenylsilyl-lithium with one of copper(I) cyanide reacted regioselectively with hex-1-yne in $<$ 20 min at 0 °C to give, after aqueous work-up, only ($>$99:1 by g.l.c.) the vinylsilane (**4**) in 94% yield. This regioselectivity is the opposite of that found by Normant[2] in the reactions of organo-copper reagents with terminal acetylenes.

The intermediate vinyl-copper reagent (**3**) reacted stereospecifically with a wide range of electrophiles, as illustrated in the Scheme. These reactions make available a variety of 2,2-disubstituted vinylsilanes, a class of vinylsilane which has hitherto been comparatively inaccessible.[3,4] That the reactions are stereospecific is shown by the production of the isomeric vinylsilanes (**5**) and (**8**). The stereochemistry of these two vinylsilanes was confirmed by comparison of the chemical shifts of the *C*-methyl hydrogens with those of *E*- and *Z*-1-dimethylphenylsilylpropene, (**9**) and (**11**), made by the routes shown in the Scheme. 2,2-Disubstituted vinylsilanes are also available using the stereospecific reaction of organocuprates with the vinyl iodide (**7**), as shown by the alternative syntheses of (**5**) and (**6**) in the Scheme.

The following notes clarify some of the finer points. (i) Use of copper(I) bromide–dimethyl sulphide[5] in place of copper(I) cyanide gave a reagent of opposite but not high (*ca.* 1:3) regioselectivity. (ii) The adduct (**3**) was configurationally stable (for at least 5 h at 0 °C), but the adduct (**10**) was not. Quenching (**10**) with methyl iodide after 2 min at -23 °C gave only (**11**), but quenching after 30 min at 0 °C gave the *trans*-isomer (**9**) as the major product. (iii) An excess of alkyne must be avoided, because it protonates the organo-copper intermediate. Thus a ten-fold excess of acetylene completely protonated (**10**) + (**12**) in $<$ 40 min at 0 °C. Hex-1-yne was slower, taking 5 h at 0 °C to protonate (**3**) completely. (iv) An excess of silyl-copper reagent should be avoided, because the excess can react with many of the electrophiles. (v) The proton on C-1 of hex-1-yne is not removed during the reaction, quenching (**3**) with D_2O gave only the monodeuterio product 2-deuterio-1-(dimethylphenylsilyl)hexene. In contrast, dialkylcuprates remove the proton from alk-1-ynes (other than acetylene itself) faster than they add.[2,6] (vi) However, when we deliberately removed the proton from C-1 (with butyl-lithium) the subsequent reaction with the silylcuprate reagent still took place with high (5:1) regio-

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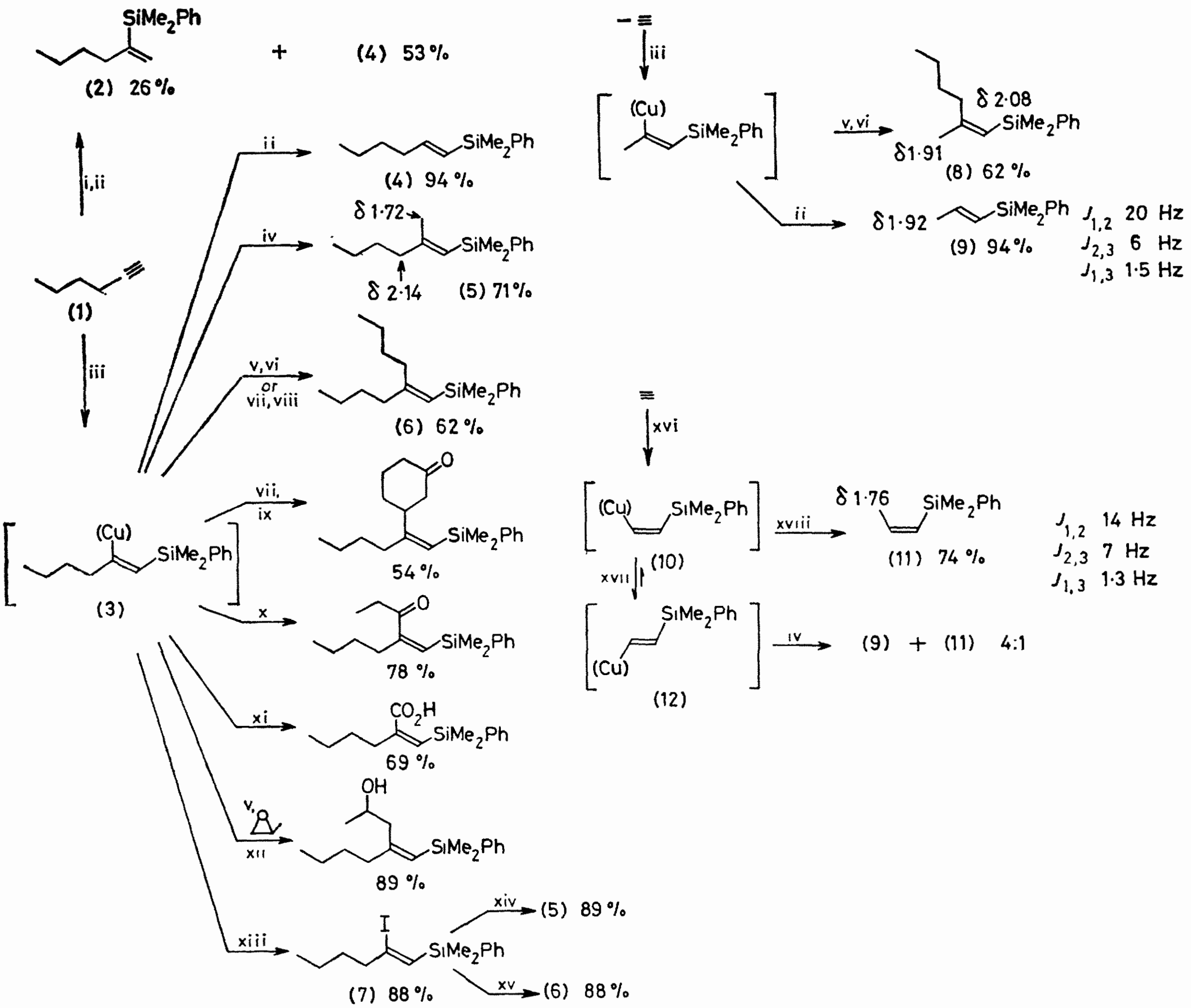
† There are no reprints of this paper.



SCHEME. *Reagents:* i, PhMe$_2$SiCu.LiCN, 0 °C, 20 min; ii, NH$_4$Cl, H$_2$O; iii, (PhMe$_2$Si)$_2$CuLi.LiCN, 0 °C, 20 min; iv, MeI, 0 °C, 40 min; v, hex-1-ynyl-lithium, −78 °C, 5 min; vi, Bu^{n}I −78 °C, 30 min, then −8 °C, 30 h, then 20 °C, 1 h; vii, hexamethylphosphoric triamide (HMPT) (2 equiv.), −23 °C, 2 min; viii, Bu^{n}I, −23 °C, 1 h, then −8 °C, 16 h; ix, cyclohexenone, −23 °C, 80 min; x, EtCOCl, 0 °C, 3 h; xi, CO$_2$, 0 °C, 1 h; xii, −78 °C, 20 min, then −8 °C, 68 h; xiii, I$_2$, 0 °C, 2 h; xiv, Me$_2$CuLi.LiCN, 0 °C, 1 h; xv, Bu$^n_2$CuLi.LiCN, 0 °C, 1 h; xvi, (PhMe$_2$Si)$_2$CuLi.LiCN, −23 °C, 2 min; xvii, 0 °C, 30 min; xviii, MeI, −23 to 0 °C, 30 min.

selectivity, and work-up with D$_2$O gave *E*-1,2-dideuterio-1-(dimethylphenylsilyl)hexene in *ca.* 80% yield.

Dimethylphenylsilyl-lithium[7] was prepared by vigorously stirring dimethylphenylchlorosilane[8] (12·5 mmol) and lithium (30 mmol, Fisons shot) in THF (25 ml) at −8 °C for 36 h. This solution (10 mmol) was added to dry copper(I) cyanide (5 mmol) at 0 °C and the mixture stirred for 20 min at 0 °C. Hex-1-yne (4·5 mmol) in THF (1 ml) was then added and the mixture stirred for 20 min at 0 °C.

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