The Syntheses of Allylsilanes and Vinylsilanes by Silyl-cupration of Allenes†

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Allenes react with silyl-cuprate reagents to give either allylsilanes or vinylsilanes, depending upon the substituents on the allene.

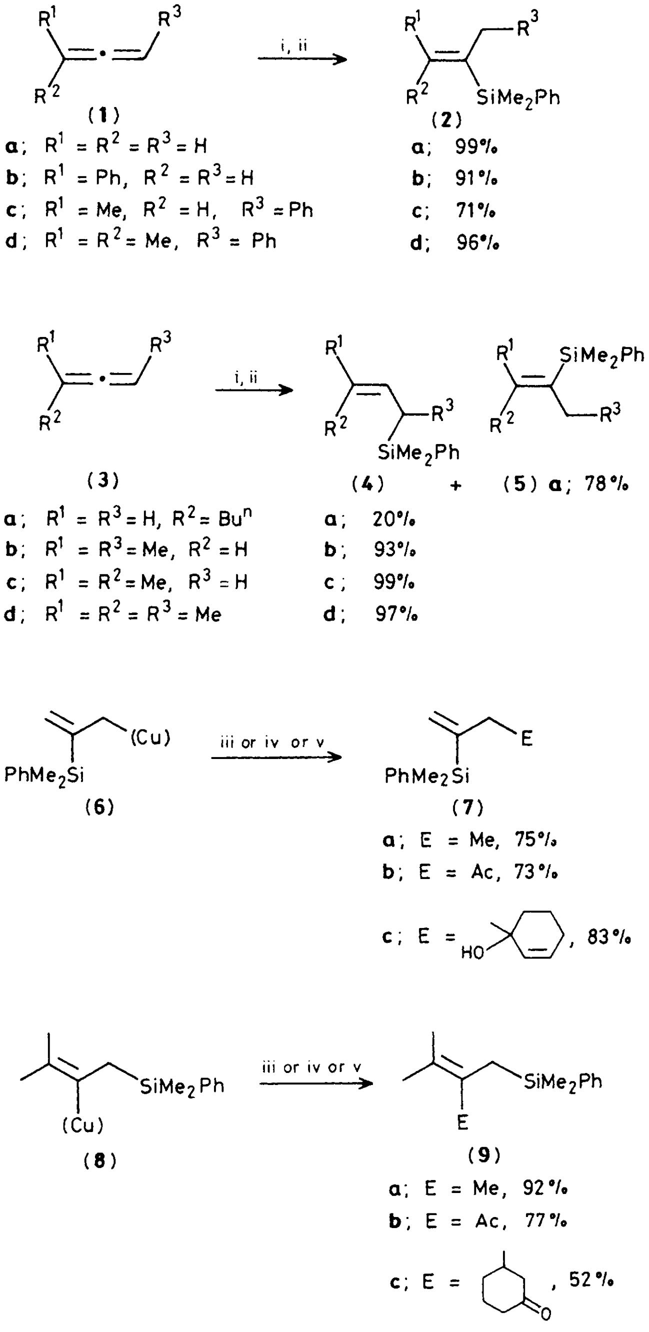
We reported earlier that our phenyldimethylsilylcuprate reagent reacts with α,β-unsaturated carbonyl compounds,[1] with acetylenes,[2] and with tertiary[3] and secondary[4] allylic acetates. In all these reactions, and in a similar reaction with acid chlorides,[5] the silyl-cuprate reagent is effectively a nucleophilic silicon species, which reacts much as alkyl-cuprates react with the same electrophiles. We now report a reaction which has no counterpart in alkyl-cuprate chemistry.

Bis(phenyldimethylsilyl)cuprate, prepared, as usual, from phenyldimethylsilyl-lithium and copper(I) cyanide,[3] reacts with allenes at dry-ice acetone temperatures within one hour, presumably by *syn* addition of the silyl and copper groups across one of the double bonds of the allene. The addition is remarkably selective, the allenes falling into two groups, one giving vinylsilanes (and allyl-copper intermediates), the other giving allylsilanes (and vinyl-copper intermediates).

Allene itself (**1a**) and the phenylallenes (**1b**—**d**) fall into the first group, each giving a single vinylsilane (**2a**—**d**) in high yield on quenching with ammonium chloride solution and methanol. The stereochemistry of the double bond in the vinylsilanes (**2b**) and (**2c**) is cleanly (*E*) [as shown by protodesilylation[6] giving the (*Z*)-alkene], as a result of the silyl-cuprate attacking the less-substituted face of the allene. The quenching of the unsymmetrical allyl-copper species is also completely selective for the formation of the more-substituted alkenes (**2b**—**d**).

Simple alkylallenes fall into the second group, the di- and tri-alkylallenes (**3b**—**d**) reacting with the silyl-cuprate reagent to give cleanly the allylsilanes (**4b**—**d**) in high yield after quenching with ammonium chloride solution and methanol. Only the monoalkylallene (**3a**) gives mixtures of regioisomers, favouring the vinylsilane (**5a**) over the allylsilane (**4a**) (4 : 1). The allylsilanes (**4b**) are a mixture of (*E*)- and (*Z*)-isomers,[4] in a ratio of 3 : 1, which is surprising because it corresponds to a preference for attack of the silyl-cuprate reagent on the more substituted face of the allene (if the addition is *syn* and the stereochemistry of the vinyl-copper intermediate is retained). When we warmed the reaction mixture to 0 °C before quenching it, the ratio was little changed (1.7 : 1). The addition of the silyl-cuprate reagent appears to be reversible: when we treated trimethylallene (**3d**) with the reagent at dry-ice acetone temperature, and quenched the intermediate at this temperature, we got only the allylsilane (**4d**); however, when we repeated the experiment, and then warmed the mixture up to 0 °C for one hour before quenching it (either at 0 °C or at dry-ice acetone temperature), we got a mixture of the allylsilane (**4d**) and the vinylsilane (**5d**) in a ratio of 55 : 45 and in 95% yield. We note in these reactions that the regioselectivity is clean not only in the sense that an allylsilane (and vinyl-copper) is formed, but also that the silyl group is selectively placed at the less substituted end of unsymmetrical allyl groups. The degree of regioselectivity of every kind seen in this work is remarkable, in view of the opportunity the reaction presents for the formation of mixtures.

The reaction is not restricted to the introduction of the phenyldimethylsilyl group. As we have shown for the other electrophiles,[7] the bis(trimethylsilyl)cuprate reacts in the same way as the more easily made bis(phenyldimethylsilyl)-cuprate, even though the former has hexamethylphosphor-



Scheme 1. *Reagents:* i, $(PhMe_2Si)_2CuLi$, tetrahydrofuran, −78 °C, 1 h; ii, NH_4Cl, H_2O, MeOH, −78 °C; iii, MeI, −78 °C, 1 h, 0 °C, 1 h; iv, AcCl, −78 °C, 1 h, 0 °C, 1 h; v, cyclohexenone, hexamethylphosphoramide, −78 °C, 1 h, 0 °C, 1 h.

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† No reprints available.

amide in it. Allene (**1a**) and 1,1-dimethylallene (**3c**) give 2-trimethylsilylpropene[8] and 3,3-dimethylallyltrimethylsilane[9] in 91% and 97% yield, respectively.

Finally, we checked that the intermediate allyl- and vinyl-copper species react with electrophiles other than a proton. The allyl-copper intermediate (**6**), prepared from allene (**1a**), reacted cleanly with methyl iodide, acetyl chloride, and cyclohexenone (by attack at the carbonyl group), to give the vinylsilanes (**7a—c**), and the vinyl-copper intermediate (**8**), prepared from 1,1-dimethylallene (**3c**), reacted with the same electrophiles (with cyclohexenone giving conjugate addition), to give the allylsilanes (**9a—c**).

We conclude that allenes are a reliable source of allylsilanes and vinylsilanes with a wide variety of substitution patterns. The allylsilanes and vinylsilanes are themselves useful carbon nucleophiles,[10] and the phenyldimethylsilyl group can be replaced by a proton[11] or (after hydrogenation of the double bond) by a hydroxy group.[12]

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