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Silylcupration of Allenes and Subsequent Electrophilic Trapping by Allylic Phosphates. A Novel Approach to Silylated 1,4-Diene Systems

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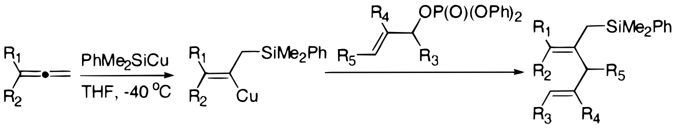
ABSTRACT



Silylcupration of allenes with a lower order silylcuprate reagent followed by an electrophilic trapping reaction with allylic diphenyl phosphates has been studied. This reaction provides a new route to 1,4-diene systems having an allylsilane moiety.

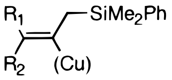
Recently the silylcupration of allenes has been thoroughly studied, mostly by Fleming and co-workers.[1] It is known that the silylcupration reaction is regioselective, with the formation of allyl- or vinyl-copper species depending on the substitution pattern of the allene.[2a,b] These copper intermediates can be trapped by a wide range of electrophiles such as alkyl halides, acyl halides, halogens, α,β-unsaturated ketones and esters, epoxides, and oxocompounds, thus providing a simple route to functionalized vinyl- or allylsilanes.[1] In most cases reported, the silylcupration of allenes is done by higher-order silyl-copper reagent **1**.[1] The regiochemistry of the silylcupration reaction is strongly dependent on the nature of the allene but not on the temperature.[1a,b]

$(PhMe_2Si)_2CuLi\cdot LiCN$ **1**

$(t\text{BuPh}_2Si)_2CuLi\cdot LiCN$ **2**

$PhMe_2SiCuCNLi$ **3**

Simple alkylallenes give vinylcopper adducts **4** with the exception of monosubstituted terminal alkylallenes, which give mixture of **4** and **5**.



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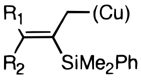

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Allene itself and the phenylallenes give allylcopper adduct **5** upon reaction with **1**.[1a,b] It has been demonstrated that by use of a more bulky silyl group attached to the copper it is possible to obtain the opposite regioisomer in the silylcupration reaction.[1d] Thus, by reaction of **2** with 1,2-propadiene, the addition product is a vinyl-copper species **4**. However, simple monoalkyl allenes gave a mixture of regioisomers, and phenylallenes were not suitable for the silylcupration reaction with **2** due to isomerization to acetylenes.[1d] Recently Pulido and co-workers reported the use of a lower-order silylcuprate reagent **3** in the silylcupration reaction of 1,2-propadiene.[3] This reagent, in analogy to the bulky reagent **2**, gives a vinylcopper species upon reaction with 1,2-propadiene at −40 °C in THF. However, only the reaction of the nonsubstituted 1,2-propadiene was investigated with **3**.

The reaction between different types of allylic substrates and cuprates or Grignard reagents under copper catalysis has

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[1] (a) Fleming, I.; Pulido, F. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1010. (b) Cuadrado, P.; Gonzalez, A. M.; Pulido, F. J.; Fleming, I. *Tetrahedron Lett.* **1988**, *29*, 1825. (c) Cuadrado, P.; Gonzalez, A. M.; Pulido, F. J.; Fleming, I.; Rowley, M. *Tetrahedron* **1989**, *45*, 413. (d) Barbero, A.; Cuadrado, P.; Gonzalez, A. M.; Pulido, F. J.; Fleming, I. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2811. (e) Fleming, I.; Landais, Y.; Raithby, P. R. *J. Chem. Soc., Perkin Trans. 1* **1991**, 715.

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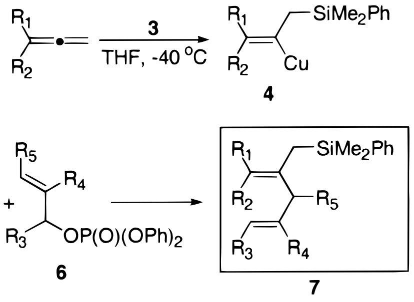
been well studied.[4] However, examples of the reactions of allylic substrates with copper species **4** and **5** are scarce.[1b]

We now report a reaction of lower order silylcopper reagent **3** with different allenes followed by electrophilic trapping of the generated organocopper intermediate by allylic phosphates.

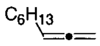
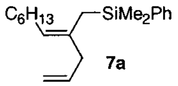
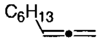
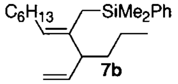
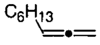
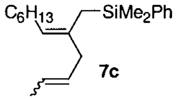
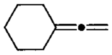
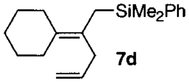
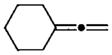
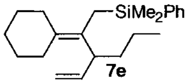
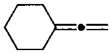
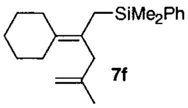
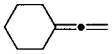
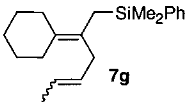
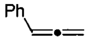
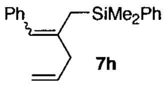
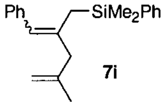
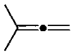
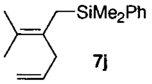
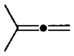
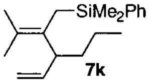
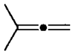
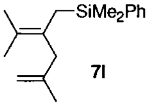
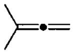
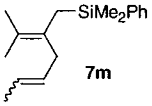
Electrophilic trapping reactions (Scheme 1) of the vinylcopper species **4** with a variety of electrophiles is well-known. However, little information is available on reactions with allylic substrates. To the best of our knowledge, only the reaction with allyl bromide has been studied.[1b]

Scheme 1



To our surprise the silylcopper reagent **3** was highly regioselective in the silylcupration reaction of allenes, and the regioselectivity did not follow the trends reported by Fleming et al.[1] concerning dependence on the allene structure in the reaction with **1** and **2**. The only observable silylcupration product in all cases studied was the vinylcopper species **4**. Our first attempt was aimed toward reaction of the vinylcopper species with allylic acetates. Unfortunately, these substrates were not suitable for this reaction due to low reactivity under the reaction conditions investigated (−40 °C, THF). Attempts to perform the reaction at higher temperature resulted in thermal decomposition of **4**. It has been reported that some Lewis acid additives can increase the reactivity of the cuprates,[2b,4] but in our case it did not result in any significant improvement. We then decided to switch to a better leaving group in place of acetate. Yamamoto has reported that the phosphate group is the most effective leaving group in allylic substitution reactions with cuprates and that it reacts mainly in an S_N2' manner with carbon nucleophiles.[5] Indeed, reaction of the vinylcopper species **4** with different allylic phosphates gave a clean and fast reaction in a complete S_N2' manner (Scheme 1, Table 1). We did not observe any S_N2 substitution reaction product, the reactions being completely S_N2'-selective.

Table 1. Allylation of Silylcuprated Allenes According to Scheme 1[a]

allene	phosphate	product	yield[b] (%)
	**6a** $R_3=R_4=R_5=H$	 **7a**	75
	**6b** $R_3=R_4=H$ $R_5=n\text{-}C_3H_7$	 **7b**	70
	**6c** $R_4=R_5=H$ $R_3=Me$	 **7c**	66 E+Z[c]
	**6a**	 **7d**	80
	**6b**	 **7e**	77
	**6d** $R_3=R_5=H$ $R_4=Me$	 **7f**	80
	**6c**	 **7g**	81 E+Z[c]
	**6a**	 **7h**	65 E+Z[c]
	**6d**	 **7i**	83 E+Z[c]
	**6a**	 **7j**	64
	**6b**	 **7k**	74
	**6d**	 **7l**	84
	**6c**	 **7m**	81 E+Z[c]

[a] Reactions were carried out according to the experimental procedure given.[7] [b] Isolated yields. [c] The E and Z isomers could not be separated.

The allene was treated with silylcuprate **3**[6] in THF at −40 °C for 1 h, and the vinylcopper species **4** generated was

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(2) (a) Blanco, F. J.; Cuadrado, P.; Gonzalez, A. M.; Pulido, F. J.; Fleming, I. *Tetrahedron Lett.* **1994**, *35*, 8881. (b) Barbero, A.; Garcia, C.; Pulido, F. J. *Tetrahedron Lett.* **1999**, *40*, 6649.

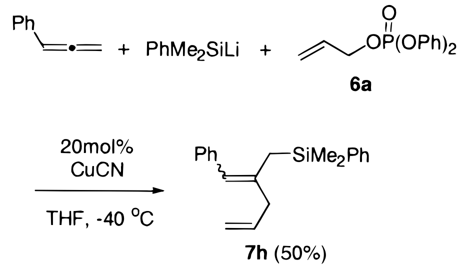
(3) (a) Posner, G. H. *Org. React.* **1975**, *22*, 253. (b) Lipshutz, B. H.; Sengupta, S. *Org. React.* **1992**, *41*, 135. (c) Bäckvall, J. E.; Sellen, M.; Grant, B. *J. Am. Chem. Soc.* **1990**, *112*, 6615. (d) Magid, R. M. *Tetrahedron* **1980**, *36*, 1901. (e) Goering, H. L.; Kantner, S. S. *J. Org. Chem.* **1984**, *49*, 422. (f) Underiner, T.; Goering, H. L. *J. Org. Chem.* **1991**, *56*, 2563, and preceding papers in this series. (g) Bäckvall, J. E.; Persson, E. S. M.; Bombrun, A. *J. Org. Chem.* **1994**, *59*, 4126. (h) Persson, E. S. M.; Bäckvall, J. E. *Acta Chem. Scand.* **1995**, *49*, 899. (i) Persson, E. S. M.; van Klaveren, M.; Grove, D. M.; Bäckvall, J. E.; van Koten, G. *Chem. Eur. J.*, **1995**, *1*, 351.

(4) (a) Yamamoto, Y. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 947. (b) Yamamoto, Y.; Yamamoto, S.; Yatagai, H.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 2318. (c) Yamamoto, Y.; Yamamoto, S.; Yatagai, H.; Ishihara, Y.; Maruyama, K. *J. Org. Chem.* **1982**, *47*, 119.

allowed to react with the appropriate allylic diphenyl phosphate at the same temperature for 1 h (Scheme 1, Table 1).[7] In all cases studied, only one regioisomer was observed as a result of a highly selective S_N2' substitution of the allylic phosphate. In some cases, double bond isomers were formed. For example, allylic phosphate **6c** gave a mixture of E and Z isomers (Table 1, products **7c**, **7g**, and **7m**). A striking difference can also be seen between 1,2-nonadiene and 1-phenyl-1,2-propadiene in the tandem silylcupration-substitution reaction. The alkylallene gives a completely stereoselective reaction, (products **7a**−**c**), whereas phenylallene gives rise to a mixture of E and Z isomers (Table 1, products **7h** and **7i**). In all other cases studied, the reaction was selective for one product.

We are now studying the catalytic version of this reaction. Preliminary experiments using 20 mol % CuCN as catalyst and slow addition of $PhMe_2SiLi$ and allylic phosphate **6a** to the reaction mixture containing phenyl allene afforded **7h** in an isolated yield of 50%, which corresponds to 2.5 turnovers (Scheme 2). Further studies on this three-component catalytic transformation are underway in our laboratory.

Scheme 2



In conclusion, a novel short synthesis of allylsilane moiety containing 1,4-diene system has been developed. These products can be widely used in organic synthesis. The allylsilanes are well-known masked carbon nucleophiles that can be utilized in a number of reactions.[8] The phenyldimethylsilyl group can also be replaced by hydrogen[9] or converted to a hydroxy group.[10]

Acknowledgment. Financial support from the Swedish Natural Science Research Council and The Swedish Foundation for Strategic Research is gratefully acknowledged.

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[5] (a) Yanagisawa, A.; Noritake, Y.; Nomura, N.; Yamamoto, H. *Synlett*, **1991**, 251. (b) Yanagisawa, A.; Nomura, N.; Yamamoto, H. *Synlett*, **1993**, 689. (c) Yanagisawa, A.; Nomura, N.; Yamamoto, H. *Tetrahedron*, **1994**, *50*, 6017.

[6] Fleming, I. In *Organocopper reagents. A practical approach*; Taylor, R. J. K., Ed.; Oxford University press: New York, 1994; Vol. 12, p 257.

[7] A total of 0.5 mmol of $PhMe_2SiLi$ (~1 M solution in THF) was added to a stirred suspension of CuCN (1 equiv) in dry THF (0.3 mL) at 0 °C and stirred at this temperature for 30 min. Then the mixture was cooled to −40 °C and 1,2-nonadiene (1 equiv) was added dropwise and reaction mixture was stirred for 1 h at this temperature. Then allylic phosphate **6a** (1.1 equiv) in 0.2 mL of THF was added slowly over 15 min. After the reaction mixture had been stirred for 1 h at −40 °C, 3 mL of saturated aqueous NH_4Cl was added and the aqueous phase was extracted with pentane (4 × 3 mL). Column chromatography on silica with pentane as eluent afforded compound **7a** as a colorless oil in 75% yield. $R_f = 0.53$ (hexane). ^1H NMR ($CDCl_3$ 400 MHz): δ 7.55 (m, 2H), 7.38 (m, 3H), 5.75 (ddt, $J = 17, 10.1, 6.8$ Hz, 1H), 5.07 (tquintet, $J = 6.8, 1$ Hz, 1H), 4.99 (ddt, $J = 10.1, 2.2, 1.1$ Hz, 1H), 4.93 (ddt, $J = 17, 2.2, 1.5$ Hz, 1H), 2.58 (dq, $J = 6.78, 1.3$ Hz, 2H), 1.88 (m, 2H), 1.78 (s, 2H), 1.28 (m, 8H), 0.92 (t, $J = 7.15$ Hz, 3H), 0.34 (s, 6H).^{13}C NMR ($CDCl_3$ 75.4 MHz): δ 139.5, 137.4, 134.3, 133.6, 128.9, 127.8, 124.1, 115.7, 43.9, 32.1, 30.1, 29.4, 28.9, 23.0, 20.8, 14.4, −1.9. MS (EI): m/z (rel) 300 (22.5, M^+), 299 (35), 285 (57), 224 (69), 223 (74), 136 (82), 135 (100).

[8] (a) Hosomi, A.; Sakurai, H. *J. Am. Chem. Soc.* **1977**, *99*, 1673. (b) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. (c) Fleming, I. *Tetrahedron* **1988**, *44*, 3761. (d) Fleming, I.; Dunogues, J.; Smithers, R. *Org. React.* **1989**, *37*, 57. (e) Castaño, A. M.; Persson, B. A.; Bäckvall, J. E. *Chem. Eur. J.* **1997**, *3*, 482.

[9] Oda, H.; Sato, M.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1983**, *24*, 2877.

[10] (a) Kumada, M.; Tamao, K.; Yoshida, J.-I. *J. Organomet. Chem.* **1982**, *239*, 115. (b) Tamao, K.; Kakui, T.; Akita, M.; Iwahara, T.; Kanatani, R.; Kumada, M. *Tetrahedron*, **1983**, *39*, 983. (c) Fleming, I.; Henning, R.; Plaut, H. *J. Chem. Soc., Chem. Commun.* **1984**, 28.