Tetrahedron Letters,Vol.30,No.44,pp 6067-6070,1989
Printed in Great Britain

0040-4039/89 $3.00 + .00
Pergamon Press plc

ALLYLSILANES DERIVED FROM α- AND β-IONONE. SYNTHESIS AND UNUSUAL REACTIVITY WITH ELECTROPHILES

Elisabetta Azzari, Cristina Faggi, Nedo Gelsomini and Maurizio Taddei*

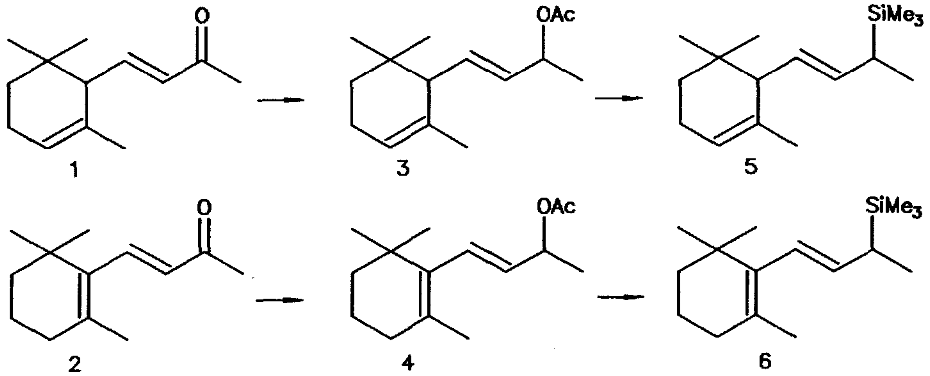
Dipartimento di Chimica Organica "Ugo Schiff", Università di Firenze,
Via G.Capponi 9 I-50121 Firenze Italy

Summary . *Silylcupration of α- and β-ionol acetates selectively gave the corresponding allylsilanes with direct substitution of the acetate with a trimethylsilyl group. Reactions of these products with electrophiles showed the unusual absence of the allylic shift, typical in nucleophilic condensations of allylsilanes. Ionotrimethylsilanes are effective building blocks for synthesis of terpenes and carotenoids.*

Ionones are useful starting materials in natural product synthesis.[1] They are commercially available in large quantities at a relatively reasonable price;[2] α-ionone can be also provided in an optically active form.

Starting from α- and β-ionone (**1** and **2**), we report the regio- and stereocontrolled preparation of the corresponding ionotrimethylsilanes (**5** and **6**) as described in scheme 1.

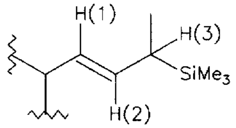
Ionones **1** and **2** were reduced with $NaBH_4/MeOH$ to the corresponding ionoles, which were further transformed with Ac_2O/Et_3N into the allylic acetates **3** and **4** in yields ranging from 75 to 85%.



Scheme 1

Acetates **3** and **4** underwent a regio- and stereocontrolled silylcupration with $(Me_3Si)_2Cu(CN)Li_2$ giving allylsilanes **5** and **6** respectively in 76 and 84% yields.

Products **5** and **6** were isolated by column chromatography and their isomerical purity was checked by capillary gas chromatography and the structure elucidated by ^1H NMR spectroscopy.[3]



The assignment was based on the multiplicity of the H(2) signal, as a doublet of doublets collapsing to a clean doublet by irradiation of H(1). Values of $J_{H(1)H(2)}$ (16 Hz for **5** and 17 Hz for **6**) confirmed the presence of the E isomer.

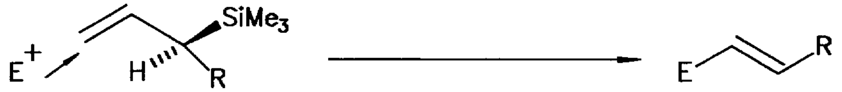
The stereocontrol in the reaction can be related to the structure of the acetates **3** and **4**. Position 1 is particularly hindered, as revealed by examination of molecular models, forcing the silylcuprate to "direct" nucleophilic substitution at the saturated C(2).

Fleming reported[4] silylcupration of secondary allylic acetates, showing that E allylic acetates give largely the allylsilane with the silyl group at the less hindered end of the allylic fragment, but with a low degree of selectivity and mediocre yields.

The structures of **3** and **4** can be considered responsible for the observed selectivity. We also suggest that the good yields can be ascribed to the presence of HMPA used in the preparation of the trimethylsilylcuprate.[5,6]

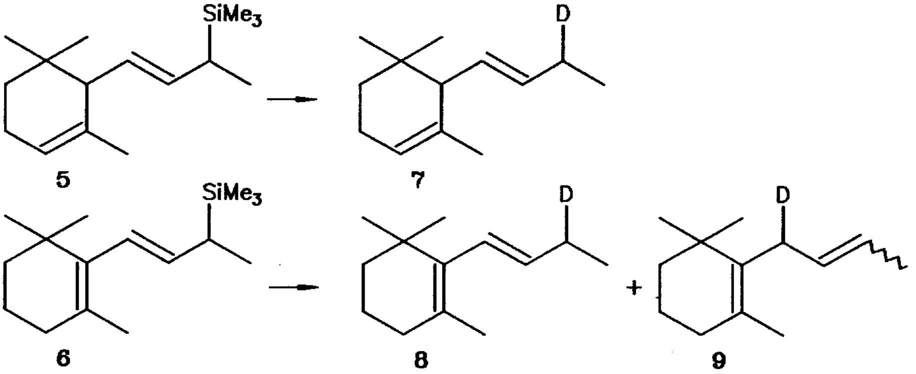
Finally we observed that both trimethylsilyl groups of $(Me_3Si)_2Cu(CN)Li_2$ were effectively transferred to the organic substrates, and that this behavior seems to be a general feature of trimethylsilylcuprate.[6]

The characteristic structure of α- and β-ionotrimethylsilane greatly affects their reactivity. Allylsilanes usually react with electrophiles in the stereochemical sense[7] described in scheme 2, characterized by attack of the electrophile at the double bond (γ to the silicon) with a subsequent allylic shift.



Scheme 2

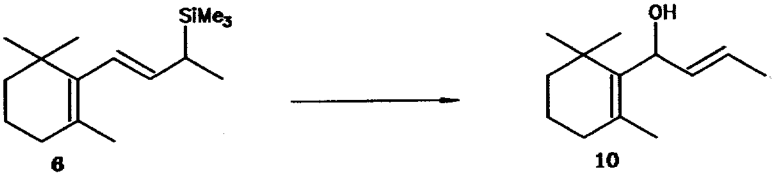
Allylsilanes **5** and **6** reacted even with a small electrophile such as D^+ (DCl/D_2O in THF, r.t., 1 h.), mainly at position 3 as described in scheme 3.



Scheme 3

An even larger difference between **5** and **6** was observed in reactions with MCPBA.

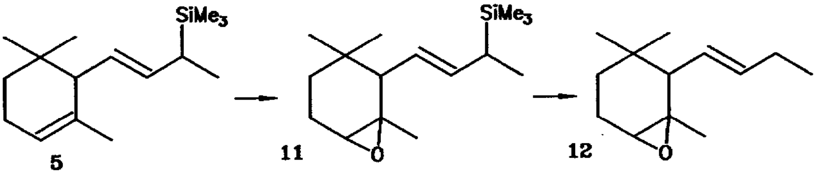
Allylsilane **6** reacted in the usual sense, giving, after treatment with TBAF (MCPBA 85% in CH_2Cl_2, r.t., 2 h., isolation of the crude, then TBAF $3H_2O$ in THF, r.t., 24 h.) alcohol **10** with complete regio- and stereochemical control in 65% yield (scheme 4).



Scheme 4

Epoxidation of the endocyclic double bond of **5** was selective, giving **11** (scheme 5).

Further treatment of product **11** with TBAF gave product **12**, once more characterized by the absence of the allylic shift (scheme 5).



Scheme 5

Finally the low reactivity of the position 4 of allylsilane **5** was confirmed in the $TiCl_4$ mediated condensation with acetaldehyde ($TiCl_4$/CH_3CHO in CH_2Cl_2 added at -78°C to **5**, quench at -50°C with Et_2O/NH_4Cl) which gave **13** as the sole product in 61% yield (scheme 6).

Scheme 6

Reaction of allylsilanes with electrophiles at the carbon carrying the trimethylsilyl group has not been documented before,[8] to our knowledge, and with ionotrimethylsilanes, this unusual reactivity seems very promising in the contest of terpene and carotenoid synthesis because the stereochemistry around the double bond remains unchanged. Projects based upon this idea are currently under way in our laboratories.

Acknowledgment. *This work was financially supported by CNR (Rome). E.A. and C.F. thank the "Consorzio del Vino Chianti Gallo Nero" and the "Cassa di Risparmio" (Florence) for a grant.*

REFERENCES AND NOTES

1) C.f. Isoe, S. Natural Product Chemistry '80A, Kagaku no Ryoiki Zokan no. 125, Nankodo, Tokyo (1980). Katsumura, S.; Kimura, A.; Isoe, S. Tetrahedron, **1989**, 45, 1337. Solladiè, A.; Girardin, A.; Lang, G. *J.Org.Chem.* **1989**, *54*, 2620.

2) For example, the price of α-ionone **2** is 55 Sfr. for 250 mL on Fluka Catalogue 88/89.

3) Typical procedure : To a solution of trimethylsilylcuprate (1.50 mmol) in THF (5 mL), prepared according to ref.6, cooled at -78°C, was added acetate **3** (650 mg, 2.75 mmol) in THF (1 mL), the mixture allowed to warm to room temperature overnight and added to Et_2O (25 mL) and to a solution of NH_4Cl/NH_4OH (5 mL), placed in a separatory funnel. The organic layer was separated, washed with brine and dried (Na_2SO_4). Removal of the solvent and purification by column chromatography on silica gel (eluant: hexane) gave 520 mg of **5** (76% yield).

5 ^{1}H NMR ($CDCl_3$, 300 mHz) -0.079 (s, 9H), 0.758 (s, 3H), 0.823 (s, 3H), 0.991 (d, 3H, J=7.2 Hz), 1.12 (m, 1H), 1.34 (m, 1H), 1.50(m, 1H), 1.536 (s, 3H), 1.94 (m, 2H), 2.013 (d, 1H, J=9 Hz), 4.946 (ddd, 1H, J_1=16 Hz, J_2=9 Hz, J_3=1 Hz, H(1)), 5.31 (m, 1H), 5.356 (ddd, 1H, J_1=16 Hz, J_2=10 Hz, J_3=1 Hz, H(2)). MS m/e 250 (M^+), 73 (base). Anal. Calcd. for $C_{16}H_{30}Si$: C, 76.77; H, 12.07. Found: C, 76.07; H, 12.10.

6 . Obtained, after column chromatography, 580 mg (84% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) -0.050 (s, 9H), 0.926 (s, 3H), 0.931 (s, 3H), 1.044 (d, 1H, J=7 Hz), 1.39 (m, 2H), 1.42 (m, 2H), 1.53 (m, 3H), 1.620 (s, 3H), 1.91 (m, 2H), 5.326 (dd, 1H, J_1=17 Hz, J_2=10 Hz, H(2)), 5.593 (d, 1H, J=17 Hz, H(1)). MS m/e 250 (M^+), 73 (base). Anal. Calcd. for $C_{16}H_{30}Si$: C, 76.77; H, 12.07. Found: C, 76.36; H, 12.11:

4) Fleming, I.; Thomas, A.P. *J.Chem.Soc.Chem.Commun.* **1985**, 411.

5) Hudrlick, P.F.; Wangh, M.A.; Hudrlick, A.M. *J.Organomet.Chem.* **1984**, *271*, 69.

6) Capella, L.; Degl'Innocenti, A.; Reginato, G.; Ricci, A.; Taddei, M.; Seconi, G. *J.Org.Chem.* **1989**, *54*, 1473.

7) See : Fleming, I.; Lawrence, N.J. *Tetrahedron Lett.* **1988**, *29*, 2077 and references therein.

8) The effects of the substituents at the opposite end to silicon in allylsilanes, in the reaction with electrophiles, are currently under way in our laboratories. See : Mordini, A.; Palio, G.; Ricci, A.; Taddei, M. *Tetrahedron Lett.* **1988**, *29*, 4991.

(Received in UK 15 September 1989)