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THE STEREOSPECIFIC SYNTHESIS OF VINYLSILANES AND 1-HALOGENO-VINYLSILANES FROM TRIPHENYLSILYLACETYLENE.

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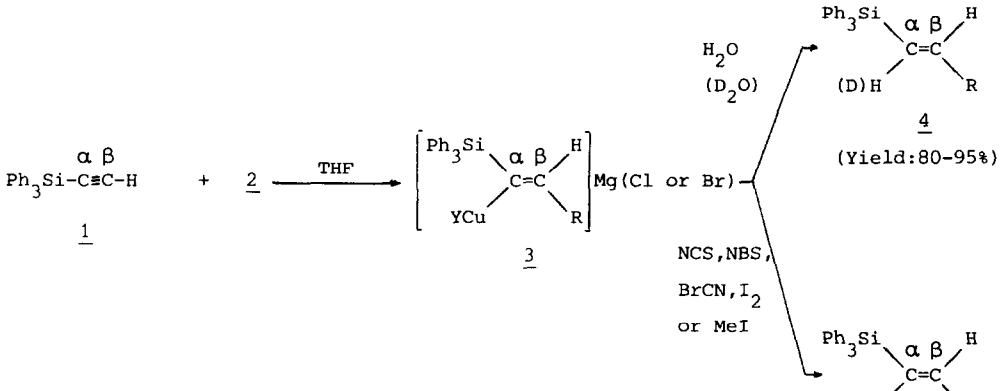
Recently several applications of vinylsilanes as precursors for various carbonyl compounds have been published [1-4] .The related α-silylated vinylcuprates are very useful acyl anion equivalents and can be applied f.i. in conjugate addition reactions [5] . Hitherto these vinylic cuprates have been prepared from the corresponding vinyllithium compounds , which can be obtained from the α-bromosilanes by metal halogen exchange (cf[5]).
In this paper we wish to report a direct synthesis of α-silylated vinylcuprates starting from the easily available triphenylsilylacetylene (1) and organocuprates [RCuY]Mg(Cl or Br) (2) in the solvent tetrahydrofuran (THF) :



R = Et , i-Pr , c-Hexyl or t- Bu
Y = R or Br

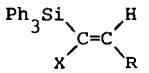
5 : X = Cl
6 : X = Br
7 : X = I
8 : X = Me

The addition of 2 to 1 occurs exclusively in a *cis* - manner as can be concluded from the ^3J(H-H) coupling in 4 : f.i. $^3J(H_1-H_2)$ in $Ph_3SiCH=CH(t\text{-}Bu)$ amounts 18,9 Hz,

which is characteristic for a *trans* orientation.
The compounds 5-8 are accessible from reaction of 3 with N-chlorosuccinimide (NCS) [6], N-bromosuccinimide (NBS) or cyanogenbromide, iodine and methyl iodide respectively.

A typical procedure is as follows :

To 0.010 mole of the cuprate 2 , prepared as described previously [7,8] in 30 ml of dry THF at -50°C - -60°C , a solution of 0.009 mole of 1 in 10 ml of dry THF was added. After stirring during 15 minutes at - 50°C , the temperature was slowly raised to +20°C. The reaction with water , cyanogen bromide , N-chloro - or N-bromosuccinimide , iodine or methyliodide was carried out at + 20°C (in THF).

Synthesis of  from 1 and 2 [9] . (Yields : 80 -95 %)

R	X	m.p. (°C)
Et	H	102 - 103
i-Pr	H	84 - 85
c-Hexyl	H	52 - 53
t-Bu	H	80 - 81
Et	Br	79 - 80
Et	I	97 - 98
i-Pr	Me	46 - 48
t-Bu	Cl	85 - 86

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9. The same results were obtained when a complex of 2 and LiBr was used (cf[8-9]).