

SYNTHESIS OF SILYL-SUBSTITUTED VINYLALLENES

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Summary : The coupling between the 5-chloro-3-en-1-yne 1a - 1e and trimethylchlorosilane gives rise to the vinylallenes 2a - 2e substituted by a trimethylsilyl group on the allenic moiety.

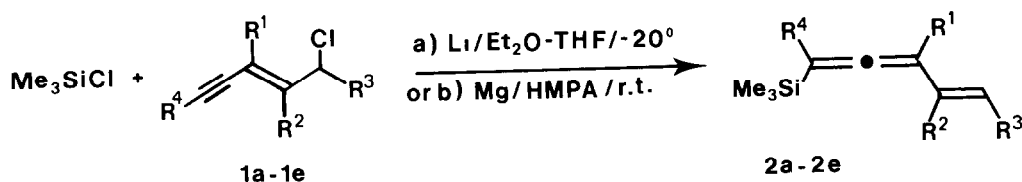
The synthetic ability of vinylallenes is well known (1), and various synthetic methods of those compounds have been reported (2).

Nevertheless, only one trimethylsilyl-substituted vinylallene has been hitherto published (3). In order to enlarge the availability of the silyl substituted derivatives 2, we investigated a new general synthetic approach.

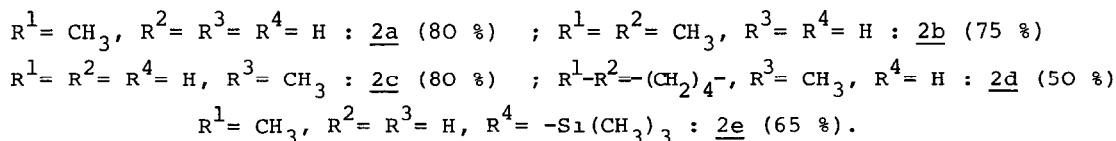
Trimethylsilyllallene is obtained in a 53 % yield when propargyl chloride is treated with the system trimethylchlorosilane/magnesium/hexamethyl phosphoric amid at 50-60 ° (4). This prompted us to apply this reaction to the enynes 1, which by analogy, should yield the silyl substituted vinylallenes 2.

We report herein two procedures a) and b) - each of them involving the coupling between the enynes 1 and trimethylchlorosilane by alkaline metals - which afford the expected compounds in good yield.

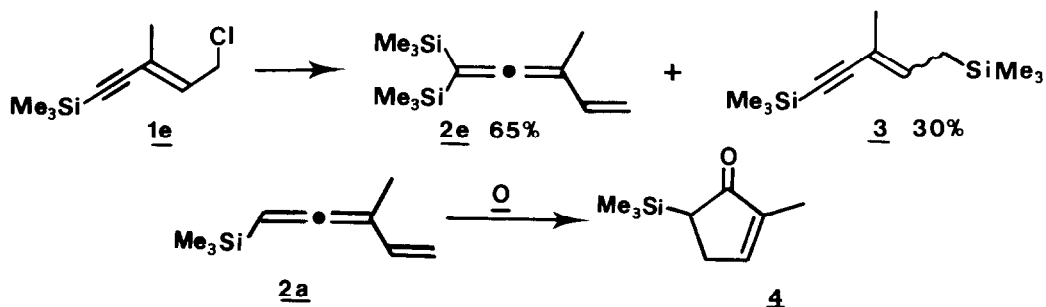
The 5-chloro-3-en-1-yne 1 are easily available by ethynylation of α,β -enones, followed by reaction of concentrated HCl with the enynol (5).



Yields are identical with procedures a) or b) :



Yields were calculated on the amount of vinylallenes recovered by distillation (2a) or t.l.c. (2b - 2e). Concerning the chloride 1e, we observe the formation of the substituted enyne 3 in a 30 % yield.



The oxidation of vinylallenes in cyclopentenones is a known reaction (1). With the silylated vinylallene **2a**, an attempt to this synthetic route was successful : the oxidation with PAYNE reagent (H_2O_2 /benzonitrile) (6), gives rise to the expected silylated cyclopentenone **4** in 60 % yield (7).

The oxidation of the silylated vinylallenes and the reactivity of the cyclopentenone **4** obtained are by now studied.

Procedure a : At -20° , under nitrogen atmosphere, the chloride **1** (10 mmol) and chlorotrimethylsilane (1.08 g, 10 mmol) in diethyl ether (15 ml) are added to lithium (0.014 g, 20 mmol) in THF (15 ml). The resulting mixture is stirred at -20° for 12 h and then poured into water. The product is extracted with pentane (3x20 ml). The extract is dried on magnesium sulfate, filtered and the solvent removed to yield the crude vinylallene which is further purified.

Procedure b : Under a nitrogen atmosphere, hexamethylphosphoric amide (12 ml) is added to the mixture of the chloride **1** (10 ml), chlorotrimethylsilane (1.08 g, 10 mmol) and magnesium (0.24 g, 10 mmol) in THF (25 ml). The resulting mixture is then allowed to react for 12 h at room temp. and then worked-up as described in procedure a .

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- 7 All the spectroscopic values are consistent with the assigned structures.