Reactivity of Acetylenic Silyl Ketones: Synthesis of Functionalized Propencylsilanes

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Abstract: Acetylenic silyl ketone 1 undergoes smooth Michael addition reaction with different silylated nucleophiles to afford β -functionalized propenoylsilanes.

The chemistry of α , β -unsaturated acylsilanes has attracted considerable attention in recent years due to some recently described interesting transformations of these compounds, which have established the utility of α , β -unsaturated acylsilanes as building blocks for the synthesis of a variety of complex organic compounds.¹ Several interesting procedures for their preparation have been recently described,² all of them leading only to alkyl or phenyl functionalized compounds. We have recently reported the reactivity of unsaturated acylsilanes and stannanes toward different silylated nucleophiles, which provides a new entry into the class of polyfunctionalized polymetalated molecules under neutral conditions³. While anyway propenoylsilanes have been extensively studied, little has been done on acetylenic silyl ketones.

We report here a novel synthetic access to a new class of α , β -unsaturated, β -functionalized acylsilanes which may be considered as useful building blocks for the synthesis of complex organic molecules.

When 1^{lb} was reacted, with different silvlated nucleophiles (see Table), a spontaneous and clean



reaction occurred, similar to those of the ethylenic series, but at a much faster rate, yielding the corresponding Michael adduct derivative in almost quantitative yield. No desilylation product was detected.

Thus, as a typical procedure, a chloroform solution of 1 (50 mg, 0.16 mmol) was treated dropwise with diethylaminotrimethylsilane (23.2 mg, 0.16 mmol) at room temperature with stirring. Progression of the reaction was monitored by NMR. Quench with satd. NH4Cl, extraction with ether and removal of the solvent afforded a crude material which was purified by the yielding 45 mg of 2a, (0.116 mmol, 73%)⁴. Results are summarized in the Table.

Although the acetylenic silvl ketone 1 may be regarded as a safer synthetic equivalent of propargylaldehyde, when the same reaction is performed on propargyl aldehyde itself, only the 1,2 adduct is formed in quantitative yields⁵, thus showing a different chemical behaviour between these two compounds.

The reactivity seems rather general, occurring with nitrogen-, sulphur- and halogen-based nucleophiles, and leads to a wide variety of 3-functionalized α , β -unsaturated acylsilanes. Interestingly, the additions of silylated nucleophiles to 1 appear to be regio- and stereospecific. No trace of the 1,2 adduct was detected in the crude reaction mixture and one isomer was obtained as the only product. It is, nevertheless, worth noting the interesting change in this selectivity, which appears to be strictly related to the nucleophile used. When, in fact, silylated secondary amines, halogens or azides are used, only the *trans* isomer is obtained. When, on the contrary, silylated ammonia or silylated primary amines or even sulphides are used, the *cis* isomer is formed selectively.



Table. Reactivity of acetylenic silyl ketone with nucleophiles^a.

^aReactions were run in chloroform at r.t. for 1h. ^bAll compounds showed analytical and spectroscopic data consistent with the assigned structure. ^cYields refer to chromatographically pure material. ^d1h, 60°C.

In the case of primary or secondary amines 2d and 2e, this behaviour can be easily explained through a preliminary formation of the *trans* isomer, which isomerizes through a highly polar zwitterionic type transition state⁶. The prevalence of *cis* population may be attributed to intramolecular hydrogen bonding, although a contribution from $N \rightarrow Si$ interaction cannot be ruled out. Accordingly, the *cis* configuration found in **2f** and **2g** might be explained with intramolecular stabilizing interactions, as already observed in vinyl sulphides⁷.

In conclusion, this reactivity allows an easy access to several functionalized acylsilanes whose reactivity as useful building blocks in organic synthesis is rather promising in relation to the new functionalities thus developed. These include enamines, vinyl sulphides and iodides, whose applications in organic synthesis are becoming increasingly popular.

References and notes.

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- 4. ¹H NMR (CDCl₃) δ ppm 1.4 (1, 6H), 2.3 (q, 4H), 5.65 (d, 1H, J= 12.9 Hz), 7.25-7.7 (m, 16 H); IR (neat) cm⁻¹ 3020, 2960, 2900, 1650, 1605, 1590, 1450, 1240, 1020, 837.
- Treatment of a chloroform solution of propargyl aldehyde (100 mg, 1.8 mmol.) with diethylaminotrimethylsilane (340 μL, 1.8 mmol) afforded 290 mg (81%) of 1-trimethylsilyloxy-1-N,N-diethylamino-2-propyn.¹H NMR (CDCl₃) δ ppm 0.05 (s, 9H) 0.90 (t, 6H), 2.37 (d, 1H, J=1.9 Hz), 2.61 (q, 4H) 5.05 (d, 1H, J=1.9Hz).
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