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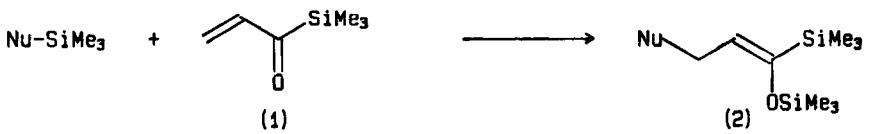
SYNTHESIS OF POLYFUNCTIONALIZED ACYLSILANES VIA PROPENOYLTRIMETHYLSILANE.

A.Ricci, A.Degl'Innocenti, G.Borselli and G.Reginato
Centro C.N.R. Composti Eterociclici e loro Applicazioni, c/o Dipartimento di Chimica Organica dell'Universita' via G.Capponi 9, I-50121 Firenze, ITALY.

Summary: Propenoyltrimethylsilane (1) reacts with silylated nucleophiles to yield the β-functionalised silyl enol ethers of acylsilanes. Further "in situ" reaction of these compounds affords an easy entry into the class of polyfunctionalised acylsilanes.

Silyl enol ethers of acylsilanes are gaining growing interest in the chemical literature[1], and although several methods have been developed for their synthesis[2], none of them appears suitable for incorporating a functional group. Moreover some β-functionalized acylsilanes have been reported[3], but the synthetic method for their preparation is not general.

As a part of our long standing and continuing interest in this field[4] we wish now to report a novel, mild and high yielding synthesis of functionalised silyl enol ethers of acylsilanes, via the Michael addition of a variety of silylated nucleophiles to a very reactive acylsilane, propenoyltrimethylsilane[5] (1).

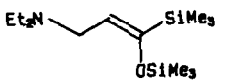
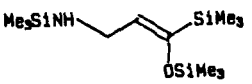
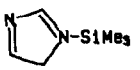
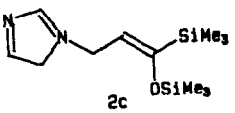
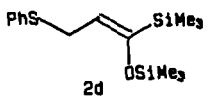
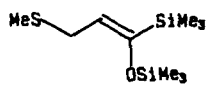
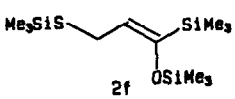
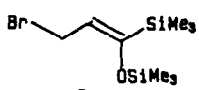
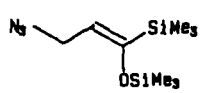
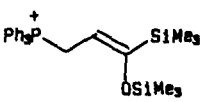


Thus, as a typical example, upon stirring for 1 h $PhSSiMe_3$ with propenoyltrimethylsilane (1) at room temperature, it is possible to isolate in 98% yield 3-phenylthio-1-trimethylsilyloxy-1-trimethylsilyl propene (2d). The compounds obtained through this procedure are usually pure enough to undergo further reactions. The results are collected in Table 1.

The reaction proceeds in the absence of any solvent, although it is possible to run it in ether or in THF, with slowing of the reaction rate. No catalyst was necessary, probably due to the high positive charge present at the carbon in the β-position.

Silyl enol ethers obtained through this Michael type addition to (1) were 95% pure E isomers, as evidenced by the NMR[6] spectra of the crude material obtained from the reaction mixtures: this feature turns out to be a very interesting one since stereochemically pure enol derivatives have important applications in stereoselective syntheses of alicyclic molecules bearing multiple asymmetric centers[7]. Interestingly the functionalization of (1) with N_3SiMe_3 affords, to our knowledge, the first example of 1,4-Michael addition of this silylated derivative, thus opening a new and easy access to β-azido ketones.

Table 1. Functionalized Silyl Enol Ethers of Acylsilanes.

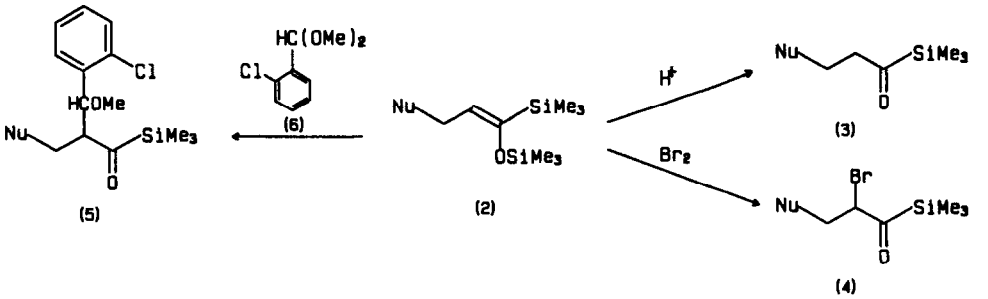
Nucleophile	Product	Yield[a]%	E:Z[b]	^{1}H NMR(ppm)
Et_2N-$SiMe_3$	 2a	98	95: 5	0.28 (s, 9H), 0.32 (s, 9H), 1.18 (q, 6H), 2.70 (m, 4H), 3.28 (d, 2H), 4.50 (t, 1H).
$(Me_3Si)_2NH$	 2b	20[c]		
	 2c	90	95: 5	0.20 (s, 9H), 0.31 (s, 9H), 4.68 (d, 2H) 5.28 (t, 1H), 7.1 (s, 2H), 7.6 (s, 1H).
PhS-$SiMe_3$	 2d	98	94: 6	0.18 (s, 9H), 0.31 (s, 9H), 3.58 (d, 2H) 5.17 (t, 1H), 7.10-7.25 (m, 5H).
MeS-$SiMe_3$	 2e	81	95: 5	0.20 (s, 9H), 0.31 (s, 9H), 2.07 (s, 3H), 3.18 (d, 2H), 5.18 (t, 1H).
$(Me_3Si)_2S$	 2f	95	91: 9	0.18 (s, 9H), 0.3 (s, 9H), 0.38 (s, 9H), 3.10 (d, 2H), 5.07 (t, 1H).
Br-$SiMe_3$	 2g	95	95: 5	0.12 (s, 9H), 0.30 (s, 9H), 4.04 (d, 2H), 5.50 (t, 1H).
N_3-$SiMe_3$	 2h	98	94: 6	0.15 (s, 9H), 0.27 (s, 9H), 3.90 (d, 2H), 5.58 (t, 1H).
PPh_3/Me_3SiCl	 2i	96	94: 6	0.15 (s, 9H), 0.27 (s, 9H), 4.73 (dd, 2H), 5.62 (m, 1H), 7.55-1.70 (m, 15H).

[a]Yields determined on the NMR spectrum of the crude product.[b] E:Z ratio determined by NMR on the chemical shifts of the vinylic protons.[c]Determined by GC/MS analysis.

By acidic hydrolysis of these new silylated enol ethers, it is possible to obtain in high yields acylsilanes variously functionalised at the β-position, with great versatility in organic synthesis, since acylsilanes are readily convertible to the corresponding aldehydes[8] and acids[9].

A further synthetic potential of compounds (2), stems from their capability to undergo the typical reactions of silyl enol ethers with electrophiles

other than H^+. To exploit this last possibility, preliminary experiments based on a one pot double functionalization of (1) were performed.



As shown by the results in Table 2, the silyl enol ethers of acylsilanes, once generated, react "in situ", in a regiospecific fashion, spontaneously or

Table 2. Reactions of silyl enol ethers of acylsilanes toward Electrophiles.

Substrate[a]	E	Product	Yield[b]%	^{1}NMR(ppm)
2a	H^+	3a	85	0.25 (s, 9H), 1.15 (t, 6H), 2.51 (q, 4H) 2.8 (t, 2H), 3.31 (t, 2H).
	Br_2	4a	95	0.3 (s, 9H), 1.13 (t, 6H), 2.55 (q, 4H), 3.27 (dd, 1H), 3.5 (dd, 1H), 4.55 (dd, 1H).
2c	H^+	3c	91	0.2 (s, 9H), 3.18 (t, 2H), 4.3 (t, 2H), 7.1 (s, 2H), 7.6 (s, 1H).
2d	H^+	3d	90	0.28 (s, 9H), 3.1 (t, 2H), 3.3 (t, 2H), 7.10-7.25 (m, 5H).
	Br_2	4d	95	0.37 (s, 9H), 3.27 (dd, 1H, J =14Hz, J =5Hz), 3.65 (dd, 1H, J =14Hz, J =10Hz), 4.55 (dd, 1H, J =10Hz, J =5Hz), 7.12-7.3 (m, 5H).
	(6)	5d	86	0.28 (s, 9H), 2.85 (m, 1H), 3.05 (m, 1H), 3.55 (s, 3H), 3.56 (m, 1H), 4.8 (d, 1H), 7.3-7.9 (m, 4H).
2e	H^+	3e	70	0.29 (s, 9H), 2.07 (s, 3H), 2.68 (t, 2H), 2.91 (t, 2H).
2f	H^+	3f	78	0.2 (s, 9H), 0.3 (s, 9H), 3.27 (t, 2H), 3.45 (t, 2H).
2g	H^+	3g	92	0.20 (s, 9H), 3.14 (t, 2H), 3.50 (t, 2H).
	(6)	5g	82	0.15 (s, 9H), 2.85-3.3 (m, 2H), 3.26 (s, 3H), 3.9-4.15 (m, 1H), 5.8 (d, 1H), 7.20-7.45, 7.70-7.90 (m, 4H).
2h	H^+	3h	95	0.31 (s, 9H), 2.93 (t, 2H), 3.53 (t, 2H).
	Br_2	4h	88	0.35 (s, 9H), 3.36 (dd, 1H, J =12.7Hz, J =6Hz), 3.75 (dd, 1H, J =12.7Hz, J =6.8Hz), 4.46 (dd, H, J =6.8Hz, J =6.0Hz).
	(6)	5h	72	0.25 (s, 9H), 2.90-3.15 (m, 2H), 3.32 (s, 3H), 3.65 (m, 1H), 4.75 (d, 1H), 7.20-7.75 (m, 4H).
2i	H^+	3i	82	0.10 (s, 9H), 3.25 (dt, J^3_{P-H}=20Hz, J =6Hz), 4.05 (m, 2H, J^2_{P-H}=13Hz, J =6Hz).

[a]All the reactions were performed "in situ". [b]Determined by GC/MS analysis or by NMR of the crude material.

under the catalytic effect of $BF_3.Et_2O$ with some representative electrophiles, leading to acysilanes with different functional groups at the α and β-positions[10].

Due to its inherent interest and wide applications in synthesis, this reactional behaviour makes compound (1) a synthetic equivalent of the poli-

(1) (6)

functional synthon (6). This is now being actively investigated in our laboratories.

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10. A typical procedure is as follows: Propenoyltrimethylsilane (1) (50 mg,0.39mmol) and Bromotrimethylsilane (60 mg, 0.39mmol) were stirred under N_2 in a flame dried flask for 1 h (completion of the reaction was monitored by GC/MS), then diluted with CH_2Cl_2 (100 μl), cooled to -78 C and treated successively with dimethoxy-(2-chlorophenyl)methane (69 mg, 0.37mmol) in 50 μl CH_2Cl_2 and $BF_3.Et_2O$ (59.5 mg, 0.37mmol) via a syringe. The obtained mixture was stirred 1h, then quenched, washed with water and brine. Purification by preparative t.l.c. afforded 96 mg of (5g) (74%).

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