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A NEW STEREOSELECTIVE SYNTHESIS OF TRANS-α, β- UNSATURATED CARBONYL COMPOUNDS.

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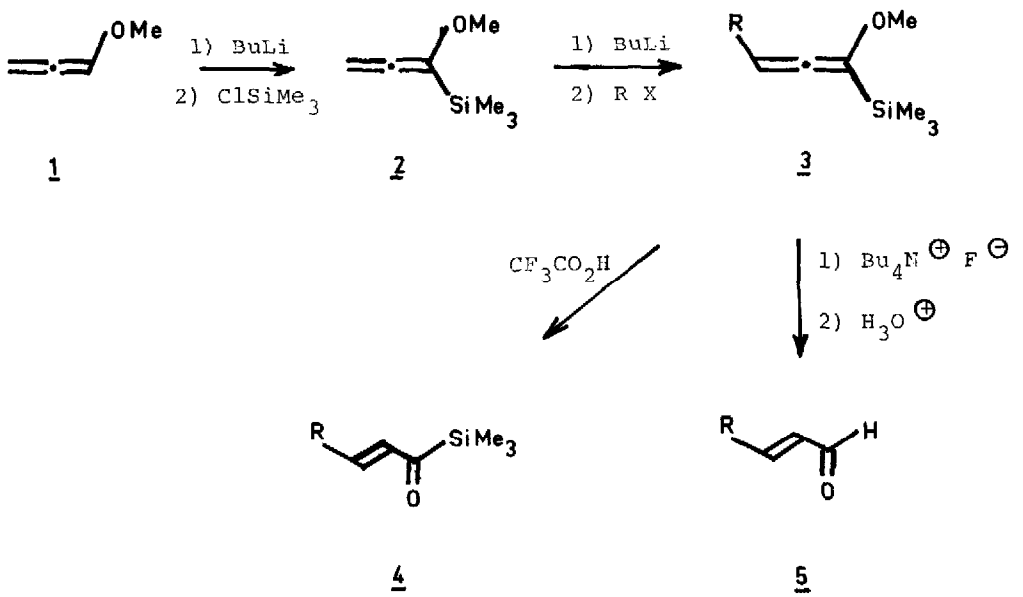
Abstract : Allenic silylated ethers are efficient precursors to unsaturated carbonyl compounds.

In connection with previous studies on lithiated allenic ethers [1], we wish to report a new efficient synthesis of α, β-unsaturated aldehydes [2,3] and acylsilanes utilizing silylated ethers.



1 2 3

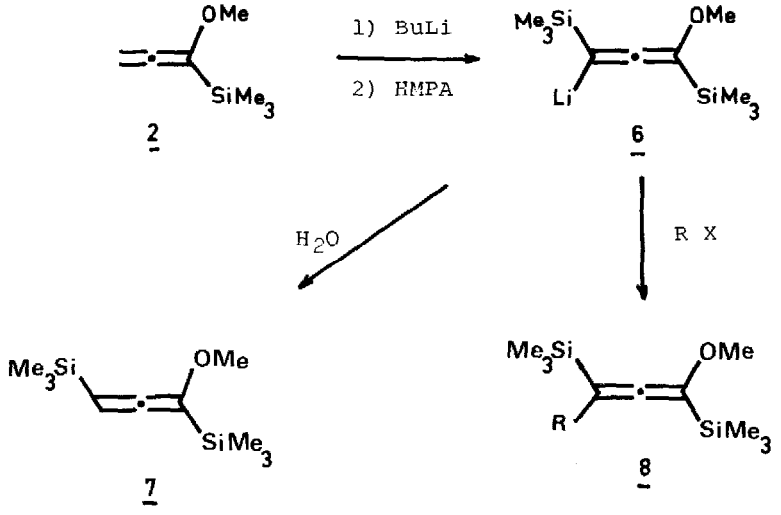
4 5

The reagent 2, easily obtainable from methoxy-allene 1 [3], was metalated [1,4] and alkylated without the formation of isomeric acetylenic by-products to provide the substituted ethers 3 [5] (R = n-C_4H_9, 82 %). Desilylation of 3 with tetrabutylammonium fluoride in THF - methanol at room temperature followed by a mild acid hydrolysis gave the trans- α, β - unsaturated aldehydes 5 in high yield (R = n-C_4H_9, 92 %).

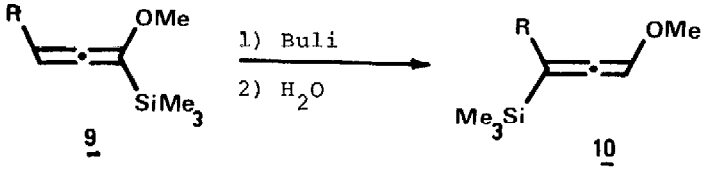
The silylated allenic ethers 3 were also found to be efficient intermediates for the synthesis of trans - α, β - unsaturated acylsilanes 4 [3b, 6].

Thus, when treated with trifluoroacetic acid in THF - water (or with IR 120 resin in methanol) at room temperature, the ether 3 (R = n-C_4H_9) gave the acylsilane 4 (R = n-C_4H_9) in 76 % yield.

In THF containing HMPA, the lithio derivative of 2 was transformed into a new allenic lithium reagent 6 [7]. Hydrolysis gave the disilylated compound 7 and alkylation with butyl chloride afforded (42 %) the substituted allene 8.



In the same way, the silylated allenic ether 9 , when treated with n-butyllithium for 6 hr at -50° C in a mixture THF - HMPA gave, after hydrolysis, the allenic ether 10 (R = n-C_6H_{13}) [3c] in 62 % yield [8] .



9 10

TYPICAL PROCEDURES :

1-trimethylsilyl-2E-hepten-1 one 4 (R = n-C_4H_9) :

1g (5 mmol) of 1-methoxy-1-trimethylsilyl-1,2-heptadiene 3 (R = n-C_4H_9) in THF (10 ml) containing 0.5 ml of water was treated with 2 ml of trifluoroacetic acid at room temperature overnight. Then, the mixture was stirred with saturated aqueous sodium carbonate solution (10 ml) for 3 hr. Work-up in the usual manner, filtration of the crude product through neutral alumina (pentane) and distillation gave 0.71 g (76 %) of pure 1-trimethylsilyl-2 E-hepten-1 one. b.p. 60 °/ 1 mm ; ν = 1620 cm^{-1} ; m/e = 184($M^{+\cdot}$) ; δ (CD_3COCD_3) : 5.98 (txd, 1H, J= 18 Hz, J = 1.5 Hz), 6.64 ppm (txd, 1H, J = 18Hz, J = 7 Hz).

(E)-2-heptenal 5 (R = n-C_4H_9) :

5.5 g (30 mmol) of 1-methoxy-1-trimethylsilyl-1,2-heptadiene 3 (R = n-C_4H_9) were treated with a solution of tetrabutylammonium fluoride (1 N in THF, 40 ml) and methanol (3 ml). The mixture was stirred overnight

at room temperature and then treated for 2 hr with aqueous HCl solution (1 N, 40 ml). Work-up in the usual manner and distillation gave 2.9 g (92 %) of pure (E)-2-heptenal.

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7) This reaction is under current investigation.

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