## Preparation of a Highly Functionalized Allylsilane for Use in Three-Bond Cascade Reactions

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This paper is dedicated to the memory of Tom Lee.

Abstract: Preparation of the novel allylsilane, methyl 3-formyl-4-(phenyldimethylsilylmethyl)pent-4enoate (2) was accomplished in 7 steps from 2,3-dibromopropene. (2) has great potential as an annulating reagent.

The utility of difunctional reagents in multiple bond formation is well-documented.<sup>1</sup> In certain cases, however, the generality of such reagents (for example, aldehydoallylsilane (1)) is hampered by retro aldol-type processes which tend to diminish conversion of starting materials into products, thereby delivering low-yielding reactions.<sup>2</sup> In an

OHC Si**Me**2Ph (1)

attempt to circumvent this pitfall, we designed trifunctional compound (2) as an efficient cascade reagent which would deliver three new bonds from reactions similar to those previously investigated. Thus, retro-aldol reaction would, it was anticipated, be retarded by trapping of the initially formed adduct by the carboxyl group, leading to lactone formation and efficient bond forming reaction (scheme 1). We herein report the synthesis of (2). The

synthetic strategy proposed to the utilize framework of 2-(5H)-furanone (3)3 to provide the oxygenation level desired, whilst introducing the



## **SCHEME 1**

allylsilane moiety by means of of a copper-catalysed addition of an organometallic reagent. This strategy is highly convergent and theoretically of short order. Thus, 2-bromo-3trialkylsilylprop-2-enes (4) and (5) were prepared by two-step procedures from

commercially available 2,3-dibromopropene (scheme 2). Copper-catalysed silylation,<sup>4</sup> followed by Grignard alkylation furnished (4) and (5). in 60 and 70% overall yields, respectively. Generation of the Grignard reagents (6) and (7) was accomplished only using activated magnesium,<sup>5</sup> but copper-catalysed addition to (3) was disappointingly inefficient



(8 and 29% respectively for addition of (6) and (7)). However, hydrolytic ringopening of the silvl lactone (8) followed by reaction of the intermediate alkoxyacid with diazomethane vielded the desired hydroxy ester (9), albeit in moderate vield (47%). Fortified by this result, the aberrant 1,4addition was rectified by addition of an activating group into the 3-position of the Michael acceptor. Thus, reaction of 3-phenylthio-2-(5H)-furanone (10)<sup>6</sup> with cuprate (7a) led to the desired product of alkylation (11); (9) was obtained in 40% yield (unoptimized) after reductive removal of the

sulphide group. Oxidation

of (9) using usual Swern oxidation conditions led to smooth formation of aldehyde, but the Et<sub>3</sub>N present induced olefin migration to give the conjugated product (12). Use of Hünig's base obviated this problem and the final product (2) was obtained in 90% (12)

R<sub>1</sub>M•2SI (12) CHO

yield. Investigations into the ability of this reagent in cascade reactions and optimization of the synthetic sequence outlined are presently underway in our laboratories.

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