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CHEMOSELECTIVE REACTION OF BIFUNCTIONAL ALDEHYDO ALLYLSILANES

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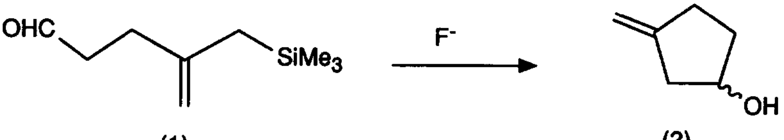
Summary: Aldehydes, such as 1, are only the second class of electrophiles found to undergo chemoselective intermolecular reaction with enolsilanes, as opposed to intramolecular attack by the allylsilane.

The preceding paper reviewed the selectivity shown by a series of acetal allylsilanes in a competitive reaction with silyl enol ethers, under electrophilic conditions[1]. It concluded that the selectivity of these reagents arises due to the potentially competitive intramolecular attack of the allylsilane on the acetal being a stereoelectronically disfavoured process[2]. It was of interest and value to see if the process could be extended to selective reaction of bifunctional reagents that possess electrophilic centres other than acetals and to establish this we have studied the reaction of the aldehydo-allylsilane 1. Beside having the additional advantage that the initial product bears a secondary alcohol function, as opposed to the synthetically limiting methoxy group obtained from the acetals, it allows the use of nucleophilic fluoride anion conditions in these reactions, as opposed to Lewis acid.

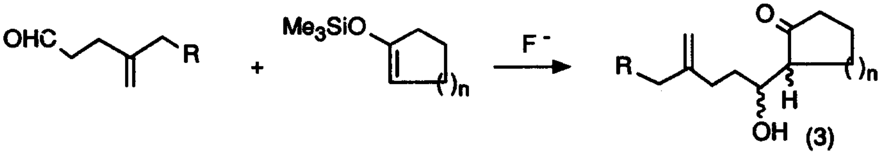
Treating 1 with fluoride does result in a high yield of the cyclised product 2 [3]. Treating 1 with fluoride anion in the presence of a trimethylsilyl enol ether gives a different outcome however, resulting in no trace of 2 but giving the ketone 3 (**Table**), as a mixture of diastereoisomers[4]. This presumably shows that the intermolecular attack of the enol silane predominates over the kinetically slower (disfavoured) intramolecular cyclisation. However, unlike in the preceding paper, this selectivity was not readily predicted since we expect such rules for ring closure to be of less utility in reactions of allylsilanes with nucleophilic fluoride. This arises since such reactions can proceed via a pentacoordinate silicon species, so promoting less predictable stereoelectronic requirements[5].



(1) (2)

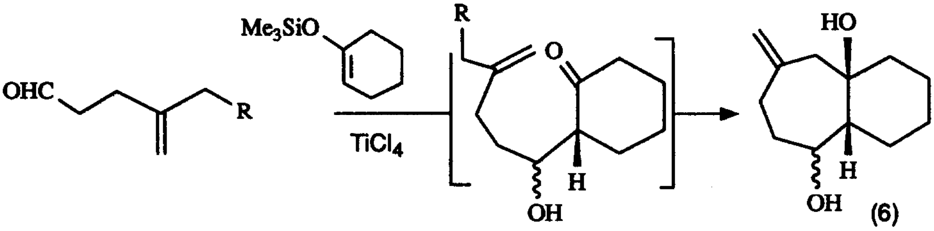
Aldehydes constitute only the second class of electrophiles that we have found that undergo this selective reaction, so avoiding "self destruction" [6]. However, within the context of using the aldehyde 1 in an annulation reaction we were unable to efficiently cyclize the intermediate 3 under the influence of fluoride[7], isolating instead the desilylated ketone 3 (R=H) as the major product. To address this problem we prepared the allylsilanes 4 and 5 [8] since they should be less prone to desilylation in the second step[9]. Although this change does prevent protiodesilylation, a retro-aldol reaction now predominates upon prolonged reaction, to regenerate the aldehyde. Furthermore, attempts to use Lewis acid catalysis for reactions of 1 were equally unsuccessful resulting only in decomposition of the allylsilane. In contrast Lewis acid induced reaction of **4** and **5** proved more useful. Upon reaction of them with an enolsilane we observed preferential intermolecular attack by the enolsilane, followed by subsequent intramolecular attack upon the initially formed ketone to form the alcohol **6** as shown below, albeit currently in low yields [10].

Table



(3)

ENTRY	R	n	(3) YIELD %
1	$SiMe_3$	1	39
2	$SiMe_3$	2	60
3	$SiMe_3$	3	38
4	$SiMe_2Ph$	2	83
5	$SiMePh_2$	2	47



(6)

(1) R = $SiMe_3$(0%) (4) R = $SiMe_2Ph$(6%) (5) R = $SiMePh_2$(20%)

The above results show that bifunctional reagents of this type are not limited to just one electrophilic centre, indicating that the synthetic utility is potentially of wider applicability.

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REFERENCES AND NOTES.

1. Preceding communication.
2. Baldwin, J.E, *J. Chem.Soc. Chem. Communs.* **1976**, 734, 736, 738.
3. cf. Sarkar, T.K; Andersen, N.H, *Tetrahedron Letters*, **1978**, 3513.
4. This is in contrast to reports on the stereoselectivity of this reaction from Nakamura, E; Yamago, S; Machii, D; Kuwajima, I, *Tetrahedron Letters*, **1988**, 29, 2207.
5. For a definite discussion, see Majetich, G; Desmond, R.W; Soria, J.J, *J. Org. Chem.*, **1986**, 51, 1753, and references therein.
6. We use the term self destruction exclusively within the context of these bifunctional reagents, since intramolecular attack of an allylsilane can be a highly desirable synthetic transformation, see Majetich, G, *Organic Synthesis: Theory and Application*, Vol.1, p.173, (JAI Press, **1989**),for an excellent review of such reactions.
7. A range of fluoride catalysts were tried, including TBAF, TBAF on SiO_2, CsF in DMF, CsF with 18-c-6, and TAS-F, with TBAF on SiO_2 giving the most reproducible results.
8. All allylsilanes were prepared according to:- Lee, T.V; Channon, J; Cregg, C; Porter, J.R; Roden, F.S, and Yeoh, H, *Tetrahedron* **1989**, 45, 5877, and all new compounds gave satisfactory analytical and/or spectroscopic data.
9. Mayr, H and Hagen, G, *J. Chem.Soc. Chem. Communs.* **1989**, 91.
10. The obvious use of the triphenyl derivative has not yet been achieved due to great difficulties in obtaining the allylsilane efficiently.

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