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PALLADIUM-CATALYZED HYDROGENOLYSIS OF ACYLDIMETHYLPHENYLSILANES TO ALDEHYDES

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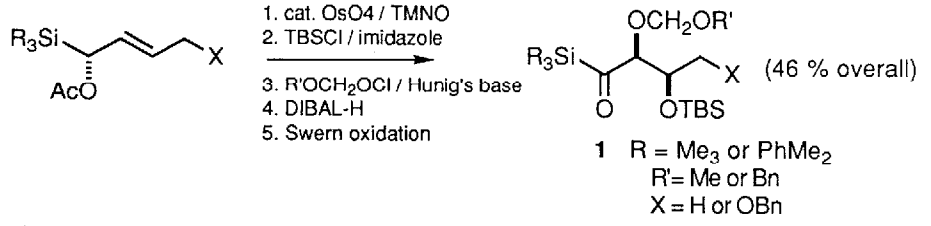
Abstract. Syn-α,β-dialkoxy-acyldimethylphenylsilanes of structural type **1**, bearing benzyl, benzyloxymethyl (BOM) ether protecting groups can be efficiently and selectively desilated to produce the corresponding aldehydes **2** by catalytic hydrogenolysis over 10% palladium on carbon in ethanol or ethyl acetate.

Acylsilanes are emerging as interesting and versatile reagents, capable of participating in a number of useful bond-forming processes.[1] As part of our continuing interest in the chemistry of C1-oxygenated allylic silanes[2] and their application in the asymmetric synthesis of polyoxygenated antitumor agents, we have developed an efficient route for the construction of enantiomerically pure syn α,β-dialkoxyacylsilanes of general structure **1** (Scheme 1), and demonstrated that these structural types participate in highly stereoselective chelation controlled nucleophilic addition reactions for the construction of 1,2,3-syn triols.[3]

Scheme 1



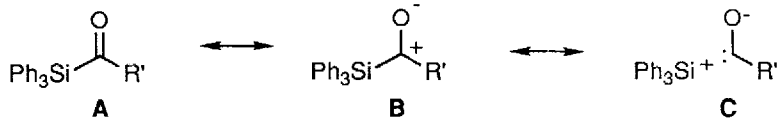
1 R = Me_3 or $PhMe_2$
R'= Me or Bn
X = H or OBn

We sought however to enhance the scope and versatility of our approach to these systems by converting the acylsilanes to aldehydes, since these structural types, although surprisingly underutilized, hold considerable potential as useful intermediates in asymmetric synthesis. The conversion of acylsilanes to aldehydes under basic conditions[4] and to acetals under photolytic conditions[5] are well documented. However these reactions seldom take place efficiently without the formation of numerous side-products, especially when sensitive substrates are involved. For instance, β-alkoxy acylsilanes readily undergo elimination in the presence of catalytic amounts of quaternary ammonium salts to form α,β-unsaturated aldehydes.[6]

An inspection of the data of a single-crystal X-ray analysis reported for acetyl triphenylsilane revealed that, whereas the phenyl-Si bond length was measured to be 1.864 Å, the silicon-carbonyl bond length was shown to be slightly longer, being measured at 1.926 Å. The data therefore suggested that three resonance forms (Figure 1) could be postulated to account for this unusual structure. These include the carbenoid-like species C as a valid canonical form, because of the large electronegativity difference between silicon and carbon.[7] The abnormal length of the Si-carbonyl bond in acylsilanes of this type led us to expect that this bond ought to be considerably weaker than a normal C-Si bond and be susceptible to cleavage under the mild conditions of catalytic hydrogenation. In this context it has been well documented that strained ring systems that possess relatively weak, elongated C-C sigma bonds resulting from poor orbital overlap, such as cyclopropanes, are reductively cleaved under catalytic

hydrogenation conditions.[8] Having established that the weak-Si-carbonyl bond may be the key feature which may effect the selective cleavage of the acylsilane to the aldehyde, we subjected a series of related acyldimethylphenylsilanes to catalytic hydrogenolysis.

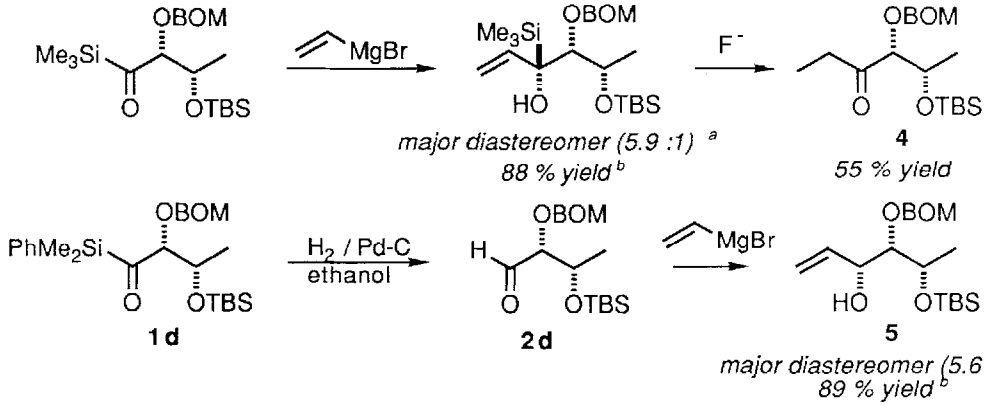
Figure 1



In this letter we would like to report the results of our experiments which describe a mild and selective conversion in the racemic series of syn-α-alkoxy-β-silyloxy acyldimethylphenylsilanes **1** to the corresponding aldehydes **2** in useful yields. This conversion is efficiently carried out over palladium on activated carbon catalyst (20% by weight catalyst / substrate) in either ethanol or ethyl acetate at room temperature, under 1-2 atmospheres of hydrogen. The reaction is accelerated in a more polar solvent such as ethanol and is typically complete in less than 24 hours whereas aprotic and less polar solvents require longer reaction times on the order of 48 to 72 hours. As illustrated in the Table, entries **a**, **b**, **d** and **e** reveal a particularly useful feature. The selective Si-carbonyl bond cleavage can be carried out in the presence of protecting groups known to be labile to catalytic hydrogenolysis such as benzyl and BOM ethers. Less surprising but still significant is the fact that acid-sensitive protecting groups such as acetonides, t-butyldimethylsilyl (TBS) and methoxymethyl (MOM) ethers are also left unaffected.

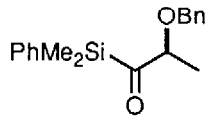
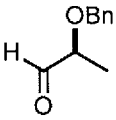
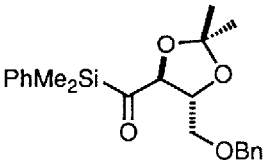
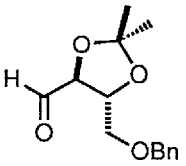
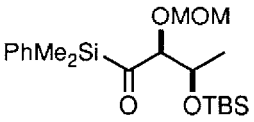
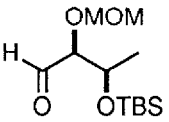
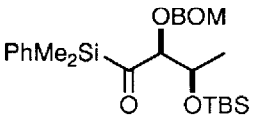
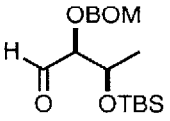
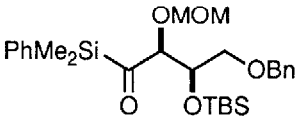
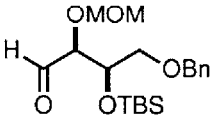
An example of the complementarity brought about by reductive cleavage of the acylsilane Si-carbon bond is illustrated in Scheme 2. By choosing the desired sequence of reactions, either compound **4** or **5** is readily available from the appropriate syn-α-alkoxy-β-silyloxy acylsilane. Thus vinyl Grignard (1.5 equiv / CH_2Cl_2 / -78 °C) addition followed by a fluoride ion catalyzed (0.2 equiv nBu_4NF / THF / -20 °C) desilylation[9] on the trimethylsilyl derivative yields ethyl ketone **4**. On the other hand, hydrogenolysis of the acylsilane **1d** to the aldehyde then addition of vinylmagnesium bromide (1.5 equiv / CH_2Cl_2 / -78 °C) yields allylic alcohol **5**.

Scheme 2



(a) Diastereomeric ratios were determined by integration of the crude proton NMR spectrum at 93.94 kG (400 MHz).
(b) Based on pure material isolated by chromatography on SiO_2 column.

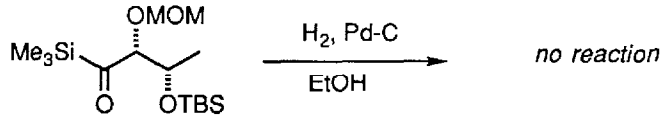
Table:Palladium-catalyzed hydrogenolysis of acylsilanes

entry	Acylsilane **1**	Time[a]	Aldehyde[b] **2**	Yield (%)[c]
a		10		80
b		24		82
c		10		75
d		10		96
e		12		82

(a) The hydrogenolysis reactions were run in ethanol, 0.1 **M** in substrate, at R. T., 1 atm. H_2, and 20% by weight of Pd on activated carbon (Aldrich). (b) All products exhibited the expected ^1H NMR (400 MHz), ^{13}C NMR (67.5 MHz), IR, MS and HRMS characteristics. (c) All yields are based on pure materials isolated by chromatography on SiO_2, and are not optimized.

In a control experiment, acylsilane **1c** was simply dissolved in ethanol and was found to be unreacted and stable after 10 hours. Moreover, the phenyl substituent on silicon is crucial in accelerating the rate of reaction, since no trace of aldehyde could be detected after 24 hours when the corresponding acyltrimethylsilane **3** was subjected to the same reaction conditions as shown in Scheme 3. Two plausible explanations for these results are that the aromatic ring maybe adsorbed onto the surface of the catalyst thereby lowering the energy of activation or it helps stabilize a transition state structure resembling resonance forms B and C so that activated hydrogen molecules on the surface of the palladium catalyst can insert between the silicon-carbonyl bond.

Scheme 3



3

In summary, the catalytic hydrogenolysis of syn-α,β-dialkoxy-acyldimethylphenylsilanes bearing benzyl and benzyloxymethyl ether protecting groups provides an efficient method to produce the corresponding aldehydes **2**. Presumably, by taking advantage of subtle structural features of phenyl-substituted acylsilanes, the reaction extends the scope and synthetic utility of C1-oxygenated allylic silanes, and breaks new ground in the area of organosilane chemistry. Further exploration of the chemistry of hetero-substituted acylsilanes and its utility in acyclic diastereoselection is currently in progress and will be reported in due course.

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