β-Lactams from Allyl- and (Allenylmethyl)-silanes

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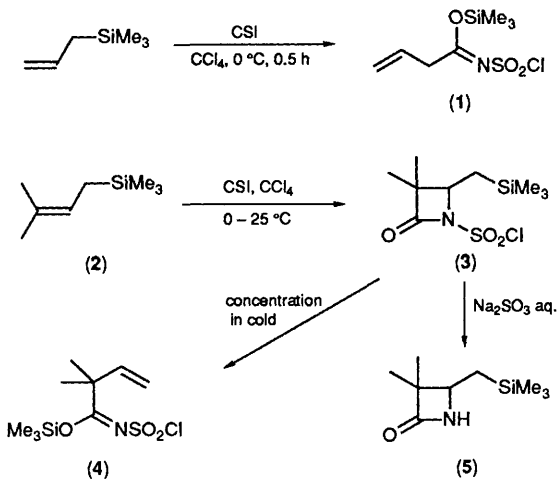
The *N*-chlorosulphonyl β-lactams formed as intermediates in the reaction between chlorosulphonyl isocyanate and allyl- and (allenylmethyl)-silanes can be intercepted by aqueous sodium sulphite; this has allowed the preparation of a range of usefully functionalised monocyclic *N*-protio β-lactams.

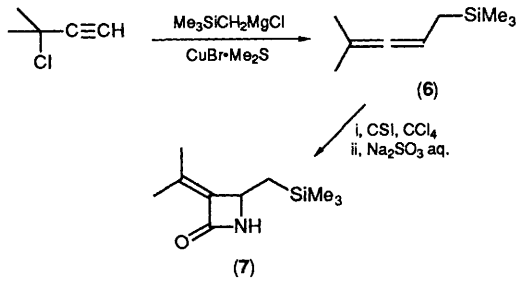
The reaction of chlorosulphonyl isocyanate (CSI) with functionalised alkenes, in particular with vinyl esters,[1] has proved to be of great utility in the preparation of monocyclic β-lactams. We were intrigued by an early report[2] by Dunoguès on the reaction between allylsilanes and CSI. Allyltrimethylsilane was reported to produce the silyl imidate (**1**) directly; however, using the dimethylallylsilane (**2**) an intermediate β-lactam (**3**) was detected by IR and ^{1}H NMR spectroscopy; this unisolated intermediate was reported to rearrange in solution over a period of one hour at ambient temperature to the acyclic imidate ester (**4**), by an implied intramolecular silatropic shift. Fleming[3] has made good use of this process in a key step in a synthesis of loganin aglycone.

In agreement with Dunoguès, we have found that allyltrimethylsilane reacts with CSI to give the silyl imidate (**1**); indeed, using low-temperature ^{1}H NMR spectroscopy and monitoring the $SiMe_3$ signal, we have found that no reaction occurs at −40 °C, whereas at 0 °C clean rearrangement takes place, with no intermediates being detected.

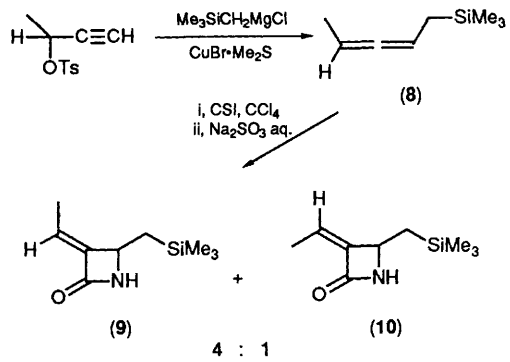
On the other hand, with the dimethylallylsilane (**2**) the intermediate *N*-chlorosulphonyl β-lactam (**3**) can be readily intercepted (Scheme 1) by *in situ* treatment with aqueous



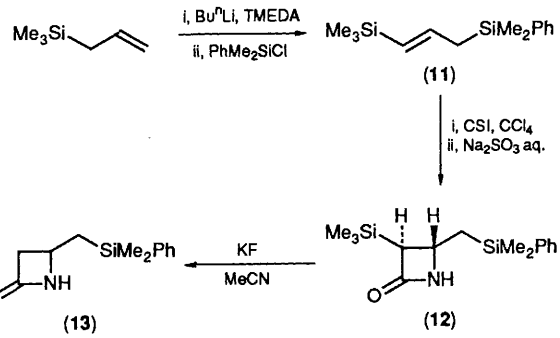
Scheme 1



Scheme 2



Scheme 3. Ts = p-$MeC_6H_4SO_2$.



Scheme 4. TMEDA = tetramethylethylenediamine.

sodium sulphite[4] to afford 3,3-dimethyl-4-(trimethylsilylmethyl)-azetidin-2-one† (**5**) as a white crystalline solid, m.p. 87–88 °C, in greater than 60% yield. Indeed, the intermediate *N*-chlorosulphonyl β-lactam (**3**) is stable in solution for at least 24 h at ambient temperature, but it does rearrange on concentration, even in the cold, to the imidate ester (**4**), suggesting a bimolecular pathway for this rearrangement.‡

We are studying this reaction with a range of allylsilanes to establish its scope and utility. However, usefully functionalised allylsilanes are relatively uncommon, and one is still left with saturated alkyl groups at C-3 and trimethylsilylmethyl groups at C-4. We are, therefore, extending this study in two complementary directions: (a) by varying the allyl substitution to provide more useful functionality at C-3, and (b) by varying the silyl substitution to allow oxidative cleavage of the C–Si bond, resulting in the overall introduction of a hydroxymethyl or oxidatively related group at C-4.

To generate more useful functionality at C-3, (allenylmethyl)silanes suggest themselves as ideally functionalised candidates: on cycloaddition, introduction of alkylidene substitution would produce potential asparenomycin and carpetimycin precursors.

(Allenylmethyl)trimethylsilanes are readily prepared by reaction between [(trimethylsilyl)methyl]copper(I) species and derivatives of propynylic alcohols.[5] The dimethylallene (**6**) reacted (Scheme 2) with CSI to give the crystalline 3-alkylidene β-lactam (**7**), m.p. 118–120 °C, in 22% yield.[6] The monomethylallene (**8**) reacted similarly, albeit in ≈10% yield, to give the β-lactams (**9**) and (**10**) as a 4:1 (*E*)-(*Z*)-mixture (Scheme 3).

The allyl/vinyldisilane[7] (**11**) reacted smoothly with CSI to provide the crystalline *trans*-β-lactam (**12**), m.p. 67–68 °C, in 50% yield (Scheme 4) suitably functionalised at C-3 for Peterson alkenation [as in the reported[8] synthesis of (−)-asparenomycin C]. Further, this β-lactam underwent quantitative desilylation at C-3 on treatment with KF–MeCN, providing access to the otherwise unobtainable (by this protocol) 3-unsubstituted β-lactam (**13**). Since phenyldimethylsilyl groups can be cleaved[9] to hydroxy groups by a sequence of protiodesilylation using HF equivalents, followed by oxidation, this provides a masked form of the synthetically useful 4-hydroxymethylazetidin-2-one.

The regiochemistry of the above cyclisation processes must be under the control of the β-effect, silicon encouraging the development of carbonium ions or partially developed such species β to it, and yet the silyl group is not lost. If a two-step zwitterionic mechanism[1] holds in such cases, this is remarkable, since it has been clearly demonstrated[10] that electrophilic attack on allylsilanes normally leads to silyl loss with the formation of substituted products with a net double bond shift, *via* an intermediate β-silyl cation.

We plan to extend these potentially useful observations, in particular by constructing suitably functionalised homochiral allenes with either phenyldimethylsilylmethyl or isopropoxydimethylsilylmethyl[11] substituents.

† All new compounds were fully characterised by elemental analysis and/or high resolution mass spectrometry, and IR, and ^1H and ^{13}C NMR spectroscopy.

‡ As a possible explanation for these differing results, it should be noted that Dunoguès operated at ≈3.5 M, Fleming at ≈2 M, whereas we used much more dilute, ≈0.2 M, conditions.

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