Rearrangement of *o*-(chloromethyldimethylsilyl)phenylmethoxide: evidence for an apical position of the migrating group in a trigonal bipyramid intermediate

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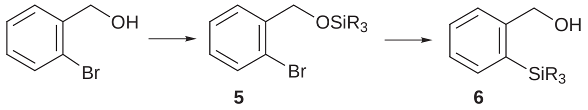
Chloromethylsilane 5a undergoes a rearrangement reaction to give oxasilacyclopentane 9 rather than oxasilacyclohexane 10, indicating that the methyl group migrates in preference to the aryl group.

Rearrangements of α-substituted organosilanes, with migration of an organic group from silicon to carbon, have been found to take place under acidic,[1] basic[1–4] or thermal[1] conditions. Little is known about the stereochemistry of the migration reaction, although migration from the apical position of a trigonal bipyramid has been suggested.[4] In contrast, the stereochemistry of nucleophilic substitutions at silicon has been extensively studied, and is generally interpreted as proceeding through pentacoordinate trigonal bipyramid intermediates, usually with entering and leaving groups in the apical positions.[5] With the increasing use of carbon-functional organosilicon compounds in organic synthesis, it is important to establish the stereochemistry of the fundamental reactions in organosilicon chemistry.[6] We report the first evidence for the stereochemistry of the base-induced rearrangement.

We have previously found the γ-oxidopropyl group on silicon to be effective as an internal nucleophile, and reported the cleavage reactions of γ-hydroxysilanes **1** (for generation of benzyl and allyl anion equivalents) (Scheme 1),[7] and the rearrangement reactions of γ-hydroxysilanes **2** (forming carbon–carbon bonds *via* a silicon template) (Scheme 2).[2]

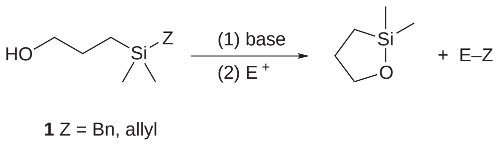
More rigid γ-hydroxysilanes would be expected to be more efficient for this purpose, and we have therefore been studying the use of *o*-silylbenzyl alcohols **6** in the cleavage and rearrangement reactions. In the course of this work, we have found that *o*-silyl benzyl alcohols **6** can be easily prepared by rearrangement of silyl ethers **5** of *o*-bromobenzyl alcohol with Li or Bu^{t}Li in Et_2O (Scheme 3).[8]



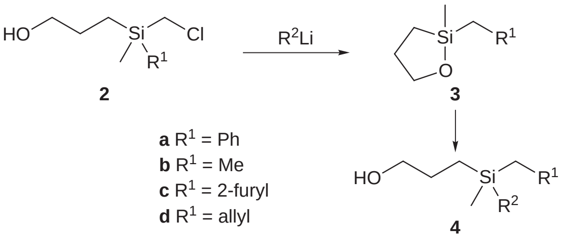
Scheme 3

Silyl ether **5a** provides an opportunity to study the relative importance of migratory aptitude (aryl *vs.* methyl) compared to stereochemical preference of the migrating group (apical *vs.* equatorial). Compound **5a**§ was prepared in 78% yield by treatment of *o*-bromobenzyl alcohol with 1.3 equiv. of $ClSiMe_2CH_2Cl$ in Et_2O–NEt_3 for 1 h at room temperature. [An impurity (*ca.* 6% by GC), believed to be $(ClCH_2Si)_2O$ was present: GC–MS *m/z* 181 (40%, $M^+ - CH_2Cl$), 153 (100); additional peaks at δ 2.76 (s) and 0.24 (s) in the ^1H NMR spectrum.] Treatment of **5a** with Bu^{t}Li in THF (30 min at −78 °C, then removal of the cold bath for 5 min, and workup by addition of saturated $NaHCO_3$) led to disappearance of **5a** with appearance of one product, assigned as oxasilacyclopentane **9**. [Some $(ClCH_2Si)_2O$ (*ca.* 7% by GC) was also observed in the GC and GC–MS.] Compound **9** is believed to arise *via* rearrangement (see Scheme 3) to γ-oxidosilane **7**, followed by methyl migration (presumably *via* trigonal bipyramid intermediate **8**, see Scheme 4). Aryl migration would have given oxasilacyclohexane **10**.

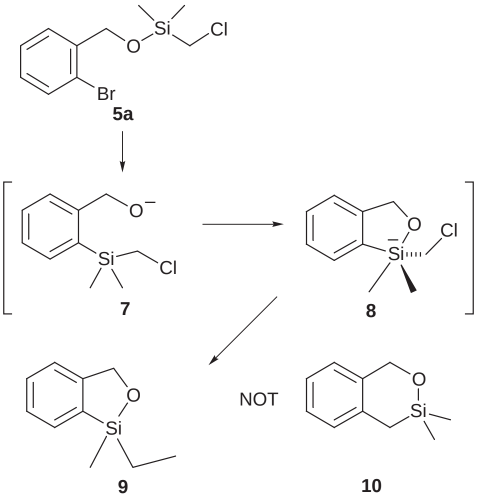
The structure of **9** was supported by the spectra, in particular the mass spectrum, which showed the base peak at 149 ($M^+ -$ Et), and the ^1H NMR spectrum, which was different from that reported for oxasilacyclohexane **10**.[9] The ^1H NMR spectrum of the crude product included δ 7.2–7.6 (m, ArH) 5.16 (s, CH_2O) and 0.39 (s, MeSi), as well as peaks due to $(ClCH_2Si)_2O$ (singlets at δ 2.76 and 0.24) and a small amount of THF. [Comparison with the reported ^1H NMR spectrum of compound **10**[9] suggested that **10**, if present, was less than 10%.] The ^{13}C NMR spectrum showed δ 6.30 (SiCH_2CH$_3$), 8.83 (SiCH$_2$$CH_3$), 71.72 ($CH_2O$), 121.55, 126.73, 129.49, 131.21, 134.14 (small), 150.07 (small), as well as 30.72 (small, $SiCH_2Cl$), peaks for THF, and three peaks in the SiMe region. The GC–MS showed *m/z* 178 (15%, M^+), 163 (8, $M^+ -$ Me), 149 (100, $M^+ -$ Et), 135 (8) and 105 (11). The structure of **9** was further confirmed by



Scheme 1



Scheme 2



Scheme 4

treatment (in THF) with excess MeLi (-78 °C, 1 h) which gave a mixture of *o*-(ethyldimethylsilyl)benzyl alcohol[8] (major) and *o*-(trimethylsilyl)benzyl alcohol[8] (minor).[10]

Migratory aptitudes in rearrangements of halomethylsilanes under basic conditions have been correlated with the ability of the migrating group to stabilize a negative charge.[3,4] In our studies of the rearrangement reactions of γ-hydroxysilanes **2**, we found that the phenyl group had a greater migratory aptitude than the methyl group, as expected.[2] Treatment of γ-hydroxysilane **2a** with several bases resulted in oxasilacyclopentane **3a**, the product of phenyl migration; in some cases, a small amount ($<5\%$) of 2-phenyl- 2-ethyl-1-oxa-2-silacyclopentane, the product of methyl migration, was also observed. (Treatment of γ-hydroxysilane **2a** with 2 equiv. of MeLi in Et_2O gave product **4a**, presumably by trapping of **3a** with MeLi.)[2]

The comparison of the migratory aptitudes in the acyclic system **2a** (phenyl migration) with those in the cyclic system **5a** (methyl migration) is very interesting. Perhaps the cyclic system **8a** has geometrical constraints which disfavor aryl migration. To the extent oxygen would prefer the apical position in a trigonal bipyramid intermediate (apical entry, electronegativity, see **8**),[11] the Si–Ar bond in the *o*-benzyl alcohol system would have to be equatorial. The preference for methyl migration in **5a** suggests that *migration is favored by an apical position of the migrating group in a trigonal bipyramid intermediate*. This work also suggests that *o*-silylbenzyl alcohol substrates should be useful for carbon–carbon bond forming reactions *via* rearrangements without interference from the aryl group.

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Notes and References

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§ The IR, ^{1}H NMR and mass spectra were in agreement with the structure.

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