Nucleophilic Substitution at a Silicon Atom: Evidence for an Equatorial Attack Mechanism

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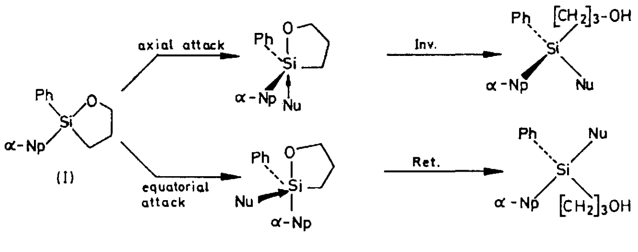
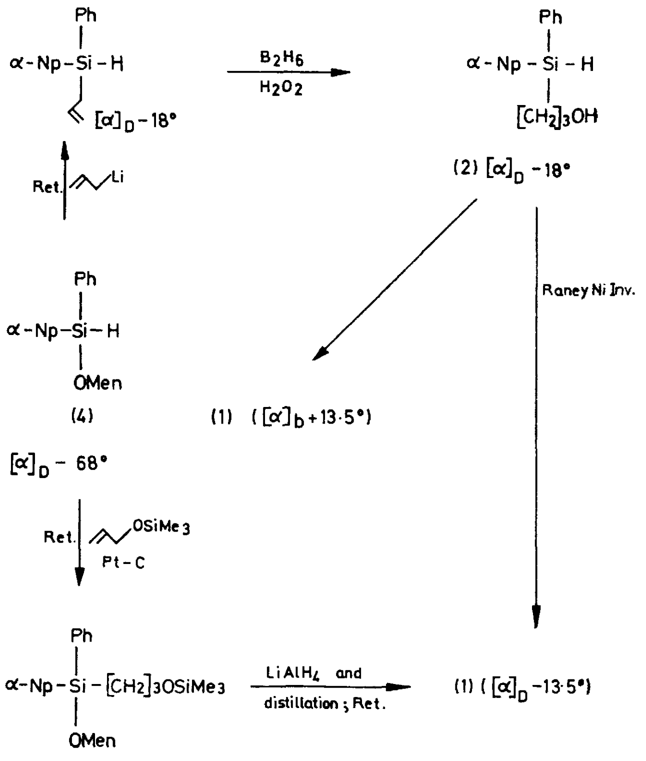
Summary The synthesis of an optically active oxasilacyclopentane is described for the first time; evidence is presented for an equatorial attack mechanism in some of its reactions.

It has been shown[1,2] that the stereochemistry of nucleophilic substitutions at silicon depends on the electronic character of the nucleophile. Further, in order to explain the results from coupling reactions of bifunctional optically active silicon compounds with organometallic compounds[3] we had suggested the possibility of an equatorial attack by the nucleophilic reagent at silicon. This hypothesis is now confirmed by studying the stereochemistry of breaking of the Si–O bond in compound (**1**). The most stable intermediate in nucleophilic substitution from (**1**) involves the equatorial–axial position of the heterocycle, with the oxygen atom in the apical position (Scheme 1). Thus



α-Np = α-naphthyl

Scheme 1



Men = menthyl

Scheme 2

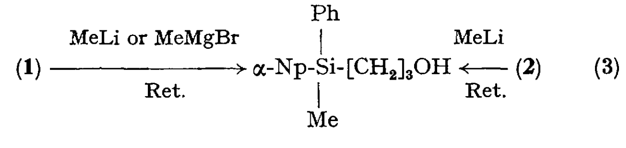
axial attack will take place with inversion and equatorial attack with retention of configuration at silicon.

Compound (**1**) was prepared as in Scheme 2. The metal-catalysed reaction of alcohols with Si–H bonds occurs with inversion[4] and thermal closure leads to retention of configuration at silicon, thus giving the enantiomeric compounds (**1**).

Reaction of (**1**) with $LiAlH_4$ or di-isobutylaluminium hydride (DIBAH)[5] in Et_2O with *NNN'N'*-tetramethylethylenediamine (TMED) occurs with retention of configuration at silicon [reactions (1) and (2)]. Opening of (**1**) with MeLi or MeMgBr also leads to equatorial attack (retention at silicon) [reaction (3)]. The stereochemistry of this reaction was shown by the following sequence: (**3**) ($[\alpha]_D$ $-2{\cdot}5^\circ$) was obtained with retention of configuration from the reaction of MeLi with (**2**) ($[\alpha]_D$ $+ 7^\circ$).[6] Compound (**3**) ($[\alpha]_D$ $- 3{\cdot}1^\circ$) was also obtained by the reaction sequence in Scheme 3.

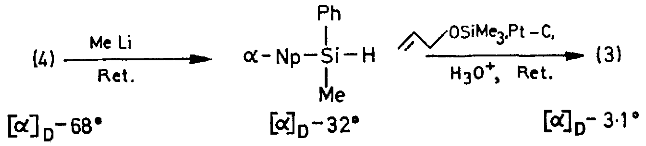
$$(\mathbf{1})\ ([\alpha]_D - 13{\cdot}5^\circ) \xrightarrow{\text{LiAlH}_4} (\mathbf{2})\ ([\alpha]_D + 7^\circ) \qquad (1)$$

$$\xrightarrow{\text{DIBAH}} (\mathbf{2})\ ([\alpha]_D + 8^\circ) \qquad (2)$$



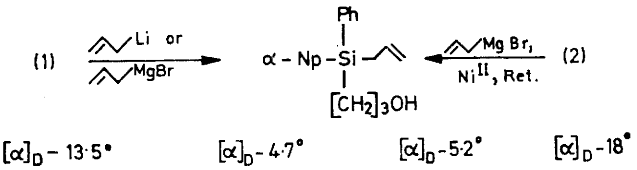
$$(\mathbf{1}) \xrightarrow[\text{Ret.}]{\text{MeLi or MeMgBr}} \alpha\text{-Np-}\overset{\text{Ph}}{\underset{\text{Me}}{\text{Si}}}\text{-[CH}_2]_3\text{OH} \xleftarrow[\text{Ret.}]{\text{MeLi}} (\mathbf{2}) \qquad (3)$$

$$[\alpha]_D - 13{\cdot}5^\circ \qquad [\alpha]_D - 5^\circ \qquad [\alpha]_D - 2{\cdot}5^\circ \qquad [\alpha]_D + 7^\circ$$



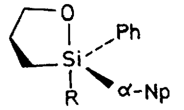
SCHEME 3

Allyl-lithium and -magnesium bromide react with (**1**) with inversion of configuration at silicon (axial attack). We have shown previously[6] that the allyl Grignard reagents activated by $\mathrm{Ni^{II}}$ complexes substitute the $\equiv$Si–H bond with retention of configuration at silicon.



The change in the stereochemistry of the breaking of the Si–O bond involves a change in the attack of nucleophilic reagent. For instance, allyl anions attack axially, in contrast to equatorial attack for propyl anions. The change in stereochemistry cannot be explained by the stability of intermediates because the most stable intermediate is always (A).

(A)



R = allyl, propyl

The present results agree with our previous hypothesis[3] on the change of stereochemistry with the nature of the nucleophile for reactions run with the same functional silane. The results could be explained by electronic factors. Hard nucleophilic reagents attack equatorially at silicon on a d_{xy} vacant orbital ('charge controlled process'). The softer nucleophiles attack axially on a d_{z^2} orbital ('frontier-orbital controlled process').

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