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Silicon-directed acid ring-opening of allyltrimethylsilane oxide. X-ray structures of 3-triisopropylsilyl-2-(2,4-dinitrobenzoyloxy)-1-propanol and 3-triisopropylsilyl-2-(2,4,6-trinitrobenzoyloxy)-1-propanol

Fatmir Badali, William Issa, Brett Pool, Jonathan M. White *

School of Chemistry, The University of Melbourne, Parkville, Victoria 3052, Australia

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Abstract

Allyltrimethylsilane oxide **5** undergoes regiospecific ring-opening with carboxylic acids in chloroform to give the hydroxy esters **6a–e**. In polar solvents competing elimination results in the formation of allyl alcohol. Allyltriisopropylsilane oxide **17** undergoes analogous reactions as **5** in chloroform but does not undergo elimination in methanol or acetone. The X-ray structures of **18b** and **18c** reveal significant lengthening of the C–O (ester) bond (a remarkable 1.502(2) Å for **18c**), these structural effects are due to strong $\sigma_{C-Si}-\sigma^{*}_{C-O}$ interactions, particularly for **18c**.

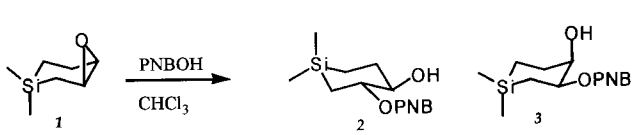
Keywords: Allyltrimethylsilane oxide; Ring opening; Regiospecific

1. Introduction

The stabilisation of positive charge at the β-position by silicon substituents, (referred to as the silicon β effect), is an extremely important property of silicon which has attracted much attention in the literature [1–3]. Theoretical, [4,5] and mechanistic [2,6,7] studies have provided valuable insight into this effect which is primarily due to hyperconjugation of the C–Si bond with the adjacent electron deficient centre. This property of silicon has been exploited in organic synthesis, where silicon substituents have been used to direct the course of reactions involving carbenium ion (or developing carbenium ion) intermediates in a useful way [3]. We recently reported an example of silicon directed carboxylic acid ring-opening of a γ,δ-epoxy silane [8], treatment of 1,1-dimethylsilacyclohex-3-ene oxide **1** with *p*-nitrobenzoic acid in chloroform (Scheme 1) resulted in the formation of the diastereomeric hydroxy esters **2** and **3** with the *p*-nitrobenzoate ester substituent at the position β- to the silicon as the only observed products.

A mechanism for the formation of **2** and **3** is summarised in Scheme 2: protonation of the epoxide oxygen is followed by ring opening to give the β-silicon stabilised carbenium ion **4** which is captured by the carboxylate ion to give the hydroxy esters **2** and **3**.

To further explore the silicon directed epoxide ring opening, we carried out a study on the reactions of the simple β,γ-silylepoxide **5** with a range of carboxylic acids and in solvents of varying polarity.



1 2 3

Scheme 1.

* Corresponding author. E-mail: j.white@secondwww.chemistry.unimelb.edu.au.

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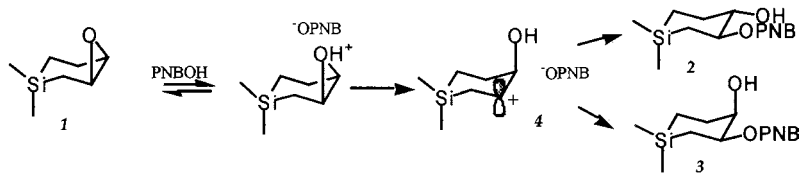
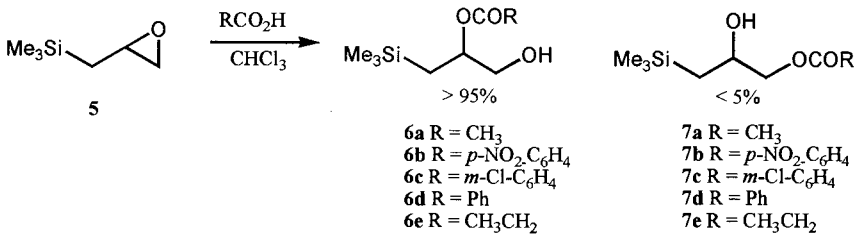
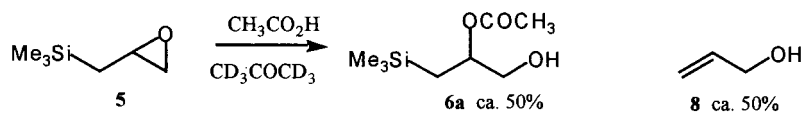


Scheme 2.



Scheme 3.



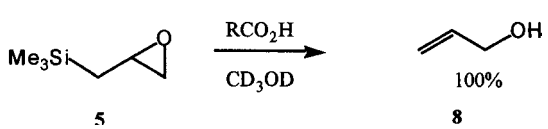
Scheme 4.

2. Results and discussion

Reactions of **5** with carboxylic acids were carried out in deuterated solvents, and monitored by ^{1}H- and ^{13}C-NMR These reactions are summarised in Scheme 3, in all examples the hydroxy esters **6a**–**e** were the only products observed. These esters were characterised by the appearance of a single proton multiplet at high frequency (in the range 5–6 ppm) corresponding to the CH–O (ester) proton, and a two proton multiplet occurring in the range 3–4 ppm corresponding to the CH_2–OH methylene protons. Signals consistent with the isomeric hydroxy esters **7a**–**e** were not detected.

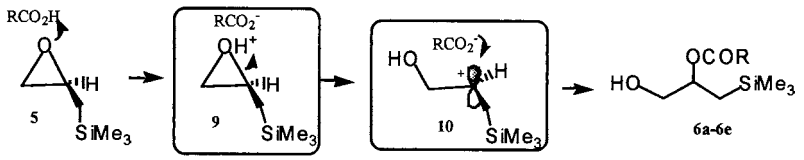
Reaction of epoxide **5** with carboxylic acids in acetone (Scheme 4, shown for reaction with acetic acid) gave rise to the same hydroxy esters **6a**–**e** but in addition there were significant quantities of allyl alcohol **8**, while reaction in methanol (Scheme 5) gave allyl alcohol as the only detectable product. The esters **6a**–**e** were found to be stable in acetone and methanol for several days without noticeable decomposition, demonstrating that allyl alcohol is not the product of further reaction under these conditions.

The formation of the products **6a**–**e** in the chloroform solvent can be accounted for by the mechanism in Scheme 6: protonation of the epoxide oxygen gives rise to the protonated intermediate **9** which in a solvent of relatively low polarity, is likely to exist as an intimate ion-pair. Ring opening of the protonated epoxide **9** giving the β-silyl stabilised carbenium ion **10** also as an intimate ion pair, is followed by capture of the carbenium ion **10** by the carboxylate anion within the intimate ion pair giving the observed hydroxy esters **6a**–**e**. Although the reaction of β-silyl carbenium ions with nucleophiles often results in preferential attack at silicon [1–3], resulting in elimination of the silicon substituent, this clearly is not occurring to any detectable extent with these reactions in chloroform.



Scheme 5.

A rationale for this can be provided, if it is assumed that in chloroform the reaction occurs within an intimate ion pair. It can be argued that the preferred conformation of the epoxide **5** has the trimethylsilyl substituent antiperiplanar to the epoxide oxygen (as shown in Scheme 6), this conformation would maximise the expected, significant, stabilising σ_{C-Si}–σ^{*}_{C-O} interaction between the C–Si bond and the C–O antibonding orbital on C_2 [9]. This interaction would be enhanced in the protonated intermediate **9**. Ring opening of the protonated epoxide **9** would then give the cation **10** with the trimethylsilyl substituent directed away from the face closest to the carboxylate ion, furthermore there would exist hindered rotation about C^{+}–C(Si) bond due to strong hyperconjugation [10], preventing rotation of the trimethylsilyl substituent towards the face closest to the carboxylate ion. Thus capture of this β-silyl carbenium ion, within the solvent cage should occur at the carbenium ion centre rather than at silicon. Evidence supporting an intimate ion pair intermediate in chloroform, is provided by the observation that reaction of allyltrimethylsilane oxide with acetic acid in



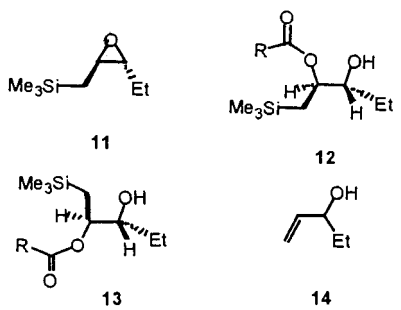
Scheme 6.

chloroform, in the presence of an equivalent of tetrabutylammonium acetate (to mimic a dissociated ion pair), results in competing elimination to give substantial quantities of allyl alcohol (Scheme 7).

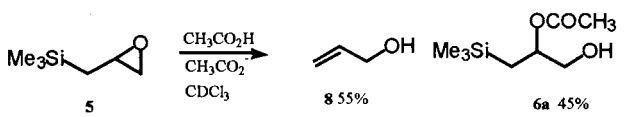
The observation of allyl alcohol as a significant product in acetone and as the only product in methanol, might be explained by the more polar solvents allowing significant dissociation of the intimate ion pair to a dissociated ion pair (Scheme 8), allowing attack at the silicon (giving allyl alcohol) to compete. An attack at the carbon giving the hydroxy esters can be envisaged to occur from either the intimate ion pair or the dissociated ion pair.

An alternative explanation for the formation of allyl alcohol is that elimination results from solvent attack at the silicon, in competition with carboxylate capture of the carbenium ion centre. Consistent with this is the greater proportion of allyl alcohol formed in the more strongly nucleophilic solvent methanol than in acetone.

To gain further support for the involvement of intimate ion pairs in chloroform we chose to study the stereochemistry of the acid ring opening of *trans*-1-trimethylsilyl-2-pentene oxide **11**. Acid ring opening of **11** within a tight ion pair would be expected to give the hydroxy ester **12** only, whereas reaction from the dissociated ion pair would be expected to give both diastereoisomers **12** and **13** in addition to the elimination product **14**.



The epoxide was prepared from the *E*-alkene **15** (Scheme 9) which was prepared by the general method



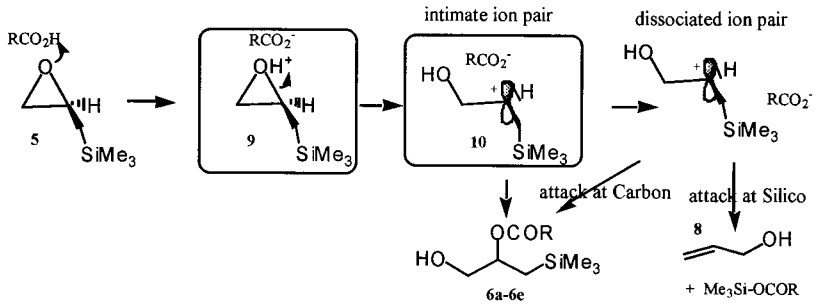
Scheme 7.

for the preparation of isomerically pure alkenylsilanes reported by Shimizu et al. [11].

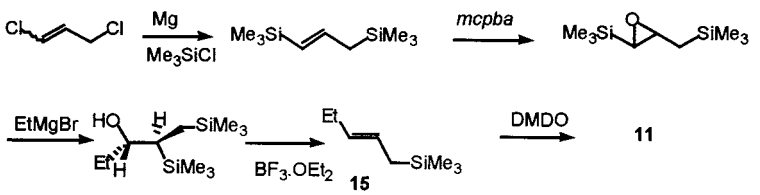
Treatment of **11** with one equivalent of acetic acid in chloroform unfortunately gave rise to a complex mixture of products which were not readily separable. ^{13}C- and ^{1}H-NMR analysis of the mixture however showed it to contain the elimination product 1-pentenol-3-ol **14** as the major product, in addition to **14**, signals consistent with the diastereoisomers **12** and **13** were also present but these could not be not isolated in pure form. This result contrasts with that obtained from the acid ring opening of **5** in chloroform where no elimination was observed. It is possible that the presence of the ethyl group on the carbenium ion **16** renders this ion stable enough to allow significant diffusion from the tight ion pair to a dissociated ion pair in this solvent, thus allowing attack of the carboxylate ion at the silicon to give the elimination product **14** in addition to attack at the carbenium ion from both faces giving **12** and **13** (Scheme 10).

We were interested to see whether the competing nuclephilic attack on the β-silyl carbenium ion **10** at the silicon which occurs in acetone and methanol could be minimised by the use of bulky substituents on the silicon, to test this end we chose the triisopropylsilyl epoxide **17** as a model substrate. Epoxide **17** was prepared from commercially available allyltriisopropylsilane by reaction with dimethyldiioxirane in acetone [12]. Reaction of **17** with *p*-nitrobenzoic acid in chloroform (Scheme 11) gave the hydroxy ester **18a** in quantitative yield as was analogous to **5**, however when the acid ring opening was conducted in acetone the hydroxy ester **18a** was the only product obtained with no evidence for the formation of allyl alcohol. Furthermore, reaction of **17** with *p*-nitrobenzoic acid in methanol gave the hydroxy methyl ether **19** as the only detectable product, presumably by competing capture of the intermediate carbenium ion by methanol, again with no evidence of allyl alcohol in the reaction mixture. This result supports the proposal that competing elimination which occurs for the ring opening of epoxide **5** in acetone and methanol occurs by nucleophilic attack at the silicon of the carbenium ion **10**.

The apparent lack of reactivity of the triisopropylsilyl substituent towards nucleophilic attack during the acid ring opening of **17**, suggested a possible method to



Scheme 8.

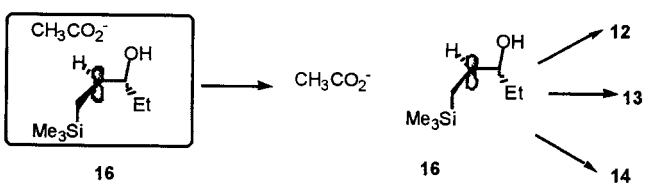


Scheme 9.

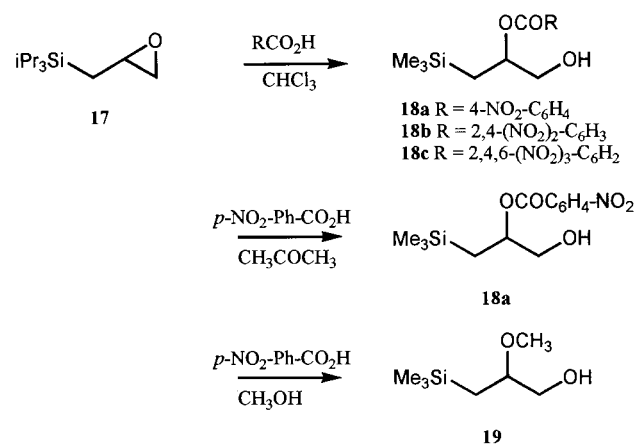
us for the preparation of β-silyl esters with strongly electron demanding ester groups for example **18b** and **18c**. We required these compounds as part of our continuing accurate structural studies on β-silyl esters with esters groups of varying electron demand [3]. However we have experienced great difficulty in the preparation of crystalline 2° β-trimethylsilyl esters with high electron demand using the conventional approach of esterifying the corresponding 2° β-trimethylsilylalcohols with an appropriate acid chloride or anhydride. These reactions are accompanied by significant amounts of olefinic products resulting from elimination of Me_3Si–OCOR. Since elimination of the silicon substituent appears to require nucleophilic assistance [13], we envisaged that reactive esters derived from acid ring opening of the epoxide **17** would be more stable and hopefully more readily handled. Thus treatment of epoxide **11** with 2,4-dinitrobenzoic acid and 2,4,6-trinitrobenzoic acid, respectively gave the 2,4-dinitrobenzoate and 2,4,6-trinitrobenzoate esters **18b** and **18c**, respectively in high yields. The structures of both these derivatives were verified by single-crystal X-ray analysis.

2.1. Molecular structures

The structures of **18b** and **18c** were determined at low temperature to minimise the effects of thermal motion, **18b** was determined at 130 K while **18c** (which under went a phase change below 160 K) was determined at 200 K. The structures of **18b** and **18c** are presented in Figs. 1 and 2, hydrogen atoms (which were refined isotropically) are omitted for clarity. Atomic coordinates for **18b** and **18c** are presented in Tables 1 and 2, respectively. Selected bond distances are presented in Table 3 and selected bond angles and dihedral angles are presented in Table 4. The dinitrobenzoate **18b** exists in the solid state as a hydrogen bonded dimer with the two molecules related by a centre of symmetry (Fig. 3). The dimer is stabilised by two hydrogen bonds between the CH_2OH group on one molecule and a NO_2 group on the second; the H···O6A distance is 2.09 Å, the O7–H···O6A angle is 165.8° and the O7…O6A distance is 2.925(1) Å. In addition to the two O–H…O hydrogen bonds the dimer is also stabilised by π–π interactions between the benzoate groups rings, the aromatic rings are parallel and the distance between the planes defined by the two aromatic rings is 3.39 Å. The trinitrobenzoate **18c** in contrast exists in the solid state



Scheme 10.



Scheme 11.

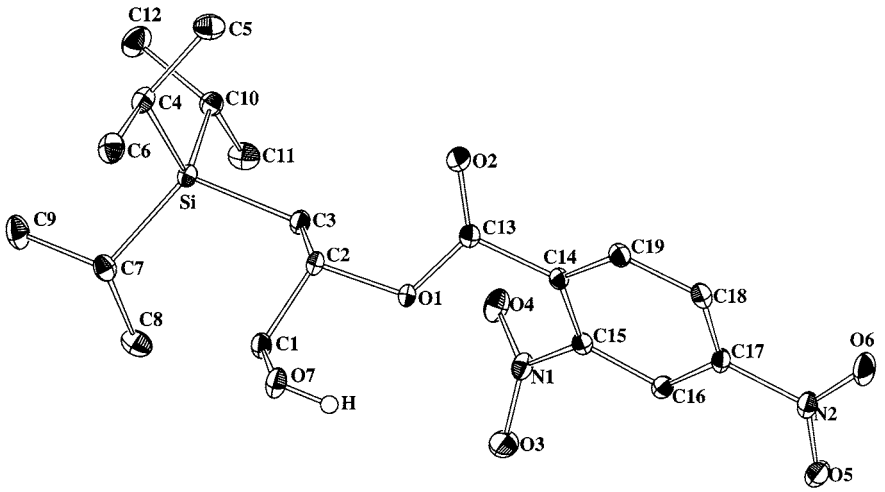


Fig. 1. Thermal ellipsoid plot for compound **18b**.

as linear chains of molecules held together by ($CH_2OH\ldots O_2N$) hydrogen bonds extending along the x direction (Fig. 4), the H1…O4 distance is 2.14 Å, the O9A–H1A…O4 angle is 171.5° and the O9…O4 distance is 3.025(2) Å.

The C2–O1 bond distances in **18b** and **18c** which are 1.480(1) and 1.502(2) Å, respectively appear to be remarkably long, carbon–oxygen bond distances in the structural fragment $R_3C–OR$ depend on the substituents attached to the carbon and upon the electron demand of the oxygen substituent (–OR) as indicated by the pK_a value for the parent acid R–OH [14,15]. A linear relationship between C–OR bond distance and pK_a for 2° alcohols and esters has been determined as: $r(\text{C–OR, Å}) = 1.475 - (2.90 \times 10^3)\ \text{p}K_a\ (\text{ROH})$. This equation leads to the prediction that a 2° C–O–(2,4-dinitrobenzoyl) distance should be 1.471 Å, and a 2° C–OC(O)(2,4,6-trinitrobenzoyl) distance should be 1.473 Å (using pK_a 2,4 $(NO_2)_2$–Ph–CO_2H as 1.42 and pK_a 2,4,6-$(NO_2)_3$–Ph–CO_2H 0.67). The lengthening of the C2–O1 bond distances in **18b** and **18c** compared to that predicted can be rationalised by examination of the Si–C3–C2–O1 dihedral angles in Table 3 which is essentially antiperiplanar in both structures, this conformation would allow for an optimum σ_{C-Si}–σ^*_{C-O} interaction between the high energy Si–C3 bonding orbital and the low lying C2–O1 antibonding orbital [9]. σ–σ^* Interactions have been previously demonstrated to lead to significant bond lengthening in cyclohexyl [3] and acyclic β-silyl esters [16]. The degree of lengthening of the C2–O1 bond in the trinitrobenzoate **18c** compared to that predicted is 0.029 Å which is larger than the bond lengthening observed for the dinitrobenzoate **18b** which is 0.09 Å. This is to be expected since the σ^*_{C-O} orbital in the more electron demanding trinitrobenzoate will lie at a lower energy than the σ^*_{C-O} orbital for the dinitrobenzoate ester **18b** resulting in a better energy match with the C–Si bond and hence a stronger σ_{C-Si}–σ^*_{C-O} interaction. The stronger σ_{C-Si}–σ^*_{C-O} interaction in **18c** compared with

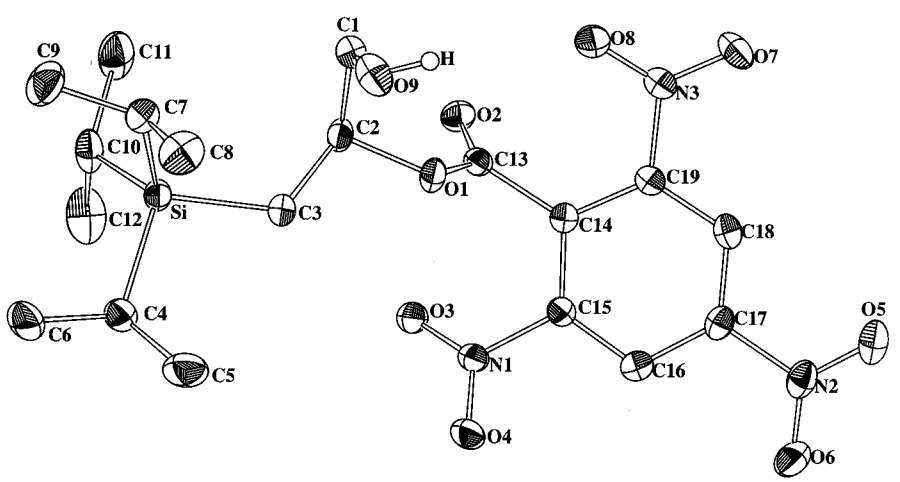


Fig. 2. Thermal ellipsoid plot for compound **18c**.

18b does not manifest in any other significant structural differences, for example the Si–C3 and C3–C2 bonds do not differ significantly between the two structures.

The silicon directed acid ring opening of allyltrimethylsilane oxide in low polarity solvents gives rise to potentially useful hydroxyesters with regiochemical control, from what is likely to be reaction within an intimate ion pair. Reaction in polar solvents, or in the presence of external nucleophiles results in significant competing elimination of the silicon. Incorporation of bulky substituent onto the silicon removes the problem of elimination in polar solvents, thus increasing the scope of this reaction as a method for the formation of hydroxyesters. With the appropriate substituents attached to silicon, a C–Si bond can be considered as a latent hydroxy group [17–19], thus simple epoxides similar to **5** might provide a useful starting point for the preparation of mixed triesters of glycerol.

3. Experimental

3.1. Crystallography

Diffraction data were recorded on an Enraf Nonius CAD4f diffractometer operating in the $\theta/2\theta$ scan mode at low temperature (130.0(1) K) for **12b** and **12c**. The crystals were flash cooled to 130.0 K using an Oxford Cryostream cooling device. Unit cell dimensions were corrected for any θ zero errors by centring reflections at both positive and negative θ angles. The data were corrected for Lorentz and Polarization effects and for Absorption (SHELX 76) [20]. Structures were solved by direct methods (SHELXS-86) [21] and were refined on F^2 (SHELXL-97) [22]. The figures were drawn using the ZORTEP program [23]. Crystal data and refinement details for **18b** and **18c** are listed in Table 4.

Table 1
Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **18b**[a]

	x/a	y/b	z/c	U_{eq}
Si	0.34082(4)	0.20185(4)	0.149944(17)	0.01931(10)
O(1)	0.67980(11)	−0.11191(11)	0.32248(4)	0.01949(19)
O(2)	0.90335(13)	−0.17349(13)	0.24137(5)	0.0324(2)
O(3)	0.48969(13)	−0.39958(16)	0.42679(6)	0.0397(3)
O(4)	0.54437(13)	−0.40887(13)	0.31265(5)	0.0314(2)
O(5)	0.99981(14)	−0.88793(13)	0.55293(5)	0.0302(2)
O(6)	1.26347(14)	−0.90354(14)	0.50589(6)	0.0365(3)
O(7)	0.58878(13)	0.20334(13)	0.37916(5)	0.0275(2)
N(1)	0.59022(14)	−0.42265(14)	0.37541(6)	0.0243(2)
N(2)	1.10234(15)	−0.83478(14)	0.50809(6)	0.0246(2)
C(1)	0.48220(17)	0.16558(17)	0.32770(7)	0.0231(3)
C(2)	0.58974(16)	0.05553(16)	0.27488(7)	0.0202(2)
C(3)	0.47853(17)	0.01477(17)	0.21901(7)	0.0218(3)
C(4)	0.47746(18)	0.35736(18)	0.10422(7)	0.0256(3)
C(5)	0.6490(2)	0.2564(2)	0.07097(9)	0.0338(3)
C(6)	0.5182(2)	0.4806(2)	0.15209(9)	0.0314(3)
C(7)	0.14018(17)	0.33674(18)	0.19471(7)	0.0247(3)
C(8)	0.0314(2)	0.2278(2)	0.24480(9)	0.0335(3)
C(9)	0.0183(2)	0.4779(2)	0.13885(9)	0.0360(3)
C(10)	0.28618(17)	0.08079(18)	0.07857(7)	0.0240(3)
C(11)	0.1677(2)	−0.0451(2)	0.10611(8)	0.0321(3)
C(12)	0.2110(2)	0.2013(2)	0.00756(8)	0.0374(4)
C(13)	0.82809(16)	−0.21147(16)	0.29705(7)	0.0208(2)
C(14)	0.89569(16)	−0.38067(16)	0.35026(6)	0.0189(2)
C(15)	0.78375(16)	−0.47484(16)	0.39028(6)	0.0189(2)
C(16)	0.84648(17)	−0.62250(17)	0.44298(7)	0.0205(2)
C(17)	1.02993(17)	−0.67732(16)	0.45270(6)	0.0208(2)
C(18)	1.14783(17)	−0.59030(17)	0.41406(7)	0.0228(3)
C(19)	1.07894(17)	−0.44060(17)	0.36273(7)	0.0223(3)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

3.2. Synthesis

General experimental details are reported elsewhere [16], allyltriisopropylsilane and allyltrimethylsilane were purchased from Aldrich and used without further purification. *E*-1-Trimethylsilyl-2-butene was prepared as reported [11].

3.3. General procedure for the ring opening of allyltrimethylsilane oxide **5** with carboxylic acids in chloroform

A solution of 50 mg of epoxide **5** in deuterated chlorform (0.5 ml) was treated with one equivalent of the carboxylic acid. Progress was monitored by ^{1}H- and ^{13}C-NMR, reactions were generally complete within 2 days. In all cases the reaction gave rise to one detectable product **6a**–**e**

^{13}C-NMR data for **6a**–**e**: δ ($CDCl_3$) are: **6a**. 171.27; 73.84; 66.15; 21.13; 18.82; −1.23; ^{1}H-NMR: 4.95 (1H, m); 3.6–3.4 (2H, m); 1.90 (3H, s); 0.9–0.7 (2H, m); (−0.10 (9H, s).

6b. 164.67; 150.49; 135.76; 130.68; 123.46; 75.98; 66.50; 19.17; −1.00; 8.25 (2H, d, $J = 7.5$ Hz); 8.15 (2H, d, $J = 7.5$ Hz); 5.35 (1H, m); 3.8–3.7 (2H, m); 2.6 (1H,br S, OH); 1.2–0.95 (2H, m); 0.0 (9H, s).

6c. 165.29; 134.31; 132.78; 132.02; 129.55; 129.50; 127.64; 75.08; 66.26; 19.06; −1.09; ^{1}H-NMR: δ ($CDCl_3$) 7.96 (1H, Br S); 7.88 (1H, Br, D = d, $J = 7$ Hz); 7.44 (1H, d, $J = 7$ Hz); 7.29 (1H, dd, $J = 7$ Hz, 7 Hz); 5.31 (1H, m); 4.8 (1H, br, S, OH); 3.8–3.6 (2H, m); 1.1–0.8 (2H, m); 0.01(9H, s).

6d. 166.54; 132.77; 130.23; 129.52; 128.14; 74.53; 66.38; 19.04; −1.09; ^{1}H-NMR: δ ($CDCl_3$) 0.8 (2H, Br, d); 7.6–7.2 (3H, m); 5.35 (91H, m); 3.8–3.6 (2H, m); 1.2–0.9 (2H, m); 0.02 (9H, s).

6e. 174.70; 73.74; 66.34; 27.14; 18.92; 8.70; −1.17, ^{1}H-NMR: δ ($CDCl_3$) 5.0 (1H, m); 3.6–3.4 (2H, m); 2.24 (2H, d); 1.05; 1.05 (3H, t); 0.85 (2H, m); −0.1 (9H, s).

Table 2
Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **18c**[a]

	x/a	y/b	z/c	U_{eq}
Si	0.87776(8)	0.84247(7)	0.079634(14)	0.03535(15)
O(1)	0.8361(2)	0.93359(17)	0.19029(3)	0.0372(3)
O(2)	0.8703(2)	1.18750(17)	0.20620(4)	0.0412(3)
O(3)	1.2210(2)	0.99779(19)	0.19871(4)	0.0467(4)
O(4)	1.3337(2)	0.78416(19)	0.22194(4)	0.0513(4)
O(5)	1.0544(3)	0.8142(2)	0.37410(4)	0.0593(5)
O(6)	1.3200(3)	0.7768(2)	0.35148(4)	0.0622(5)
O(7)	0.5739(2)	1.0674(2)	0.30382(4)	0.0521(4)
O(8)	0.5772(2)	1.0606(2)	0.24625(4)	0.0565(5)
O(9)	0.5195(3)	0.8003(2)	0.15152(5)	0.0600(5)
N(1)	1.2329(2)	0.8986(2)	0.22215(5)	0.0369(4)
N(2)	1.1594(3)	0.8186(2)	0.34965(5)	0.0452(5)
N(3)	0.6506(2)	1.0449(2)	0.27622(5)	0.0370(4)
C(1)	0.5795(3)	0.9560(3)	0.14732(6)	0.0476(6)
C(2)	0.7865(3)	0.9696(3)	0.15161(5)	0.0391(5)
C(3)	0.8953(3)	0.8551(3)	0.13052(5)	0.0397(5)
C(4)	1.0714(3)	0.7043(3)	0.07008(6)	0.0447(5)
C(5)	1.0855(5)	0.5590(4)	0.09428(10)	0.0697(8)
C(6)	1.0744(5)	0.6592(5)	0.03075(8)	0.0695(9)
C(7)	0.6436(3)	0.7693(3)	0.06269(6)	0.0473(5)
C(8)	0.6047(5)	0.6019(4)	0.07398(10)	0.0663(8)
C(9)	0.6037(5)	0.7904(5)	0.02211(8)	0.0730(9)
C(10)	0.9241(4)	1.0347(3)	0.05711(6)	0.0502(6)
C(11)	0.7817(6)	1.1601(4)	0.06451(9)	0.0747(10)
C(12)	1.1185(6)	1.0944(4)	0.06473(10)	0.0768(10)
C(13)	0.8770(3)	1.0503(2)	0.21223(5)	0.0323(4)
C(14)	0.9450(3)	0.9850(2)	0.24846(5)	0.0300(4)
C(15)	1.1180(3)	0.9164(2)	0.25318(5)	0.0312(4)
C(16)	1.1922(3)	0.8621(2)	0.28562(5)	0.0345(4)
C(17)	1.0846(3)	0.8778(2)	0.31459(5)	0.0350(4)
C(18)	0.9112(3)	0.9400(2)	0.31204(5)	0.0351(4)
C(19)	0.8433(3)	0.9912(2)	0.27898(5)	0.0311(4)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

3.4. General procedure for the ring opening of allyltrimethylsilane oxide **5** with carboxylic acids in acetone

A solution of 50 mg of epoxide **5** in hexadeuteroacetone (0.5 ml) was treated with one equivalent of the carboxylic acid.

Reaction with *p*-nitrobenzoic acid gave **62** (ca. 50%) and allyl alcohol (ca. 50%). ^{13}C-NMR: δ ($CDCl_3$) 138.86; 114.88; 63.93.

3.5. 1-Trimethylsilyl-2-pentene oxide **11**

A solution of *E*-1-trimethylsilyl-2-butene (500 mg) in dichloromethane (20 ml) was treated with a solution of dimethyldioxirane in acetone (ca. 0.09 M 1.5 equivalents) as 0°C. The resulting solution was stirred for 60 min, dried ($MgSO_4$) filtered and evaporated down to an oil which was pure by ^{13}C-NMR: δ ($CDCl_3$) 61.35; 56.74; 25.28; 20.79; 9.90; −1.30.

3.6. Reaction of 1-trimethylsilyl-2-pentene oxide with acetic acid in chloroform

trans-1-Trimethylsilyl-2-pentene oxide (0.11 g, 7.0×10^{-4} mol) was placed in a NMR tube with acetic acid (0.038 g, 6.3×10^{-4} mol) in $CDCl_3$. This was left for a week with occasional shaking to give a complex mixture containing 3-hydroxy-1-pentene; ^{1}H-NMR: δ ($CDCl_3$) 5.80 (1H, m); 5.16 (1H, d, $J = 17$ Hz); 5.06 (1H, d, $J = 11$ Hz); 4.01 (1H, m) 1.50 (2H, m) 1.83 (3H, m) ^{13}C-NMR: δ 140.60; 114.74; 74.56; 29.92; 9.90; Other signals 171.5; 171.01; 80.43; 80.23; 77.19; 77.19; 76.75; 75.99; 75.78; 74.67; 74.61; 70.30; 68.46; 70.95; 68.46; 52.84; 39.52; 38.3; 36.75; 35.01; 33.40.

3.7. Allyltriisopropylsilane oxide **17**

A solution of allyltriisopropylsilane (0.5 g) was treated with an acetone solution of dimethyldioxirane (ca. 0.09 M, 1.5 equivalents). After stirring for 60 min at room temperature the solvent was removed giving **17** as a colourless oil 98%. ^{13}C-NMR: δ ($CDCl_3$) 10.95; 14.10; 18.56; 49.56; 50.54. ^{1}H-NMR: δ ($CDCl_3$) (2H, m); 1.02 (20H, s); 1.25 (1H, m); 2.43 (1H, m); 2.77 (1H, m); 3.00 (1H, m).

Table 3
Selected distances (Å), angles (°) and dihedral angles (°) for **18b** and **18c**

Bond distances (Å)		
Si–C3	1.9044(13)	1.901(2)
Si–C4	1.8906(14)	1.888(2)
Si–C7	1.8946(14)	1.890(3)
Si–C10	1.9003(14)	1.886(2)
C1–C2	1.5106(17)	1.509(3)
C2–C3	1.5158(17)	1.508(3)
C2–O1	1.4802(14)	1.502(2)
C1–O	1.4184(15)	1.413(3)
O1–C13	1.3335(15)	1.315(2)
O2–C13	1.1978(16)	1.196(2)
Bond angles (°)		
C10–Si–C3	110.97(6)	113.10(11)
C10–Si–C7	115.14(6)	108.61(12)
C10–Si–C4	107.53(6)	107.97(11)
C4–Si–C7	108.30(6)	113.39(11)
C4–Si–C3	111.57(6)	102.39(10)
C7–Si–C3	110.97(6)	111.32(11)
Si–C3–C2	120.40(9)	123.40(15)
C3–C2–C1	114.32(11)	116.3(2)
C3–C2–O1	103.10(9)	105.28(16)
C2–C1–O	113.43(11)	111.9(2)
C2–O1–C13	117.25(9)	118.54(16)
Dihedral angles (°)		
Si–C3–C2–O1	178.83(8)	177.40(16)
Si–C3–C2–C1	63.81(14)	60.7(3)
C3–C2–C1–O	−179.56(10)	49.0(3)
O1–C2–C1–O	61.78(13)	−67.5(2)
C3–C2–O1–C13	80.29(13)	133.68(19)
C1–C2–O1–C13	−157.68(10)	−102.6(2)

Table 4
Crystal data and structure refinement for **18b** and **18c**

Empirical formula	$C_{19}H_{30}N_2O_7Si$	$C_{19}H_{29}N_3O_9Si$
Formula weight	426.54	471.54
Temperature (K)	130.0(1)	200.0(1)
Radiation	Cu–K_α, Nickel filtered	Cu–K_α, Nickel filtered
Wavelength (Å)	1.54180	1.54180
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
Unit cell dimensions		
a (Å)	7.7517(9)	7.2718(7)
b (Å)	7.9090(10)	8.5559(9)
c (Å)	18.7240(10)	37.350(4)
α (°)	79.600(10)	
β (°)	87.140(10)	93.140(10)
γ (°)	74.930(10)	
V (Å^3)	1090.2(2)	2320.3(4)
Z	2	4
$D_{calc.}$ (g m^{-3})	1.299	1.350
Absorption coefficient (mm^{-1})	0.316	1.371
$F(000)$	456	1000
Crystal size (mm)	$0.42 \times 0.14 \times 0.14$	$0.36 \times 0.12 \times 0.02$
θ range for data collection (°)	2.40–74.88	2.37–74.91
Index ranges	$-9 \le h \le 9,\ 0 \le k \le 9,\ -23 \le l \le 23$	$0 \le h \le 9,\ -10 \le k \le 0,\ -46 \le l \le 46$
Intensity control reflections	3	3
Measurement interval (min)	60	60
Decomposition	Insignificant	Insignificant
Reflections collected	4819	5147
Independent reflections	4480 [$R_{int} = 0.0161$]	4760 [$R_{int} = 0.0179$]
No. of observed reflections	4014 [$I > 2\sigma(I)$]	3510 [$I > 2\sigma(I)$]
Refinement method	Full-matrix on F^2	Full-matrix on F^2
Data/restraints/parameters	4480/0/383	4760/0/406
Goodness-of-fit on F^2	1.010	1.034
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0317$, [a]$wR_2 = 0.0847$	$R_1 = 0.0422$, [a]$wR_2 = 0.0950$
R indices (all data)	$R_1 = 0.0364$, [a]$wR_2 = 0.0885$	$R_1 = 0.0654$, [a]$wR_2 = 0.1066$
A	0.0515	0.0442
B	0.3316	0.6839
Extinction coefficient	0.0035(4)	0.00019(8)
Absorption: max. min. trans.	0.88 and 0.68	0.97 and 0.78
Maximum shift/S.D.	0.012	0.002
Largest difference peak and hole (e Å^{-3})	0.390 and −0.198	0.258 and −0.213

[a] Weighting scheme calc. $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$ where $P = (F_o^2 + 2F_c^2)/3$.

3.8. Reaction of allyltriisopropylsilane oxide **17** with p-nitrobenzoic acid in chloroform: preparation of 2-(p-nitrobenzoyloxy)-3-triisopropylsilyl-1-propanol **18a**

Allyltriisopropylsilane oxide **17** (0.50 g, 2.3×10^{-3} mol) and *p*-nitrobenzoic acid (0.39 g, 2.3×10^{-3} mol) were stirred in chloroform (20 ml) overnight, then filtered and the solvent was removed under reduced pressure to give **18a** (0.79 g, 89%) with m.p. (97.5–99.5°C). ^{13}C-NMR: δ ($CDCl_3$) 11.32; 11.71; 18.64; 66.90; 75.97; 123.46; 123.52; 130.70; 133.36; 164.79. ^{1}H-NMR: δ ($CDCl_3$) 1.05 (21H, m); 1.10 (1H, dd, $J = 6.8$, 15 Hz); 1.22 (1H, dd, $J = 7.7$, 15 Hz); 2.00 (1H, s) [OH]; 3.74 (1H, dd, $J = 6.6$, 12 Hz); 3.87 (1H, dd, $J = 3.2$, 12 Hz); 5.45 (1H, m); 8.21 (2H, d, $J = 11$ Hz), 8.30 (2H, d, $J = 11$ Hz). υ(nujol) 3523.9, 1715.9 cm^{-1}.

3.9. Reaction of allyltriisopropylsilane oxide **17** with p-nitrobenzoic acid in acetone

Allyltriisopropylsilane oxide **17** (0.50 g, 2.3×10^{-3} mol) and *p*-nitrobenzoic acid (0.39 g, 2.3×10^{-3} mol) were stirred in acetone (20 ml) overnight, and the solvent was removed under reduced pressure to give **18a** (0.8 g, 89%).

3.10. Reaction of allyltriisopropylsilane oxide **17** with p-nitrobenzoic acid in methanol: preparation of 2-methoxy-3-triisopropylsilyl-1-propanol **19**

Allyltriisopropylsilane oxide (0.44 g, 2.0×10^{-3} mol) and *p*-nitrobenzoic acid (0.34 g, 2.0×10^{-3} mol) were stirred in methanol (20 ml) overnight, then filtered and the solvent was removed under reduced pressure to give

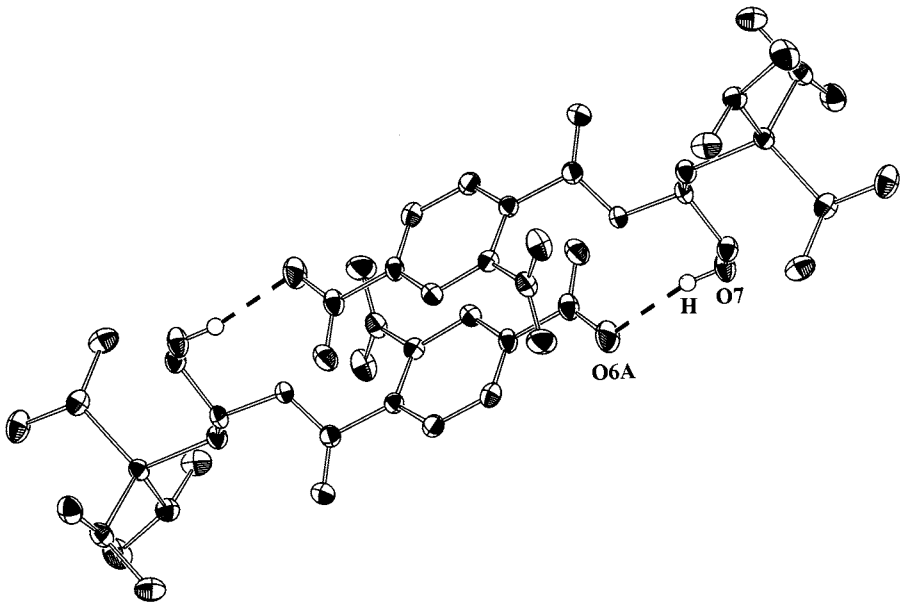


Fig. 3. H-Bonding in **18b**.

2-methoxy-1-triisopropylsilyl-3-propanol. ^{13}C-NMR: δ ($CDCl_3$) 11.39; 11.48; 18.75; 56.04; 65.60; 79.37. ^{1}H-NMR: δ ($CDCl_3$) 0.72 (1H, dd, $J = 8.1$, 15 Hz); 1.05 (21H, m); 1.85 (1H, dd, $J = 5.8$, 15 Hz); 2.55 (1H, s); 3.35 (3H, s); 3.42 (1H, dd, $J = 6.2$, 11 Hz); 3.50 (1H, m); 3.75 (1H, dd, $J = 3.1$, 11 Hz).

3.11. 2-(2,4-Dinitrobenzoyloxy)-3-triisopropylsilyl-1-propanol ***18b***

From 2,4-dinitrobenzoic acid, procedure as for **18a**. 85% yield, m.p. 171–172°C, ^{1}H-NMR: δ ($CDCl_3$) 1.05 (21H, m); 1.10 (1H, dd, 8.6, 15 Hz) 1.22 (1H, dd, 6.3, 15 Hz); 2.51 (1H, s) [OH]; 3.70 (1H, dd, 6.1, 12 Hz); 3.95 (1H, dd, 2.4, 12 Hz); 5.45 (1H, m); 7.98 (1H, m); 8.56 (1H, m) 8.78 (1H, m).

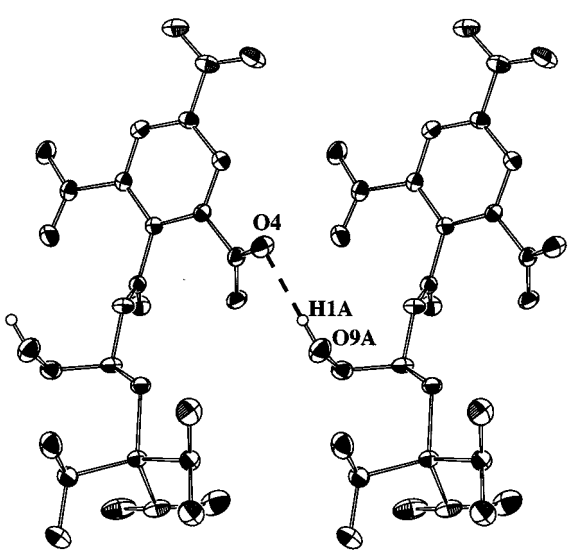


Fig. 4. H-Bonding in **18c**.

3.12. 2-(2,4,6-Trinitrobenzoyloxy)-3-triisopropylsilyl-1-propanol ***55c***

From 2,4-dinitrobenzoic acid, procedure as for **18a**. 80% yield, m.p. 98–99°C, ^{13}C-NMR: δ ($CDCl_3$) 10.79; 11.39; 18.66; 64.74; 81.00; 123.71; 124.54; 130.17; 133.35; 160.29 ^{1}H-NMR: δ ($CDCl_3$) 1.05 (21H, m); 1.10 (1H, m); 1.15 (1H, m); 2.45 (1H, s) [OH] 3.75 (1H, dd, $J = 6.8$, 14 Hz); 4.00 (1H, dd, $J = 3.4$, 14 Hz); 5.55 (1H, m) 9.21 (1H, s).

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