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Evidence for Silicon-Directed Acid-Catalysed Ring Opening of a β,γ-Epoxy Silane: Reaction of 1,1-Dimethyl-1-silacyclohex-3-ene Oxide with *p*-Nitrobenzoic Acid

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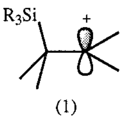
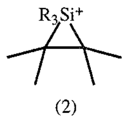
The ring-opening reaction of the β,γ-epoxy silane (4) with *p*-nitrobenzoic acid in chloroform occurs regiospecifically to give the two hydroxy esters (14) and (15). The mechanism involves regiospecific ring opening giving the β-silicon-stabilized carbenium ion (18) which is captured by the *p*-nitrobenzoate counter ion. The solution conformation of (14) provides evidence for the presence of $\sigma_{C-Si}-\sigma^*_{C-O}$ interactions between the ring C–Si bonding orbital and the C–$OCOC_6H_4NO_2$ antibonding orbital. In acetone, reaction of (4) with *p*-nitrobenzoic acid takes a different pathway and results in acyclic products from solvent attack at the silicon.

Introduction

The remarkable stabilizing effect of silicon substituents on positive charge at the β-position is referred to as the silicon β-effect, and has been used to great effect in organic synthesis.[1,2] Silicon is particularly useful in controlling the course of reactions and rearrangements which involve carbenium (or developing carbenium ion) intermediates.[3] These reactions generally occur in such a way that the positive charge is located β to the silicon substituent. The magnitude of the stabilization of positive charge by a β-silyl substituent depends on the electron demand of the carbenium ion,[1] and has been calculated to be 160 kJ/mol primary, 120 kJ/mol for secondary, and 75 kJ/mol for tertiary carbenium ions in the gas phase,[4,5] and *c.* 75 kJ/mol for secondary carbenium ions in solution.[6] The origin of this remarkable stabilization is believed to be substantially due to hyperconjugation (σ–π conjugation)[1,2] between the C–Si σ bonding orbital and the vacant carbocation p orbital as represented by (1); stabilization involving the non-classical ion (2) appears to be important in primary systems.[1–3]



(1)



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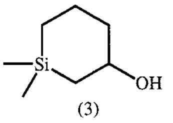

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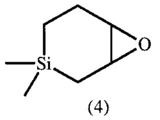
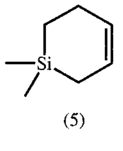
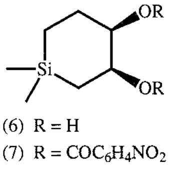


(4)



(5)



(6) R = H
(7) R = $COC_6H_4NO_2$

As part of our studies on the ground-state effects of silicon substituents on leaving groups at the β-position[1,7–9] we attempted to synthesize 1,1-dimethyl-1-silacyclohexan-3-ol (3) for which the epoxide (4) was seen as a possible precursor. Initial attempts to synthesize this epoxide, involving treatment of the known alkene (5) with *m*-chloroperoxybenzoic acid in dichloromethane, unfortunately gave a complex mixture. Reduction of this mixture with lithium aluminium hydride gave the *cis*-diol (6) as the major product which was characterized by X-ray analysis of the bis-*p*-nitrobenzoate ester derivative (7).[10] It appeared that the epoxide (4) was sensitive to the *m*-chlorobenzoic acid by-product of this procedure and that further reactions of the epoxide (4) with this acid were occurring. We subsequently synthesized the epoxide (4) under neutral conditions using a modified Payne epoxidation procedure.[11] The apparent sensitivity of epoxide (4) to acid prompted us to investigate the acid-catalysed ring opening of this epoxide under controlled reaction conditions in order to assess any directing effects that the silicon substituent might exert on the epoxide ring opening.

Results and Discussion

1,1-Dimethyl-1-silacyclohex-3-ene (5) was synthesized in 7 steps starting from dichlorodimethylsilane following reported procedures[12–14] with minor modifica-

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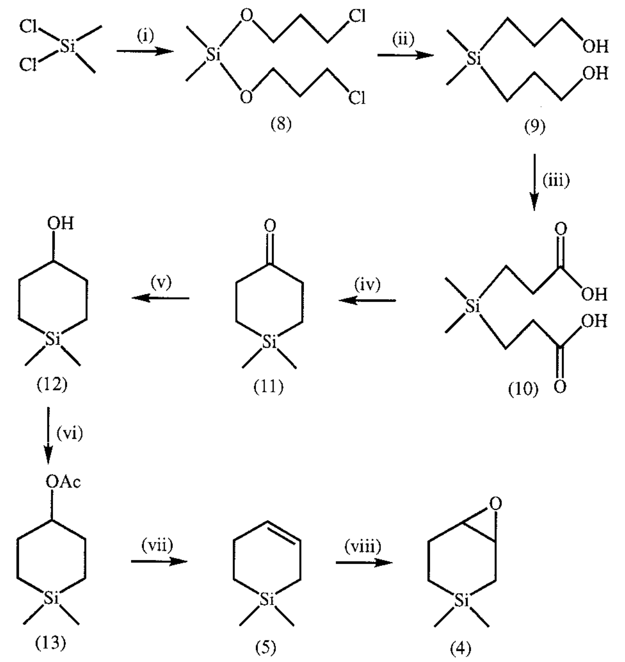
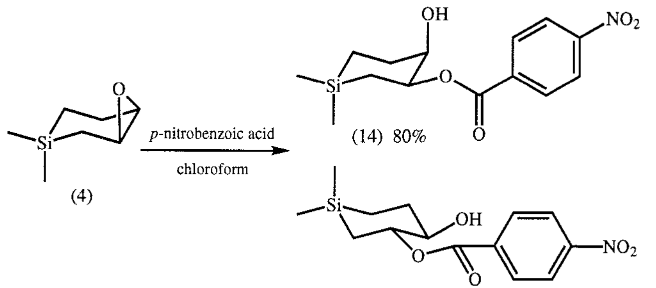


Scheme 1. Reagents: (i) $Cl(CH_2)_3OH$/pyridine; (ii) Na, Me_3SiCl, toluene, Δ; (iii) Jones reagent, acetone; (iv) 2 equiv. NaOH in EtOH, $Th(NO_3)_4$, filter, Δ 400°; (v) $LiAlH_4$; (vi) MeCOCl, pyridine; (vii) f.v.p., 600°/0·1 Torr; (viii) MeCN, MeOH, H_2O_2.

tions which are summarized in Scheme 1. Epoxidation of the alkene (5) with *in situ* generated peroxyacetamidic acid[11] gave the epoxide (4) (80%) as an air-sensitive oil. Reaction of the epoxide (4) with 1 equiv. of *p*-nitrobenzoic acid in chloroform gave a mixture of the *cis* and *trans* hydroxy esters (14) and (15) in the ratio *c.* 4 : 1 as the only detectable products by ^{1}H and ^{13}C n.m.r. (Scheme 2); these hydroxy esters were separated by fractional crystallization from methanol.



Scheme 2

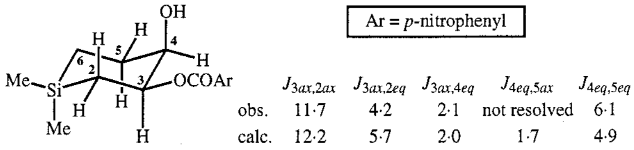
The structure of the *trans* hydroxy ester (15) was proven by single-crystal analysis (below), while the structure of the major component was assigned on the basis of the ^{1}H n.m.r. data. The important feature of the ^{1}H n.m.r. spectrum of hydroxy ester (14) was the appearance of a single-proton resonance at δ 5·31 characteristic of the $CHOCOC_6H_4NO_2$-*p* as a doublet of doublet of doublets with coupling constants of 11·7, 4·2 and 2·0 Hz, consistent with an axially disposed proton on the ester-bearing carbon. A single-proton resonance at δ 4·11 characteristic of the CHOH proton on the other hand appeared as a doublet (6·1 Hz) of broad lines with other coupling constants being not resolved, consistent with an equatorially disposed proton on the hydroxy-bearing carbon. Thus a *cis* stereochemical relationship between the ester and hydroxy substituents was established, but it was necessary to distinguish between (14) and its regioisomer (16).

Table 1. ^{1}H n.m.r. data for the *cis* hydroxy ester (14)
Chemical shifts in ppm, coupling constants in Hz

Proton	Chemical shift	Multi-plicity	Coupling constants
H2*ax*	1·36	dd	13·3, 11·7
H2*eq*	1·07	dd	13·3, 4·2
H3	5·305	ddd	11·7, 4·2, 2·0
H4	4·11	d	6·1, 2·0,^{A} 2·0^{A}
H5*ax*	1·76	dddd	14·4, 12·7, 4·2, 2·0
H5*eq*	2·21	dddd	14·4, 6·1, 5·7, 5·7
H6*ax*	0·87	ddd	14·7, 12·7, 5·7
H6*eq*	0·54	ddd	14·7, 5·7, 4·2

^{A} Not resolved.

This was achieved from analysis of the COSY data which allowed the chemical shift assignment of all the ring protons which were fully resolved; the proton n.m.r. parameters for (14) are summarized in Table 1. Notable was the observation that H3*ax* was coupled to a proton at δ 4·11, assigned as H4*eq*, and to two other protons. These two protons were geminally coupled to each other but showed no other couplings except to H3*ax* and were thus assigned as H2*ax* and H2*eq*. Thus the structure (14) was assigned.

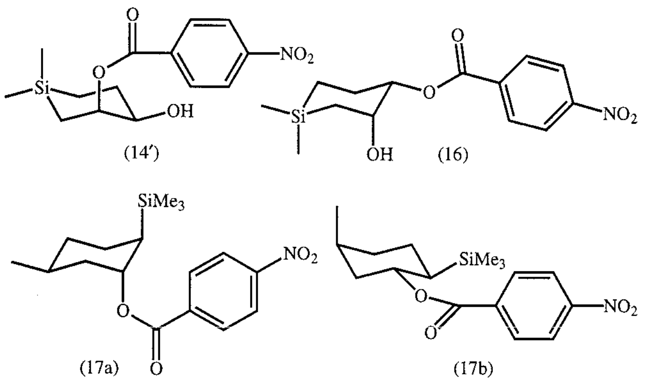


	$J_{3ax,2ax}$	$J_{3ax,2eq}$	$J_{3ax,4eq}$	$J_{4eq,5ax}$	$J_{4eq,5eq}$
obs.	11·7	4·2	2·1	not resolved	6·1
calc.	12·2	5·7	2·0	1·7	4·9

Fig. 1. Observed and calculated (PCMODEL) vicinal coupling constants (Hz) for the *cis* hydroxy ester (14).

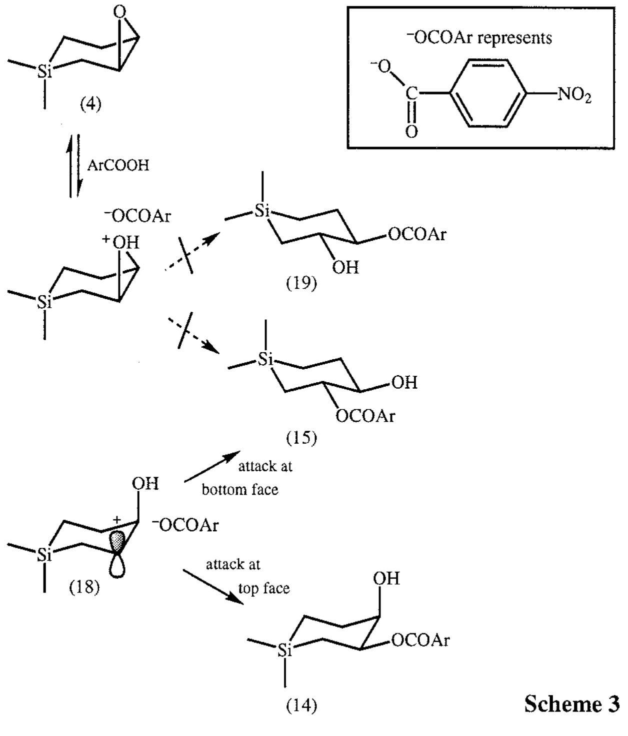
There is close agreement between the observed vicinal ^{1}H–^{1}H coupling constants for (14) and those calculated from a molecular mechanics minimized structure (Fig. 1)[15] suggesting that (14) exists substantially in the conformation having the C3 substituent equatorial and the C4 substituent axial, rather than the alternative conformer (14′) having the C3 substituent axial and the C4 substituent equatorial. It is interesting to note that this contrasts with our molecular mechanics calculations which predict the latter conformation to be more stable by 1·8 kJ/mol. The prediction that (14′) is more stable was surprising to us in view of the *syn*-1,3-diaxial relationship between the Si-CH_3 group and the axial ester substituent in conformation (14′) which we expected to be strongly destabilizing (based on analogies with all carbon cyclohexane derivatives). This 1,3-diaxial interaction is apparently relieved by the Si–C bonds in the ring which, being longer than

C–C bonds (*c.* 1·87 Å), would significantly diminish this effect and may even result in van der Waals attraction.[16,17]



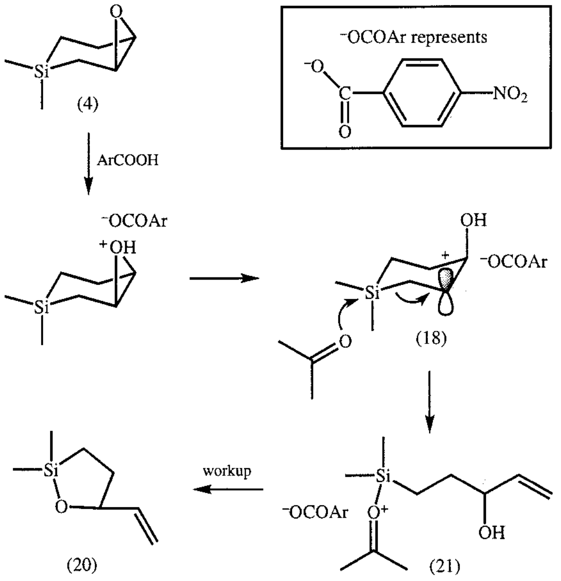
(14′) (16) (17a) (17b)

The observation that the preferred conformation is represented by structure (14) can be rationalized in terms of the stabilizing σ_{C-Si}–σ^*_{C-O} interaction which is present in (14) where the Si–C–C–O dihedral angle is 180° but much smaller in conformation (14′) where the Si–C–C–O dihedral angle is likely to be *c.* 60°. This type of interaction has previously been shown to exert a strong influence on the preferred conformations of flexible systems containing the Si–C–C–O moiety;[9] for example, 5-methyl-2-trimethylsilylcyclohexyl *p*-nitrobenzoate exists in solution predominantly in the diaxial conformation (17a), whereas molecular mechanics predict the diequatorial conformation (17b) to be more stable. Tentative structural evidence for the σ_{C-Si}–σ^*_{C-O} interaction in (15) is apparent from the crystal structure, which is discussed below.



Scheme 3

The proposed mechanism of the formation of (14) and (15) is outlined in Scheme 3; protonation of the epoxide oxygen by the carboxylic acid, is associated with rapid ring opening of the epoxide to give the β-silyl-stabilized carbenium ion (18), which is captured by the *p*-nitrobenzoate anion from the top face resulting in the formation of the major *cis* product (14). The minor *trans* product (15) arises from capture of the cation (18) from the bottom face by the *p*-nitrobenzoate anion. The relative proportions of the *cis* and *trans* isomers could simply reflect the preferred direction of approach of the *p*-nitrobenzoate anion to the carbenium ion intermediate (18); attack from the top face is possibly assisted by hydrogen bonding to the axial OH group. Alternatively the predominance of the *cis* isomer (14) could reflect a rapid epoxide ring opening upon protonation, followed by rapid capture of the cation by the carboxylate anion at the top face before much diffusion to the lower face (resulting in *trans* products) can occur. The fact that the isomer (19) was not observed tends to rule against the possibility that (15) arose from S_N2-type attack by the benzoate anion on the protonated epoxide.



Scheme 4

To investigate the effect of solvent on this acid-catalysed epoxide ring opening, we repeated the reaction of (4) with *p*-nitrobenzoic acid in acetone. The reaction in this solvent resulted in the formation of a major product which was tentatively identified as the cyclic alkenylsiloxane structure (20) based on the ^1H and ^{13}C n.m.r. data and i.r. data. The hydroxy esters (14) or (15) were not detected by n.m.r. The mechanism proposed for the formation of (20) is outlined in Scheme 4; protonation of the epoxide oxygen is again followed by rapid ring opening to give the β-silyl-stabilized cation (18). The carbenium ion (18) rapidly undergoes a solvent-assisted desilylation to give the acyclic alkene

(21) which upon workup gives (20). The susceptibility of β-silyl cations to solvent-assisted desilylation is well known (even with weakly nucleophilic solvents),[18] and is a major reason that these reactive intermediates have been so difficult to observe.[19]

Table 2. Crystal data and refinement details for the *trans* hydroxy ester (15)

Empirical formula	$C_{14}H_{19}NO_5Si$
Formula weight	309·39
Temperature	293(2) K
Wavelength	1·54180 Å (Cu Kα radiation)
Crystal system	monoclinic
Space group	$P2_1/c$
a	6·772(1) Å
b	34·293(3) Å
c	7·2461(8) Å
β	110·12(1)°
Volume	1580·1(3) Å^3
Z	4
Density (calculated)	1·301 g/cm^3
Absorption coefficient	1·502 mm^{-1}
$F(000)$	656
Crystal size	0·5 by 0·5 by 0·05 mm
θ range for data collection	2·58–74·90°
Index ranges	$0 \leq h \leq 7,\ 0 \leq k \leq 42,\ -9 \leq l \leq 8$
No. of control reflections	3
Measurement interval	180 min
Decomposition	not significant
Reflections collected	3399
Independent reflections	3133 ($R_{\text{int}} = 0{\cdot}0294$)
No. of obs. reflections	2496
Criterion obs. reflections	$I > 2\sigma(I)$
Refinement method	full matrix least squares on F^2
Data/restraints/parameters	3132/0/267
Goodness of fit on F^2	1·033
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0{\cdot}0438$, $wR_2 = 0{\cdot}1186$
R indices (all data)	$R_1 = 0{\cdot}0565$, $wR_2 = 0{\cdot}1354$
Weighting scheme	$w = 1/[\sigma^2(F_o{}^2)+(0{\cdot}0742P)^2+0{\cdot}2801P]$ where $P = (F_o{}^2+2F_c{}^2)/3$
Absorption correction	SHELX76[A]
Max., min. transmission	0·93, 0·57
Extinction method	SHELXL[B]
Extinction coefficient	0·0014(4)
Maximum shift/e.s.d.	−0·022
Largest diff. peak, hole	0·254, −0·216 e/Å^3

[A] Sheldrick, G. M., SHELX76, Program for Crystal Structure Determination, Cambridge, England, 1976.
[B] Sheldrick, G. M., SHELXL-93, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1993.

Table 3. Atomic coordinates and equivalent isotropic displacement parameters for (15)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Atom	X/a	Y/b	Z/c	U_{eq} (Å^2)
Si	0·26968(11)	0·31084(2)	0·81562(9)	0·0652(2)
O(1)	0·1246(2)	0·40655(4)	0·4491(2)	0·0528(3)
O(2)	−0·2651(3)	0·37385(6)	0·3635(3)	0·0826(5)
O(3)	0·2604(2)	0·44372(4)	0·7176(2)	0·0578(4)
O(4)	0·3050(3)	0·55497(5)	−0·1106(2)	0·0709(4)
O(5)	0·2286(3)	0·59517(4)	0·0810(3)	0·0753(5)
N(1)	0·2660(3)	0·56244(5)	0·0378(2)	0·0531(4)
C(2)	0·3016(4)	0·35248(7)	0·6617(4)	0·0635(5)
C(3)	0·0986(3)	0·37450(5)	0·5747(3)	0·0509(4)
C(4)	−0·0828(4)	0·35038(6)	0·4430(3)	0·0620(5)
C(5)	−0·1443(5)	0·31779(8)	0·5557(4)	0·0772(7)
C(6)	0·0268(6)	0·28743(7)	0·6460(5)	0·0837(8)
C(7)	0·5054(8)	0·27889(13)	0·8855(8)	0·1108(13)
C(8)	0·2252(6)	0·32850(11)	1·0398(4)	0·0873(8)
C(9)	0·2083(3)	0·43918(5)	0·5424(3)	0·0465(4)
C(10)	0·2285(3)	0·47035(5)	0·4060(3)	0·0442(4)
C(11)	0·2399(3)	0·46225(5)	0·2220(3)	0·0480(4)
C(12)	0·2584(3)	0·49236(5)	0·1024(3)	0·0489(4)
C(13)	0·2595(3)	0·53008(5)	0·1690(3)	0·0452(4)
C(14)	0·2512(3)	0·53900(5)	0·3518(3)	0·0474(4)
C(15)	0·2381(3)	0·50862(5)	0·4710(3)	0·0464(4)

Molecular Structure of (15)

Crystals of (15) were grown by slow evaporation from methanol. The data collection and refinement parameters are presented in Table 2, atomic coordinates and displacement factors in Table 3, and selected bond lengths, angles and dihedral angles are given in Tables 4–6. A perspective diagram of (15) which is presented in Fig. 2 was drawn with ORTEPII[20] and depicts 50% ellipsoids.

The conformation of the silacyclohexane ring is best described as a flattened chair, with distortions

Table 4. Selected bond distances (Å) for (15)

Atoms	Distance	Atoms	Distance
Si–C(8)	1·853(3)	Si–C(7)	1·857(3)
Si–C(6)	1·863(3)	Si–C(2)	1·870(2)
O(1)–C(3)	1·475(2)	O(1)–C(9)	1·329(2)
C(2)–C(3)	1·504(3)	C(5)–C(6)	1·527(4)
C(3)–C(4)	1·516(3)	C(4)–C(5)	1·524(3)
O(2)–C(4)	1·420(3)		

Table 5. Selected bond angles (degrees) for (15)

Atoms	Angle	Atoms	Angle
C(8)–Si–C(7)	109·7(2)	C(8)–Si–C(6)	110·3(2)
C(7)–Si–C(6)	114·0(2)	C(8)–Si–C(2)	111·1(2)
C(7)–Si–C(2)	110·4(2)	C(6)–Si–C(2)	101·11(12)
C(3)–C(2)–Si	110·9(2)	O(1)–C(3)–C(2)	110·3(2)
O(1)–C(3)–C(4)	105·1(2)	C(2)–C(3)–C(4)	114·6(2)
O(2)–C(4)–C(3)	110·5(2)	O(2)–C(4)–C(5)	105·9(2)
C(3)–C(4)–C(5)	112·0(2)	C(4)–C(5)–C(6)	115·0(3)
C(5)–C(6)–Si	110·9(2)		

Table 6. Selected torsion angles (degrees) for (15)

Atoms	Angle	Atoms	Angle
C(8)–Si–C(2)–C(3)	−68·0(2)	C(7)–Si–C(2)–C(3)	170·0(2)
C(6)–Si–C(2)–C(3)	49·0(2)	C(9)–O(1)–C(3)–C(2)	−82·6(2)
Si–C(2)–C(3)–C(4)	−60·0(2)	O(1)–C(3)–C(4)–O(2)	−57·0(2)
C(2)–C(3)–C(4)–O(2)	−178·3(2)	O(1)–C(3)–C(4)–C(5)	−174·7(2)
C(2)–C(3)–C(4)–C(5)	64·0(3)	O(2)–C(4)–C(5)–C(6)	177·0(2)
C(3)–C(4)–C(5)–C(6)	−62·6(3)	C(4)–C(5)–C(6)–Si	57·5(3)
C(8)–Si–C(6)–C(5)	70·1(3)	C(7)–Si–C(6)–C(5)	−166·0(2)
C(2)–Si–C(6)–C(5)	−47·6(3)	C(3)–O(1)–C(9)–O(3)	−0·6(3)
Si–C(2)–C(3)–O(1)	−178·37(13)		

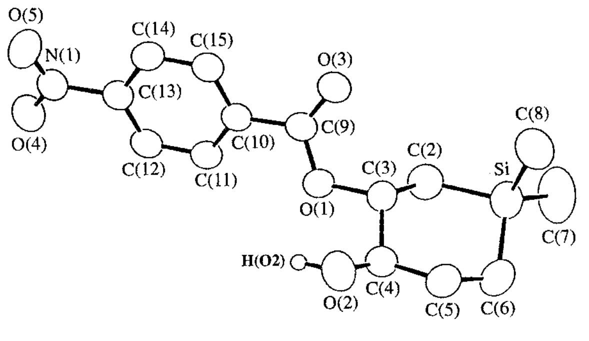
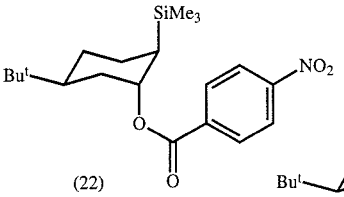


Fig. 2. Perspective diagram of (15), with the atom numbering scheme.

away from the idealized chair geometry being due to the presence of the C-Si bonds in the ring [Si–C(2) 1·870(2), Si–C(6) 1·863(3) Å]. These distortions manifest in dihedral angles in the vicinity of the silicon deviating markedly from 60° [C(6)–Si–C(2)–C(3) 49·0(2), C(2)–Si–C(6)–C(5) −47·6(3)°] and closing up of the internal C–Si–C bond angle to 101·11(12)°. The C(3)–O(1) bond length is 1·475(2) Å which represents a slight lengthening when compared with C–O bond lengths observed in room-temperature structural analyses of other equatorial cyclohexyl *p*-nitrobenzoates.† These have C–O bond lengths in the range 1·462–1·467 Å; the slight lengthening of the C(3)–O(1) bond length in (15), when compared to these structures, gives tentative support for the $\sigma_{\text{C-Si}}$–$\sigma^*_{\text{C-O}}$ interaction between the Si–C(2) bond and the C(3)–O(1) bond, an interaction which was proposed above to account for the conformational preferences of the *cis* hydroxy ester (14). The dihedral angle Si–C(2)–C(3)–O(1) [−178·37(13)°] suggests a close to optimum geometry for this interaction. Structural evidence for $\sigma_{\text{C-Si}}$–$\sigma^*_{\text{C-O}}$ interactions in the antiperiplanar geometry[7] has been seen previously in the esters (22)–(24) which show significant lengthening of the C(alkyl)–O(ester) bond.



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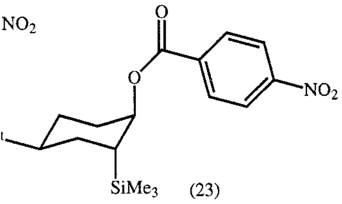

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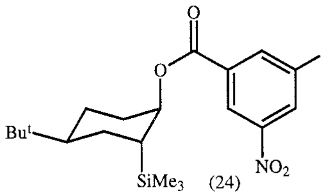

(24)

Conclusion

Silicon directs the carboxylic-acid-catalysed ring opening of the β,γ-epoxide (4) so that the positive charge is on the β-carbon; this allows the positive charge to benefit from the remarkable stabilization of the silicon β-effect. While this is not a surprising result, it is to the best of our knowledge the first example of a silicon-directed acid-catalysed ring opening of a β,γ-epoxide. The result (in a non-nucleophilic solvent) is a silicon-substituted diol which has the hydroxy substituent β to the silicon protected as an ester function while the hydroxy substituent γ to the silicon is not protected and can potentially undergo further chemistry. The synthetic utility of this directed epoxide ring opening deserves to be further explored.

Experimental

Crystallography

Diffraction data were recorded on an Enraf Nonius CAD4f diffractometer operating in the $\theta/2\theta$ scan mode at room temperature (298 K). Data were corrected for Lorentz and polarization effects and for absorption (SHELX76).[25] Structures were solved by direct methods (SHELXS-86)[26] and were refined on F^2 (SHELXL-93).[27] Hydrogen atoms were located from difference-Fourier maps and allowed to refine, without restraint, with isotropic thermal parameters. Crystal data and refinement details for (15) are listed in Table 2.‡

Synthesis

Melting points were determined on a Gallenkamp melting point apparatus. Infrared spectra were run on a Perkin–Elmer 983G infrared spectrometer. N.m.r. spectra were run on a Varian Unity-300 spectrometer operating at 299·9 MHz for ^{1}H spectra, and 75 MHz for ^{13}C. Reactions involving ultrasound were conducted in a Soniclean 160 HT ultrasound bath at room temperature.

Bis(3-chloropropoxy)dimethylsilane (8) was prepared in 77% yield following a similar procedure to that reported by Speier[13] from dichlorodimethylsilane (204 g, 1·58 mol), 3-chloropropan-1-ol (230 g, 3·51 mol) and pyridine (500 ml). The product boiled at 82°C/2 mm. ^{13}C n.m.r. δ ($CDCl_3$) 58·69, 41·46, 35·02, −3·55. ^{1}H n.m.r. δ ($CDCl_3$) 3·9, t, 4H; 3·7, t, 4H; 2·0, quintet, 4H; 0·18, s, 6H. ν_{max} (thin film) 1299, 1257, 1097, 1069, 851, 799 cm^{-1}.

Bis(3-hydroxypropyl)dimethylsilane (9) was synthesized in 68% yield following the procedure outlined by Speier[13] from bis(3-chloropropoxy)dimethylsilane (8). The procedure used sodium metal (133·6 g, 5·81 mol), toluene (750 ml), chlorotrimethylsilane (319 ml) and bis(3-chloropropoxy)dimethylsilane (8). The product (9) was obtained as a viscous clear oil ^{13}C n.m.r. δ 65·24, 26·89, 10·69, −3·61. ^{1}H n.m.r. δ ($CDCl_3$) 3·54, 4H, t; 3·1, 2H, br s; 1·4–1·6, 4H, m; 0·4–0·55, 4H, m; −0·75, 6H, s. ν_{max} (thin film) 3332, 2870, 1249, 1053, 840 cm^{-1}.

Bis(2-carboxyethyl)dimethylsilane (10)[12]

The dialcohol (9) (50 g, 0·28 mol) was dissolved in acetone (500 ml) and chilled with stirring to 0°C. To this solution, freshly prepared Jones reagent (8 N with respect to oxygen, 242 ml) was added dropwise with stirring, and the resultant mixture was stirred at room temperature for 2 h after addition was complete. Aqueous sodium bisulfite solution was added to destroy the remaining oxidant. The product was then extracted into ether (3×100 ml), dried ($MgSO_4$) and evaporated under reduced pressure to yield the diacid (10) (44·4 g, 78%) as an orange semicrystalline solid. ^{13}C n.m.r. δ ($CDCl_3$) 181·07, 28·46, 9·72, −3·99. ^{1}H n.m.r. δ 2·3, t, 4H; 0·8, t, 4H; −0·05, s, 6H. ν_{max} (thin film) 1709, 1253, 1047, 839 cm^{-1}.

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† C–O distances in R^1–O–R^2 fragments depend on the nature of R^1 and R^2.[21] Literature values for an equatorial cyclohexyl *p*-nitrobenzoate are 1·462(3) and 1·467 Å in 2-hydroxy[4.2.2]propellan-1-yl *p*-nitrobenzoate[22] and (1*R**,4a*S**,8a*S**)-5,5,8a-trimethyldecahydro-1-naphthyl *p*-nitrobenzoate[23] respectively, and 1·464(2) and 1·468(2) Å for the two molecules of *trans*-4-t-butylcyclohexyl *p*-nitrobenzoate.[24]

‡ An Accessory Publication (bond distances, bond angles, torsion angles, anisotropic displacement parameters, hydrogen atom parameters, and structure factors) is available, until 31 December 2001, from the Australian Journal of Chemistry, P.O. Box 1139, Collingwood, Vic. 3066.

Thorium Salt of the Diacid (10)

Phenolphthalein indicator (5 drops) was added to a stirred solution of the diacid (10) (44·4 g, 0·22 mol) in hot ethanol (80 ml). A 20% solution of NaOH (aqueous) was added until the acid was neutralized. A solution of $Th(NO_3)_4.4H_2O$ (85·1 g, 0·15 mol) in warm H_2O was added slowly with rapid stirring. Once the gelatinous solid had given way to a white precipitate, the precipitate was filtered off and washed with copious amounts of H_2O. The solid was dried under high vacuum (0·1 mmHg) to yield the thorium salt as an off-white crystalline solid (81·81 g).

Pyrolysis of Thorium Salt of (10): Preparation of 1,1-Dimethyl-1-silacyclohexan-4-one (11), and Subsequent Reactions

The general procedure outlined by Benseker[12] was followed and employed 81·81 g of the thorium salt which was placed into a 100-ml round-bottom flask. The salt was heated in a Wood's metal bath (400°C) under vacuum (15 mm) to effect the pyrolysis. The crude product was collected in a liquid-nitrogen trap, and was further distilled (150°/20 mm) giving (11) (7·57 g, 35%) as a clear yellow oil. ^{13}C n.m.r. δ ($CDCl_3$) 178·31, 37·40, 10·42, −3·39. ^{1}H n.m.r. δ 2·4, t, 4H; 0·6–1·4, m, 4H; −0·15, s, 6H. ν_{max} (thin film) 1702, 1249, 1050, 840, 783 cm^{-1}.

1,1-Dimethyl-1-silacyclohexan-4-ol (12) was prepared, by reduction of the ketone (11) (12·89 g, 0·092 mol) by the procedure of Washburne,[14] as a colourless oil (11·39 g, 88%). ^{13}C n.m.r. δ ($CDCl_3$) 72·18, 32·36, 10·42, −3·07, −4·30. ^{1}H n.m.r. δ 3·4–3·7, m, 4H; 0·3, s, 3H; 0·1, s, 3H. ν_{max} (thin film) 3343, 1461, 1248, 1038, 837 cm^{-1}.

1,1-Dimethyl-1-silacyclohexan-4-yl acetate (13) was prepared in 81% yield, according to the procedure of Washburne,[14] as a clear yellow oil. ^{13}C n.m.r. δ ($CDCl_3$) 184·5, 74·4, 28·83, 20·40, 10·40, −3·38, −4·15. ν_{max} (thin film) 1737, 1244, 840 cm^{-1}.

Preparation of 1,1-Dimethyl-1-silacyclohex-3-ene (5)

In a modification of the procedure reported by Washburne,[14] the acetate (13) (1·86 g, 0·01 mol) was passed through a horizontally mounted vacuum pyrolysis column (600°C/0·1 mmHg). 1,1-Dimethyl-1-silacyclohex-3-ene (5) was collected in a liquid-nitrogen trap as a yellow oil (1·14 g, 90%). ^{13}C n.m.r. δ ($CDCl_3$) 130·03, 125·75, 22·66, 13·08, 9·99, −2·74. ^{1}H n.m.r. δ ($CDCl_3$) 5·25–5·40, m, 2H; 3·12, m, 2H; 2·10, m, 2H; 0·32, m, 2H; 0·0, m, 6H. ν_{max} (thin film) 1247, 1155, 1027, 840 cm^{-1}.

Preparation of 1,1-Dimethyl-1-silacyclohex-3-ene Oxide (4)†

The olefin (5) (1·12 g, 8·87 mmol) was added to a solution of methanol (10 ml), acetonitrile (2 ml), H_2O_2 (30% solution, 2·8 ml), and $KHCO_3$ (0·15 g), and stirred at room temperature for 90 h. The resulting solution was diluted with H_2O (50 ml) and extracted with ether (3×50 ml); the combined organic extracts were washed with H_2O (3×50 ml), dried ($MgSO_4$) and evaporated under reduced pressure. Kugelrohr distillation (115°C/20 mm) yielded the epoxide (4) (990 mg, 88%) as a clear, colourless oil. ^{13}C n.m.r. δ ($CDCl_3$) 54·24, 52·52, 20·36, 12·34, 6·03, −0·95, −1·89. ^{1}H n.m.r. δ ($CDCl_3$) 3·2–3·3, m, 1H; 3·0–3·1, m, 1H; 2·2–2·4, m, 1H; 1·88–2·0, m, 1H; 1·35–1·25, m, 1H; 1·05–1·0, m, 1H; 0·74–0·6, m, 1H; 0·5–0·4, m, 1H; 0·0, s, 3H; −0·1, s, 3H. ν_{max} (thin film) 1246, 842 cm^{-1}.

Reaction of Epoxide (4) with p-*Nitrobenzoic Acid in Chloroform*

A solution of the epoxide (4) (200 mg, 1·41 mmol) in chloroform (10 ml) was treated with *p*-nitrobenzoic acid (1·05 equiv.) and then stirred for 24 h under an atmosphere of nitrogen. After filtration of the excess *p*-nitrobenzoic acid, the chloroform was removed under reduced pressure, leaving a creamy solid (430 mg) which was shown by n.m.r. (^{1}H and ^{13}C) to be a *c.* 4:1 mixture of (14) and (15).‡

Fractional crystallization of the crude product gave the *trans* hydroxy ester (15), m.p. 141–142°C. ^{13}C n.m.r. δ ($CDCl_3$) 164·6, CO; 150·45, CNO_2; 136·04, **C**CO; 130·64; 123·5; 80·21, C3; 76·68, C4; 29·61, C5; 19·74, C2; 10·63, C6; −2·3, −3·9. ^{1}H n.m.r. δ ($CDCl_3$) 8·28, 1H, d, *J* 8·7 Hz; 8·20, 1H, *J* 8·7 Hz; 5·05–5·16, 1H, m, H3; 3·60–3·69, 1H, m, H4; 2·2–2·3, 2H, m; 1·62–1·7, 1H, m; 1·41–1·5, 1H, m; 0·88–0·95, 1H, m; 0·6–0·7, 1H, m; 0·2, 3H, s, CH_3; 0·10, 3H, s, CH_3.

Crystallization of the mother liquors gave the *cis* hydroxy ester (14), m.p. 84·5–85°C (Found: C, 53·9; H, 6·1; N, 4·3. $C_{14}H_{19}NO_5Si$ requires C, 54·3; H, 6·2; N, 4·5%). ν_{max} (Nujol) 3578s (OH), 1706s (CO), 1248s (C–Si), 846s (C–Si) 862s (C–Si), 874s cm^{-1} (C–Si). ^{13}C n.m.r. δ ($CDCl_3$) 164·12, CO; 150·46, CNO_2; 136·04, (**C**CO); 130·64; 123·52; 78·27, C3; 70·80, C4; 27·02, C5; 15·89, C2; 6·28, C6; −2·0, CH_3; −3·7, CH_3. ^{1}H n.m.r. δ ($CDCl_3$) 8·27, 1H, d, *J* 8·9; 8·20, 1H, d, *J* 8·9; 5·31, 1H, ddd, *J* 11·7, 4·2, 2·0 Hz, H3; 4·11, 1H, d, *J* 6·1 Hz; 2·4, 1H, br, OH; 2·21, 1H, dddd, *J* 14·4, 6·1, 5·7, 5·7 Hz, H5*eq*; 1·76, 1H, dddd, *J* 14·4, 12·7, 4·2, 2·0 Hz, H5*ax*; 1·36, 1H, dd, *J* 13·3, 11·7 Hz, H2*ax*; 1·07, 1H, dd, *J* 13·3, 4·2 Hz, H2*eq*; 0·87, 1H, ddd, *J* 14·7, 12·7, 5·7 Hz, H6*ax*; 0·54, 1H, ddd, *J* 14·7, 5·7, 4·2 Hz, H6*eq*; 0·13, 3H, s, CH_3; 0·12, 3H, CH_3.

Reaction of Epoxide (4) with p-*Nitrobenzoic Acid in Acetone: Isolation of (20)*

A solution of the epoxide (4) (100 mg, 0·75 mmol) in acetone (5 ml) was treated with *p*-nitrobenzoic acid (131 mg, 1·05 equiv.). The resulting solution was stirred overnight. The solvent was removed under reduced pressure leaving an oily solid. (D)Chloroform was added to the residue and the *p*-nitrobenzoic acid precipitate filtered off; the soluble material gave the following spectra. ^{13}C n.m.r. δ ($CDCl_3$) 140·50, **C**H=C; 115·04, **C**H_2=C; 75·29, CHO; 30·52, CH_2; 13·35, CH_2; 0·25, CH_3. ^{1}H n.m.r. δ 6·1–5·6, m, 1H, CH=C; 5·4–5·0, m, 2H, CH_2=C; 4·1–3·9, m, 1H, CHO; 1·7–1·3, m, 2H, CH_2; 0·7–0·4, m, 2H, CH_2Si; 0·10, s, 6H, CH_3Si. ν_{max} (thin film) 1252s (Si–C), 1055s (Si–O), 900–830s cm^{-1} (Si–C).

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† Best name for indexing purposes: 3,3-dimethyl-7-oxa-3-silabicyclo[4.1.0]heptane.

‡ 4-Hydroxy-1,1-dimethyl-1-silacyclohexan-3-yl *p*-nitrobenzoate.

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