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Unprecedented effects of the trimethylsilyl group on the reactivity of 3C-silylated silacyclopentenes and their derivatives

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Abstract

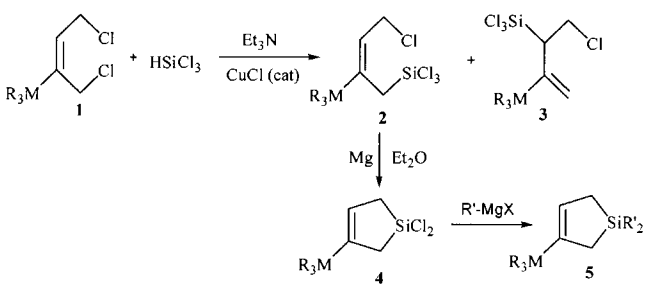
We have synthesised new 3C-silylated silacyclopentenes from the corresponding 3-trimethylsilyl-1,1-dichloro-1-silacyclopent-3-enes. The presence of two metal centres M (M = Si) in α and β-positions confers an original structure for these new heterocycles. The chemical behaviour of such compounds and their derivatives was studied and compared to the results obtained in the non-substituted silacyclopentane series. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Silicon; Synthesis; 3-Trimethylsilyl-3-silacyclopentenes; Vinylsilanes; Epoxysilanes

1. Introduction

We have been interested by silacyclopentenes for a long time. Such compounds have generated a large interest in both fundamental and applied organometallic chemistry [1]. The chemistry of these heterocycles is governed mainly by the presence of two reactive sites in the same molecule: an electron deficient centre M (Si) and an electron rich carbon–carbon double bond, in allylic position to the metal M. For example, organolithium compounds (RLi) induce a ring-opening polymerisation of these metallacycles resulting from the nucleophilic attack of R^- on the silicon to yield poly(1-sila-*cis*-pent-3-enes), precursors of ceramics [1c]. On the other hand, 3,4-amino-1-silacyclopentanols, prepared in two steps from corresponding silacyclopentenes, have shown a biological activity as serotonin antagonists [1b].

We have already reported the synthesis of a series of 3C-silylated 1,1-dichloro-1-silacyclopent-3-enes (**4**) in two steps, using the reaction of the trichlorosilylation of allylic chlorides followed by a ring closure with magnesium in diethyl ether [2]. In fact, hydrosilylation of the commercially available 1,4-dichlorobut-2-yne with various silanes and germanes in the presence of chloroplatinic acid as a catalyst yields *cis*-1,4-dichlorobut-2-enes (**1**) bearing corresponding silyl and germyl groups in 2-position. 2-Substituted *cis*-1,4-dichloro-2-butenes (**1**) react with trichlorosilane in the presence of triethylamine and catalytic amounts of cuprous chloride (CuCl) to give a mixture of two products, **2** and **3**. The ratio of the S_N2 and S_N2' products varies as a function of the electronegativity of the groups directly attached to the metal. Reaction of **2**, present in the mixture, with magnesium powder in Et_2O leads to corresponding 3C-substituted 1,1-dichloro-1-silacyclopent-3-enes (**4**), in good yields [2].



R_3M = Cl_3Si, $MeCl_2Si$, Et_3Si, Me_3Si, $PhMe_2Si$, Et_3Ge...

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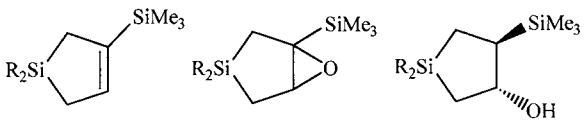
In this paper, we wish to report the synthesis and the reactivity of the 3C-trimethylsilyl-1,1-dimethyl (and 1,1-diphenyl)-1-silacyclopent-3-enes (**5a**,**b**) and their derivatives **6** and **7** with hydrogen halides, lithium dialkylamides, bromomagnesium dialkylamides, and Grignard reagents.



R = Me **5a** **6a** **7a**

R = Ph **5b** **6b** **7b**

In this new 3C-silylated silacyclic series, we will examine the effect of the trimethylsilyl (TMS) group on the reactivity of such systems and compare our results to those reported in the literature in the carbon series and also to those already reported in the non-silylated silacyclopentene series.

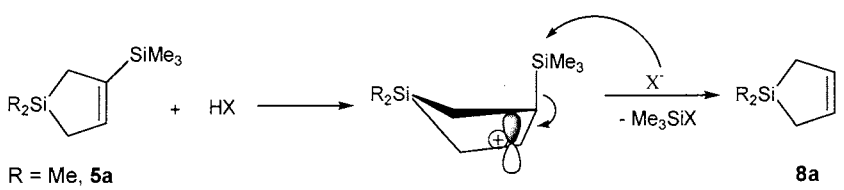
2. Results and discussion

2.1. 3-Trimethylsilyl-1-silacyclopentenes (*5a,b*)

3C-silylated 1-silacyclopent-3-enes (**5a**,**b**) were prepared from the dichlorosilacyclopentene derivatives (**4**) and an excess of the corresponding Grignard reagent R–MgX (R = Me, Ph), respectively in 81 and 90% yield.

Treatment of **5a,b** with concentrated hydrogen halides (HCl, HBr and HI) leads to the quantitative formation of 1,1-dimethyl (diphenyl)-1-silacyclopent-3-enes (**8a,b**) [3] and trimethylsilyl halides Me_3SiX (X = Cl, Br, I) resulting from a protodesilylation reaction.

This reaction may proceed by the protonation of the π-electron rich carbon–carbon double bond, followed by a nucleophilic attack of the counteranion X^- on the trimethylsilyl group, inducing the corresponding trimethylsilyl halide elimination [4]

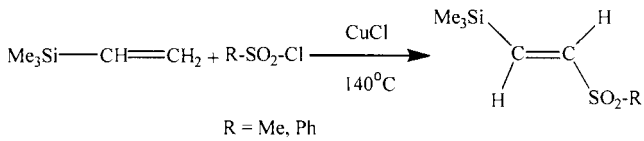


R = Me, **5a** **8a**

R = Ph, **5b** **8b**

The protodesilylation reaction is regioselective. There was no attack of the X^- on the ring-bound silicon (Si). We did not detect products resulting from a nucleophilic displacement of an intracyclic Si–C bond, leading to a ring-opening reaction.

In the same conditions as those reported for the synthesis of allyl and (trimethylsilyl) vinyl sulfones, no reaction occurred when **5** and methane sulfonyl chloride, in a mixture of CH_2Cl_2–CH_3CN in the presence of catalytic amounts of cuprous chloride (CuCl), were heated in a sealed tube at 140°C [5].

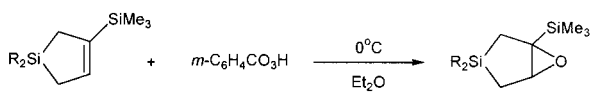


R = Me, Ph

Only the starting material was recovered and small amounts of **8**, resulting most likely from a partial hydrolysis of the methane sulfonyl chloride, generating HCl. Resulting HCl may induce a protodesilylation reaction of the 3C-silylated silacycles **5**.

2.2. 1-Trimethylsilyl-3,3-dimethyl (diphenyl)-6-oxa-3-silabicyclo[3.1.0]hexane (*6a,b*)

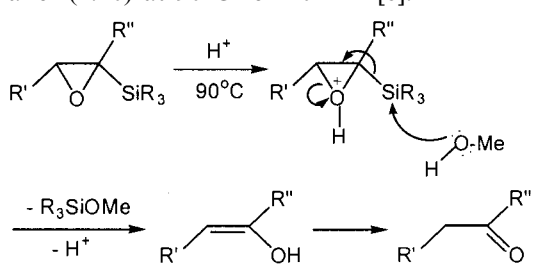
Oxidation of the carbon–carbon double bond was achieved using *m*-chloroperbenzoic acid in diethyl ether [3a] in high yields.



R = Me, **5a** **6a**

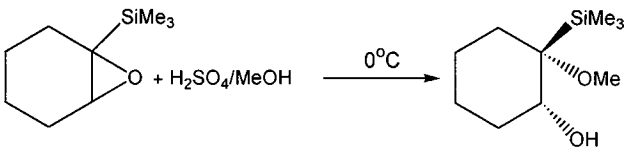
R = Ph, **5b** **6b**

Various examples are reported in the literature concerning the chemical behaviour of α,β-epoxysilanes [6,7]. For example, such derivatives give aldehydes and ketones when treated with a solution of sulfuric acid in methanol (1:10) at 90°C for 10 min [8].

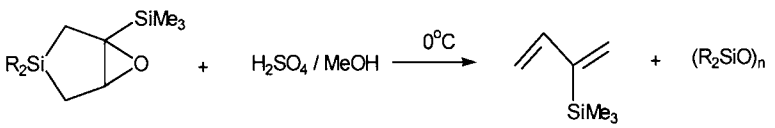


Ring-opening of α,β-epoxysilanes with different nucleophiles (HBr, MeOH, AcOH) under different conditions has shown that these epoxides undergo nucleophilic attack at the carbon α to silicon [9,10]. For example, when the reaction of 1,2-epoxy-1-trimethylsilylcyclohexane was carried out with 5% sulfuric acid

in methanol at 0°C, the *trans*-2-methoxy-2-trimethylsilylcyclohexan-1-ol was obtained in 78% yield:

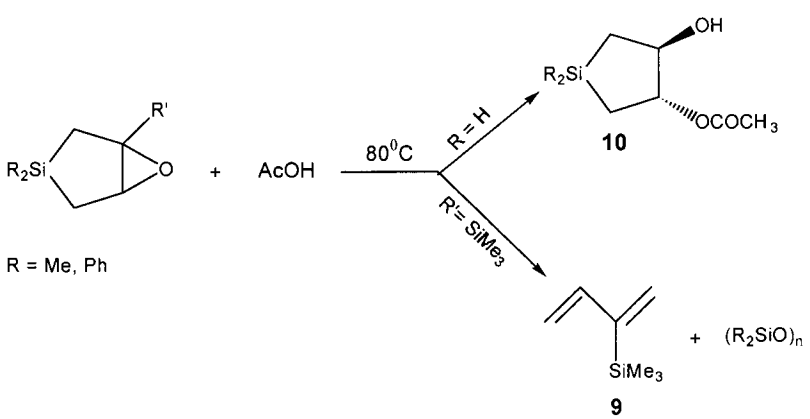


Epoxides **6a,b** behave differently in acidic media. The reaction with H_2SO_4–MeOH (1:10) at −20 or 0°C yields 2-trimethylsilyl-1,3-butadiene (**9**) [11] and the corresponding siloxanes:



R = Me, Ph **6a, b** **9**

The reaction with acetic acid shows a difference with the non-substituted analogue. In fact, 6-oxa-3,3-dimethyl(or diphenyl)-3-silabicyclo[3.1.0]hexanes when heated at 80°C in neat acetic acid (AcOH) gave the corresponding silacyclic acetoxy alcohol (**10**) as a result of the ring-opening of the oxirane bridge [1b]:



R = Me, Ph

We assume that the mechanism of this reaction is similar to the one reported by Stork et al. [8] involving methanolic solution of H_2SO_4 and α,β-epoxysilanes. The first step corresponds to the protonation of the oxygen of the oxirane ring. The presence of the trimethylsilyl group facilitates nucleophilic displacement of the silicon–carbon bond α to silicon and thus favours the formation of a carbonium ion in a β-position to the intracyclic silicon. Nucleophilic attack of MeOH on silicon in the β-position leads to the ring-opening product. The protonation of the hydroxyl group of the intermediate alcohol, in the acidic media, followed by a second nucleophilic attack of MeOH on the methoxysilyl group yields 2-trimethylsilyl-1,3-butadiene (**9**) and the corresponding dialkyldimethoxysilanes. Nucleophilic displacement occurs at the silicon bearing a methoxy group rather than at the TMS group because of the electron deficiency at the first silyl group (Scheme 1).

Besides the steric effect of the trimethylsilyl group, the presence of a second intracyclic silicon in β-position induces the ring opening of the silacycle. The nucleophilic reaction of MeOH or AcOH could be rationalised as a result of a β-effect of silicon.

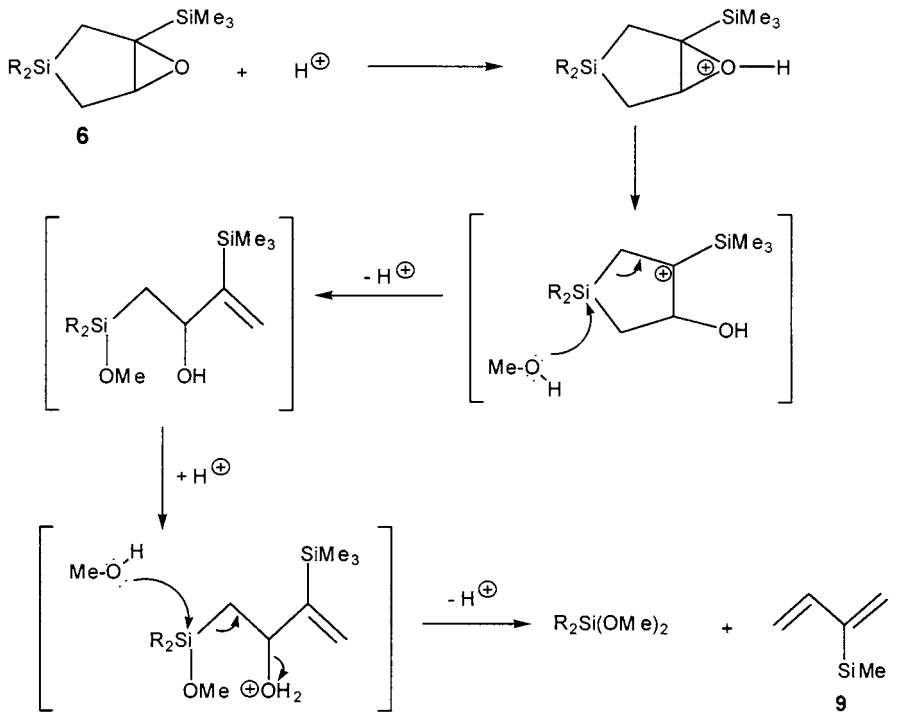
The same dienic product (**9**) was isolated when epoxides **6** and catalytic amounts of boron trifluoride etherate (BF_3, Et_2O) [12] were allowed to react in $CDCl_3$ at room temperature (r.t.) or in dichloromethane at 0°C. The mechanism of the decomposition of the silyloxirane (**6**) is proposed in Scheme 2

The first step corresponds to the complexation of the Lewis acid (BF_3) by oxygen. The subsequent heterolytic cleavage of a silicon–carbon bond leads to the formation of a positive charge in α-position to the trimethylsilyl group. Nucleophilic attack of the electron rich oxygen on the intracyclic silicon, in β-position, gives the intermediate resulting from the ring-opening reaction of the silacycle with regeneration of BF_3 and formation of silaoxetane. Thermal decomposition of the silaoxetane intermediate leads to 2-trimethylsilyl-1,3-butadiene (**9**) and silanones. Cyclooligomerisation of the silanones gives corresponding siloxanes. Similarly, 1,3-butadiene and corresponding siloxanes were obtained when unsubstituted oxasilabicyclo-[3.1.0]hexanes were reacted with catalytic amounts of boron trifluoride.

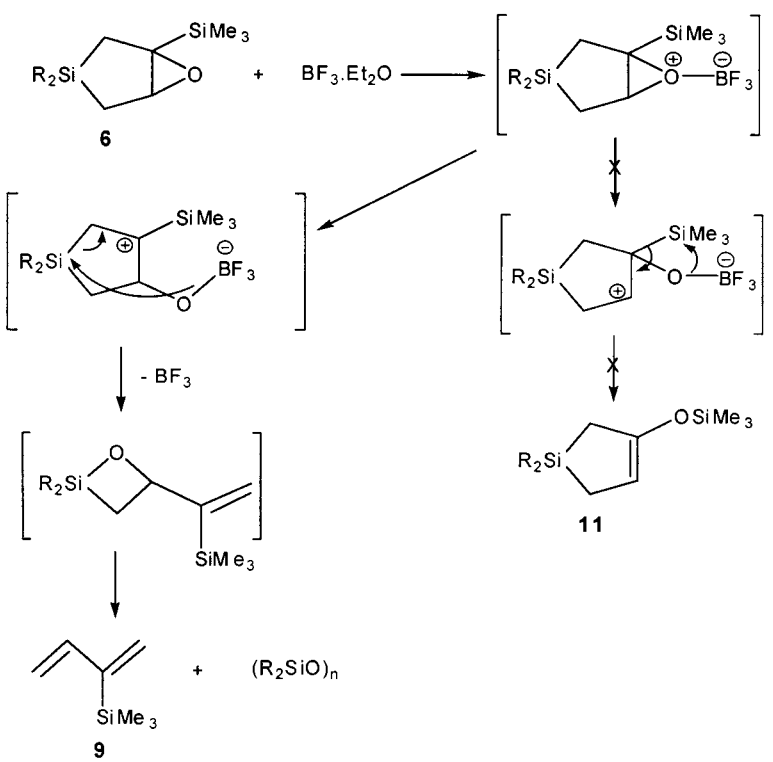
An alternative mechanism in which free fluoride anion (F^-) attacks the ring-bound silicon was suggested by Weber et al. [13]. BF_3 may induce complexation rather than decomposition because BF_3 forms stable complexes with ethers. Nucleophilic attack by F^- is less probable in this case even though the final products are the same.

The same behaviour was observed when 3,3-dimethyl (and 3,3-diphenyl)-6-oxa-3-silabicyclo[3.1.0]hexanes were reacted, respectively with *N*-benzyltriphenylphosphinimine ($Ph_3P^+–N^––CH_2–Ph$) [14] and tetra-*n*-butylammonium bromide [15].

There is no spectroscopic evidence (^{1}H-NMR, IR) for the formation of the isomeric silylenol ether (**11**) resulting from a β-cleavage of a carbon–oxygen bond induced by the strong Lewis acid BF_3 followed by a migration of the trimethylsilyl group from



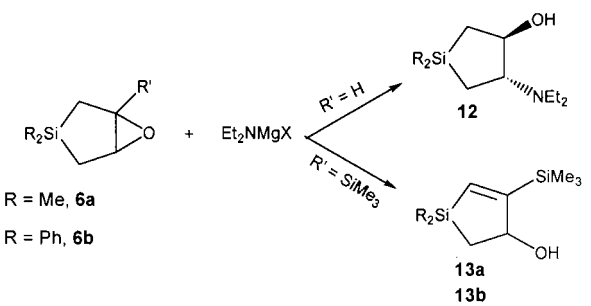
Scheme 1.



Scheme 2.

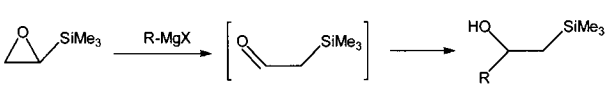
carbon to an α-oxygen as reported for α,β-epoxysilanes [12].

Addition of one equivalent of bromomagnesium diethylamide, Et_2NMgBr to the cyclic α,β-epoxysilanes (**6**) gave the silacyclopentenol (**13**) in contrast to the unsubstituted isologue, which afforded the corresponding α, β-aminoalcohol (**12**) [1b]:

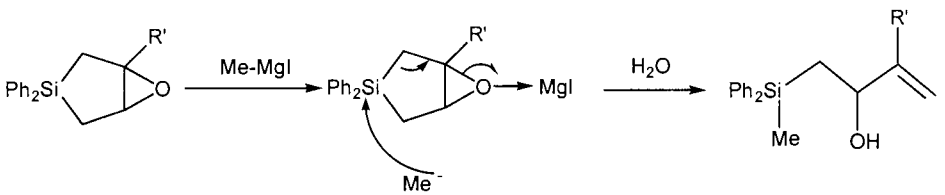


Same results were obtained when the reaction was carried out in the presence of lithium diethylamide, Et_2NLi and HX (X = Cl, Br). This regiochemistry of the silylated epoxide is enhanced by the presence of the trimethylsilyl group. Abstraction of the hydrogen in the α-position to the intracyclic metal by relatively weak bases ($X^- = Cl^-$, Br^-) may be attributed to the increase of the acidity of this atom. On the other hand, the steric hindrance of the trimethylsilyl group may direct the reaction in the observed path. Both R_2NMgBr and HX (X = Cl, Br) open the epoxide to give the corresponding amino alcohols and halohydrins, respectively, when they are reacted with the unsubstituted 6-oxa-3-silabicyclo[3.1.0]hexanes (R′ = H) 1b, 16.

Hudrlik et al. [17] have shown that an α,β-epoxysilane could be considered as a masked aldehyde or ketone and gave an example illustrating this hypothesis by reacting these epoxides with Grignard reagents. Corresponding β-alcohols are isolated:



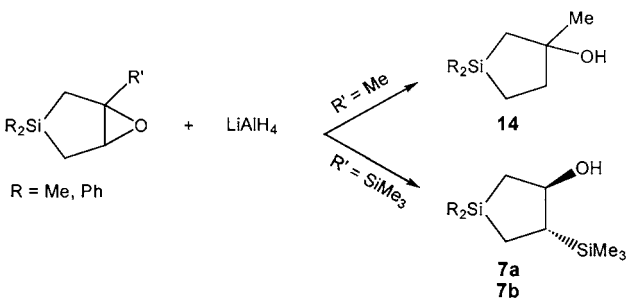
When 1-trimethylsilyl-3,3-diphenyl-6-oxa-3-silabicyclo[3.1.0]hexane (**6b**) and an ethereal solution of methylmagnesium iodide were refluxed for 1 h, only linear γ-ethylenic silacompound (**14b**) was formed quantitatively. The reaction is similar in the unsubstituted epoxide series:



The reaction is regioselective. The nucleophilic displacement occurs at the Si–C bond α to TMS group. There was no spectroscopic evidence for the formation of a tertiary alcohol resulting from the cleavage of the silicon–carbon bond β to the TMS group. The high stereospecificity of this reaction suggests that the trimethylsilyl group facilitates displacement α to silicon and a β-elimination process due to the presence of the intracyclic silicon.

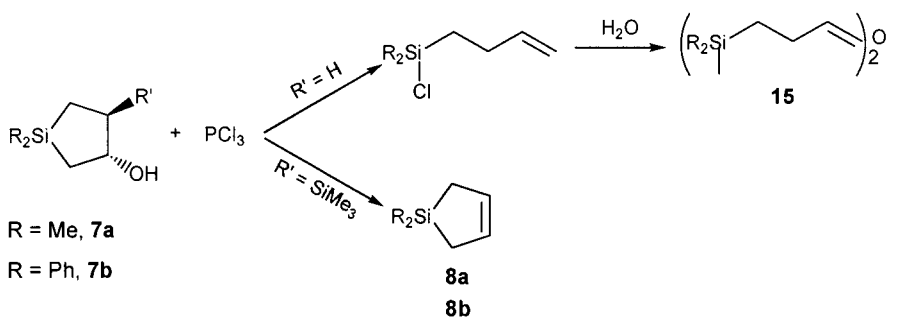
*2.3. 3-Trimethylsilyl-1,1-dimethyl(diphenyl)-1-silacyclopentan-4-ol (**7a,b**)*

Reduction of the epoxides **6a,b** with lithium aluminium hydride in diethyl ether produced the secondary alcohols **7a,b**. This is in agreement with the previous observations regarding the lithium aluminium hydride reduction of α,β-epoxysilanes. The mechanism of this reaction is elucidated in the literature [18]. Reduction of the 3C-methylated epoxides offers the corresponding tertiary alcohols [19]. These epoxides undergo reduction with hydride attack at the more sterically accessible carbon in contrast to the 3-silylated oxiranes where the nucleophilic displacement occurs at the carbon bearing the bulky trimethylsilyl group. This result is consistent with the previous observations concerning the nucleophilic attack at the α-carbon.

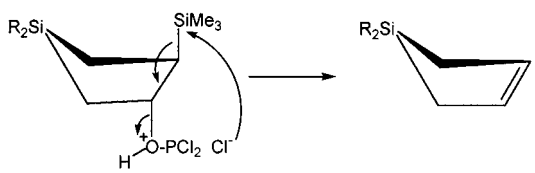


Treatment of alcohols **7a,b** with hydrogen halides HX (X = Cl, Br, I) or phosphorus trichloride gave the corresponding 1,1-dimethyl(diphenyl)-silacyclo-

pent-3-enes (**8a,b**) and Me_3SiX (X = Cl, Br, I) or $HOPCl_2$:



The first reaction corresponds to the protonation of the alcohol function or to the nucleophilic substitution at the phosphorus atom. The counteranion X^- attacks the electron deficient metal (Si) in the β-position. In the case of the non-substituted alcohol, nucleophilic attack occurs at the intracyclic silicon to give the ring-opening product **15** after hydrolysis. With the substituted alcohol (R′=$SiMe_3$), the S_N2' reaction takes place at the trimethylsilyl group resulting in an anti-elimination reaction of chlorotrimethylsilane (TMSCl) and formation of the corresponding silacyclopentene (**8a,b**).



3. Conclusions

We have shown that the chemical properties of the 3-trimethylsilyl silacyclopentenes (**5**) follow the trends of simple vinylsilanes while the presence of a trimethylsilyl group on the oxiranes (**6**) and alcohols (**7**) modified the chemical behaviour of such series. These results underline the electronic and steric properties of the trimethylsilyl group in the β-position of the silicon atom present in the heterocycle.

Further investigations on the scope of these reactions are in progress.

4. Experimental

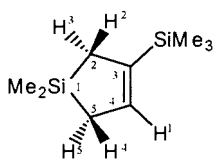
All experiments were carried out in flame-dried glassware under an atmosphere of argon. Diethyl ether and pentane were distilled freshly from sodium–benzophenone ketyl prior to use. Methyl iodide, bromobenzene and diethylamine were obtained from Aldrich Chemical Co., *m*-chloroperbenzoic acid (85%) was purchased from Air Liquide and used without additional purification. All NMR spectra were recorded at 25°C on a Bruker AC 80 and 250 MHz spectrometer in deuteriochloroform ($CDCl_3$). The ^1H and ^{13}C chemical shifts (δ) are given in ppm and referenced relative to Me_4Si. The coupling constants are given in Hz. Melting points were determined in evacuated capillaries with a Buchi–Tottoli apparatus. IR spectra were recorded as thin films on a Perkin–Elmer System Series 1600 FT-IR spectrometer. Low-resolution mass spectra were determined by GC–MS using a Hewlett–Packard 5890 Serie II gas chromatograph equipped with a HP/MS 5989A mass selective detector. An ionising voltage of 70 eV was used (mass spectra are reported in mass-to-charge units, m/z, with ion identity and peak intensities relative to the base peak in parentheses).

4.1. Synthesis of 3-trimethylsilyl-1,1-dimethyl-1-silacyclopent-3-ene (*5a*)

To a solution of methyl magnesium iodide MeMgI (prepared from 4.5 g of magnesium turnings and 25 g of methyl iodide in 100 ml of diethyl ether), was added dropwise, under vigorous stirring, 13.1 g (58.24 mmol) of 3-trimethylsilyl-1,1-dichlorosilacyclopent-3-ene (**4a**) in 60 ml of Et_2O. After refluxing for 21 h, the mixture was cooled to 0°C (ice bath) and hydrolysed with 30 ml of a saturated ammonium chloride aqueous solution, and washed with water (2 × 50 ml). The aqueous layer was extracted with pentane.

The combined organic layers were dried over sodium sulphate and the solvents were removed in vacuo. 8.68 g of the product **5a** were isolated after distillation of the crude liquid. B.p: 73°C/20 mmHg. Yield: 81%. Anal. Calc. For $C_9H_{20}Si_2$: C, 58.62; H, 10.93. Found: C, 58.67; H, 10.87%.

IR: 2994, 2955, 2898 (C–H stretch), 1577 (C=C), 1398, 1247, 1146, 1096, 1002, 957, 837, 787, 749, 724, 690 cm^{-1}.



^{1}H-NMR δ: 0.05 (s, 9H, Me_3Si), 0.15 (s, 6H, Me_2Si), 1.33 (m, 4H, H^2, H^3, H^4, H^5), 6.15 (m, 1H, H^1). ^{13}C-NMR δ: −2.13 (Me_2Si), −1.96 (Me_3Si), 19.98 (C^2), 20.78 (C^5), 139.61 (C^4), 144.89 (C^3). GC–MS *m/e* (relative intensity): 184 (25) $(M)^+$, 169 (71) $(M–Me)^+$, 141 (23) $(M–MeSi)^+$, 111 (4) $(M–Me_3Si)^+$, 96 (10) $(M–Me_4Si)^+$, 73 (100) $(Me_3Si)^+$, 59 (38) $(Me_2SiH)^+$, 58 (20) $(Me_2Si)^+$, 43 (51) $(MeSi)^+$, 29 (13) $(C_2H_5)^+$.

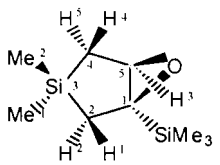
4.2. Synthesis of 3-trimethylsilyl-1,1-diphenyl-1-silacyclopent-3-ene (**5b**)

In a 500 ml two-neck round-bottom flask, containing an ethereal solution of phenylmagnesium bromide (prepared from 34.6 g of bromobenzene and 11.0 g of magnesium turnings in 100 ml of ether), were added at 0°C (ice bath), 15.69 g (69.65 mmol) of 3-trimethylsilyl-1,1-dichloro-1-silacyclopent-3-ene (**4b**) in 100 ml of diethyl ether. The flask was allowed to warm up gradually to r.t. and then the mixture was refluxed for 48 h. After hydrolysis and the usual work up, 19.24 g of the product were distilled as a colourless liquid. Bp: 130°C/0.1 mmHg. Yield: 90%. IR: 3067, 3049, 2997, 2953, 2894, 1953, 1889, 1818, 1765, 1578 (C=C), 1485, 1427, 1391, 1303, 1259, 1246, 1188, 1145, 1065, 1028, 1002, 955, 909, 836, 811, 770, 725, 697 cm^{-1}. ^{1}H-NMR δ: 0.37 (s, 9H, Me_3Si), 2.16 (m, 4H, H^2, H^3, H^4, H^5), 6.56 (m, 1H, H^1), 7.51–7.86 (m, 10H, Ph_2Si). ^{13}C-NMR δ: −1.58 (Me_3Si), 19.34 (C^2), 20.21 (C^5), 127.45, 127.53, 128.23, 129.05, 129.72, 135.03, 136.38 (aromatics), 139.75 (C^4), 145.49 (C^3). GC–MS *m/e* (relative intensity): 308 (24) $(M)^+$, 293 (32) $(M–Me)^+$, 265 (3) $(M–MeSi)^+$, 231 (6) $(M–C_6H_5)^+$, 197 (26) $(Ph_2SiMe)^+$, 181 (31) $(197\text{-}CH_4)^+$, 135 (38) $(PhSiMe_2)^+$, 105 (67) $(PhSi)^+$, 77 (8) $(C_6H_5)^+$, 73 (100) $(Me_3Si)^+$, 59 (44) $(Me_2SiH)^+$, 58 (28) $(Me_2Si)^+$, 53 (35) $(C_4H_5)^+$, 43 (73) $(MeSi)^+$.

4.3. 1-Trimethylsilyl-3,3-dimethyl-6-oxa-3-silabicyclo[3.1.0]hexane (**6a**)

In a 250 ml two-neck round-bottom flask, were placed 5.1 g (25 mmol) of *m*-chloroperbenzoic acid (85%) and 50 ml of diethyl ether. The flask was cooled to 0°C and an ethereal solution of the metallacyclopentene (**5a**) [4.1 g (22 mmol) in 30 ml of ether)] was added dropwise with stirring. The flask was left to warm up gradually to r.t. and kept at this temperature for another 12 h. The mixture was then treated with 50 ml of a 10% sodium hydroxide aqueous solution and washed with water (2 × 50 ml). The aqueous layers were extracted with Et_2O. The combined organic layers were dried over Na_2SO_4 and the solvents were removed under pressure. Distillation of the residual liquid gave 3.71 g of **6a** as a colourless liquid. B.p.: 83°C/18 mmHg. Yield: 83%. IR: 2956, 2926, 2896, 1398, 1358, 1249, 1173, 1121, 1083, 988, 974, 897, 838, 747, 734, 704, 648, 636 cm^{-1}. ^{1}H-NMR δ: −0.00 (s, 9H, Me_3Si), 0.05 (s, 3H, Me^1Si), 0.07 (s, 3H, Me^2Si), 0.94 (ddd, $J(H^1H^2) = 15.7$ Hz; $^4J(H^1H^3) = {}^4J(H^2H^3) = 0.6$ Hz, 2H, H^1, H^2), 0.99 (ddd, $J(H^4H^5) = 15.7$ Hz; $^3J(H^4H^3) = {}^3J(H^5H^3) = 2.0$ Hz, 2H, H^4, H^5), 3.27 (td, $^3J(H^3H^4) = {}^3J(H^3H^5) = 2.0$ Hz; $^4J(H^3H^1) = {}^4J(H^3H^2) =$ 0.6 Hz, 1H, H^3). ^{13}C-NMR δ: −3.64 (Me_3Si), −1.27 (Me^1Si), 0.49 (Me^2Si), 16.76 (C^2), 17.09 (C^4), 61.67 (C^1), 61.80 (C^5).

GC–MS *m/e* (relative intensity): 200 (2) $(M)^+$, 185 (15) $(M–Me)^+$, 157 (17) $(M–SiMe)^+$, 147 (63) $(Me_3SiOSiMe_2)^+$, 117 (17) $(Me_3SiC_2H_4)^+$, 101 (39) $(Me_3SiCO)^+$, 85 (12) $(Me_2SiC_2H_3)^+$, 73 (100) $(Me_3Si)^+$, 59 (54) $(Me_2SiH)^+$, 58 (24) $(Me_2Si)^+$, 45 (73) $(MeSiH_2)^+$, 43 (62) $(MeSi)^+$, 29 (21) $(HSi)^+$.



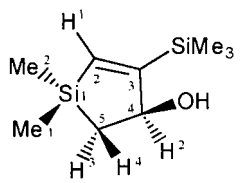
4.4. 1-Trimethylsilyl-3,3-diphenyl-6-oxa-3-silabicyclo[3.1.0]hexane (**6b**)

As previously, epoxidation of 2.0 g (6.48 mmol) ethylenic heterocycle (**5b**) gave after recrystallisation in pentane, 2.0 g of white crystals of **6b**. M.p.: 58°C. Yield: 95%. IR: 3069, 3061, 2998, 2958, 2898, 1954, 1881, 1428, 1393, 1358, 1250, 1189, 1173, 1114, 1083, 987, 889, 841, 784, 726, 698, 641 cm^{-1}. ^{1}H-NMR δ: 0.10 (s, 9H, Me_3Si), 1.48 (ddd, $J(H^1H^2) = 15.9$ Hz; $^4J(H^1H^3) \neq {}^4J(H^2H^3) = 1.6$ Hz, 2H, H^1, H^2), 1.68 (ddd, $J(H^4H^5) = 15.9$ Hz; $^3J(H^4H^3) \neq {}^3J(H^5H^3) = 2.2$ Hz, 2H, H^4, H^5), 3.49 (td, $^3J(H^3H^4) = {}^3J(H^3H^5) = 2.2$ Hz; $^4J(H^3H^1) = {}^4J(H^3H^2) = 1.6$ Hz, 1H, H^3). ^{13}C-NMR δ: −3.45 (Me_3Si), 16.29 (C^2), 16.41 (C^4), 61.49 (C^1), 61.59 (C^5), 127.34, 128.12, 128.85, 129.54, 134.92, 135.52, 135.86, 136.13 (aromatic carbons). MS *m/e* (relative intensity): 324 (7) $(M)^+$, 309 (8) $(M–MeSi)^+$, 281 (10) $(Ph_2SiCH_2CSiMe_3)^+$, 271 (50) $(Ph_2SiOSiMe)^+$, 225 (46) $(Ph_2SiCH_2CHO)^+$, 193 (100) $(271\text{-}C_6H_6)^+$, 183 (76) $(Ph_2SiH)^+$, 182 (9) $(Ph_2Si)^+$, 181 (38) $(271\text{-}Me_3SiOH)^+$, 135 (37) $(PhSiMe_2)^+$, 121 (14) $(PhSiHMe)^+$, 105 (47) $(PhSi)^+$, 77 (13) $(C_6H_5)^+$, 73 (58) $(Me_3Si)^+$, 53 (13) $(C_4H_5)^+$, 45 (41) $(MeSiH_2)^+$, 43 (16) $(MeSi)^+$, 29 (5) $(HSi)^+$.

4.5. 3-Trimethylsilyl-1,1-dimethyl-1-silacyclopent-2-ene-4-ol (**13a**)

In a 100 ml two-neck round-bottom flask, was placed a solution of Et_2NLi in pentane, prepared by addition of 10 ml of *n*-BuLi (1.6 M in hexanes) to an excess of diethylamine (1.3 g) in 20 ml of pentane. To this

solution, was added dropwise using a syringe, 2.45 g (12.22 mmol) of **6a** solution in 15 ml of ether at 0°C. The flask was allowed to warm up to r.t. and kept at this temperature for an additional 12 h, hydrolysed with a saturated aqueous solution of NH_4Cl and washed with water (2×25 ml). The aqueous layers were extracted with ether. The organic layers were combined, dried over Na_2SO_4 and the solvents were removed under pressure. Distillation of the residual liquid gave 1.18 g of the allylic alcohol **12a** as a colourless liquid. Bp: 42°C/0.1 mmHg, Yield: 48%. Anal. Calc. For $C_9H_{20}OSi_2$: C, 53.93; H, 10.06. Found: C, 54.06; H, 10.37%. IR: 3601 (free OH), 3404 (associated OH), 2954, 2898, 1405, 1317, 1247, 1221, 1142, 1044, 910, 874, 843, 801, 751, 735, 691, 669, 642, 618 cm^{-1}.



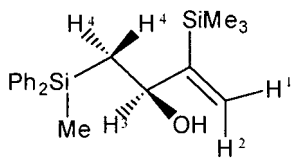
^{1}H-NMR δ: 0.08 (s, 3H, *Me*^{1}Si), 0.13 (s, 9H, *Me*$_3$Si), 0.18 (s, 3H, *Me*^{2}Si), 0.63 (dd, $J(H^3H^4) = 14.5$ Hz, $^3J(H^3H^2) = 5.7$ Hz, 1H, H^3), 1.39 (dd, $J(H^4H^3) = 14.5$ Hz, $^3J(H^4H^3) = 7.2$ Hz, 1H, H^4), 1.58 (m, 1H, OH), 4.87 (ddd, $^3J(H^2H^4) = 7.2$ Hz; $^3J(H^2H^3) = 5.7$ Hz, $^4J(H^2H^1) = 1.7$ Hz, 1H, H^2), 6.6 (d, $^4J(H^1H^2) = 1.7$ Hz, 1H, H^1). ^{13}C-NMR δ: -1.89 (*Me*^{1}Si), -0.82 (*Me*$_3$Si), -0.61 (*Me*^{2}Si), 24.50 (C^5), 79.84 (C^4), 144.40 (C^2), 173.42 (C^3). GC–MS *m*/*e* (relative intensity): 185 (11) $(M–Me)^+$, 183 (14) $(M + 1\text{-}H_2O)^+$, 169 (7) $(M + 1\text{-}MeOH)^+$, 157 (29) $(Me_2SiCH{=}CHSiMe_3)^+$, 141 (17) $(M–Me_2SiH)^+$, 110 (29) $(Me_2SiC_4H_4)^+$, 85 (14) $(MeSiC_4H_4)^+$, 75 (66) $(Me_2SiOH)^+$, 73 (100) $(Me_3Si)^+$, 59 (18) $(Me_2SiH)^+$, 58 (11) $(Me_2Si)^+$, 45 (69) $(MeSiH_2)^+$, 43 (59) $(MeSi)^+$, 29 (15) $(HSi)^+$.

4.6. 3-Trimethylsilyl-1,1-diphenyl-1-silacyclopent-2-ene 4-ol (13b)

As previously, 0.53 g (1.63 mmol) of epoxide **6b** in 5 ml of diethyl ether were added slowly at 0°C to a solution of Et_2NLi in pentane [prepared by addition of 1.6 ml (2.54 mmol) of *n*-BuLi (1.6 M in hexanes) to 0.3 g (4.1 mmol) of Et_2NH in 5 ml of pentane]. The flask was allowed to warm up to r.t. with stirring and kept at this temperature for 12 h. After the usual work up and purification of the crude product by chromatography on silica gel (50 g of SiO_2) using a mixture of pentane–Et_2O (95/5) as eluent, 0.10 g of the product were isolated as a colourless liquid. Yield: 19%. ^{1}H-NMR δ: 0.26 (s, 9H, Me_3Si), 1.22 (dd, $J(H^3H^4) = 14.8$ Hz; $^3J(H^3H^2) = 5.6$ Hz, 1H, H^3), 1.96 (dd, $J(H^4H^3) = 14.8$ Hz; $^3J(H^4H^2) = 7.1$ Hz, 1H, H^4), 5.15 (ddd, $^3J(H^2H^3) = 5.6$ Hz, $^3J(H^2H^4) = 7.1$ Hz, $^4J(H^2H^1) = 1.7$ Hz, 1H, H^2), 6.79 (d, $^4J(H^1H^2) = 1.7$ Hz, 1H, H^1). ^{13}C-NMR δ: -0.68 (*Me*$_3$Si), 23.56 (C^5), 80.07 (C^4), 128.11, 129.73, 129.78, 130.12, 134.78, 135.04, 135.51 (aromatics).

4.7. 4-Diphenyl(methyl)silyl-2-trimethylsilylbut-1-ene 3-ol (14b)

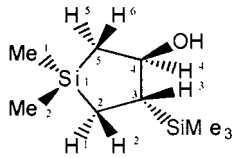
To an ethereal solution of MeMgI [prepared from 1.5 g (10 mmol) of iodomethane and 0.5 g (21 mmol) of magnesium turnings in 10 ml of Et_2O], were added dropwise 0.65g (2 mmol) of epoxide **6b** in 5 ml of ether. The solution was refluxed for 1 h and then hydrolysed at r.t. with a saturated aqueous solution of NH_4Cl. After the usual work up, the crude product was purified by chromatography on silica gel using a mixture of pentane–ether = 95:5 as eluent to yield 0.60 g. Yield: 88%.



^{1}H-NMR δ: 0.11 (s, 9H, *Me*$_3$Si), 0.14 (s, 3H, *Me*Si), 1.49 (d, $^3J(H^4H^3) = 7.0$ Hz, $2H^4$), 4.52 (td, $^3J(H^3H^4) = 7.0$ Hz, $^4J(H^3H^1) = 1.0$ Hz, $^4J(H^4H^2) = 1.3$ Hz, 1H, H^3), 5.34 (dd, $J(H^1H^2) = 2.4$ Hz, $^4J(H^1H^3) = 1.0$ Hz, 1H, H^1), 5.72 (dd, $J(H^2H^1) = 2.4$ Hz, $^4J(H^2H^3) = 1.3$ Hz, 1H, H^2). ^{13}C-NMR δ: -0.21 (*Me*Si), 1.13 (*Me*$_3$Si), 24.56 (C^4), 74.12 (C^3), 122.73 (C^1), 127.95, 127.97, 129.29, 134.63, 134.68, 137.21, 137.49 (aromatic carbons), 157.78 (C^2). GC–MS *m*/*e* (relative intensity): 322 (1) $(M–H_2O)^+$, 214 (1) $(Ph_2MeSiOH)^+$, 211 (4) $(Ph_2MeSiCH_2)^+$, 210 (9) $(Ph_2SiCO)^+$, 199 (40) $(Ph_2SiOH)^+$, 198 (22) $(Ph_2SiO)^+$, 197 (100) $(Ph_2SiMe)^+$, 181 (9) $(197\text{-}CH_4)^+$, 105 (15) $(PhSi)^+$, 77 (5) $(C_6H_5)^+$, 73 (36) $(Me_3Si)^+$, 53 (6) $(C_4H_5)^+$, 43 (11) $(MeSi)^+$.

4.8. 3-Trimethylsilyl-1,1-dimethyl-1-silacyclopentan-4-ol (7a)

In a 50 ml two-neck round-bottom flask, were placed 0.32 g (excess) of $LiAlH_4$ suspension in 10 ml of diethyl ether. To this solution, were added, via a syringe, 0.74 g (3.70 mmol) of epoxide **6a** solution in 5 ml of ether with stirring. The mixture was refluxed for 3 h, hydrolysed at r.t. with 0.5 ml of water. The white precipitate (aluminium salts) was filtered over a glass fritte and washed with diethyl ether. The solvents were removed in vacuo and the residual liquid was purified by chromatography on silica gel using a mixture of pentane–ether = 90:10 as eluent, to give 0.66 g of **7a** as a colourless liquid. Yield: 89%. Anal. Calc. for $C_9H_{22}OSi_2$:



C, 53.39; H, 10.95. Found: C, 53.60; H, 11.14%. IR: 3623 (free OH), 3483 (associated OH), 2952, 2898, 1403, 1319, 1247, 1142, 1104, 1071, 1001, 986, 939, 909, 883, 837, 736, 699, 661, 644 cm^{-1}. ^{1}H-NMR δ: 0.05 (s, 9H, Me_3Si), 0.08 (s, 3H, Me^1Si), 0.20 (s, 3H, Me^2Si), 0.65 (m, 1H, OH), 1.00 (m, 5H, H^1, H^2, H^3, H^5, H^6), 4.59 (m, 1H, H^4). ^{13}C-NMR δ: −1.79 (Me_3Si), −1.51 (Me^1Si), −0.43 (Me^2Si), 9.89 (C^2), 27.00 (C^5), 34.42 (C^3), 75.87 (C^4).

4.9. 3-Trimethylsilyl-1,1-diphenyl-1-silacyclopentan-4-ol (7b)

As above, from 1.34 g (4.13 mmol) of epoxide **6b**, we distilled after reduction, 1.01 g of the alcohol **7b.** Bp: 140°C/0.05 mmHg. Yield: 75%. IR: 3582 (free OH), 3458 (associated OH), 3067, 3948, 3019, 2949, 2901, 1486, 1427, 1403, 1317, 1245, 1141, 1113, 1073, 998, 938, 879, 638, 810, 786, 728, 698, 624 cm^{-1}. ^{1}H-NMR δ: 0.13 (s, 9H, Me_3Si), 1.14 (m, 5H, H^1, H^2, H^3, H^5, H^6), 1.20 (m, 1H, OH), 4.81 (m, 1H, H^4), 7.3–7.8 (m, 10H, Ph_2Si). ^{13}C-NMR δ: −1.67 (Me_3Si), 9.37 (C^2), 26.13 (C^5), 35.24 (C^3), 75.73 (C^4), 127.91, 128.02, 129.33, 134.90, 135.22, 136.71 (aromatic carbons). MS *m/e* (relative intensity): 311 (1) $(M–Me)^+$, 282 (1) $(Ph_2SiCH_2CHSiMe_3)^+$, 236 (78) $(M–Me_3SiOH)^+$, 225 (15) $(Ph_2SiCH_2CHO)^+$, 199 (33) $(Ph_2SiOH)^+$, 183 (22) $(Ph_2SiH)^+$, 182 (33) $(Ph_2Si)^+$, 181 (49) $(199\text{-}H_2O)^+$, 158 (100) $(M–Me_3SiOH–C_6H_6)^+$, 135 (16) $(PhSiCH_2O)^+$, 121 (10) $(PhSiOH)^+$, 105 (24) $(PhSi)^+$, 77 (10) $(C_6H_5)^+$, 73 (23) $(Me_3Si)^+$, 53 (5) $(C_4H_5)^+$.

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