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Synthesis of Six-Membered Silaheterocycles by the Ring Enlargement of 1,1-Diphenyl-1-silacyclopent-3-ene

György Keglevich,[1] Mónika Trecska,[1] Kálmán Újszászy,[2] Krisztina Ludányi,[3] Áron Szöllősy,[4] László Tőke,[1] and Serge Mignani[5]

[1]*Department of Organic Chemical Technology, Technical University of Budapest, 1521 Budapest, Hungary*

[2]*Department of General and Inorganic Chemistry, Eötvös University, 1518 Budapest, Hungary*

[3]*Institute of Chemistry of the Hungarian Academy of Sciences, 1525 Budapest, Hungary*

[4]*Department of General and Analytical Chemistry, Technical University of Budapest, 1521 Budapest, Hungary*

[5]*Rhone-Poulenc Rorer, Centre de Recherche de Vitry-Alfortville, 13 Quai Jules Guesde BP14, 94403 Vitry-sur-Seine Cedex, France*

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ABSTRACT: *Silabicyclo[3.1.0]hexane* **2** *obtained from silacyclopent-3-ene* **1** *by dichlorocarbene addition is useful in the synthesis of ring-expanded products, such as silacyclohexa-2,4-diene* **3** *and 5-alkoxy-silacyclohex-3-enes* **5.** *Catalytic hydrogenation of compound* **3** *affords silacyclohexane* **4.** *The new heterocycles are characterized by* ^{13}C *and* ^{1}H *NMR, as well as mass spectroscopic data.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10: 171–175, 1999

INTRODUCTION

Recently, silicon-containing heterocycles have attracted much attention [1,2]. The simplest heterocyclic families include silacyclopentenes that are useful in the synthesis of other silicon-containing ring compounds. Mignani et al. [3] have developed an efficient one-step synthesis of 1,1-diphenyl-1-silacyclopent-3-ene (**1**). Although the possibility of the dichlorocarbene ring enlargement of silacyclopent-3-enes was recognized more than two decades ago [4,5], this procedure was not studied in detail. We decided to revisit this challenge and to work out simple and easily applicable synthetic methods for the ring enlargement of silacyclopentene **1** to different six-membered silacycles.

RESULTS AND DISCUSSION

According to the method of Manuel et al. [4], the key intermediate, 3-silabicyclo[3.1.0]hexane **2**, was prepared by the reaction of silacyclopentene **1** with dichlorocarbene generated from chloroform by potassium *tert*-butylate. After treatment with several portions of $CHCl_3$-KOBu-t, the yield of **2** was 60%. We have now found that the dichlorocyclopropanation of **1** carried out under phase transfer catalytic

Correspondence to: György Keglevich
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conditions using the chloroform—50% aqueous sodium hydroxide—triethylbenzylammonium chloride system, which was used for 3-phospholene 1-oxides [6], gave the product **(2)** in an almost quantitative yield (96%) already after a one-portion treatment (Scheme 1). Earlier, the dichlorocarbene adduct **(2)** was characterized only by melting point and by ^{1}H NMR data obtained by a low-performance spectrometer [4]. Adduct **2** with an ABX system has now been characterized by refined ^{1}H NMR parameters (see Experimental); the ^{13}C NMR (Table 1) and mass spectral data are also provided. Here we note that the French group prepared some other silabicyclohexanes too by the $CHCl_3$-KOBu-*t* method [4,5]. A Russian research group reported the synthesis of the 3,3-dichloro derivative [7]. They reacted 1,1-dichloro-1-silacyclopent-3-ene with dichlorocarbene generated from trichloromethyl-trichlorosilane.

The silabicyclohexanes of type **2** may be versatile intermediates for ring-expanded products. Manuel et al. observed that a mixture of cyclic and linear dienes is formed in the thermolysis of the 1,1-disubstituted silabicyclohexanes [4,5]. Consequently, these reactions are not of practical importance. We thought it to be useful to map the thermostability of dichlorocarbene adduct **2** by TG, DTG, and DSC. These examinations suggested the cyclopropane ring opening to occur in the range of 160–250°C. A thermolysis of neat **2** at 180°C for 25 minutes afforded silacyclohexadiene **3** in 85% yield after column chromatography (Scheme 1). At 180°C, the thermolysis of **2** is a clean reaction without any by-products. Product **3,** prepared by us for the first time, was characterized by ^{13}C and ^{1}H NMR, as well as mass spectral data. The ^{13}C NMR spectral parameters are listed in Table 1.

We tried to synthesize 3,3-diphenyl-3-silabicyclo[3.1.0]hexane by the catalytic hydrogenation of the 6,6-dichloro derivative **(2)**. This reaction failed, as only unidentified by-products could be isolated from the mixture. So, for the preparation of the dehalogenated product, the reaction of silacyclopentene with carbene as suggested in the literature [8] remains the best method.

Silacyclohexadiene **3** offered itself for utilization in the preparation of silacyclohexane **4.** Catalytic hydrogenation of **3** indeed led to product **4;** the yield was, unfortunately, only 31% (Scheme 2). Still, this method serves as an alternative beside the different cyclization [9,10] and substitution [11] techniques described. Product **4** was characterized by ^{13}C and ^{1}H NMR, as well as mass spectral data. For ^{13}C NMR data, see Table 1.

Finally, we aimed at the synthesis of alkoxy-silacyclohexenes **5.** Solvolysis of the dichlorocarbene adduct **2** in different alcohols in the presence of silver nitrate furnished the expected silacyclohexenes **(5)** (Scheme 3). The yield of the products **(5)** was 31–58% after column chromatography. In all cases, the corresponding $Ph_2Si(OR)_2$ could be pointed out in the reaction mixture as the by-product. The structures of the products **(5)** were supported by ^{13}C and ^{1}H NMR, as well as mass spectral data. The ^{13}C and ^{1}H NMR data are listed in Tables 2 and 3, respectively. ^{13}C NMR assignments were confirmed by spectra obtained by the Attached Proton Test technique. Signals in the ^{1}H NMR spectrum of **5a** and **5c** were fully resolved. The multiplicity of H–2, H–3, H–5, and H–6 is a doublet of doublets in all cases. Due to the diastereotopy, the OCH_2 or the $OCH(CH_3)_2$ signals were doubled in the ^{1}H NMR spectrum of **5a** and **5b,** respectively. In the mass spectrum of the products **(5)**, the molecular ions were of weak intensity, but the fragments formed by the loss of ROH were more intensive. The base peak was the Ph_2SiOR^{7+} fragment in all cases; it may be formed by an intramolecular rearrangement. For **5a,** the elemental composition of Ph_2SiOEt^{7+} was confirmed by HRMS (M^+_{found} = 227.0859, $C_{14}H_{15}OSi$ requires 227.0892).

It is worth mentioning that the mass spectrum of all silacycles containing a chloro substituent in position 4 (**2**, **3**, and **5**) revealed the presence of the Ph_2SiCl fragment (*m/z* = 217). Elemental composition of this fragment was confirmed by HRMS (M^+_{found} = 217.0225, $C_{12}H_{10}ClSi$ requires 217.0240). The fragmentations of six-membered silacycles leading to Ph_2SiCl^{7+} and to Ph_2SiOR^{7+} may be of general value.

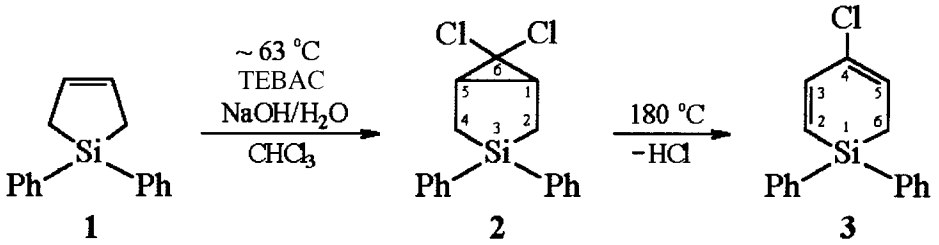
An excellent review on five- and six-membered silicon-carbon heterocycles have been published by Schmidt [12].

EXPERIMENTAL

^{13}C and ^{1}H NMR spectra were obtained on a Bruker DRX-500 spectrometer at 125.7 and 500 MHz, respectively, with tetramethylsilane as the standard. Mass spectra were recorded on a MS 25-RFA instrument at 70 eV.

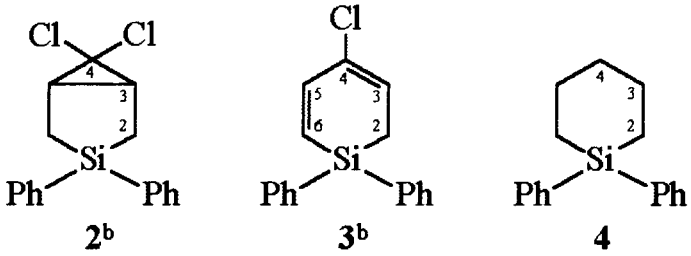
6,6-Dichloro-3,3-diphenyl-3-silabicyclo[3.1.0]hexane **(2)**

A solution of sodium hydroxide (25 g, 0.625 mol) in water (25 mL) was added dropwise to the mixture of silacyclopentene **1** (10.0 g, 42.4 mmol) [3], triethylbenzylammonium chloride (0.3 g, 1.32 mmol), and alcohol-free chloroform (100 mL) that was stirred at room temperature. The temperature of the mixture rose gradually to reflux. After stirring for 4 hours, contents of the flask were filtered. The residue obtained after evaporating the solvent of the organic



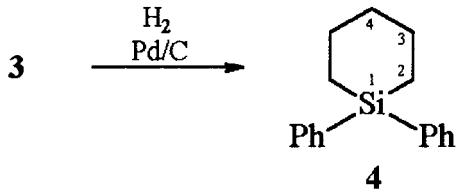
SCHEME 1

TABLE 1 ^{13}C NMR Data for Silacycles **2–4**[a]



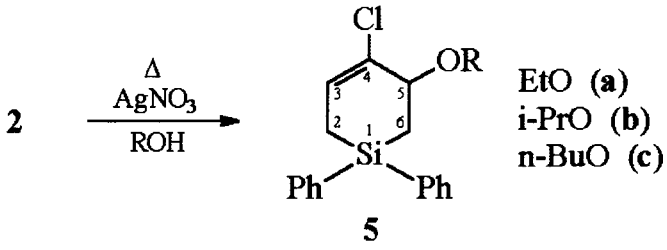
Comp.	$\delta_C(CDCl_3)$ C_2	C_3	C_4	C_5	C_6
2[c]	11.7	34.8	69.7	—	—
3[d]	13.1	126.2[e]	130.6	124.2[e]	146.0
4[f]	11.8	24.5[g]	30.2[g]	—	—

[a]The assignments were confirmed by spectra obtained by the Attached Proton Test Technique.
[b]Occasional numbering.
[c]127.9, 128.1 ($C_{3'}$, $C_{3''}$), 129.6, 129.7 ($C_{4'}$, $C_{4''}$), 134.3, 134.8 ($C_{2'}$, $C_{2''}$), 133.8, 135.9 ($C_{1'}$; $C_{1''}$).
[d]127.8, 128.3 ($C_{3'}$, $C_{3''}$), 130.1, 130.2 ($C_{4'}$, $C_{4''}$), 134.5, 134.9 ($C_{2'}$, $C_{2''}$), 134.6, 134.8 ($C_{1'}$, $C_{1''}$).
[e,g]May be reversed.
[f]128.0 ($C_{3'}$, $C_{3''}$), 129.3 ($C_{4'}$, $C_{4''}$), 134.7 ($C_{2'}$, $C_{2''}$), 136.9 ($C_{1'}$, $C_{1''}$).



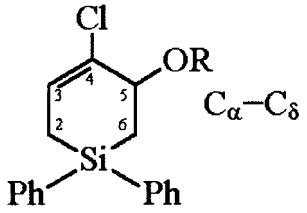
SCHEME 2

phase was purified by column chromatography (silica gel, 1% methanol in chloroform) to give **2** (13.0 g, 96%). ^{13}C NMR, Table 1; ^1H NMR ($CDCl_3$) δ 1.44 (d, ^2J = 16.1, 2H, C(2)H_A), 1.63 (dd, ^2J = 15.7, ^3J = 7.7, 2H, C(2)H_B), 2.22 (d, ^3J = 7.0, 2H, C(3)H), 7.28–7.57 (m, 10H, Ar), (Ref. [4]: 1.5 (C(2)H_2), 2.2 (C(1)H), 7.3 (Ar)); MS, *m/z* (relative intensity) 318 (M^+, <1), 282 (M − 35 − H, 43), 217 (Ph_2SiCl, 100).



SCHEME 3

TABLE 2 ^{13}C NMR Spectral Data for 5-Alkoxy-Silacyclohex-3-enes **5a–c**



Comp.	$\delta_C(CDCl_3)$ C_2	C_3	C_4	C_4	C_5	C_α	C_β	C_γ	C_δ
5a	12.6	126.7	134.6	78.9	17.9	63.9	15.5	—	—
5b	12.7	126.5	134.4	76.3	18.7	69.7	22.0[b] 23.0[b]	—	—
5c	12.7	126.5	[a]	79.3	18.0	68.4	32.2	19.6	14.1

[a]Not resolved.
[b]The two signals are due to diastereotopy.

4-Chloro-1,1-diphenyl-1-silacyclohexa-2,4-diene (3)

Adduct **2** (4.1 g, 12.9 mol) was heated at 180°C in an opened flask for 25 minutes. The crude product was taken up in chloroform and purified by column chromatography (silica gel, 1% methanol in chloroform) to give **3** (3.1 g, 85%). ^{13}C NMR, Table 1; ^1H NMR ($CDCl_3$) δ 2.15 (d, J = 5.6, 2H, CH_2), 6.21 (t, J = 5.5, 1H, C(3)H), 6.40 (d, J = 14.5, 1H, C(5)H*), 6.91 (d, J = 14.5, 1H, C(6)H*), 7.20–7.60 (m, 10H, Ar) *may be reversed; MS, *m/z* (relative intensity) 282 (M^+,

TABLE 3 ^{1}H NMR Data for 3-Alkoxy-Silacyclohex-4-enes **5a–c** in $CDCl_3$ Solution[a]

	δ_H, *multiplicity* (*J in Hz*)						
Comp.	*H-2*	*H-6*	*H-3*	*H-5*	*OCH-*	*CH_2*	*CH_3*
5a	1.92 dd ($J_{2,2'}$ = 16.8, $J_{3,2}$ = 8.3) 2.01 dd ($J_{2,2'}$ = 17.0, $J_{3,2'}$ = 3.8)	1.65 dd ($J_{6,6'}$ = 14.7, $J_{6,5}$ = 4.5) 1.72 dd ($J_{6,6'}$ = 14.6, $J_{6',5}$ = 6.2)	6.26 dd ($J_{3,2}$ = 8.3, $J_{3,2'}$ = 3.8)	4.32 dd ($J_{6,5}$ = 5.2, $J_{6',5}$ = 5.3)	3.60 dq 1H (J_{gem} = 9.4, J = 7.5) 3.56 dq 1H (J_{gem} = 9.4, J = 7.5)	—	1.18 t (J = 7.0)
5b	1.89 dd ($J_{2,2'}$ = 16.7, $J_{3,2}$ = 8.5) 1.99 dd ($J_{2,2'}$ = 16.8, $J_{3,2'}$ = 3.3)	not resolved	6.20 dd ($J_{3,2}$ = 8.3, $J_{3,2'}$ = 3.6)	4.40 dd ($J_{6,5}$ = 4.6, $J_{6',5}$ = 4.9)	3.77–3.83 m 1H	— 1.13 d 3H	1.17 d 3H (J = 6.0) (J = 6.0)
5c	1.90 dd ($J_{2,2'}$ = 16.8, $J_{3,2}$ = 8.4) 1.97 dd ($J_{2,2'}$ = 16.9, $J_{3,2'}$ = 3.8)	1.62 dd ($J_{6,6'}$ = 14.6, $J_{6,5}$ = 4.4) 1.70 dd ($J_{6,6'}$ = 14.7, $J_{6',5}$ = 5.9)	6.25 dd ($J_{3,2}$ = 8.5, $J_{3,2'}$ = 3.8)	4.32 dd ($J_{6,5}$ = 5.0, $J_{6',5}$ = 5.4)	3.44–3.56 m 2H	1.33 sx (J = 7.2) 2H 1.48–1.58 m 2H	0.88 t (J = 7.5)

[a]Aromatic signals for the phenyl groups of the products (**5a–c**): 7.10–7.65 m 10H

38), 246 (M − 35 − H, 15), 217 (Ph_2SiCl, 100), 204 (M − 77 − H, 20), 181 (217 − 35 − H, 24), 142 (M − 77 − 35 − CH_2CH − H, 77).

1,1-Diphenyl-1-silacyclohexane (4)

To the mixture of diene **3** (2.0 g, 7.08 mol) in methanol (50 mL) was added 5% palladium on carbon (0.2 g), and the suspension was hydrogenated at 450 kPa and at 26 → 90°C until 3 equivalents of hydrogen were absorbed. The mixture was filtered, the solvent evaporated, and the residue distilled *in vacuo* to yield **4** (0.55 g, 31%). bp: 136–140°C (0.25 mmHg) [Ref. [10]: 122°C (0.12 mmHg)]; ^{13}C NMR, Table 1; ^{1}H NMR ($CDCl_3$) δ 1.38–1.48 (m, 4H, C(2)H_2), 1.70–1.78 (m, 2H, C(4)H_2), 1.95–2.05 (m, 2H, C(3)H_2), 7.51–7.85 (m, 10H, Ar); MS, *m/z* (relative intensity) 252 (M^+, 45), 209 (M − $(CH_2)_3$ − H, 22), 174 (M − 77, 100).

General Procedure for the Preparation of 5-Alkoxy-4-chloro-1,1-diphenyl-1-silacyclohex-3-enes 5a–c

The mixture adduct **2** (1.0 g, 3.14 mmol) and silver nitrate (6.0 g, 35.3 mmol) in the corresponding alcohol (50 mL) was stirred at the boiling point for 6 hours. The solid components were removed by filtration and the filtrate evaporated. The residue so obtained was purified by repeated column chromatography (silica gel; 2% methanol in chloroform) to give **5a–c**.

The following products were thus prepared.

4-Chloro-1,1-diphenyl-5-ethoxy-1-silacyclohex-3-ene **(5a)**. The alcohol: ethyl alcohol; yield: 58%; ^{13}C NMR, Table 2; ^{1}H NMR, Table 3; MS, *m/z* (relative intensity) 328 (M^+, 2), 282 (M − EtOH, 13), 227 (100), 217 (Ph_2SiCl, 30).

4-Chloro-1,1-diphenyl-5-(2-propoxy)-1-silacyclohex-3-ene **(5b)**. The alcohol: *i*-propyl alcohol; yield: 45%, ^{13}C NMR, Table 2; ^{1}H NMR, Table 3; MS, *m/z* (relative intensity) 342 (M^+, 2), 282 (M − *i*-PrOH, 29), 241 (100), 217 (Ph_2SiCl, 41).

5-(1-Butoxy)-4-chloro-1,1-diphenyl-1-silacyclohex-3-ene **(5c)**. The alcohol: *n*-butyl alcohol; yield: 31%, ^{13}C NMR, Table 2; ^{1}H NMR, Table 3; MS, *m/z* (relative intensity) 356 (M^+, <1), 282 (M − *n*-BuOH, 7), 255 (100), 217 (Ph_2SiCl, 15).

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