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THERMAL ISOMERIZATION OF 3-SILABICYCLO[3.1.0]HEXANES: A NEW ROUTE TO SILACYCLOPENTENES AND SILACYCLOHEXENES *

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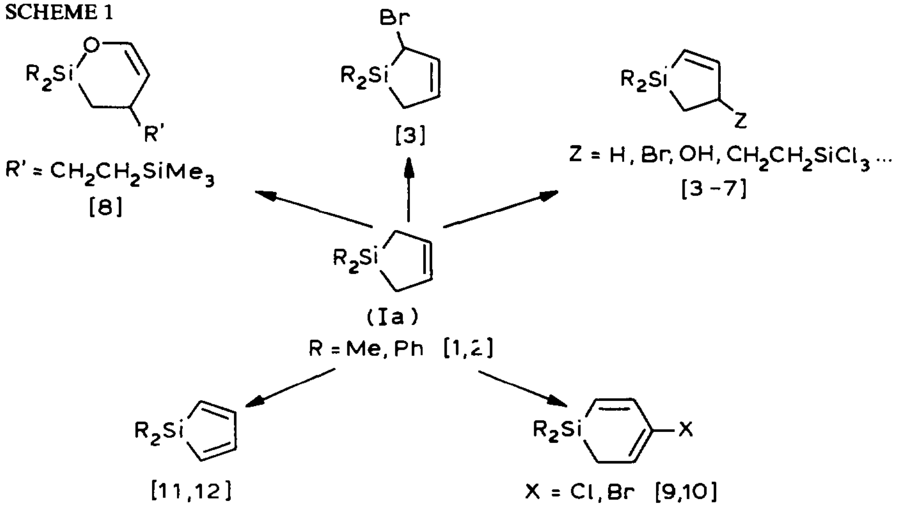
Summary

By thermolysis, 3-silabicyclo[3.1.0]hexanes lead to silacyclohexenes as major products and also to silacyclopentenes. The ratio of the different isomeric silicon rings is strongly dependent on the nature of the C(1) and C(5) substituents (R, R′ = H, Me).

Introduction

1-Silacyclopent-3-enes are good starting compounds for the synthesis of new types of five- and six-membered cyclic organosilicon derivatives, especially those

SCHEME 1



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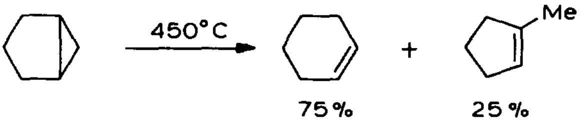
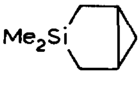
* Dedicated to Dean R. Calas on the occasion of his 70th birthday.

with one or two double bonds in the ring. The main results obtained in our laboratory in this area are illustrated in Scheme 1.

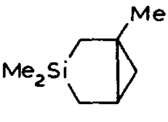
In the light of the results observed in the carbon series on the thermal rearrangement of bicyclo[3.1.0]hexane [13] (eq. 1) we investigated the best suitable experimen-



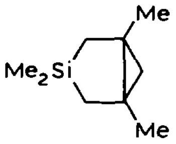
(1)



(IIa)



(IIb)

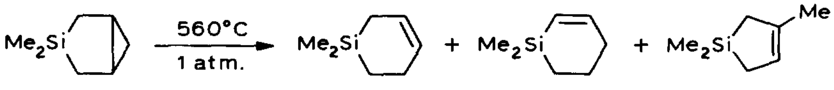


(IIc)

tal conditions for the thermolysis of analogous organosilicon derivatives IIa, IIb and IIc, which are available from the corresponding silacyclopent-3-enes Ia, Ib and Ic [2]. Thus, we hoped to obtain silacyclohexenes in one-step and to determine the effects of the silicon atom and the methyl substituents on the isomerization process.

Thermolysis of 3,3-dimethyl-3-silabicyclo[3.1.0]hexane (IIa)

When heated at 450°C in a sealed tube, the bicyclic compound IIa gave unidentified decomposition products. On the other hand, thermolysis in a flow system gave 1,1-dimethyl-1-silacyclohex-3-ene (IIIa) in good yield, along with small amounts of 1,1-dimethyl-1-silacyclohex-2-ene (III'a) and 1,1,3-trimethyl-1-silacyclopent-3-ene (Ib) (eq. 2).



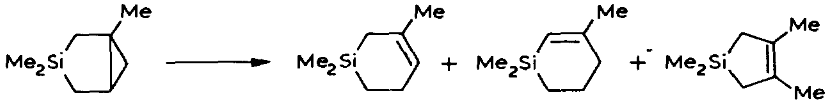
(IIa) (IIIa) (90%) (III'a) (5%) (Ib) (5%)

(2)

Derivatives IIIa, III'a and Ib are known compounds, but were made in other ways (IIIa, [15,16]; III'a [17,18]; Ib, [1,19]).

Thermolysis of 1,3,3-trimethyl-3-silabicyclo[3.1.0]hexane (IIb)

The thermolysis of the compound IIb in a sealed tube at 410°C for 5 h gives mainly a mixture of the silacyclohexene isomers IIIb and III'b and a small amount of disubstituted silacyclopentene Ic (eq. 3)

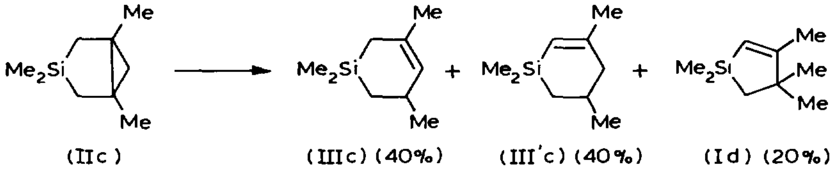


(IIb) (IIIb) (45%) (III'b) (45%) (Ic) (10%)

(3)

Thermolysis of 1,3,3,5-tetramethyl-3-silabicyclo[3.1.0]hexane (IIc)

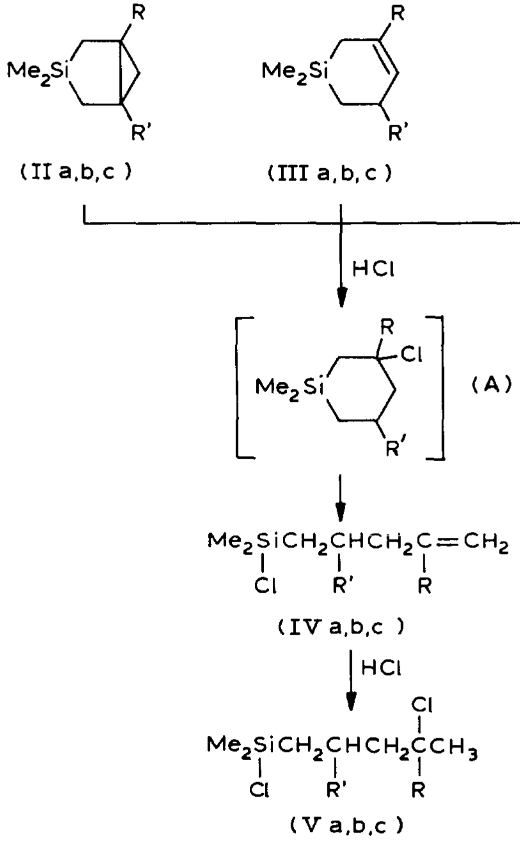
Thermal isomerization of compound IIc in a sealed tube at 330°C takes place within 5 h. In this case also, two isomeric silacyclohexenes were isolated and characterized, along with a smaller amount of trisubstituted silacyclopent-2-ene (eq. 4).



(4)

Reaction of hydrogen chloride with 3-silabicyclo[3.1.0]hexanes and silacyclohexenes (III and III')

In order to confirm the structures inferred from the spectral study (see Experimental) we treated the different compounds obtained in the pyrolytic reactions with HCl gas. The results are summarized in Scheme 2:



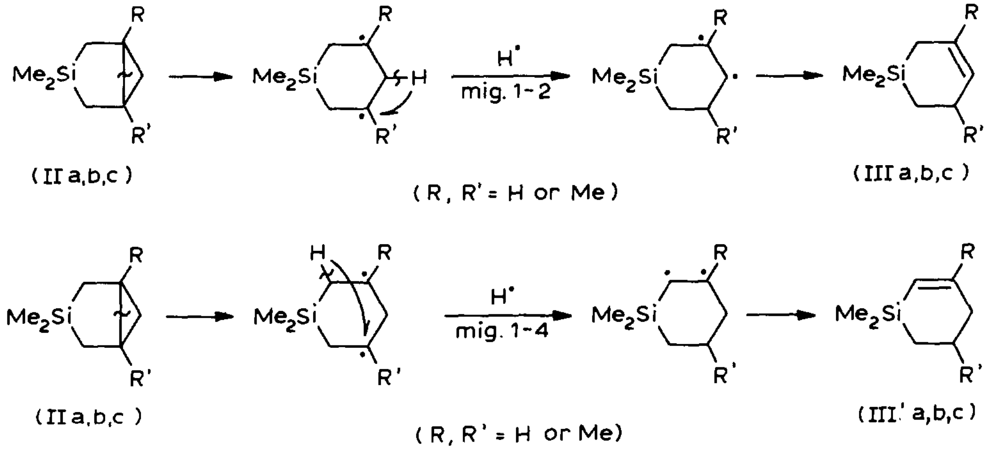
SCHEME 2. IIa, IIIa, III'a, IVa: R = R' = H; IIb, IIIb, III'b, IVb, Vb: R = Me, R' = H; IIc, IIIc, III'c, IVc, Vc: R = R' = Me.

The cleavage with HCl of the bridging bond in the bicyclic derivatives II leads to β-chlorosilacyclohexanes (A). These compounds undergo a β-elimination to give linear β-ethylenic compounds IV. For R = Me, these derivatives readily add a further HCl molecule, giving the dichloro compounds V. Markownikoff addition of HCl to the unsaturated species III and III′ initially gives the same compound (A) and then the linear derivatives IV and V.

Discussion, Mechanism

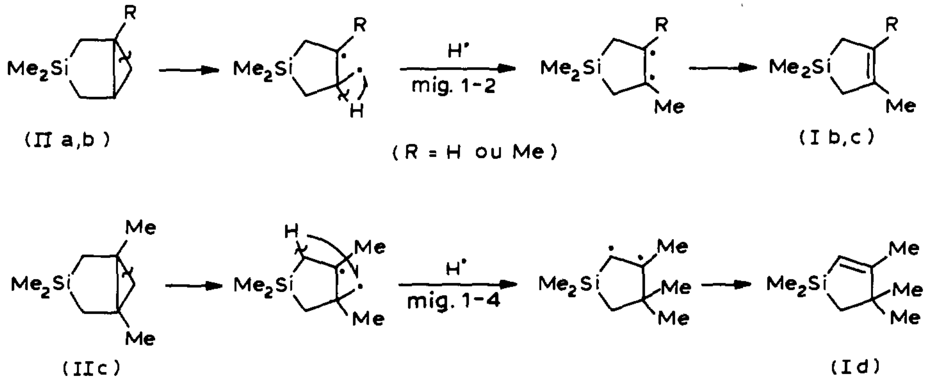
The six-membered ethylenic rings produced in the thermolysis arise from the homolytic cleavage of the bridging C(1)–C(5) bond. The most substituted biradical thus formed leads to the β-ethylenic (III) or α-ethylenic (III′) compounds after 1-2 or 1-4 migration of a H˙ radical (Scheme 3).

SCHEME 3



The silacyclopentenes Ib, Ic and Id formed in reactions 2, 3 and 4, probably result from C(1)–C(6) cleavage. The transient biradical is converted to the α- or β-ethylenic five-membered ring via 1-2 or 1-4 migration of one H˙ radical (Scheme 4).

SCHEME 4



These results show that 1-4 migrations occur during the formation of a carbon–carbon double bond α to the heteroatom; they emphasize the influence of the silicon which, through its *d* orbitals, stabilises a radical in the α position and, then, an α-ethylenic system, in a five- or six-membered ring.

Methyl substituents on carbon atoms 1 and 5 in silabicyclo[3.1.0]hexane (II), stabilise the formation of tertiary radicals and so affect the isomerization temperature and the nature and proportions of the isomers obtained. In the absence of C-methyl groups, the extent of 1-4 migration leading to an α-ethylenic six-membered silicon ring, is markedly reduced.

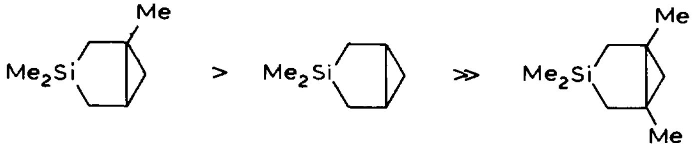
Conclusion

This work shows that the thermolysis of 3-silabicyclo[3.1.0]hexanes under suitable conditions provides a new and potentially valuable route for the synthesis of 1-silacyclohex-2-(and 3-)enes.

Experimental

NMR spectra (^1H) were recorded with a VARIAN EM 360A spectrometer (solvent: CCl_4 with TMS as internal standard; chemical shifts (ppm); s, singlet; s′, divided singlet; t, triplet; m, multiplet), IR spectra were recorded on a Perkin–Elmer 457 spectrometer (liquid film between NaCl windows). Girdel 3000 (10′ 1/4″ SE30 column) and Varian 712 (20′ 1/2″ SE30 20% column) chromatographs were used for analytical and preparative chromatography, respectively.

Compounds IIa [14], IIb and IIc were synthesized from the corresponding silacyclopentenes I by the Simmons–Smith process [20] as modified by Rawson and Harrison [21]. We observed that while the formation of the methylene bridge was faster for the monosubstituted silacyclopentene than for the unsubstituted derivative (due to the polarization of the double bond by the methyl group), it was markedly slowed down when the ring was substituted with two methyl groups (steric effect). Thus the ease of formation of silabicyclohexanes decreases in the order:



(IIb) (IIa) (IIc)

To increase the yield of II, it is necessary to add several portions of $Zn/CuCl/CH_2I_2$ during the reaction.

IIb. A mixture of Ib (26.5 g), active Zn (52 g), anhydrous cuprous chloride (80 g), methylene iodide (54 g) and anhydrous diethyl ether (200 ml) was refluxed for 24 h. After this time, the yield was about 70% (VPC). Zn (26 g), CuCl (40 g) and CH_2I_2 (54 g) were introduced and the mixture boiled again for 24 h. After centrifugation, the solution was neutralized ($NaHCO_3$), dried (sodium sulphate) and distilled; b.p. 139°C/760 mmHg, yield 50%. Analysis. Found: C, 68.40; H, 11.34. $C_8H_{16}Si$ calcd.: C, 68.48; H; 11.49%. IR spectrum: 3040 cm^{-1} (cyclopropane C–H), 1250 cm^{-1} (Me_2Si). NMR spectrum: δ 0.06(s), 0.10(s) (Me_2Si), 0.9(m) (CH_2SiCH_2), 1.15(s)

(C–Me). The signals corresponding to cyclopropane protons at high field overlapped with the Me_2Si signals.

IIc. The same procedure was used but starting from Ic. After three additions of a mixture Zn/Cu and CH_2I_2, IIc was obtained, containing about 5% unreacted Ic. IIc was purified by preparative VPC. b.p. 86°C/32 mmHg, yield 20%. Analysis. Found: C, 69.81; H, 11.62. $C_9H_{18}Si$ calcd.: C, 70.04; H, 11.75%. IR spectrum: 3040 cm^{-1} (cyclopropane C–H), 1250 cm^{-1} (Me_2Si). NMR spectrum: δ 0.03(s), 0.07(s) (Me_2Si), 0.9(m) (CH_2SiCH_2), 1.15(s) ($2CH_3$–C). Other signals, at high field, were not resolvable.

Thermolysis of IIa

A 20% solution of IIa in pentane was slowly introduced (syringe with PRECIDOR pump, 10 ml/h) in a slow nitrogen flow into a vertical quartz tube (30 cm long, 1 cm inside diam.) filled with quartz helices which was contained in an oven at 560 ± 4°C. The products resulting from the pyrolysis were collected in a condenser cooled with dry-ice and were analyzed by VPC and by IR and NMR spectroscopy. In addition to small amount of unreacted IIa, three other products were identified and isolated: 1,1,3-trimethyl-1-silacyclopent-3-ene (Ib) [2], 1,1-dimethyl-1-silacyclohex-2-ene (III′a) [17,18] and 1,1-dimethyl-1-silacyclohex-3-ene (IIIc) [15,16] b.p. 131°C/760 mmHg, yield 65% (after recycling four times at 560°C). IR spectrum (in CCl_4): 1620 cm^{-1} (weak band) (ν(C=C)). NMR spectrum: δ 0.05(s) (Me_2Si) 0.65 (t, J 7 Hz)($SiCH_2CH_2$), 1.05–1.25(m) ($SiCH_2CH$), 2.0–2.4(m) (CH_2CH_2CH), 5.3–5.9(m) (CH=CH).

Thermolysis of IIb

After IIb had been kept for 5 h at 410°C in a sealed tube, the liquid was dark yellow. VPC showed the formation of three new products, which were isolated by distillation between 120 and 130°C followed by preparative chromatography: (a) unreacted starting product IIb; (b) 1,1,3,4-tetramethyl-1-silacyclopent-3-ene (Ic) [2]; (c) 1-silacyclohex-2-ene (III′b); (d) 1-silacyclohex-3-ene (IIIb). The last two six-membered rings have almost the same retention time.

IIIb. IR spectrum: 1630 cm^{-1} (very weak band) (ν(C=C)). NMR spectrum: 0.04(s) (Me_2Si), 0.60(t, J 7 Hz)($SiCH_2CH_2$) 1.7(s′) (CH_3–C), 2.0–2.4(m) (CH_2CH), 5.3–5.5(complex m) (CH=C).

III′b. IR spectrum: 1610 cm^{-1} (strong band) (ν(C=C)). NMR spectrum: δ 0.02(s) (Me_2Si), 0.5–0.8(m) ($SiCH_2$), 1.1–1.4(m) ($CH_2CH_2CH_2$), 1.8(s′) (CH_3–C), 1.8–2.0(m) (CH_2C=), 5.3(s′) (CH=C).

Thermolysis of IIc

Isomerization of IIc was almost complete within 5 h at 330°C, the mixture being yellow-green after this time. VPC showed the formation of three new peaks. The fraction distilling between 135 and 142°C was separated by preparative VPC, to give the following products in order of increasing retention time: 1,1,3,4,4-pentamethyl-1-silacyclopent-2-ene (Id), the unreacted bicyclic derivative IIc and silacyclohexenes III′c and IIIc.

Id. IR spectrum: 1580 cm^{-1} (ν(C=C)). NMR spectrum: δ 0.10(s) (Me_2Si), 0.70(s) ($SiCH_2$), 1.10(s) (Me_2C), 1.80(s′) (CH_3–C=), 5.3(s′) (CH=C).

IIIc. IR spectrum: 1630 cm^{-1} (ν(C=C)). NMR spectrum: δ 0.02(s) (Me_2Si), 0.60(d) ($SiCH_2$), 0.8–1.3(m) ($CH{-}CH_3$), 1.20(s′) ($SiCH_2C{=}$), 1.80(s′) ($CH_3C{=}$), 5.4(m) ($CH{=}C$).

III′c. IR spectrum: 1610 cm^{-1} (strong intensity) (ν(C=C)). NMR spectrum: δ 0.01(s) (Me_2Si), 0.60(d) ($SiCH_2$), 0.8–1.3(m) ($CH_3{-}CH$), 1.7(s′) ($CH_3C{=}$), 5.4(s′) ($CH{=}C$).

Reaction of hydrogen chloride

With IIa and IIIa. The reaction was monitored by VPC; $Me_2Si(Cl)(CH_2)_3CH{=}CH_2$. IVa was obtained. b.p. 153°C/760 mmHg, yield 80%. Analysis. Found: C, 51.60; H, 9.34; Cl, 21.01. $C_7H_{15}SiCl$ calcd.: C, 51.66; H; 9.29; Cl, 21.79%. IR spectrum: 1640 cm^{-1} (ν(C=C)). NMR spectrum: δ 0.40(s) (Me_2Si), 0.6–1.0(m) ($SiCH_2$), 1.2–1.8(m) ($CH_2\mathit{CH}_2CH_2$), 1.8–2.4(m) ($CH_2C{=}$), 4.7–5.2(m) ($CH_2{=}C$), 5.4–6.2(m) ($CH{=}C$).

With IIb, IIIb and III′b. In all cases the IVb, $Me_2Si(Cl)(CH_2)_3C(Me){=}CH_2$, was obtained. IR spectrum: 1645 cm^{-1} (ν(C=C)). NMR spectrum: δ 0.40(s) (Me_2Si), 0.7–2.0(m) ($CH_2CH_2CH_2$), 1.65(s′) ($Me{-}C{=}$), 4.65(s′) ($CH_2{=}C$).

Compound IVb reacts readily with HCl gas to give $Me_2Si(Cl)CH_2CH_2CH_2C{-}ClMe_2$ (Vb); NMR spectrum: δ 0.45(s) (Me_2Si), 0.7–1.8(m) ($CH_2CH_2CH_2$), 1.60(s) ($Me{-}C{-}Me$).

Compounds IIc, IIIc and III′c, similarly gave IVc $Me_2Si(Cl)CH_2C(Me){-}HCH_2C(Me){=}CH_2$; IR spectrum:1645 cm^{-1} (ν(C=C)); NMR spectrum: δ 0.42(s) (Me_2Si), 0.6–1.8(m) (CH_2CHCH_3), 2.4(s′) ($CH_3C{=}$), 2.7(m) ($CH_2C{=}$), 4.7(m) ($CH_2{=}C$).

Compound IVc also readily reacts with HCl gas to give $Me_2Si(Cl)CH_2C(Me)HC{-}ClMe_2$ (Vc), which was characterized by its NMR spectrum: δ 0.45(s) (Me_2Si), 1.60(s) ($Me{-}C{-}Me$).

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