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Synthesis and ring opening reactions of a 2-silabicyclo[2.1.0]pentane†

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Methyl 2-silabicyclo[2.1.0]pentane-1-carboxylate, obtained by a photochemical intramolecular cyclopropanation reaction of an α-allylsilyl-α-diazoacetate, undergoes ring opening reactions under different conditions leading to methyl 2-[diisopropyl(methoxy)silylmethyl]cyclopropane-1-carboxylate, a 1-sila-4-cyclopentene-2-carboxylate or an allyl(methoxysilyl)ketene.

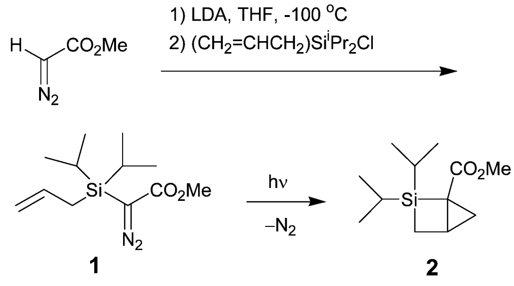
Intramolecular carbene and metal–carbene reactions of appropriately functionalized diazo compounds allow the ready construction of a broad range of carbo- and heterocyclic rings.[1–5] Starting from silyldiazoalkanes and silyldiazoacetates, this strategy gives access to various silaheterocycles[6] mainly by C,H insertion,[7–10] intramolecular cyclopropanation,[10] and reaction at a C≡C bond.[11] Successful intramolecular cyclopropanation reactions with allyloxysilyl- and [(3-butenyl)oxysilyl]-diazoacetates[10] led us to wonder whether the tether between the two reacting functionalities could be shortened by one member, *i.e.* whether (allylsilyl)diazoacetates would still undergo an intramolecular cyclopropanation reaction, yielding the so far unknown 2-silabicyclo[2.1.0]pentane skeleton.

For the synthesis of silyl-functionalized α-silyl-α-diazoacetates, we have introduced a procedure in which a silyl bis(triflate) is reacted with an alkyl diazoacetate and a (hetero)nucleophile.[12] Efforts to prepare **2** by this method gave unsatisfactory results, and therefore an alternative was developed: reaction of allyl(chloro)(diisopropyl)silane, readily prepared from dichloro(diisopropyl)silane and allylmagnesium chloride, with an excess (3–4 equiv.) of methyl α-lithio-α-diazoacetate[13] gave **1** in yields of up to 81% based on the silane (Scheme 1).

We were pleased to find that irradiation of diazoacetate **1** with 300 nm light (toluene, 2.5 h) gave 2-silabicyclo[2.1.0]pentane **2** which could be isolated in 68% yield. In contrast, thermal (180–250 °C) and catalytic ($Rh_2(OOCC_3F_7)_4$) decomposition of **1** was unspecific and no products were identified.

The constitution of **2** was established by 1D and 2D NMR spectroscopy. In addition to these data,‡ the shielding effect of silicon on the adjacent CH_2 group, as compared to the ^1H and ^{13}C chemical shifts of the parent bicyclo[2.1.0]pentane,[14] and the coupling constants ^1J(C-4,H) (181 Hz) and ^1J(C-5,H) (165 Hz) leave no doubt about the silabicyclopentane structure.

Obviously, **2** is formed by an intramolecular [2+1] cycloaddition reaction of the carbene intermediate derived from **1**. This is a remarkable result, since the formation of bicyclo[2.1.0]pentane ring systems by intramolecular carbene cyclopropanation is rare, in contrast to bicyclo[3.1.0]- and bicyclo[4.1.0]alkane systems. While the intermediacy of bicyclo[2.1.0]pentan-2-ones in the so-called vinylogous Wolff rearrangement of γ,δ-unsaturated α-diazoketones[15] has been known for some time, the first isolation of bicyclo[2.1.0]pentane-1-carboxylates from diazo compounds, namely by Rh(II)-catalysed decomposition of 2-diazo-3,3-difluoro-5-hexenoates, has been reported only recently.[16]

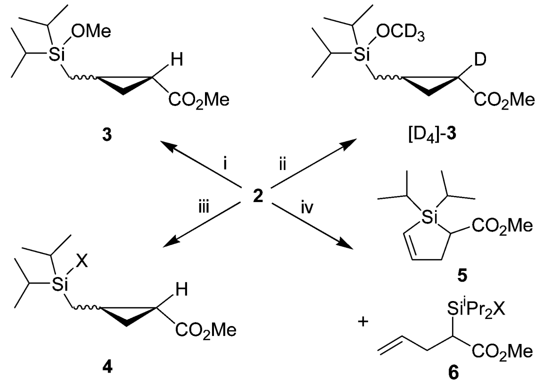


Scheme 1

Compound **2** is the first sila analogue of bicyclo[2.1.0]pentane ("housane"), which was reported as long ago as 1957,[17] and of 1-methoxycarbonylbicyclo[2.1.0]pentane.[18] Some chemical properties of compound **2** are described briefly in the following (Scheme 2). The compound remains unchanged for at least 1–2 weeks in solutions of pure $CDCl_3$, CD_3CN and [D_6]-EtOH. Also, heating of acetonitrile or ethanol solutions of **2** at 60 °C for 1 day left **2** unchanged. However, after 15 h in methanol solution, **2** had disappeared completely and methyl 2-[diisopropyl(methoxy)silylmethyl]cyclopropane-1-carboxylate (**3**) was isolated in 48% yield (*ca.* 90% yield before distillation according to ^1H NMR) as a diastereomeric mixture ($E : Z = 53 : 47$). Similarly, treatment of **2** with [D_4]-methanol gave the expected [D_4]-**3**. The nearly complete loss of stereochemical information at the cyclopropane ring indicates that the ring opening of **2** occurs by a nucleophilic attack at silicon followed by Si–C bond cleavage with the acceptor-substituted cyclopropyl anion as the leaving group. The configurational instability of ester-substituted cyclopropyl anions is a known fact. The analogous reaction with EtOH was achieved only by catalysis with aqueous conc. HCl and was found to be less clean by ^1H NMR. According to GC/MS analysis, **4**-OEt (73%), **4**-OH (23.5%), and **4**-Cl (1%) were the major volatile components.

The nucleophile-induced Si–C cleavage of **2** by MeOH is reminiscent of solvent-induced isomerization[19] and nucleophilic substitution[20] of monocyclic 1-halo- and 1-alkoxysilacyclobutanes. It has been suggested that the ready reaction of silacyclobutanes with Lewis bases is due to the formation of a pentacoordinate silicon species with concomitant release of angle strain.[21]

When **2** was treated in chloroform solution with a catalytic amount of *p*-toluenesulfonic acid, an 85 : 15 mixture of two



Scheme 2 *Reactions and conditions*: (i) CH_3OH, 15 h, rt, 48% yield; (ii) CD_3OD, 15 h, rt; (iii) EtOH, conc. HCl; X = Cl, OEt, OH; (iv) $CHCl_3$, cat. TsOH, 5 days, 62%.

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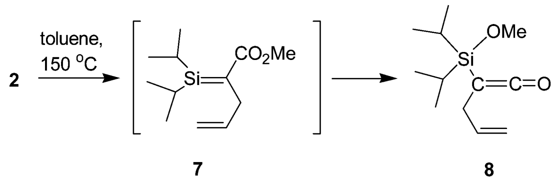
† Electronic supplementary information (ESI) available: experimental procedures, and physical and spectroscopic data for compounds **1–3**, **5** and **7**. See http://www.rsc.org/suppdata/cc/b3/b312110k/



Scheme 3

products was obtained with 1-sila-4-cyclopentene **5** as the major product. The double bond position in **5** could be derived from the proton coupling in the ^{1}H NMR spectrum;‡ furthermore, the IR absorption at 1545 cm^{-1} (C=C stretching mode) is considered characteristic of 1-sila-2-cyclopentenes, while 1-sila-3-cyclopentenes have an absorption at 1610–1620 cm^{-1}.[22] With the small quantities obtained, the minor product could not be separated from **5**, but its ^{1}H NMR signals suggest a 2-silylated 4-pentenoate **6**, the (Si)–X substituent of which is perhaps OH or a condensation product of SiOH. It is reasonable to assume that the formation of both products begins with the H^{+}-induced opening of the C1–C4 bond (possibly initiated by protonation of the carbonyl function) of silabicyclopentane **2** leading to a 3-silacyclopentyl cation which can either lose a proton to form silacyclopentene **5** or fragment to give acyclic alkene **6**.

Silabicyclopentane **2** is a thermally quite stable compound. However, thermolysis in toluene solution at 150 °C was completed in 29 h and according to GC/MS analysis gave a mixture of at least ten products from which only allyl(alkoxysilyl)ketene **8** could be isolated in 7% yield (Scheme 3).‡ After only 19 h of thermolysis (87% conversion), the yield of **8** was 20%. When the thermolysis of **2** was performed in methanol (110 °C, 24 h), an 83 : 17 mixture of cyclopropane **3** and i-$Pr_2Si(OMe)CH(CO_2Me)CH_2CH{=}CH_2$, the methanol addition product of **7**, was obtained. The isomerization **2**$\rightarrow$**8** is likely to proceed through a [2+2] cycloreversion of **2** generating the silaethene intermediate **7** which rearranges to form ketene **8** by a 1,3(C$\rightarrow$Si) OMe shift. While similar short-lived alkoxycarbonyl-silenes have been generated from appropriate silyldiazoacetates by a Wolff-type carbene-to-silene rearrangement,[23] the thermal cycloreversion of silabicyclopentane **2** represents a novel access to acyl-substituted silaethenes. It should be noted that the generation of simple silaethenes by [2+2] cycloreversion from monocyclic silacyclobutanes requires pyrolysis or laser photolysis conditions.[24]

In conclusion, we have prepared the first 2-silabicyclo[2.1.0]pentane by a photochemical intramolecular cyclopropanation. Three ring opening modes were found, namely cleavage of the Si–C1 bond to form a (silylmethyl)cyclopropane, opening of the C1–C4 bond to form a 1-sila-2-cyclopentene, and [2+2] cycloreversion yielding an acylsilene intermediate which rearranges to an (alkoxysilyl)ketene.

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Notes and references

‡ Selected physical and spectroscopic data. Compound **2**: δ_{H} (500.14 MHz, $CDCl_3$) 0.67 (dd, ^{2}J 14.1, ^{3}J 1.2, 1H, 3-H_{endo}), 1.03 (“s”, 4H, CH*Me* + C*H*Me$_2$), 1.06 (d, 3H, CH*Me*), 1.07 (dd, 1H, 3-H_{exo}, obscured by *i*-Pr signals), 1.08 and 1.11 (each d, ^{3}J 7.5, 3H, CH*Me*), 1.29 (pseudo-t, 1H, 5-H_{syn}), 1.33 (sept, 2H, C*H*Me$_2$), 1.72 (mc (centered multiplet), 1H, 5-H_{anti}), 2.25 (mc, 1H, 4-H), 3.61 (s, 3H, OMe); δ_{C} (100.6 MHz, $CDCl_3$) 8.4 (C-3), 11.8/13.1 (*C*HMe$_2$), 16.99 (C-1), 17.01/17.13/17.28/18.31 (CH*Me*$_2$), 23.9 (^{2}J(C,H) 165, C-5), 26.6 (^{2}J(C,H) 181, C-4), 51.3 (OMe), 174.5 (C=O); δ_{Si} (99.36 MHz) 10.7. Compound **5**: δ_{H} (400.14 MHz, $CDCl_3$) 0.91/0.97/1.01/1.05 (4 d, 12 H, CH*Me*$_2$), *ca*. 0.90–1.00 (1H, C*H*Me$_2$, covered by other signals), 1.08 (sept, 1H, C*H*Me$_2$), 2.43 (dd, ^{3}J 8.7, J 6.3, 1H, 2-H), 2.64 (^{2}J 18.4, ^{3}J 8.7, ^{3}J 2.9, ^{4}J 1.9, 1H, 3-H), 2.92 (^{2}J 18.4, ^{3}J 6.3, $^{3}J = {}^{4}J = 2.4$, 1H, 3-H), 3.64 (s, 3H, OMe), 5.73 (dt, ^{3}J 10.4, ^{4}J 2.2, 1H, 5-H), 6.83 (dt, ^{3}J 10.4, 2.7, 1H, 4-H); δ_{C} (100.6 MHz) 11.5 (*C*HMe$_2$), 17.81/17.87/18.21 (CH*Me*$_2$), 28.6 (C-2), 35.7 (C-3), 51.5 (OMe), 123.6 (C-5), 153.0 (C-4), 176.2 (C=O). Compound **8**: δ_{H} (200.13 MHz, $CDCl_3$) 0.98–1.04 (m, 14H, C*HMe*$_2$), 2.59–2.64 (dt, 2H, CH_2-allyl), 3.47 (s, 3H, OMe), 4.96 (ddt, ^{3}J 10.5, $^{2}J = {}^{4}J = 1.5$), 5.10 (ddt, ^{3}J 16.7, $^{2}J = {}^{4}J = 1.5$), 5.74–5.94 (m, 1H); δ_{C} (50.32 MHz) 9.3 (*C*=C=O), 13.0 (SiCH), 17.3 (CH*Me*$_2$), 25.9 (CH_2-allyl), 51.5 (OMe), 115.3, 136.6, 181.7 (C=*C*=O); ν(film)/cm^{-1} 2089 (s, C=C=O).

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