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Preliminary communication

A novel ring-opening reaction of 2,2-dimethyl-2-silabicyclo[3.1.0]hexane

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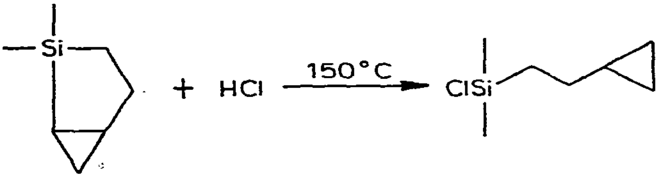
SUMMARY

The compound 2,2-dimethyl-2-silabicyclo[3.1.0]hexane reacts with hydrogen chloride in the gas phase to give a high yield of β-(chlorodimethylsilyl)ethylcyclopropane.

It is well known that there is a rather sharp line of demarcation between the reactivity of cyclic organosilanes where the silicon is in a five- or large-membered ring. The larger silacycloalkanes undergo silicon–carbon cleavage reactions under essentially the same conditions as do open chain organosilanes, whereas silacyclobutanes[1] and silacyclopropanes[2] react under mild conditions with a variety of polar reagents to yield ring-opened products.

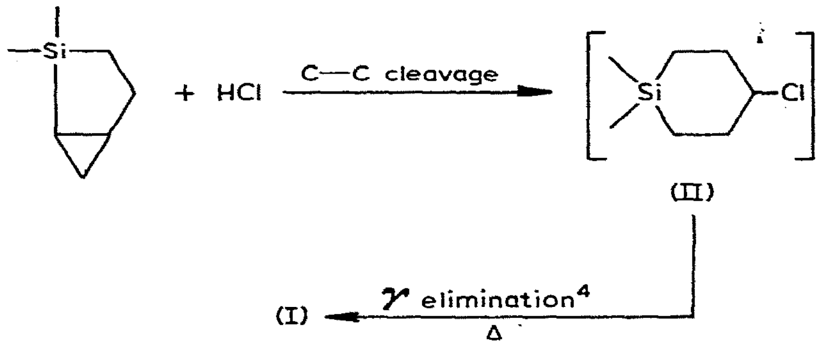
We have found that 2,2-dimethyl-2-silabicyclo[3.1.0]hexane[3], while containing silicon in a five-membered ring, reacts with hydrogen chloride under mild conditions to give silicon–carbon cleavage (eqn. 1).



(1)

(I)

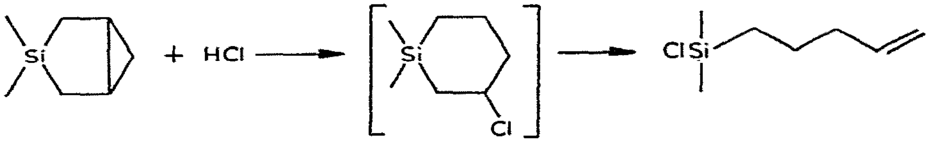
It is possible to propose a mechanism whereby the above product (I) is the result of carbon–carbon cleavage (eqn. 2).



(2)

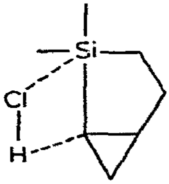
However, we have ruled out this possibility with an experiment using DCl in place of HCl, which showed that all of the deuterium was incorporated into the cyclopropyl group rather than half of it, as would be required by an intermediate such as II.

The gas phase reaction of 3,3-dimethyl-3-silabicyclo[3.1.0]hexane has been shown to proceed by carbon—carbon cleavage[5] (eqn. 3). Moreover, we have shown that neither 1,1-dimethyl-1-silacyclopentane nor trimethylsilylcyclopropane react with hydrogen chloride under the conditions of reaction 1.

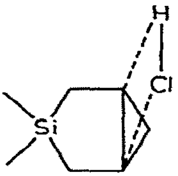


(3)

Both reactions 1 and 3 can be viewed as electrophilic attacks on cyclopropane, with reaction 1 proceeding through transition state III and reaction 3 proceeding through transition state IV.



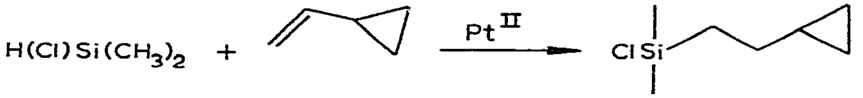
(III)



(IV)

Transition state III presumably is operative as a result of the polarity of the silicon—carbon bond but the distance between the cyclopropyl ring and the silicon atom in IV prevents direct interaction of the chlorine with the silicon.

The hydrogen chloride cleavage of 2,2-dimethyl-2-silabicyclo[3.1.0]hexane was carried out by sealing 1.1 mmol of 2,2-dimethyl-2-silabicyclo[3.1.0]hexane and 2.02 mmol hydrogen chloride in a 50 ml glass vessel and placing the vessel in an oven at 150° for 6 h. Hydrogen chloride (1.04 mmol) was recovered and 0.148 g (0.92 mmol) of crude product was isolated. This proved to be 91% pure by gas chromatographic analysis. An unmeasured quantity of non-volatile liquid remained in the reaction vessel. The product showed a parent *m/e* peak at 162 and was identified as β-(chlorodimethylsilyl)ethylcyclopropane (I) by comparison of its gas chromatographic retention time, IR and NMR spectra with an independently synthesized sample. The latter was prepared by Pt^{II}-catalyzed addition of dimethylchlorosilane to vinylcyclopropane (eqn. 4). Dimethylchlorosilane, 9g, 95 mmol, was added to 6g (88 mmol) of vinylcyclopropane in the presence of a few drops of Speier's catalyst[6]. The mixture was heated at reflux for 1 hour and then was distilled, the product being purified by preparative gas chromatography on an 8 'X 3/8" column packed with SE 30 on chromosorb W at 230°. The yield of crude product was 3.5g (25%). (Calcd.: C, 51.69; H, 9.23; Found: C, 51.23: H, 9.29%.) Selected IR bands include (cm^{-1}): 3080 (cyclopropyl CH stretch), 1250 (silicon methyl), 1010 (cyclopropyl breathing), 470 (Si—Cl stretch). The NMR spectrum of this compound is discussed below.



(4)

The reaction between 0.5g of 2,2-dimethyl-2-silabicyclo[3.1.0]hexane and a 40% excess of DCl was 90% complete after 66 h at 145°. The product obtained had a gas chromatographic retention time identical to that of β-(chlorodimethylsilyl)ethylcyclopropane and showed a parent *m/e* peak at 163.

For undeuterated I the following NMR data (40% in CCl$_4$, benzene internal standard) was obtained: The β-CH$_2$ appears as a multiplet at τ8.63, the α-CH$_2$ as a multiplet at τ8.93, the methyl groups on silicon as a singlet at τ9.55. The region from τ8.85 to 9.75 shows an integral value of 11 protons, indicating that signals due to three of the cyclopropyl protons are found in this region. There is a multiplet at τ9.86 which is the signal due to the other two cyclopropyl protons. For deuterated I the NMR data are the same, except that the τ9.86 signal has an integral value of one proton.

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