Synthesis of difunctional 1,4-dimethyl-1,4-disilacyclohexanes

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Transformations of HVinSiCl₂, HVinSi(Me)Cl, HVinSi(Me)Ph, and HVinSi(Me)NEt₂ in the presence of Pt catalyst were studied. In dilute solutions, the reaction gave a mixture of structural and stereoisomers of five- and six-membered disilacyclanes, resulting from intramolecular cyclization of the initially formed linear dimer. In the case of methyl(phenyl)dilsilacyclane, the structural isomers were separated and trans-1,4-dimethyl-1,4-diphenyl-1,4-disilacyclohexane was isolated. The reaction of this product with HCl in the presence of AlCl₃ followed by hydrolysis resulted in the synthesis of trans-1,4-dichloro- and trans-1,4-dihydroxy-1,4-dimethyl-1,4-disilacyclohexanes. The structures of the structural and stereoisomers synthesized were confirmed by ¹H, ¹³C, and ²⁹Si NMR and IR spectroscopies and mass spectrometry.

Key words: hydrosilylation, chlorination, hydrolysis, intramolecular cyclization, disilacycloalkanes, structural and stereoisomerism.

The purpose of this work was an attempt to prepare difunctional 1,4-diorgano-1,4-disilacyclohexanes, which could serve as the basis for the synthesis of cyclolinear polyorganocarbosiloxanes or polyorganocarbosilanes. These polymers present a certain interest as self-organizing systems and can be used to prepare monomolecular Langmuir films. No data on polymers with disilacyclohexane units in the chain can be found in the literature. Organodisilacyclanes are formed in 5–19% yields as by-products in the syntheses of linear polycarbosilanes by polyaddition of organovinylhydrogensilanes in the presence of Pt catalysts.¹–¹⁰

Based on IR spectra, organodisilacyclanes prepared from vinylhydrogensilanes ¹a–d via linear dimers ²a–d (reaction (1)) were assumed¹ to have structures ³a–d and ⁴d. Later, it was found by NMR spectroscopy that they are mixtures of structural isomers, whose ratio depends on the substituents at the silicon atom.² In a study of stepwise hydrosilylation of dimethyl(divinyl)silane with chlorodimethylsilane followed by reduction of ClMe₂SiCH₂CH₂SiMe₂Vin isolated in the first step, it has been shown that structural isomers are formed from dimethyl(vinyl)silane (1a) at the step of intramolecular cyclization; the ratio of five- to six-membered disilacyclanes is 70 : 30.³ Compound ³a was synthesized from bis(trimethylsilyl)ethane by elimination of SiMe₄ in the presence of AlBr₃⁴ and by methylation of tetrachlorodisilacyclohexane ³e.⁶ Crystalline compounds ³e,f were isolated from the products of polyaddition of dichlorovinylsilane (1e) and chlorophenylvinylsilane (1f) in 5 and 9% yield, respectively,⁷ whereas chloro(methyl)vinylsilane (1g) and chloro(ethyl)vinylsilane form mixtures of structural isomers of disilacyclanes ³ and ⁴.⁷ However, based on the data on the reduction of the reaction mixture, it was concluded⁸,⁹ that dichlorosilane ¹e is also converted into a mixture of isomers ³e and ⁴e. Note that 1,1,4,4-tetrafluoro-1,4-disilacyclohexane was obtained by hydrosilylation of diphenyldivinylsilane by diphenylsilane followed by chlorination and fluorination.¹⁰

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is based on the preparation of 1,1,4,4-tetrachloro-
1,4-disilacyclohexane (3f) followed by Grignard phenyl-
ation. Upon homohydrosilylation of dichlorovinylsilane (1f) in the presence of a Pt complex of tetramethyl-
divinylsiloxane (Carsted catalyst) in hexane, we ob-
tained products (18%) which partially crystallized during distillation. Judging by the 1H NMR spectroscopy and
GLC data, the crystals separated by filtration represented compound 3f of 90% purity. The liquid product was
found to be a mixture of isomers 4f and 3f in 85 : 15 ratio. However, the reaction of this mixture with
phenylmagnesium bromide did not give compound 3f.

We further studied homohydrosilylation of diethyl-
amino(methyl)vinylsilane (1h) in the presence of the
Carsted catalyst and H2PtCl6·6H2O both in solution and
without a solvent. The reaction in hexane gave 5% distillable products. According to GLC, the product
isolated by distillation was a mixture of three com-
 pounds. The chemical shifts and absorption bands ob-
served in the 1H NMR and IR spectra correspond to
the SiCH2CH2Si, SiCH(Me)Si, CH2=CHSi, and HSi
groups, indicating the presence of three structural iso-
mers 2h—4h, i.e., intramolecular hydrosilylation in so-
lution does not occur completely. We were unable to
separate the isomers by conventional techniques. Even
under rigorous conditions (7 h at 200—215 °C), in-
tramolecular hydrosilylation in block did not occur to
completion, and unreacted Si—Vin and Si—H groups
remained in the polymer.

The third approach to the synthesis of difunctional
diorganocyclohexanes studied here is based on homo-
 hydrosilylation of chloro(methyl)vinylsilane (1g) in a
10% hexane solution in the presence of the Carsted
catalyst. This gave volatile products (17%); judging by
the 1H NMR spectrum, they were a mixture of isomers
4g and 3g in 65 : 35 ratio, which is consistent with the
published data.7

Comparison of published data with those obtained in
this study shows that the structural isomers can be
separated for R1 = Cl and Ph, because in these cases, isomer 3 predominates. We decided to separate isomers
3d and 4d, in view of the fact that the majority of
organosilicon compounds with phenyl substituents ex-
hibit an enhanced tendency for crystallization.

We studied the influence of the concentration of the
solution (in hexane or toluene) and the type of Pt
catalyst used (H2PtCl6, Carsted catalyst, metallic and
bimetallic Pt—Pt and Pt/Pd colloids in a polystyrene—
4-vinylpyridine block copolymer micelle) on the yield
and the composition of the cyclic products of homo-
hydrosilylation of methyl(phenyl)vinylsilanes (1d).
According to 1H and 13C NMR spectra, the type of the
catalyst does not influence significantly the quantitative
or qualitative composition of the resulting structural
and stereoisomers. Dilution of the reaction mixture
increases the yield of distillable products to 35—40%.
According to 1H NMR spectra, the products distilled
after the synthesis in a 1% hexane—toluene solution
contained up to 1.5% linear dimer 2d apart from iso-
mers 3d and 4d. The reaction in a 10% solution af-
curred up to 30% of a mixture of disilacyclanes 3d and
4d without linear isomer 2d. Analysis of the 1H NMR
spectra of this mixture shows that the δ 0.16—0.37
region has five signals due to the methyl groups at the
silicon atoms; of these signals, three low-field signals
correspond to the five-membered disilacyclane 4d. This
assignment was based on the integrals of the three
doublets due to the protons of the methyl group at-
tached to the CH group, occurring at 0.811—0.831,
1.007—1.026, and 1.190—1.209 ppm. Two high-field
signals corresponding to the protons of the Me groups
at the silicon atoms belong apparently to two stereo-
isomers, cis- and trans-1,4-dimethyl-1,4-diphenyl-
1,4-disilacyclohexane (3d).

After some period at room temperature, crystals
(10—12%) precipitate from a mixture of disilacyclanes
3d and 4d. According to GLC data, this substance
becomes chromatographically pure after recrystalliza-
tion. Single crystals grown from a solution proved to be
systematic twins, which precluded their complete X-ray
diffraction study. The differential scanning calorimetry
(DSC) curves of the crystal of 3d exhibit one peak,
matched by the melting point at 93 °C.

Since the X-ray diffraction study did not allow us to
find out which of the spatial isomers had been isolated
as crystals, we attempted to elucidate their structure
more precisely using a semiempirical method based on
the use of increments for some organocycloctetrasiloxanes
found by 1H NMR spectroscopy.13 The 1H NMR spec-
trum of a mixture of disilacyclanes 3d and 4d recorded
in a CC14—C6D6 mixture, in addition to complex mul-
tiplets at δ 7.1—7.5 and 0.8—1.3 due to the protons of
the phenyl and methylene groups, exhibits two singlets
at δ 0.223 and 0.178 with a ratio of integral intensities of
1.0 : 0.3, corresponding to the protons of the methylsilyl
groups of the cis- and trans-isomers of 3d. The crystal-
line product isolated from the mixture exhibits a high-
field 1H NMR signal at δ 0.178 due to the methylsilyl
groups. Data on the increments for a phenyl group and a
hydrogen atom can be found in the literature but no
data for methyl groups have been reported. However, in
view of the fact that the protons of two methyl groups at
one silicon atom in the two stereoisomers of planar
organocycloctetrasiloxanes are indistinguishable and are
identical for cis- and trans-isomers, it can be assumed
with a high degree of certainty that the effects of the
methyl group and the hydrogen atoms attached directly
to silicon on the chemical shifts of the protons of the
Me groups attached to the neighboring silicon atom are
nearly identical. In this case, an estimate of chemical
shifts by the increment scheme13 shows that the signal
of the methyl group in the trans-isomer should be
shifted upfield from the corresponding signal of the cis-
isomer by 0.043 ppm. Based on this fact, we believe
that the crystalline product that we isolated is the trans-
isomer of 3d.