Five- and six-membered silicon–carbon heterocycles. Part 2. Synthetic modifications and applications of silacycles

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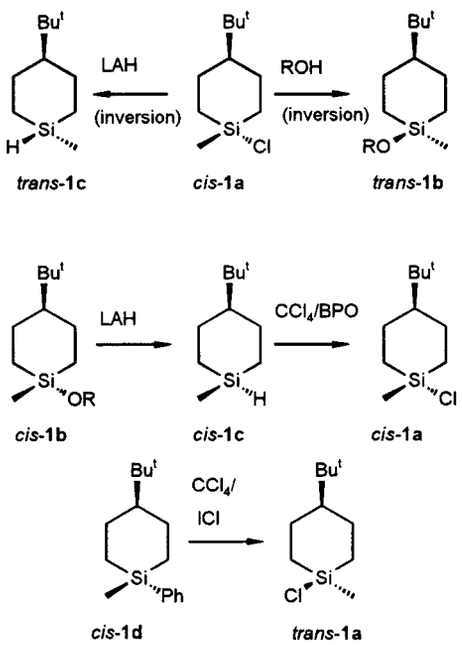
1 Reactions at the silicon atom

1.1 Nucleophilic substitutions

Silaheterocycles, as silicon compounds in general, offer many possibilities for substitution reactions at the silicon center. Early investigations in this field address the problem of stereochemistry in these types of transformation. Thus, conformationally stable silacyclohexanes have been used as model compounds by Sakurai and Murakami to gain insight into stereoselectivity of substitution reactions at the silicon center.[1] Chlorosilacyclohexane **1a** reacts with nucleophiles with inversion of configuration (Scheme 1, formation of *trans*-**1c** and *trans*-**1b**), whereas alkoxysilacyclohexane *cis*-**1b** reacts with LAH with retention to give *cis*-**1c**. The latter finding may be interpreted by coordination of the oxygen to the aluminium leading to a front-side attack. Stereoselective substitution of hydrogen by chlorine is possible *via* a radical mechanism.[2] Thus, *cis*-**1c** can be transformed to *cis*-**1a** with retention of configuration. Recently, attempts have been made to use this type of radical substitution to bring about kinetic resolution of *trans*-2,5-dimethyl-1-phenylsilacyclopentane using a chiral thiol catalyst.[3]

The 4-*tert*-butylsilacyclohexane model system has also proved useful for an investigation into the stereochemistry of halodesilylation.[4] Here a silicon-bound phenyl group is stereoselectively substituted by a halogen with inversion (Scheme 1, formation of *trans*-**1a** from *cis*-**1d**).

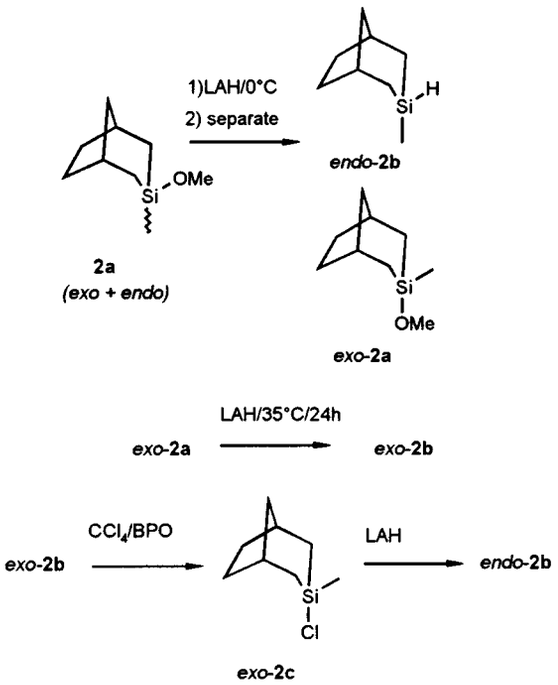


Scheme 1

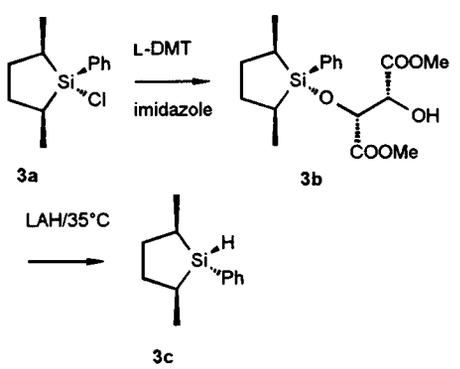
Similar stereochemical observations for nucleophilic substitutions were made by Cremer and Blankenship.[5] They found that reduction of the methoxy substituted bicyclic silanes *exo*- and *endo*-**2a** with LAH occurs stereoselectively with retention of configuration. Furthermore a significant difference in reactivity allows kinetic resolution of the diastereoisomers (Scheme 2): *endo*-**2a** is reduced with LAH at 0 °C with retention within a few hours, whereas the *exo*-isomer requires higher reaction temperatures. A sequence for the inversion of configuration at a silicon center is presented in Scheme 2 for the transformation of *exo*-**2b** to *endo*-**2b** *via* the intermediate chlorosilane *exo*-**2c**.

Different results concerning the stereochemistry of nucleophilic substitution reactions at silicon atoms in silacyclopentanes have been obtained more recently by Roberts *et al.* In the course of their studies of optical resolution and absolute stereochemistry of silacyclopentanes, the authors investigated the stereochemistry of several substitution reactions at silicon. For example, chlorosilacyclopentane **3a** reacts with dimethyl L-tartrate (L-DMT) in the presence of imidazole with apparent retention of configuration to give **3b**, which was reduced with LAH predominantly with inversion to give **3c** (Scheme 3). Similar observations were made for the C_2-symmetric (and hence chiral) *trans*-isomers, which allows the preparation of optically pure C_2-symmetric silacyclopentanes.[6]

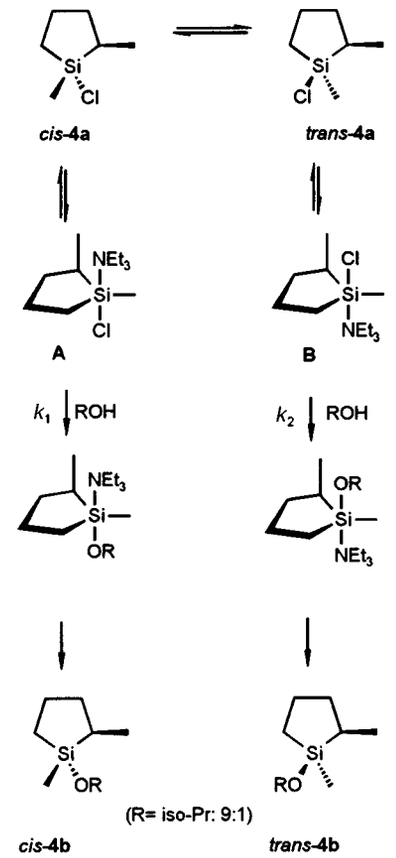
From these results it can be concluded that the stereochemical outcome of substitution reactions is not easy to predict. Dubac and Cartledge addressed this problem twenty years ago when they studied the stereoselectivity of a variety of



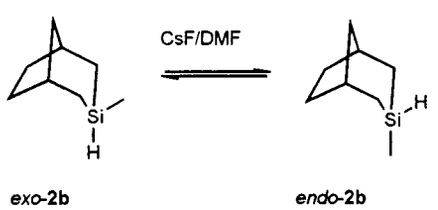
Scheme 2



Scheme 3



Scheme 4



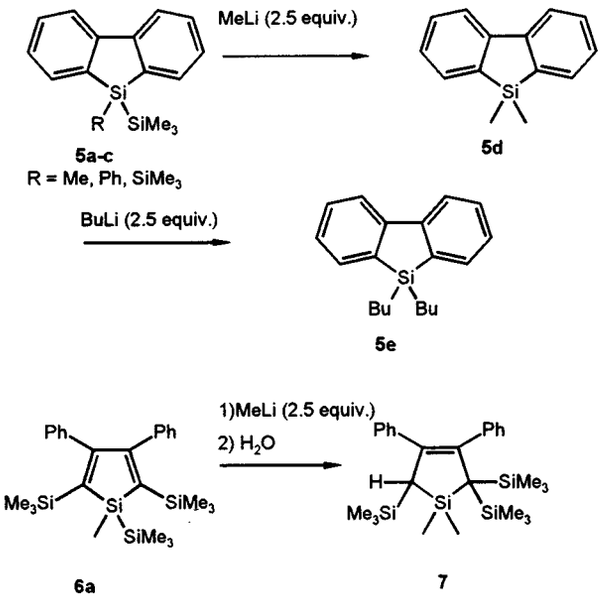
Scheme 5

substitution reactions in 1,2-dimethylsilacyclopentanes.[7] The authors postulate a pentacoordinate intermediate for substitution reactions which is in agreement with their observation that 'with silanes there is frequently a substantial energetic bias toward inversion, so that the inversion pathway will be followed unless there is some very compelling reason for front-side attack'. Pentacoordination at silicon and subsequent pseudorotation is a possible explanation for the different stereochemical outcome of the alcoholysis of chlorosilanes in the presence of an amine (see above). This reaction has been investigated by Dubac and Cartledge for the 1,2-dimethylsilacyclopentane model system.[8] Starting from a 1:1 mixture of chlorosilacyclopentanes *cis*- and *trans*-**4a**, a 9:1 mixture of alkoxysilanes *cis*- and *trans*-**4b** was obtained after reaction with triethylamine and propan-2-ol. For sterically less demanding alcohols diastereoselectivity was lower. These findings can be explained by the assumption of pentacoordinate intermediates **A** and **B**, which may interconvert by pseudorotation (Scheme 4).

Equilibration of different isomers of organosilanes in the presence of fluoride ions also seems to proceed *via* pseudorotation of pentacoordinate intermediates. Blankenship and Cremer were able to demonstrate that both isomers of **2b** equilibrate in the presence of CsF in DMF to yield a 70:30 mixture of *exo*- and *endo*-**2b** (Scheme 5).[9]

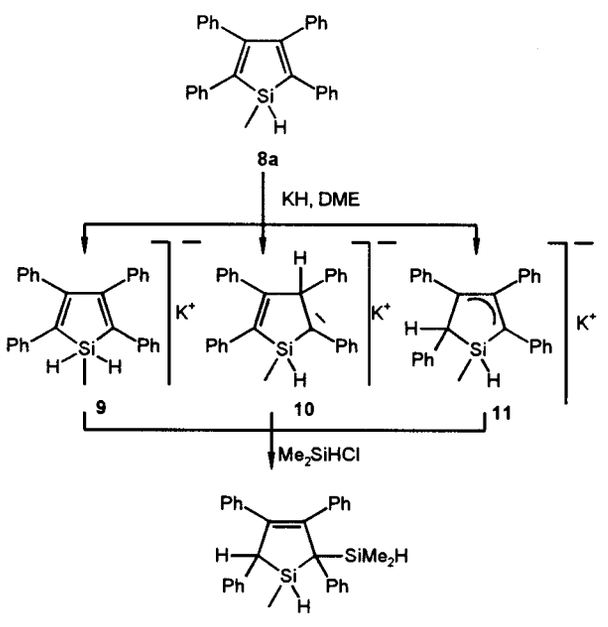
Ab initio calculations as well as spectroscopic observations at low temperature indicate that pentacoordinate silacyclopentanes undergo pseudorotation much faster than pentacoordinate silacyclopentadienes (siloles).[10] Consequently, in order to gain insight into the nature of pentacoordinate intermediates of silicon, siloles and their benzoannellated analogs have been studied in far more detail than other organosilanes. Thus, Klumpp *et al.* were able to detect pentaorganosilicates resulting from the reaction of MeLi with siloles, benzosiloles and dibenzosiloles at low temperatures by means of NMR spectroscopy. Addition of HMPA strongly stabilizes the pentaorganosilicates.[11] From NMR spectroscopic measurements the activation parameters for the pseudorotation process have been determined for one example by the same authors.[12] Pentaorganosilicates were earlier postulated as intermediates in substitution reactions by Ishikawa *et al.* who showed that dibenzosiloles **5a**–**c**, upon treatment with excess MeLi, undergo substitution of the substituents attached to the silicon to give **5d**. The methyl groups in **5d** can be replaced by butyl groups with excess BuLi. Different results were obtained by the same authors when silole **6a** was treated with MeLi under the same conditions as described above for dibenzosiloles **5**. Here migration of a TMS group from the silicon to an adjacent carbon was observed, leading (after hydrolysis) to a silacyclopentene **7**. In both cases pentacoordinated species are assumed to be formed initially (Scheme 6).[13]

Similar observations were made more recently for 1-methyl-2,3,4,5-tetraphenylsilole (**8a**). Upon treatment with potassium



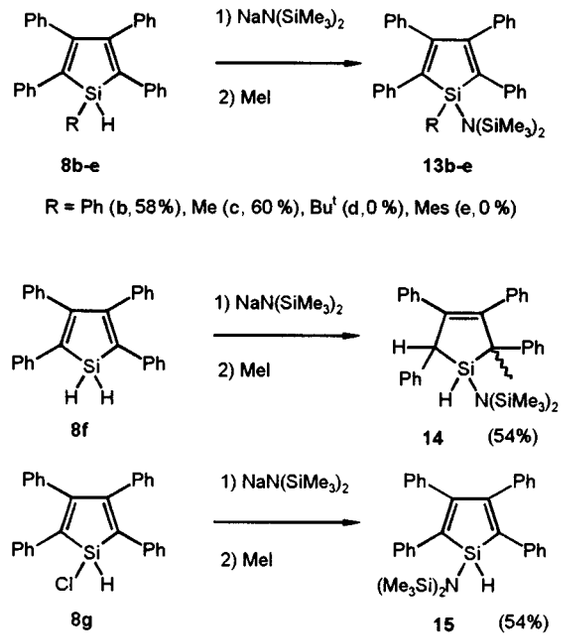
Scheme 6

hydride, a dark purple solution was produced from which the silacyclopentene **12** was isolated in good yield after quenching the mixture with chlorodimethylsilane. By means of ^{1}H, ^{13}C and ^{29}Si-NMR spectroscopy of the dark purple solution the authors were able to identify three different intermediates **9**, **10** and **11** (Scheme 7).[14]



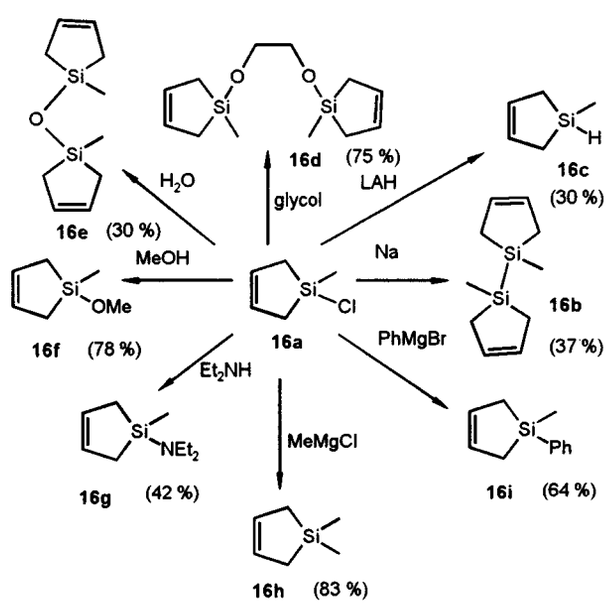
Scheme 7

The same authors investigated the reaction of a variety of 1-hydrosiloles **8** with sodium bis(trimethylsilyl)amide, a base which is not a strong nucleophile. Surprisingly, no products resulting from deprotonation were observed. Instead, depending on the substitution pattern of the initial silole **8**, substitution at the silicon center (products **13** and **15**) or migration of a hydride from the silicon to an adjacent carbon atom was observed (**14**). The experimental findings are consistent with a mechanism that involves nucleophilic attack of the amide at the silicon center to give a bipyramidal pentacoordinated intermediate, which may then undergo hydride migration (leading to silacyclopentene **14** after quenching with MeI) or pseudorotation (bringing the leaving group into a favored apical position). Extrusion of the leaving group leads to the formation of siloles **13** and **15**. The assumption of a pseudorotation prior to extrusion of the leaving group explains the complete failure of the substitution reaction when sterically demanding substituents are attached to the silicon (siloles **8d** and **8e**) (Scheme 8).[15]



Scheme 8

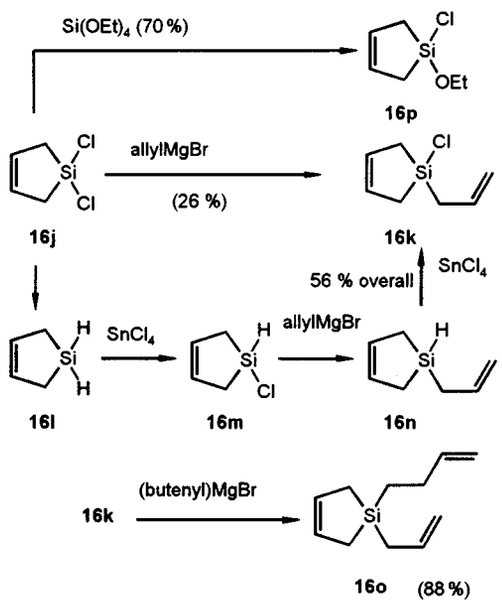
After these mechanistic considerations we now wish to summarize preparatively useful substitution reactions. Probably the most useful type of compounds for this purpose are 1-chlorosilacycloalkanes. Thus, 1-chlorosilacyclopentene **16a** reacts with a variety of nucleophiles to give 1-functionalized silacyclopentenes **16b–i** in good to moderate yield. Compound **16b** is formed by a reductive coupling with elemental sodium (Scheme 9).[16] However, for the preparation of 1-hydrosilacyclopentenes such as **16c**, reduction of the 1-alkoxysilacyclopentenes with LAH normally gives better yields than the corresponding chloro derivatives.[17]



Scheme 9

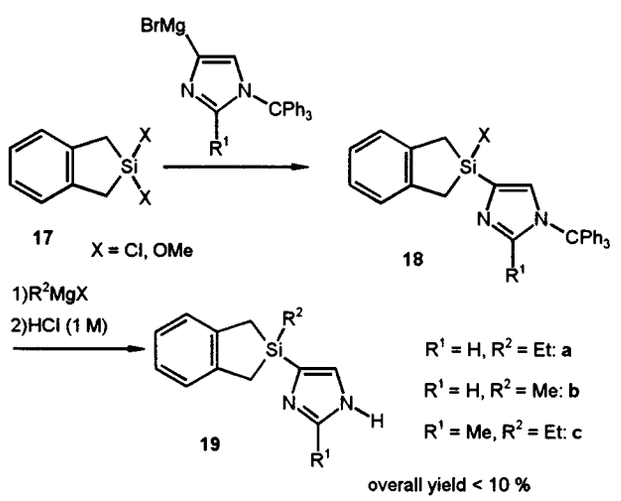
The preparation of unsymmetrically substituted silacyclopentenes from 1,1-dichlorosilacyclopentenes has been investi-

gated by Ushakov and Pritula. Treatment of dichlorosilacyclopentene **16j** with allylmagnesium bromide gives the unsymmetrically substituted silacyclopentene **16k** in 26% yield along with a considerable amount of diallylation product. Better yields are obtained by a four-step procedure, which involves double reduction of **16j** with LAH to give **16l**, selective exchange of one hydrogen by chlorine using $SnCl_4$ (**16m**), allylation (**16n**), and again $SnCl_4$-mediated exchange of hydrogen by chlorine (**16k**). Using the latter procedure, **16k** is formed in 56% overall yield. Addition of butenylmagnesium bromide to **16k** gives **16o**, which may be used as a starting material in metathesis reactions. The four-step procedure may turn out to be advantageous whenever double alkylation at the silicon is a problem.[18] Selective substitution of one chlorine in **16j** by an ethoxy group was achieved by Chernyshev using tetraethoxysilane (**16p**) (Scheme 10).[19]



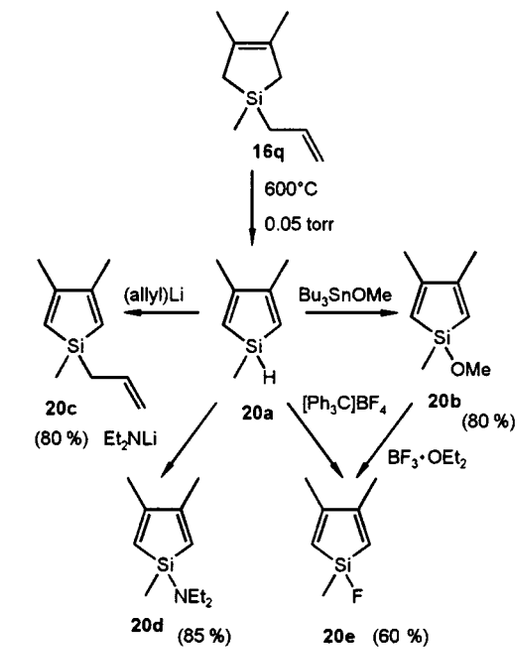
Scheme 10

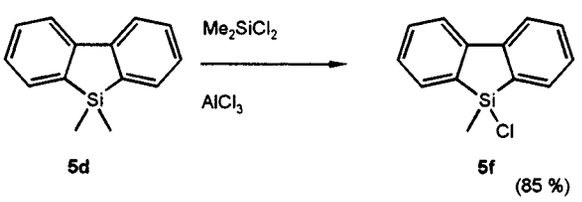
The synthesis of unsymmetrically substituted silaindanes **19** bearing an imidazole substituent at the silicon atom has been achieved by subsequent treatment of 1,1-dichloro- or 1,1-dimethoxy-silaindane **17** with two different Grignard reagents, albeit in very low yield. Silaindanes **19a–c** are sila analogs of the drug atipemazole, an α_2-adrenergic receptor antagonist. Pharmacokinetic properties of compound **19a** are very similar to those of the commercially available drug (Scheme 11).[20]



Scheme 11

While for saturated silacycloalkanes and silacycloalkenes, 1-chloro and 1-alkoxy derivatives are the starting materials of choice for substitution reactions at the silicon atom, appropriately functionalized siloles are not that easily accessible.[21] However, 1-hydrosiloles, which have been prepared by flash vacuum pyrolysis of 1-allylsilacyclopentenes such as **16q**,[17,22,23] may serve as starting materials for nucleophilic substitution reactions (see also Scheme 8).[24] Thus, substitution of hydrogen in silole **20a** leads to a variety of other functionalized siloles **20b–e** in preparatively useful yields and quantities. The formation of **20b** and **20e** seems to be favored by the presence of Lewis acids. The selective Lewis-acid supported substitution of one methyl group in dibenzosilole **5d** has also been described (Scheme 12).[25]





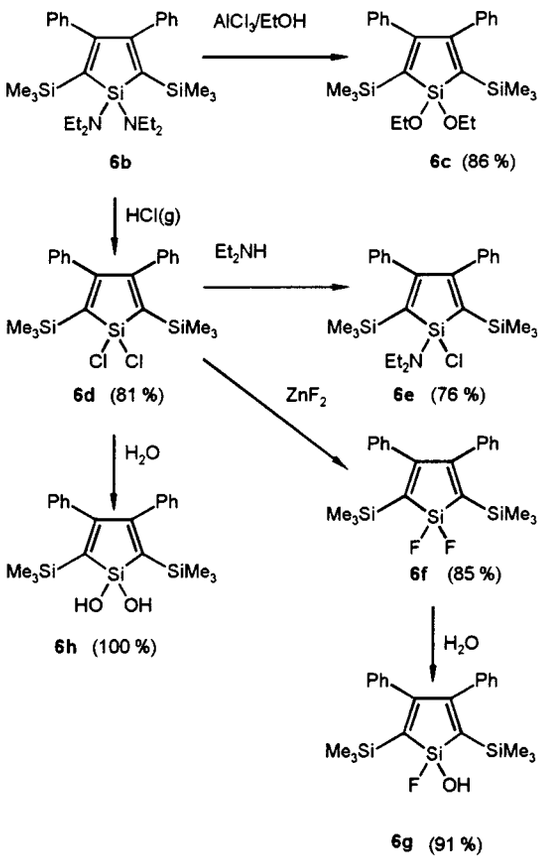
Scheme 12

Recent work by Tamao *et al.* opens up an efficient path towards a variety of functionalized siloles starting from the bis(diethylamino) substituted derivative **6b**, which are directly accessible from acyclic precursors.[26] Scheme 13 summarizes synthetically useful transformations of **6b**.

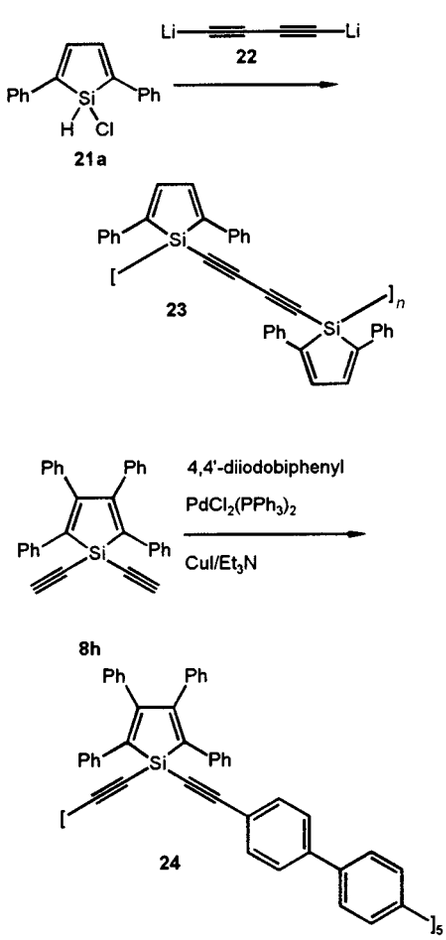
Double functionalization of siloles at the silicon atom provides a route towards polymers with a mixed acetylene–silole backbone. For example, reaction of dilithiobutadiyne **22** with silole **21a** results in the formation of a dodecamer **23**.[27] Related oligomers **24** have been prepared using palladium catalyzed cross coupling reactions of silole **8h** and dihalogenated aromatic compounds.[28] These investigations have been motivated by the search for new electrically conducting polymers (Scheme 14). Indeed, **23** and **24** show electrical conductivity when they are doped with iron chloride.[29]

1.2 Aromaticity of silole anions and their reactions with electrophiles

1,1-Dichlorosilole **8i** undergoes reduction with elemental sodium to give a disodio compound **25**, which is amenable to

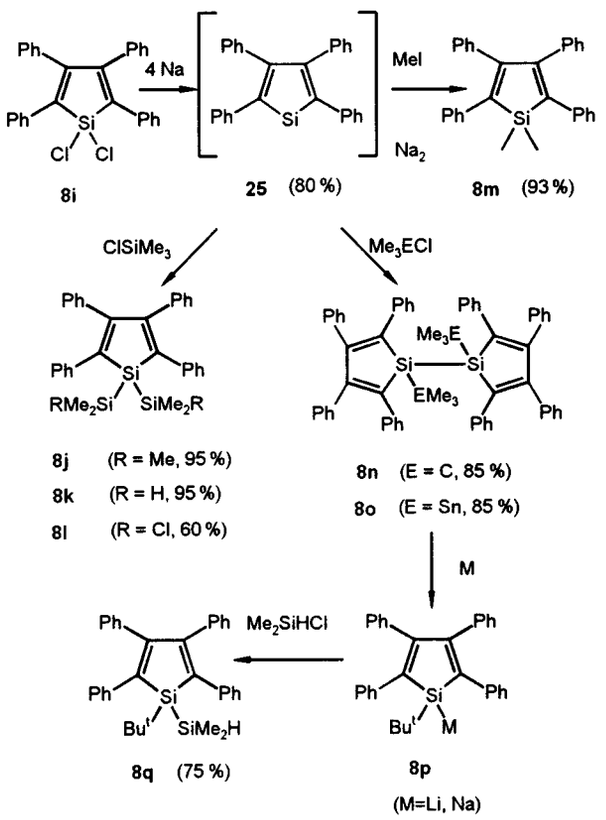


Scheme 13



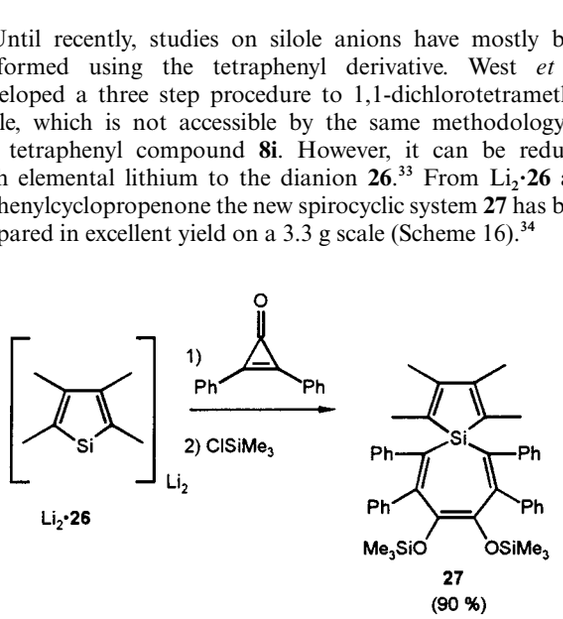
Scheme 14

subsequent synthetic modifications. For example, treatment with MeI or various chlorosilanes gives **8j**–**m** in excellent yields. Treatment of **25** with *tert*-butyl chloride or Me_3SnCl does not give the expected substitution products, instead dimeric species **8n**,**o** are formed (Scheme 15).[30] **8n** is a valuable starting material for monometallated species Li·**8p** and Na·**8p**, respectively. By quenching with a chlorosilane, silole **8q** with two different substituents at the silicon has been prepared.[31] A recent study by Wakahara and Ando provides some insight into the mechanism of the formation of silole mono- and di-anions. From trapping experiments at low temperatures it was concluded that in a first step the conjugated diene system is reduced to a butadiene dianion, which then undergoes subsequent elimination of the substituents at silicon.[32]



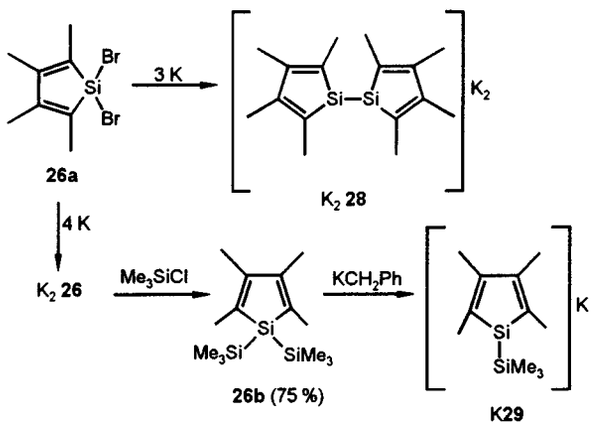
Scheme 15

Until recently, studies on silole anions have mostly been performed using the tetraphenyl derivative. West *et al.* developed a three step procedure to 1,1-dichlorotetramethylsilole, which is not accessible by the same methodology as the tetraphenyl compound **8i**. However, it can be reduced with elemental lithium to the dianion **26**.[33] From Li_2·**26** and diphenylcyclopropenone the new spirocyclic system **27** has been prepared in excellent yield on a 3.3 g scale (Scheme 16).[34]



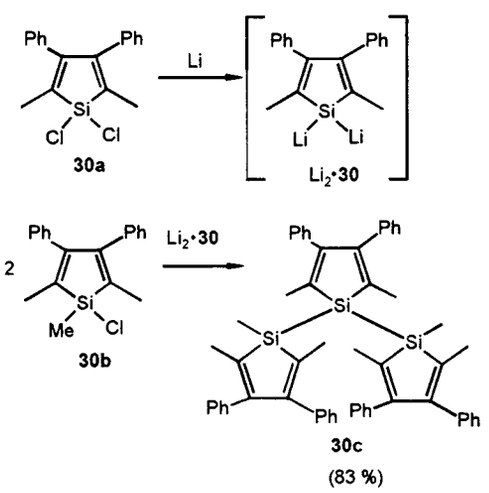
Scheme 16

1,1-Dibromotetramethylsilole **26a** can be used as an alternative precursor for silole anions and silole dianions.[35,36] Compound **26a** undergoes reduction to anionic species in the presence of elemental potassium. The course of the reaction depends on the amount of potassium employed, as outlined in Scheme 17. Selective desilylation of **26b** with benzylpotassium is an alternative path to monoanions.



Scheme 17

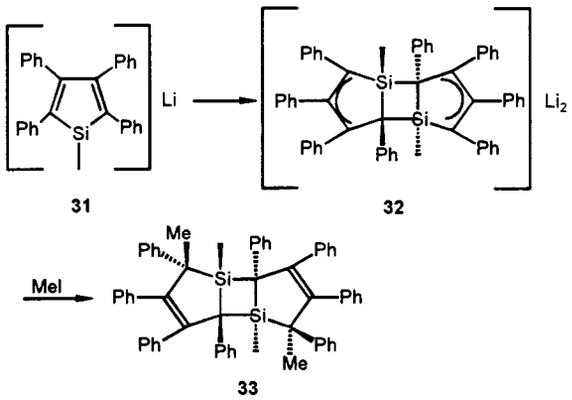
Silole dianions are useful starting compounds for the preparation of oligomers with an all-silicon backbone. Recently, Tamao *et al.* reported the formation of trimer **30c** in good yield starting from the dilithio compound Li_2·**30** and **30b** (Scheme 18). An analogous tetramer has also been obtained, albeit in somewhat lower yield.[37] Polysiloles with a silicon backbone are expected to have unique spectroscopic and optoelectronic properties resulting from σ*–π* interaction between the σ* orbitals of the polysilane chain and the π* orbitals of the butadiene moiety. Therefore, oligosiloles have been thoroughly characterized by UV–VIS spectra, indicating a correlation between chain length and absorption maximum.[38]



Scheme 18

On the basis of ^{13}C- and ^{29}Si-NMR spectra, delocalized structures have been proposed for anions of siloles,[39] but not for anions of dibenzosiloles.[40] In the latter case, negative charge seems to be located on the silicon. Delocalization of negative charge through the butadiene moiety in tetraphenylsilole anion **31** is nicely illustrated by its dimerization to the dianion **32**, which, upon treatment with MeI, stereoselectively reacts to give **33** (Scheme 19).[41]

The question whether silole anions are aromatic or not has caused many structural,[35,42] spectroscopical[43] and theoretical[44,45] investigations.[46] From the results it was concluded that silole



Scheme 19

*di*anions show a high degree of aromaticity, whereas the silole *mono*anions do not. The reason for this is a pyramidal structure around the silicon atom observed for the latter species, which results in poor conjugation.[36,47]

1.3 Silaheterocycles as auxiliaries

Silacycles have been used to modify structure and reactivity of organic and organometallic compounds. Some examples for compounds in which structures are determined by the silacyclic unit are given in Fig. 1. In all cases, the silacycle has been used to obtain rigid systems which were required for the fine tuning of certain properties. For example cyclopentadienes **34**[48] and **35**[49,50] form rigid zirconium complexes which have been tested for the Ziegler–Natta polymerization of olefins. The degree of rigidity in the ligand sphere of the catalysts exerts an influence on the structure and hence on the macroscopic properties of the resulting polyolefins. Polythiophenes are of interest for molecular electronic devices because of their electrochemical properties. In compound **36** a silaspirocyclic center has been used to force both oligomeric chains into an orthogonal arrangement, which is necessary to avoid electronic interactions between the two chains.[51] Compound **37** has been used to mimic copper–bipyridyl complexes in order to gain some insight into their binding to catalytic antibodies.[52] Silacycloalkanes attached to pharmacologically active compounds can be expected to alter geometry and shape of the molecules, and hence the pharmacological properties. Steroids with silicon containing side chains as potential antifertility agents[53] and platinum compounds with silylamine ligands[54] are examples where silicon–carbon heterocycles have been investigated.

Silicon–carbon heterocycles have been used as auxiliaries for hydrosilation and silicon mediated aldol reactions. Unlike ketone substrates, hydrosilation of olefins is normally not a facile process. The reaction may suffer from low rates, sometimes low regioselectivities and double bond migrations. In the case of prochiral olefins, enantioselectivity of the hydrosilation becomes an additional problem, and—if this can be overcome—problems may arise from selective carbon–silicon bond cleavage to transform the initial hydrosilation products into useful organic compounds without racemization. Some of the problems mentioned above can be overcome by conducting the hydrosilation as an intramolecular process starting from an allyl alcohol attached to a dialkyl- or diarylhydrosilane. Bosnich *et al.* used this approach to investigate the possibilities of asymmetric catalysis for hydrosilation of olefins. From the results summarized in Scheme 20 it becomes clear that the substitution pattern at the silicon exerts a significant influence on the yield and on the enantioselectivity. For **39a–c** best results are observed when the silicon is part of a five- or six-membered ring. In the case of dimethylsilyl derivative **39a** the reaction does not give any cyclized product. For related cyclizations using a diphenylsilyl moiety, the conversion was

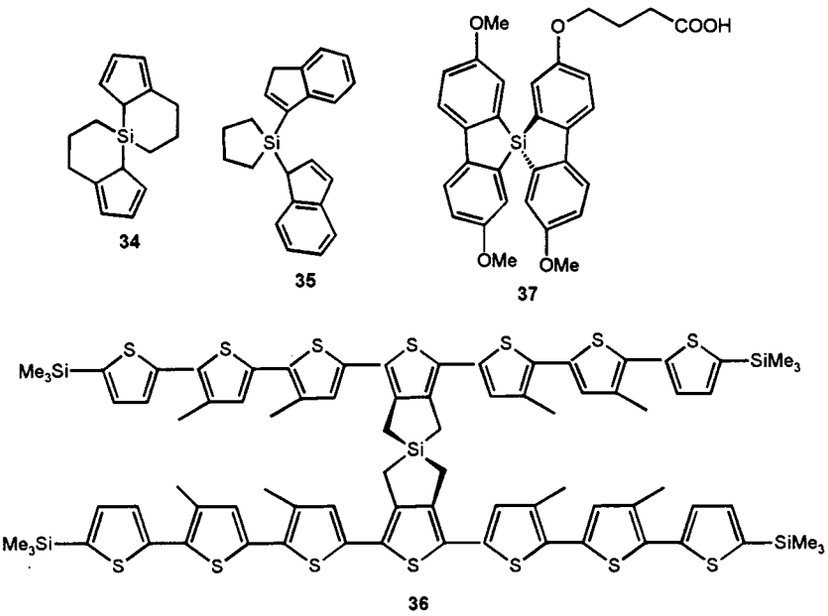
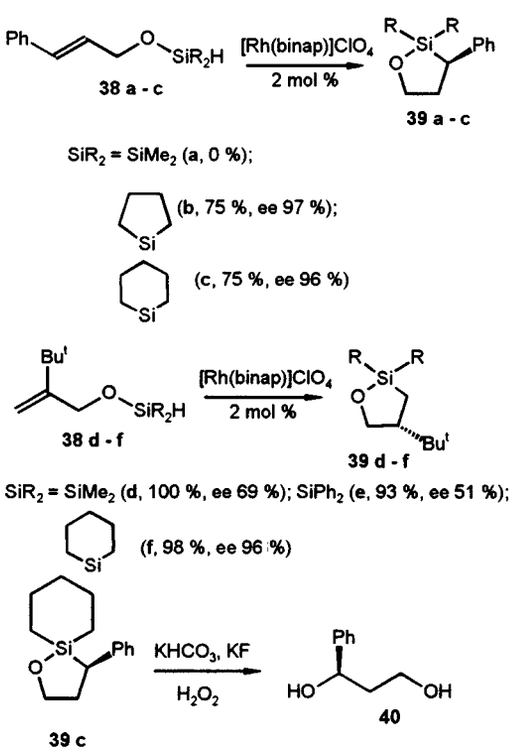


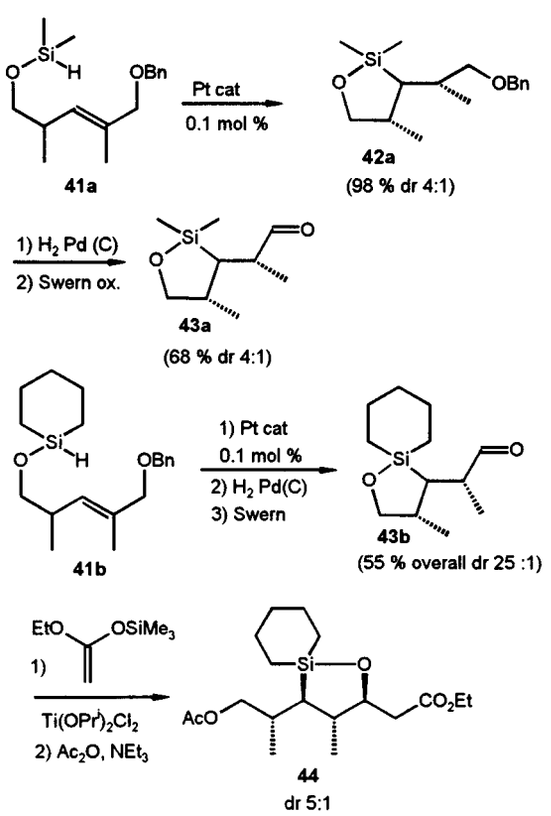
Fig. 1

satisfactory but enantioselectivity was low. Silacyclic auxiliaries do not solve all problems in hydrosilation reactions. Apart from the substitution pattern at the silicon atom, the substituents at the allyl moiety and the chiral ligand influence yield and ee. For example, substrates with terminal substituents are only cyclized in good yield and enantioselectivity when silacycloalkyl auxiliaries are used, when the terminal substituent is an aryl group and when the chiral ligand is binap.[55,56] The conversions of **38d–f** exemplify that intramolecular hydrosilation is also possible with bulky substituents at the internal olefin carbon. For this example good enantioselectivity is only observed for substrate **38f** bearing a silacyclohexyl substituent. In contrast, dimethyl- and diphenyl-silyl groups (**38d**,**e**) give only moderate ee's.[57] Oxidative cleavage of the cyclic siloxanes **39** yields chiral butane-1,4-diols **40**, which is illustrated for one example. In section 4.2 this transformation will be discussed in more detail.[58]



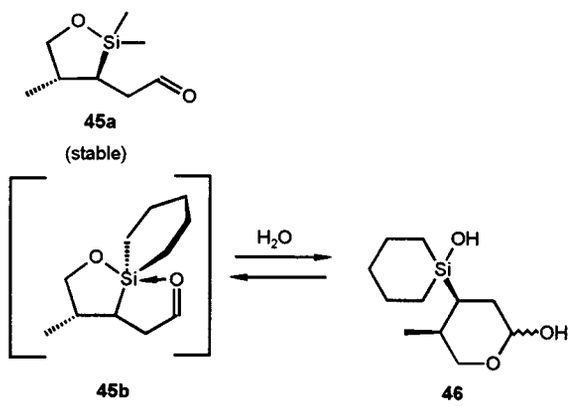
Scheme 20

Intramolecular hydrosilation of silicon tethered homoallylic alcohols bearing an additional substituent in the allylic position has been investigated, too. Here diastereoselectivity becomes a problem: **41a** has been converted to siloxane **42a** in excellent yield but moderate diastereoselectivity to afford, after deprotection and Swern oxidation, the aldehyde **43a**. Hoveyda *et al.* were able to show that diastereoselectivity improves significantly (from 4 : 1 for **41a** to 25 : 1 for **41b**) if the dimethylsilyl moiety is substituted by a silacyclohexyl moiety.[59] If **43b** is subsequently treated with a silyl ketene acetal an aldol reaction occurs, followed by a rearrangement of the silacyclohexane moiety. Acetylation drives the rearrangement to completion giving the cyclic silyl ether **44** with high regioselectivity (Scheme 21).[60]



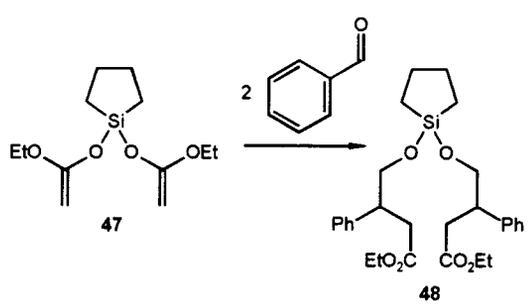
Scheme 21

Obviously the rearrangement leading to **44** is strongly facilitated by the tendency of the silicon atom to pentacoordination, which may also be regarded as Lewis-acidity. There is strong evidence that ring strain significantly enhances the Lewis-acidity (and hence the ability to form pentacoordinated intermediates). An instructive example is the following: aldehyde **45a** has been obtained by a sequence analogous to the one described above for **43a**. Attempted isolation of aldehyde **45b** using the same procedure failed, because this compound spontaneously adds one equivalent of water and rearranges to the hemiacetal **46** (Scheme 22).[59]



Scheme 22

The enhanced Lewis-acidity of silicon centers embedded in ring systems has practical consequences for silicon-directed aldol reactions. Here substrates with Lewis-basic sites (carbonyl compounds) are expected to coordinate to the silicon atom prior to C–C bond formation. As a consequence, enhanced reactivity, even in the absence of an external Lewis acid, is observed. For example, silacyclopentane substituted ketene acetal **47** reacts with benzaldehyde at ambient temperature to give the addition product **48** (Scheme 23).[61]



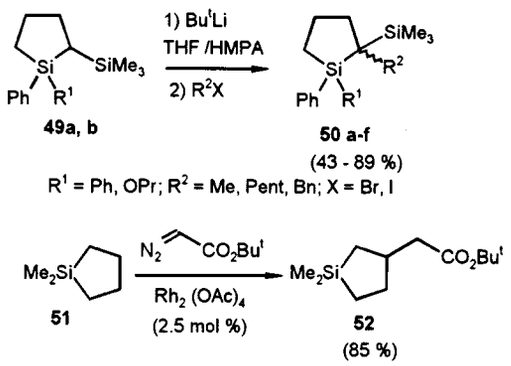
Scheme 23

Similar results have been obtained with *O*-silyl-*N*,*O*-ketene acetals, where a significant rate acceleration is observed for silacycloalkyl structures.[62] The effect becomes even more pronounced, when silacyclobutane ketene acetals are reacted with aldehydes. Furthermore, diastereoselectivity is usually high in these cases.[63] The chemistry of siloxycyclobutanes is beyond the scope of this review and will therefore not be discussed in detail. It should be mentioned that there is evidence for enhanced tendency towards pentacoordination for cyclic organosilanes from their ^{29}Si-NMR chemical shifts and from crystal structures of derivatives bearing an internal donor substituent.[64]

2 Reactions at the α-position

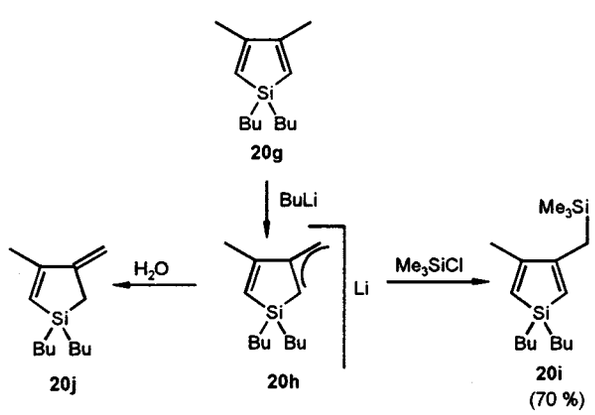
2.1 Addition of electrophiles to lithiated silacycles

The stabilization of carbanions by an adjacent silicon substituent has been exploited for a variety of synthetic methods. For example, metallation of silicon–carbon heterocycles and subsequent treatment with electrophiles has been used for the introduction of substituents in the α-position in some cases. Thus, regioselective lithiation of silacyclopentanes **49a**,**b** with an additional TMS-substituent in the 2-position and subsequent treatment with alkyl halides exclusively yields silacyclopentanes **50**. No stereoselectivity was observed for derivatives with two different substituents at the silicon (Scheme 24).[65] As C–C bond-forming reactions starting from saturated silacycles are rare, a recent report dealing with the rhodium-catalyzed insertion of diazoesters into C–H bonds of saturated silicon–carbon heterocycles (*e.g.* **51**) seems to be especially remarkable and should be mentioned here (Scheme 24).[66]



Scheme 24

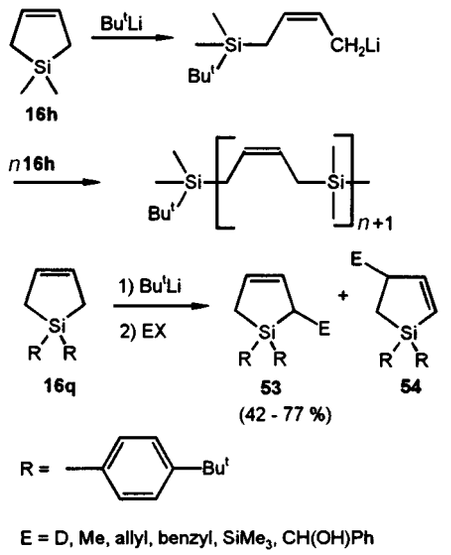
Other reports describe the lithiation of silacycloalkenes by deprotonation in an allylic or benzylic position. Obviously, these transformations differ significantly from the one described above, as the acidity is enhanced by the formation of delocalized carbanions. In cases where delocalized carbanions are formed, regioselectivity of the electrophilic attack may become a problem. This is clearly demonstrated by the metallation of **20g**. The silylallyl anion **20h** reacts with water by attack at the α-position (**20j**) and with chlorotrimethylsilane by attack at the γ-position (**20i**) (Scheme 25).[24]



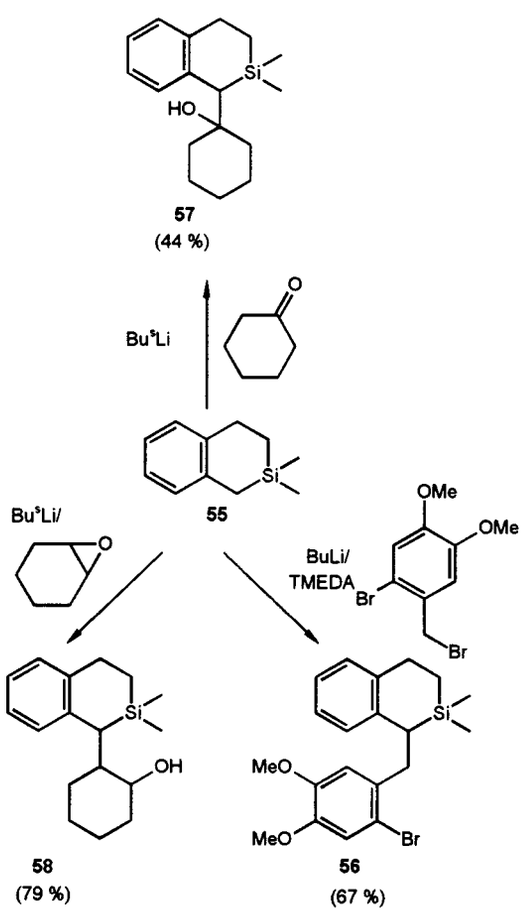
Scheme 25

Acyclic silylallyl anions are interesting building blocks for organic synthesis, as they react with electrophiles regio- and stereoselectively to (*E*)-vinylsilanes.[67] Consequently, there have been attempts to prepare and derivatize cyclic silylallyl anions. Horvath and Chan have intensively investigated the lithiation and subsequent functionalization of silacyclopentenes.[68] The success of the reaction critically depends on the substituents at silicon: 1,1-dimethylsilacyclopentene (**16h**) reacts with Bu′Li exclusively by attack at the silicon inducing a ring opening polymerization. This difficulty was circumvented by enhancing the electron density at the silicon atom. Thus, starting from a silacyclopentene **16q** with *p*-Bu′-phenyl substituents attached to the silicon, no polymerization was observed and the

silacyclopentene cleanly metallated at the allylic position. Regioselectivity depends very much on the type of electrophile employed. If EX = D_2O, only the isomer **53** was isolated. For MeBr or MeI **54** was isolated as the major product. All other electrophiles, including chlorosilanes, other alkylhalides or aldehydes, showed a slight preference of the γ-isomer **54** (Scheme 26).



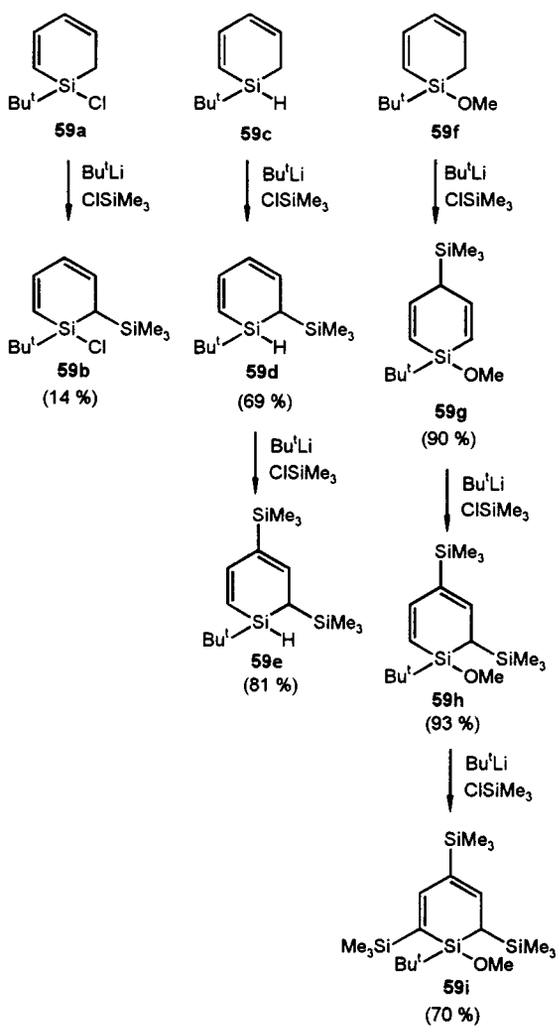
Scheme 26



Scheme 27

The strong preference for nucleophilic attack at the silicon observed for simple silacyclopentenes is probably caused to a certain extent by release of ring strain. In the case of six-membered rings, lithiation in the α-position seems to proceed without ring opening side reactions. This has, for example, been demonstrated by Hoshino *et al.* in their studies on the functionalization of silatetralins. Silatetralin **55**[69] can be deprotonated in the benzylic position using BuLi–TMEDA and subsequently functionalized with benzyl halides. The products **56** have been tested in intramolecular radical cyclizations directed towards the construction of polycyclic silicon-containing systems.[70] Metallated silatetralin **55** has also been reacted with cyclohexanone to give tertiary alcohol **57** and with cyclohexene oxide to give alcohol **58** (Scheme 27).[71]

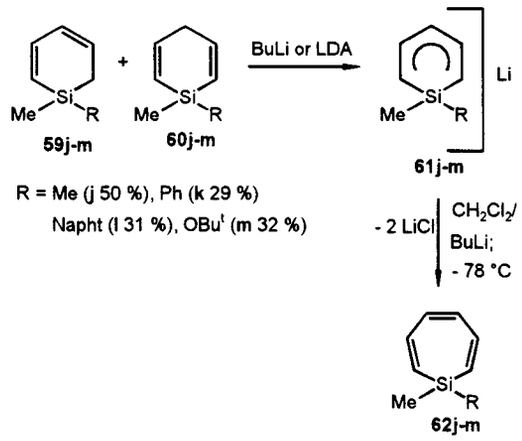
Other six-membered silacycles which have been reported to be easily functionalized by metallation and subsequent trapping reactions are silacyclohexadienes **59**. From a systematic study by Jutzi *et al.* it becomes clear that the reactivity in lithiation reactions depends on the substitution pattern at the silicon atom. Undesired side reactions can be suppressed by conducting the lithiation at low temperatures in THF using Bu′Li as a base.[72] Except for the chloro derivative **59a**, lithiation and silylation proceed with excellent yields and regioselectivities. A few points are worth mentioning here: a) obviously an alkoxy substituent at silicon increases the acidity of the allylic position, compared to a hydrogen; b) the substitution pattern at the silicon influences the regioselectivity of the electrophilic attack (compare **59d**, **59g**); c) the second silylation step is highly diastereoselective for the methoxy derivative **59h**, whereas **59e** is formed as a 1 : 1 mixture of diastereomers (Scheme 28).



Scheme 28

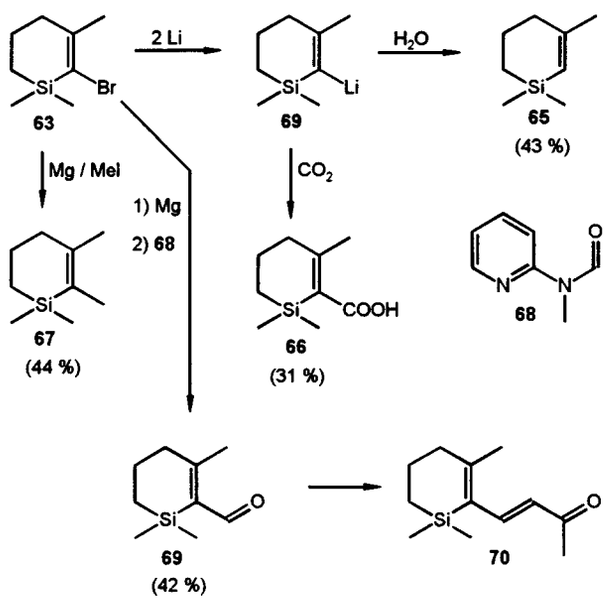
The lithiation of a mixture of silacyclohexadienes **59** and **60** with BuLi or LDA leads to silacyclohexadiene anions **61j–m**, which react with chlorocarbene, generated *in situ* from DCM, with ring enlargement to yield silepines **62j–m** in moderate yields (Scheme 29).[73]

α-Lithiated and α-magnesiated silacyclohex-2-enes are available from the 2-bromo derivative **63** by treatment with



Scheme 29

elemental lithium or magnesium.[74] The lithio and the magnesio compounds have been quenched with a variety of electrophiles: water (giving **65**), carbon dioxide (giving carboxylic acid **66**), methyl iodide (giving **67**) and *N*-formyl compound **68** (giving aldehyde **69**). The latter compound has been used as a starting material for a synthesis of β-silaionone **70** (Scheme 30). The olfactory properties of **70** and related silacyclic compounds have been evaluated and compared to those of the carbon analogs in order to gain insight into structure–odor relationships.[75]

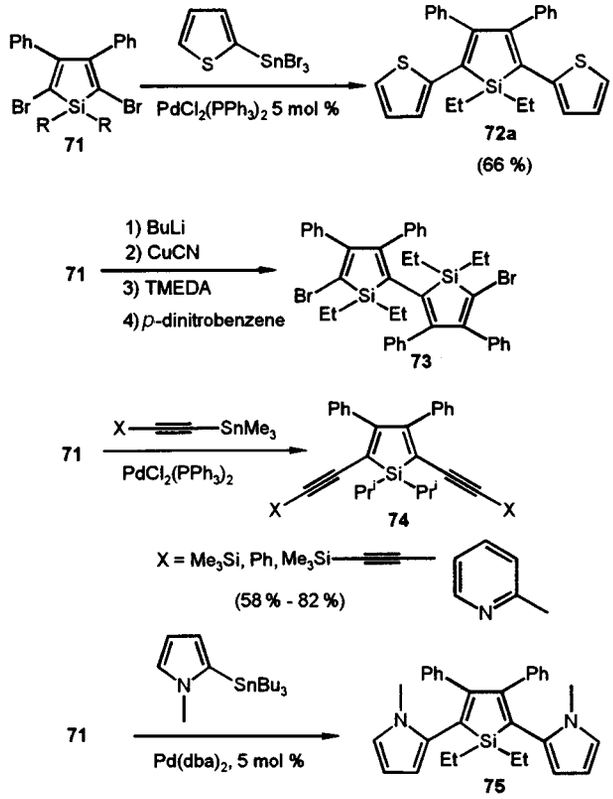


Scheme 30

2.2 Transition metal catalyzed C–C bond forming reactions

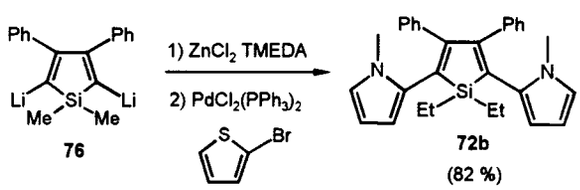
Over the past few years the increasing interest in siloles as building blocks for π-conjugated polymers has led to the development of a variety of synthetic methods for the functionalization of this particular ring system. Many of these transformations start from the dibromo derivative **71**. For example, Pd-catalyzed cross coupling reactions have been described with thienyl tin derivatives (**72**),[76] pyrrole tin derivatives (**75**)[77] and stannylated acetylenes (**74**).[78] The formation of **73** from **71** proceeds *via* Br–Li exchange,[79] transmetallation with CuCN and oxidative removal of the copper with dinitrobenzene as an oxidant, leading to a direct coupling of two silole units (Scheme 31).[76]

Alternatively, aryl substituents can be introduced into the 2-position of siloles starting from the dilithio compound **76**,



Scheme 31

followed by transmetallation with $ZnCl_2$ and palladium catalyzed cross coupling with aryl halides.[80] This sequence is outlined in Scheme 32, for example **72b**.



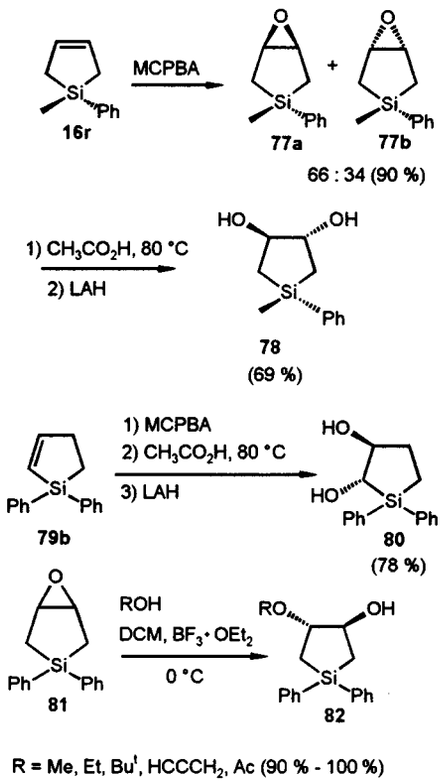
Scheme 32

3 Addition reactions to double bonds

3.1 Epoxidation of endocyclic double bonds and subsequent reactions

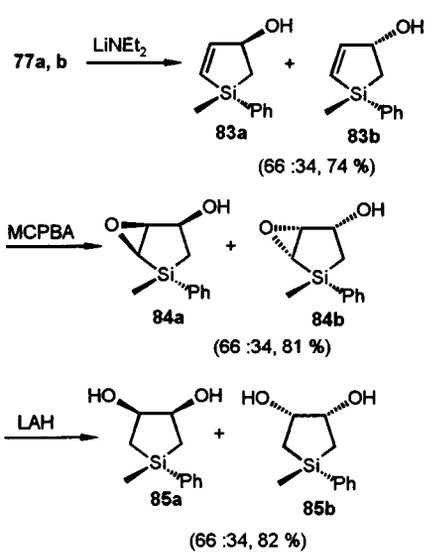
In silacycloalkenes the internal double bonds may be epoxidized under standard conditions (for example using MCPBA) in good yields, leaving the carbon–silicon bonds unaffected. Thus, dihydroxylated silacyclopentanes become accessible from silacyclopentenes in a few steps. If the unsymmetrically substituted silacyclopentene **16r** is treated with MCPBA, two diastereomeric epoxides **77a**,**b** are formed in a 2:1 ratio in excellent yield. Epoxide opening in refluxing acetic acid and subsequent reduction of the ester with LAH yields one diastereoisomer of *trans*-3,4-diol **78**. Similarly, epoxidation of vinylsilane **79b** followed by ring opening with acetic acid and reduction of the intermediate ester with LAH gives *trans*-2,3-diol **80**.[81] *trans*-Selective epoxide opening occurs under milder conditions in the presence of a catalytic amount of $BF_3{\cdot}OEt_2$. This has been demonstrated for epoxide **81** and a variety of nucleophiles leading to products **82** in excellent yields (Scheme 33).[82]

Treatment of **77a**,**b** with $LiNEt_2$ induces a rearrangement to the allylic alcohols **83a**,**b**, with the ratio of diastereomers being the same as in the starting material. Alkyllithiums are too nucleophilic for this purpose; they add to the silicon atom



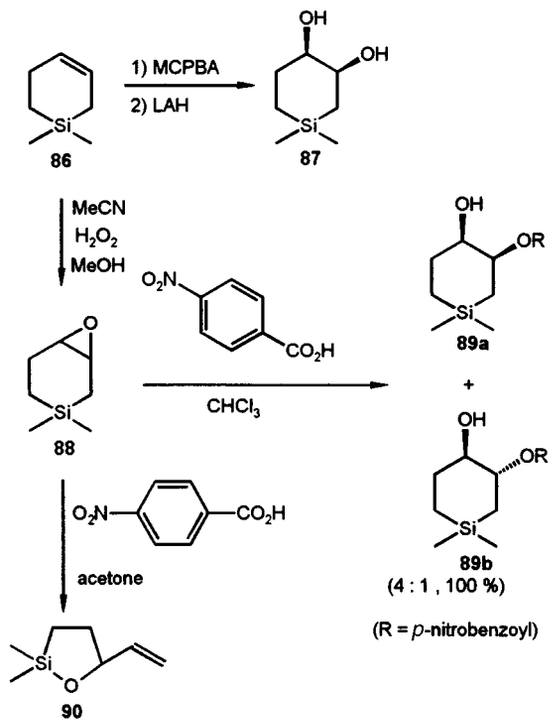
Scheme 33

and induce a ring opening leading to acyclic allyl alcohols.[83] Epoxidation of **83a**,**b** proceeds in good yield and high diastereoselectivity leading to the epoxides **84a**,**b** with hydroxy group and ring oxygen on the same side of the molecule. Reduction of **84a**,**b** with LAH occurs highly regioselectively and yields a mixture of the two *cis*-diols **85a**,**b** (Scheme 34).[81]



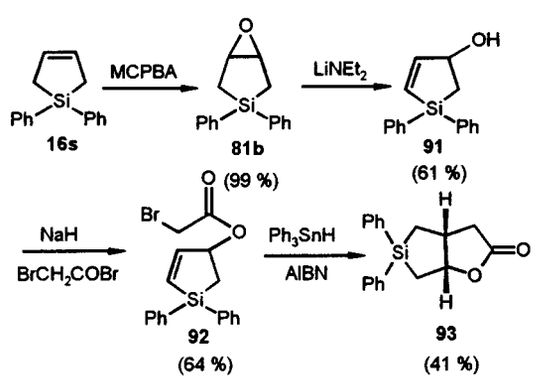
Scheme 34

Epoxidation and epoxide opening reactions have also been studied for silacyclohexenes, however with different results. When White *et al.* tried to epoxidize the silacyclohexene **86** with MCPBA under standard conditions, they obtained a complex mixture, from which—after reduction with LAH—they isolated the *cis*-diol **87** as the major component. The relative stereochemistry of **87** was verified by crystal structure analysis of its bis(*p*-nitrobenzoate).[84] The formation of a *cis*-diol by ring opening of an epoxide is somewhat surprising. In order to solve this problem, the ring opening of epoxide **88** was studied under controlled conditions. **88** has been synthesized in good yield using acetonitrile–hydrogen peroxide. Treatment with *p*-nitrobenzoic acid in chloroform gave a 4 : 1 mixture of the two diastereomers **89a**,**b**. Obviously, in the case of six-membered silacycles the β-effect of silicon directs the regio- and stereochemistry of epoxide opening reactions. The preferred formation of the *cis*-product may be explained by hydroxy group assisted attack of the carboxylic acid. Further evidence that in the case of six-membered silacycles a strong β-effect is working stems from a remarkable solvent effect: with coordinating solvents such as acetone, silicon–carbon bond cleavage occurs leading to a cyclic siloxane **90** (Scheme 35).[85]



Scheme 35

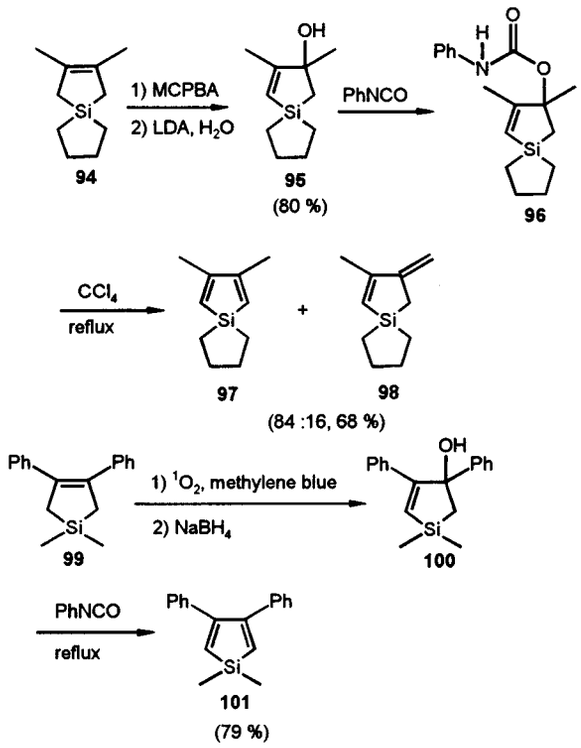
Apart from the synthesis of *cis*-diols, as outlined in Scheme 34, the base-induced rearrangement of silacyclopentene oxides opens up a pathway to bicyclic structures and to siloles. Thus, epoxide **81b**, which is prepared in nearly quantitative yield from silacyclopentene **16s**, undergoes base-induced rearrangement to give allyl alcohol **91**. Deprotonation and esterification lead to the 2-bromo ester **92**, which undergoes free radical induced cyclization to the *cis*-lactone **93** (Scheme 36).[86]



Scheme 36

Allyl alcohols of type **91** may also serve as precursors for siloles. For example, starting from spirocyclic silacyclopentene **94** the allyl alcohol **95** is prepared in two steps and good yield. Treatment of **95** with phenylisocyanate gives the urea intermediate **96**, which undergoes elimination upon heating.

Silole **97** is isolated along with byproduct **98**.[87] An alternative preparation of the allyl alcohol intermediates involves ene reaction of silacyclopentenes with photochemically generated singlet oxygen, followed by reduction with sodium borohydride. The preparation of silole **101** from silacyclopentene **99** along these lines is shown in Scheme 37.[88]

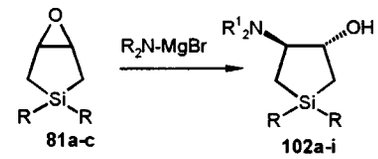


Scheme 37

The formation of β-amino alcohols from silacyclopentene oxides is not as straightforward as the formation of diols. Manuel *et al.* were able to demonstrate that treatment of epoxides with amines leaves the starting material unchanged, while treatment with lithium amides gives the base-induced rearrangement mentioned above. Bromomagnesium dialkylamides turned out to be the reagents of choice for the preparation of β-amino alcohols. Thus, epoxides **81a–c** underwent ring opening with a variety of weakly basic magnesium dialkylamides to give amino alcohols **102a–i** (Scheme 38, Table 1). Control of reaction temperature is crucial, as at elevated temperatures nucleophilic attack at the silicon atom may occur, leading to silicon–carbon bond cleavage and formation of acyclic siloxanes.[82]

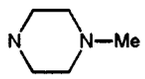
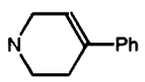
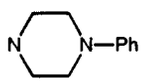
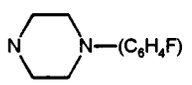
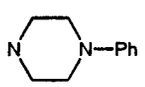
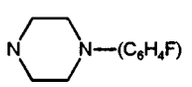
Introduction of an amino group is best achieved by Lewis acid catalyzed epoxide opening with trimethylsilyl azide (**103a**,**b** from **81a**,**b**)[82] or by epoxide opening with sodium azide and subsequent reduction (**102j** from **81b**). Compound **102j** serves as a valuable starting material for aziridine **104b** which is available by tritylation of the amino function and subsequent treatment with sulfuryl chloride. An oxysulfonamido species is proposed as an intermediate, from which **104b** is formed by extrusion of sulfur trioxide (Scheme 39).[89]

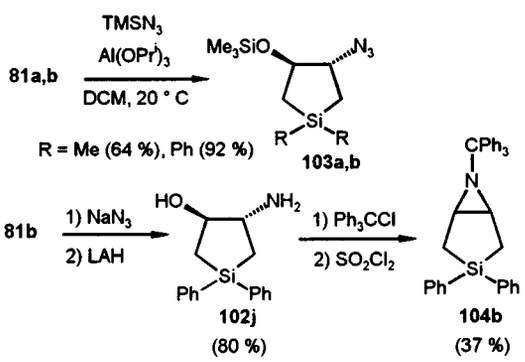
Vacuum pyrolysis of silacyclopentene oxide **105** has been used to generate monomeric silicon dioxide (**106**) for characterization by means of matrix IR spectroscopy (Scheme 40).[90,91]



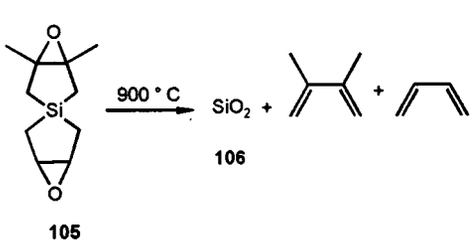
Scheme 38

Table 1 Amino alcohols from epoxides

	R	$R^1{}_2N$	No.	Yield
81a	Me	NMe_2	**71a**	72
	Me	NEt_2	**71b**	71
	Me	$NMeCH_2Ph$	**71c**	78
	Me		**71d**	24
81b	Ph		**71e**	56
	Ph		**71f**	71
	Ph		**71g**	69
81c	C_6H_4F		**71h**	56
	C_6H_4F		**71i**	67



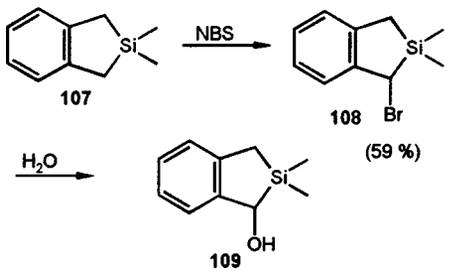
Scheme 39



Scheme 40

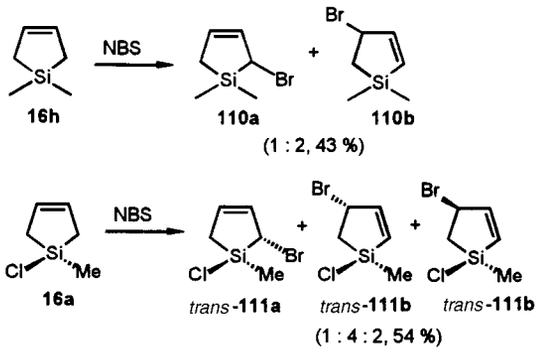
3.2 Other reactions of silacycloalkenes

Addition of halogens or halogen containing compounds and allylic halogenations represent an important class of reactions of silacycloalkenes. Radical-induced substitution of allylic hydrogen by bromine is possible using NBS under standard conditions. Silaindane **107** has been brominated in this way to provide **108** as a starting material for a kinetic study on the effect of silicon substituents on the rate of hydrolysis. In **108**, nucleophilic substitution of the bromine is 500 times slower compared to the carbon analog (Scheme 41).[92]



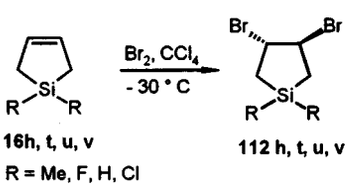
Scheme 41

If the bromination with NBS is performed for silacyclopentene **16h**, the 2-bromo **110a** and the 4-bromo regioisomer **110b** are formed in a 1 : 2 ratio. For the 1-chlorosilacyclopentene **16a** the 4-bromo isomer **111b** is preferred over the 2-isomer **111a**, which is probably due to repulsive interactions between chlorine in the 1- and bromine in the 2-position. This may also explain why **111a** is formed as a single *trans*-diastereoisomer, whereas **111b** is obtained as a 1 : 2 mixture of *cis* : *trans* isomers (Scheme 42).[16]



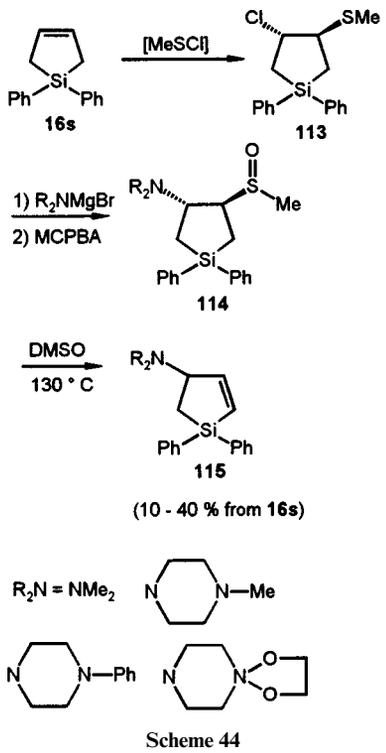
Scheme 42

Addition of bromine across the double bond of **16a** occurs readily and is *trans*-stereospecific.[16] The influence of the substitution pattern at silicon on the rate constant of bromine addition has been systematically investigated by Chernyshev *et al.*[93] Thus, the reactivity of silacyclopentenes **16h**,**t**,**u**,**v** towards addition of bromine seems to be determined by the size of the substituents at silicon, with the rate constant decreasing in the order F > H > Me > Cl. Low reaction temperatures are necessary in the case of **16u** (R = H) to avoid direct bromination of the silicon (Scheme 43).



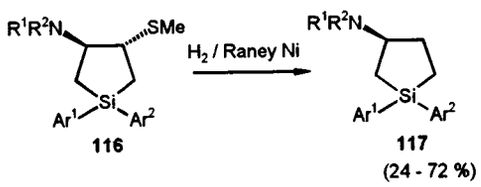
Scheme 43

Addition of methanesulfenyl chloride across the double bond of **16s** also occurs with high *trans*-selectivity. This reaction has been used as a key step for the preparation of 4-amino functionalized silacyclopent-2-enes **115**: nucleophilic substitution of the chlorine in **113** by secondary bromomagnesium amides, followed by oxidation of the thioether to the sulfoxides **114** and subsequent regioselective elimination gave silacyclopent-2-enes **115** (Scheme 44).[94] The photochemically induced radical addition of methanesulfonyl bromide to silacyclopentene **16h** leads to a sulfone related to the thioether **113**. However, this reaction has only been investigated from a mechanistic point of view and will therefore not be discussed in detail.[95]



Scheme 44

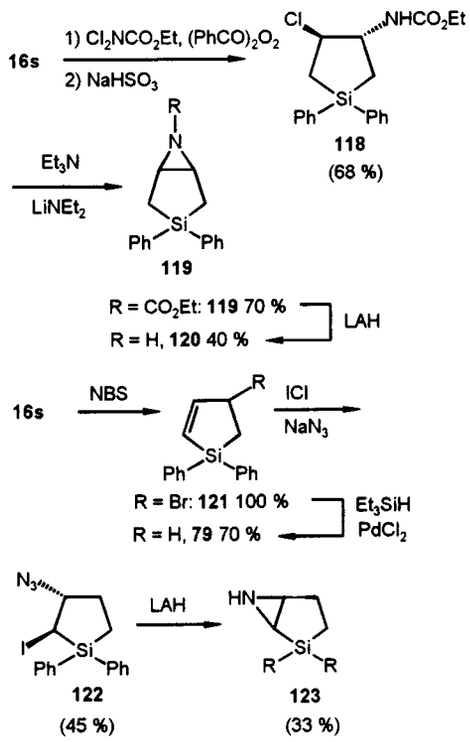
Hydrogenation of silacyclopentanes **116** leads to removal of the sulfur giving 3-amino substituted silacyclopentanes **117** (Scheme 45).[96] A large variety of derivatives has been prepared *via* this method and tested for their pharmacological activity as serotonin antagonists.[97] For 3-aminosilacyclopentenes such as **115**[98] and alkoxy(amino)-substituted silacyclopentanes (*e.g.* **102**)[99] pharmaceutical formulations are claimed as well. Reviews on pharmacologically active organosilanes, including some examples for silacycles, are available.[100,101]



Scheme 45

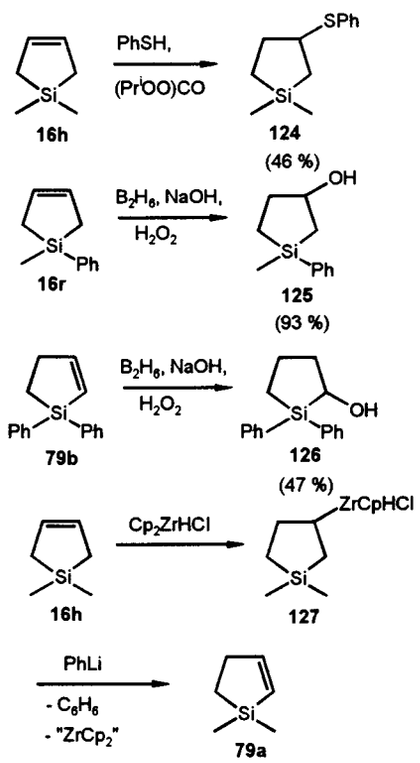
Simultaneous addition of halogen and nitrogen functionality has also proven useful for further synthetic modifications of silacyclopentenes. Thus, **16s** reacts with *N*,*N*-dichlorourethane in the presence of a radical initiator to give carbamate **118**. Subsequent treatment with a base leads to aziridine **119** which is reduced with LAH to give **120**. Regioisomer **123** has also been obtained starting from **16s**: NBS-induced isomerization leads to vinylsilane **121**, reductive removal of the bromine gives vinylsilane **79b**. Formal addition of iodine azide across the double bond and reduction of azide **122** with LAH results in the formation of aziridine **123** (Scheme 46).[89]

Silacyclopentenes do not seem to be particularly reactive towards element–hydrogen bonds. Thus, hydrosilation of the double bond in **16a** failed under different conditions as well as the addition of phosphines. The addition of thiophenol to the double bond of **16h** has been performed on a preparatively useful scale in the presence of a radical initiator, giving thioether **124** in moderate yield.[16] In contrast, hydroboration of **16r** or **79b** proceeds in good yields, giving after oxidative cleavage the silacyclopentanols **125** and **126** respectively.[102] Silacyclopentene **16h** has also been investigated in a hydrozirconation reaction. Upon treatment with the Schwartz reagent, the stable zirconium complex **127** is formed quanti-



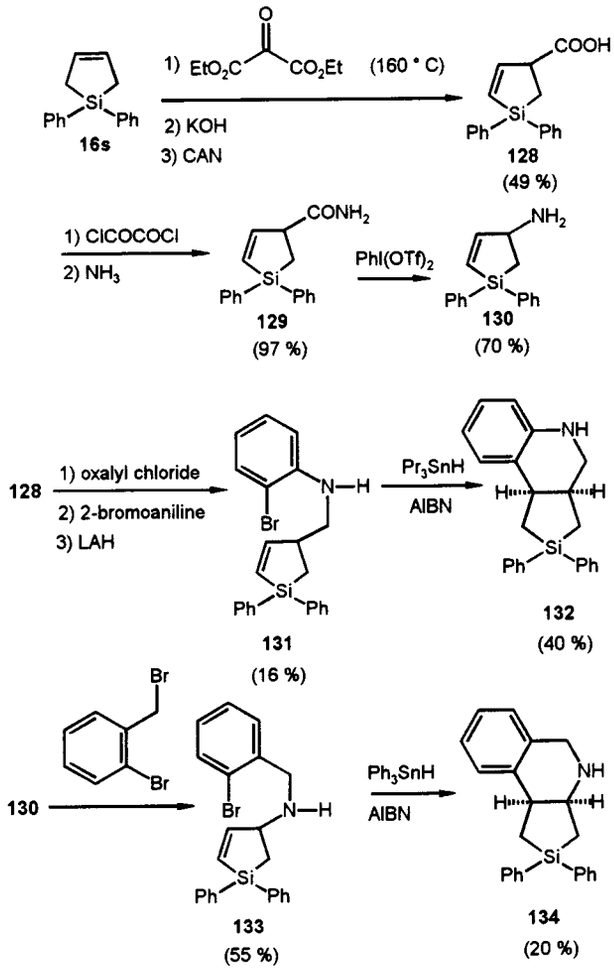
Scheme 46

tatively, which—after substitution of the chlorine by phenyllithium—slowly eliminates to the vinylsilane **79a**. No ring opening reaction, which is the usual reaction path for element heterocycles with donor atoms, is observed here (Scheme 47).[103]



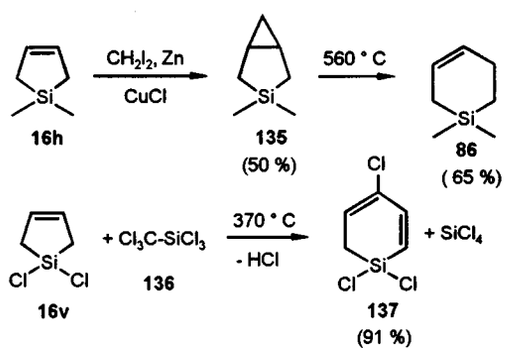
Scheme 47

Silacyclopent-2-enes with additional substituents in the 4-position are interesting precursors for silabicyclic molecules. One approach towards this structural pattern has already been described in Scheme 36. Scheme 48 presents another approach: ene-reaction between silacyclopentene **16s** and diethyl oxomalonate causes introduction of a substituent in the 4-position and rearrangement of the double bond simultaneously. Hydrolysis and oxidation with CAN gives **128** in nearly 50% overall yield. Amide **129** is obtained from carboxylic acid **128**. The former may serve as a precursor for **130**, which is accessible from the amide by Hofmann degradation. **128** and **130** are starting materials for azasilabicyclic structures **132** and **134**, respectively, which have been prepared by radical induced cyclization of **131** and **133** respectively.[104]



Scheme 48

Cyclopropanation reactions of silacyclopentenes have been achieved by carbene or carbenoid insertion to the endocyclic double bond. Thus, cyclopropane **135** has been prepared by Simmons–Smith reaction of **16h**. Upon thermolysis, **135** undergoes isomerization to give silacyclohexene **86** in good yield, along with minor amounts of isomers.[105] Silacyclohexadiene **137** becomes accessible from silacyclopentene **16v** and dichlorocarbene (generated from **136**). A bicyclic compound analogous to **135** is formed as an intermediate, which undergoes isomerization and elimination of HCl leading to **137** (Scheme 49).[106]

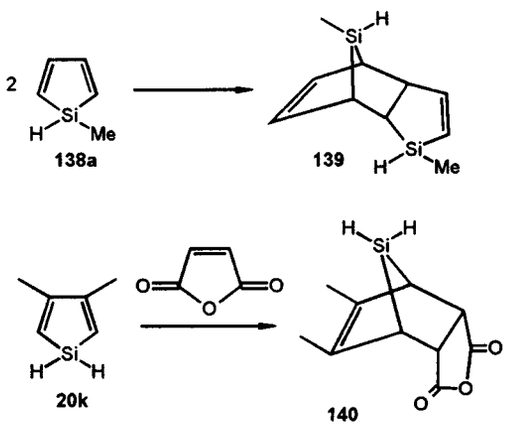


Scheme 49

3.3 Cycloaddition reactions

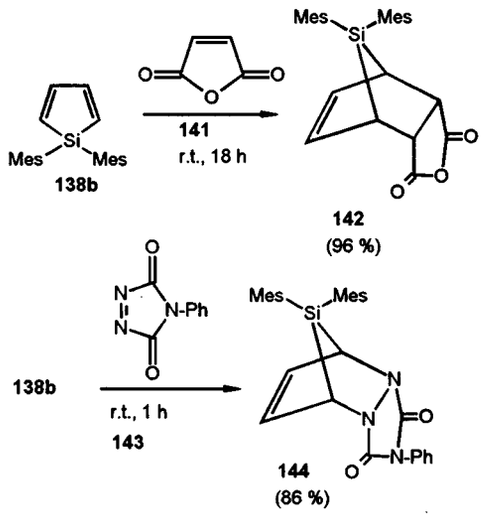
Three different types of cycloaddition reactions will be discussed in this chapter: [4 + 2], [2 + 2] and [3 + 2] cycloadditions.

The first type is characteristic for siloles: derivatives without sterically demanding substituents such as **138a**, are so reactive in Diels–Alder reactions that they are not isolable in monomeric form but dimerize spontaneously.[107] Introduction of two methyl groups to the 3- and 4-position provides enough steric hindrance to stop the dimerization reaction. For example, silole **20k** has been characterized in monomeric form and as its Diels–Alder adduct (**140**) with maleic acid anhydride (Scheme 50).[17]



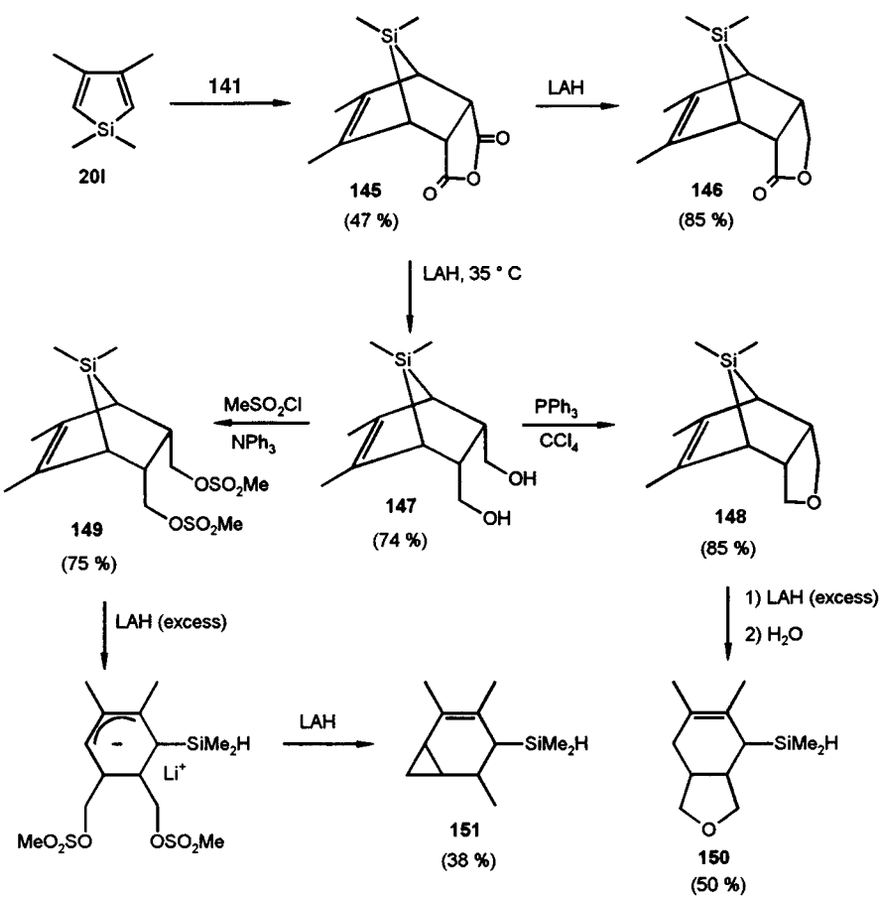
Scheme 50

A different strategy for the isolation of monomeric siloles is the introduction of sterically demanding substituents at the silicon. Thus, 1,1-dimesitylsilole (**138b**) is stable towards dimerization even in refluxing toluene after a prolonged period of time, but undergoes [4 + 2] cycloaddition with reactive dienophiles **141** and **143** readily at room temperature to give the adducts **142** and **144** respectively (Scheme 51).[108]



Scheme 51

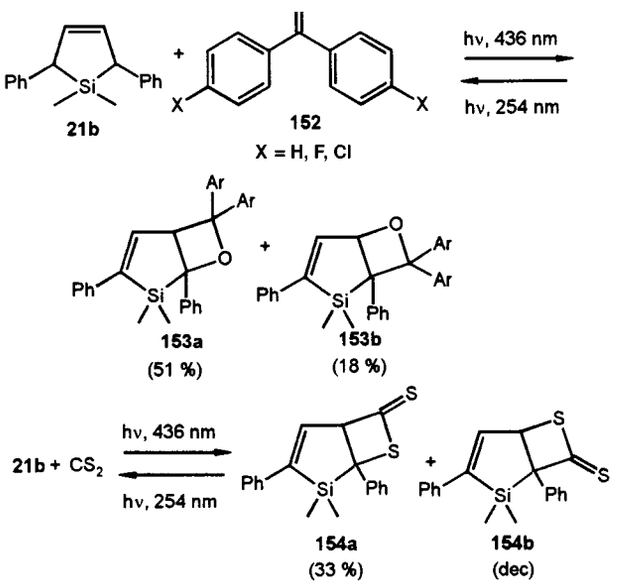
Diels–Alder reaction of siloles with maleic acid anhydride provides a pathway to a variety of 7-silanorbornene derivatives. Thus, starting from silole **20l**, adduct **145** becomes accessible which can be reduced with LAH to give either the tricyclic lactone **146** or the diol **147**, depending on the conditions employed. Diol **147** was transformed into the tetrahydrofuran **148** and the dimesylate **149**. Treatment of **148** and **149** with a large excess of LAH results in nucleophilic attack at the silicon leading to cleavage of one silicon–carbon bond and formation of the bicyclic structures **150** and **151** (Scheme 52).[109] Similar sensitivity of 7-silanorbornenes towards nucleophilic attack at



Scheme 52

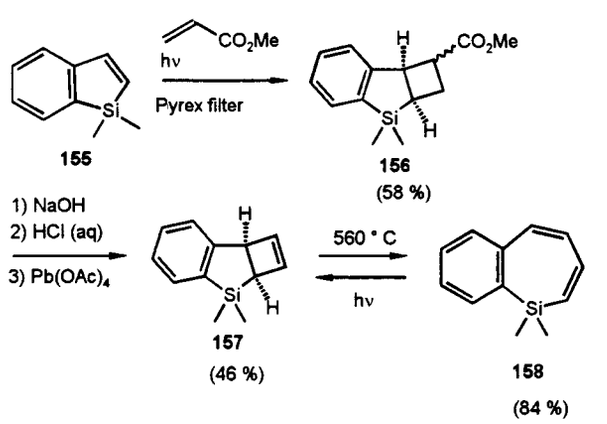
the silicon and subsequent cleavage of one silicon–carbon bond had previously been reported. The ease of Si–C bond cleavage is probably caused by release of ring strain.[110]

Siloles have also been reported to undergo [2 + 2] cycloadditions. However, these processes are less facile and require activation by irradiation. When the photoaddition of substituted benzophenones **152** to silole **21b** to give oxetanes **153a**,**b** was investigated, substituent effects indicated that the reaction proceeds *via* a single electron transfer rather than a concerted mechanism with the silole being the electron donor.[111] This mechanistic assumption is further supported by the observation that carbon disulfide undergoes [2 + 2] cycloaddition to **21b**, in contrast to carbon dioxide, which is not easily reduced. Cycloadducts **154a**,**b** are formed in a 1 : 1 ratio almost quantitatively. **154b** decomposes quite readily on silica gel and could therefore only be characterized from the reaction mixture (Scheme 53).[112] The cycloaddition reactions leading to **153** and **154** are reversible. Upon irradiation at 254 nm the starting materials are re-formed.



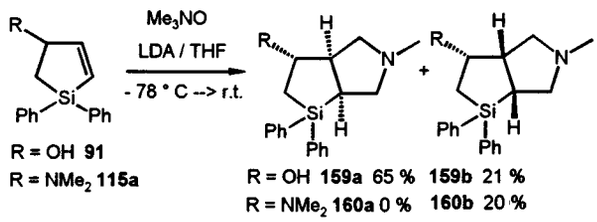
Scheme 53

Electron-deficient alkenes also undergo [2 + 2] cycloaddition reactions. Benzosilole **155** reacts with methyl acrylate under irradiation to the cyclobutane **156**, which has been isolated as a mixture of diastereomers but as a single regioisomer. Oxidative removal of the ester functionality makes cyclobutene **157** accessible, which rearranges at high temperatures to benzosilepine **158**. Prolonged heating of **158** results in the formation of naphthalene, whereas irradiation induces ring contraction to give **157** (Scheme 54).[113,114] The butadiene moiety in benzosilepine **158** may serve as a diene as well as an alkene component in Diels–Alder reactions.[114]



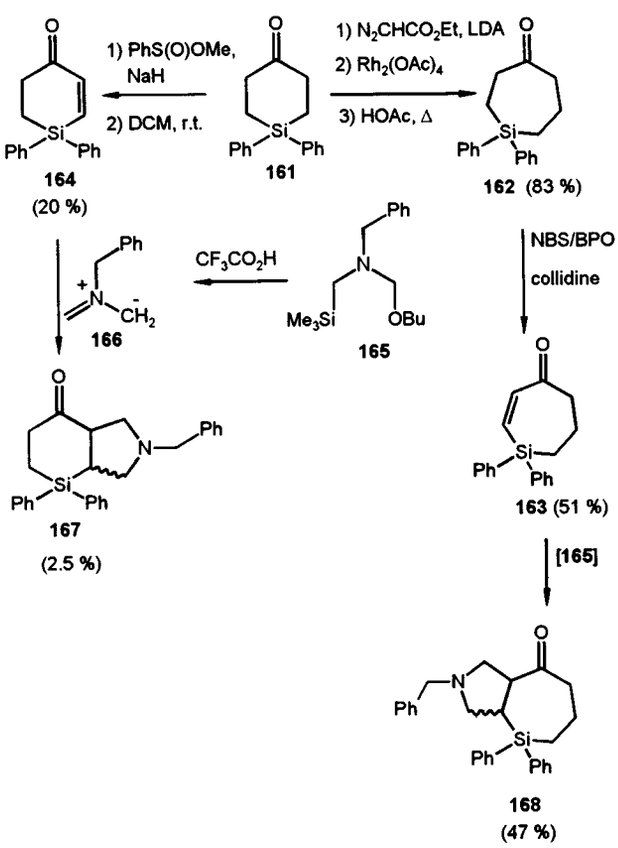
Scheme 54

[3 + 2] Cycloaddition reactions of azomethine ylides to cyclic vinylsilanes have been used to prepare azasilabicyclic compounds. For example, from silacyclopentenes **91** and **115a** bicyclic compounds **159a**,**b** and **160b** are accessible by reaction with trimethylamine *N*-oxide and LDA. While **159** was obtained as a 3 : 1 mixture of diastereoisomers, **160** was formed as a single (*cis*) stereoisomer, albeit in low yield (Scheme 55).[115]



Scheme 55

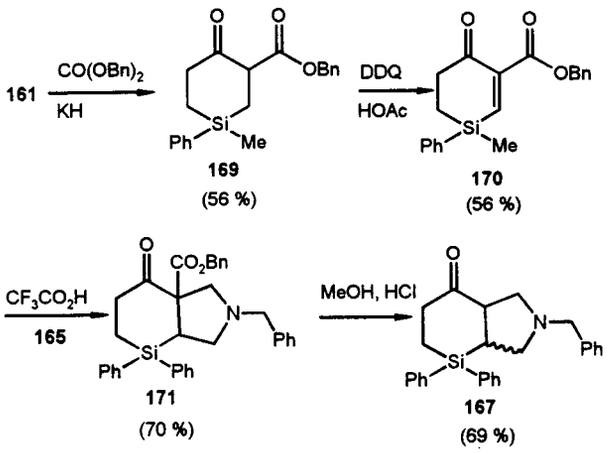
The reactivity of silacycloalkenes in [3 + 2] cycloaddition reactions critically depends on the ring size. This has been illustrated for silacyclohexenone **164** and silacycloheptenone **163**: while **163** readily adds the azomethine ylide **166** (generated *in situ* from **165** by acid catalyzed elimination of TMSOBu) to give the bicyclic derivative **168** as a mixture of diastereoisomers, the analogous compound **167** is formed from **164** only in very low yield. A few comments should be made on the synthesis of the precursors: **164** has been prepared from **161** by condensation of methyl benzenesulfinate and subsequent elimination. **163** is also accessible from **161** by addition of ethyl diazoacetate to the carbonyl function and subsequent rhodium-catalyzed ring enlargement (giving intermediate **162**).[116] Bromination with NBS and elimination of HBr leads to **163** (Scheme 56).[117]



Scheme 56

Successful preparation of **167** requires the introduction of an additional electron withdrawing group. This has been achieved by alkylation of **161** with dibenzyl carbonate (leading to **169**)

followed by oxidation with DDQ. Compound **170** reacts in good yield with azomethine ylide **166** (generated *in situ* from **165**) to give the bicyclic compound **171**. Removal of the ester functionality finally gives **167** (Scheme 57).[117]

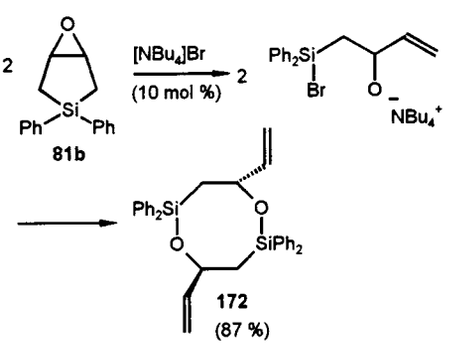


Scheme 57

4 Cleavage of silicon–carbon bonds

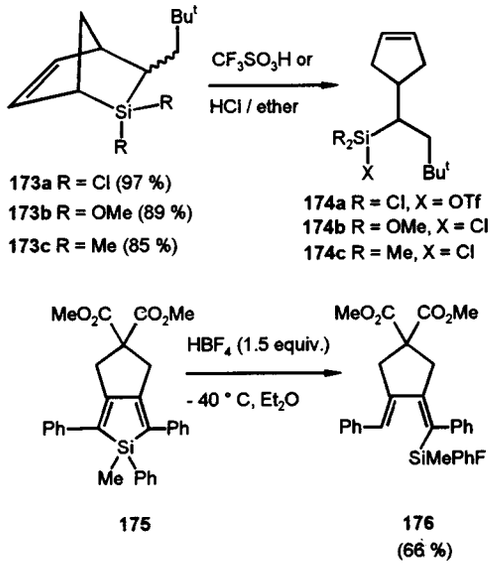
4.1 Cleavage of silicon–carbon bonds by protodesilylation or attack of nucleophiles

Attack of nucleophiles or acids on silacyclic compounds may result in the cleavage of one silicon–carbon bond. Two examples for this behavior have already been given above (Scheme 52) for the reaction of silanorbornenes with LAH. Related cleavage products of tricyclic system **148** have also been detected from the reaction with alkyllithium or TBAF.[109] Even if the silicon atom is not part of a bicyclic structure, nucleophile induced Si–C bond cleavage may proceed efficiently. A catalytic version of such a process has been presented by Weber *et al.*: epoxide **81b** was converted in the presence of a substoichiometric amount of tetrabutylammonium bromide to the eight-membered ring **172**. The reaction proceeds *via* nucleophilic attack of bromide at the silicon atom, cleavage of one Si–C bond with formation of the double bond and subsequent dimerization with liberation of the bromide (Scheme 58).[118]



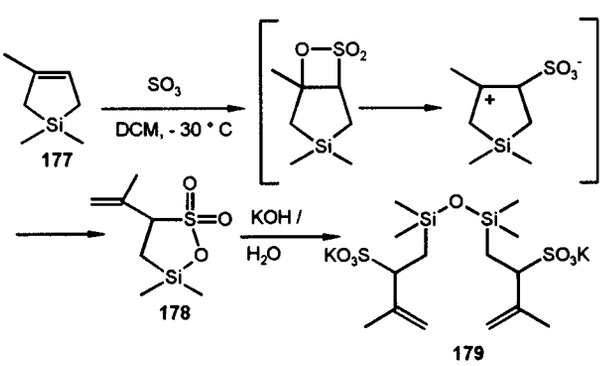
Scheme 58

2-Silanorbornenes can be transformed into substituted cyclopentenes **174a–c** by selective cleavage of one Si–C bond with triflic acid or HCl in anhydrous ether. The conditions depend on the substitution pattern at silicon: for the dichloro derivative **173a** triflic acid has to be used for the cleavage reaction as HCl in ether adds to the double bond. In contrast, cleavage with HCl–ether works well for dimethoxy (**173b**) and dimethyl derivative **173c**.[119] Formation of a conjugated diene **176** with a (*Z*)-vinylsilane moiety has been achieved starting from silole **175** by treatment with tetrafluoroboric acid at low temperatures (Scheme 59).[120]



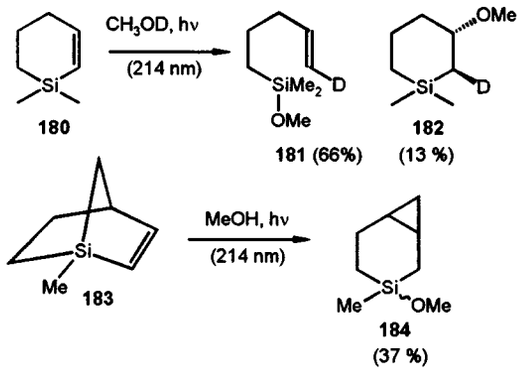
Scheme 59

As part of their study on the reactivity of allylsilanes towards sulfur trioxide, Cerfontain *et al.* investigated the silicon–carbon bond cleavage reaction of silacyclopentene **177**. In the first step SO_3 is thought to add to the double bond in a [2 + 2] mode, followed by cleavage of the C–O bond leading to a species with a positive charge in the β-position to the silicon. Rearrangement gives intermediate **178**, which can be cleaved by KOH–water to give sulfonate **179**. The final product has some structural similarities to the one isolated from the bromide catalyzed opening of epoxide **81b** (Scheme 58): in both cases a but-1-ene with a silicon functionality in the 4-position and a heterosubstituent in the allylic position is formed (Scheme 60).[121]



Scheme 60

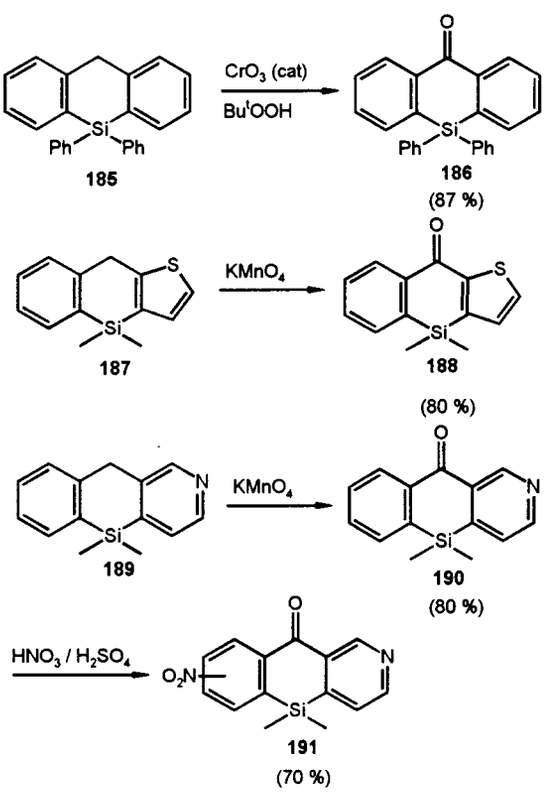
Cleavage of silicon–carbon bonds under acid-free conditions has been investigated by photolysis of various organosilanes in alcohols.[122,123] These investigations are primarily interesting from the mechanistic point of view. However, two reactions investigated by Steinmetz *et al.* should be mentioned here. Photolysis of silacyclohexene **180** in deuterated methanol leads to the formation of two products, a cleavage product **181** and an alcoholysis product **182**. Formation of both products occurs stereoselectively, indicating the intermediacy of a cyclic silicon-stabilized carbenium ion. Similar results have been obtained for 1,1-dimethylsilacyclopent-2-ene.[124] A second example is the photoalcoholysis of silanorbornene **183**. Here the six-membered silacycle remains intact, but formation of cyclopropane **184** *via* [1,3-C] migration has been observed. The reaction is thought to proceed *via* a silene intermediate which is quenched by methanol (Scheme 61).[125,126]



Scheme 61

4.2 Oxidative cleavage of silicon–carbon bonds

Oxidation of organosilanes does not necessarily lead to silicon–carbon bond cleavage. For example, silaanthracene **185** is transformed selectively in good yield to the ketone **186** using *tert*-butyl hydroperoxide as an oxidant and chromium trioxide as a catalyst.[127] In other cases, potassium permanganate has been efficiently used as an oxidant, for example for the preparation of **188**[128] and **190**[129] from **187** and **189**, respectively. Ketones **186**, **188** and **190** are useful precursors for 9-functionalized-10-silaanthracene derivatives.[130,131] The silicon–carbon bonds in **190** are stable even towards mixtures of nitric acid and sulfuric acid. Under these conditions three regioisomers of the nitro compound **191** are isolable in good yield (Scheme 62).[132]

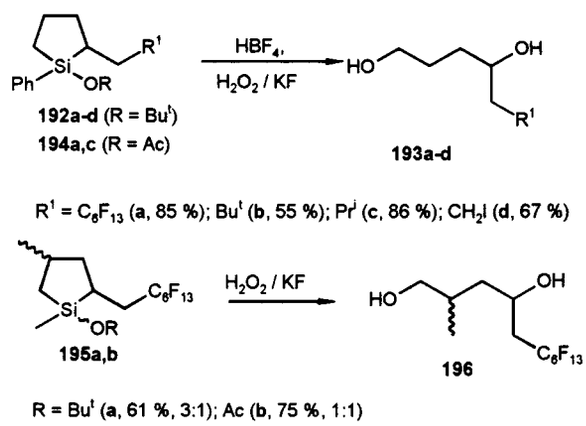


Scheme 62

Oxidative cleavage of silicon–carbon bonds provides a convenient access to hydroxylated compounds.[133] Silicon–carbon heterocycles contain two endocyclic Si–C bonds, so in principle two functional groups can be introduced in one step. Several preparatively useful transformations have been described and these will be discussed below. The reactions can be distinguished according to the structural patterns formed.

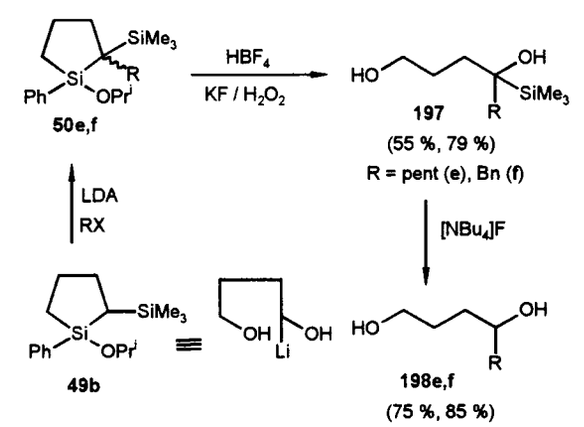
4.2.1 1,4-Diols

Silacyclopentanes with at least one phenyl or one alkoxysubstituent at the silicon atom can be transformed into diols *via* oxidative cleavage of both silicon–carbon bonds. In a first step, a Si–phenyl bond is cleaved by action of tetrafluoroboric acid, followed by treatment with KF–H_2O_2 (Fleming–Tamao oxidation) to give the corresponding diol. Scheme 63 summarizes some examples starting from silacyclopentanes **192a–d** with one phenyl and one alkoxysubstituent. Diols **193a**,**c** have also been obtained from the acetoxy compounds **194a**,**c**, albeit in lower yield.[134] Although one heterosubstituent is present in the molecule, conversion of **192b–d** to diols **193b–d** requires the action of HBF_4 prior to oxidative cleavage.[135] The diastereomeric ratio of the cleavage product **196** reflects the diastereomeric ratio in the starting silacyclopentanes **195a**,**b**.[134]



Scheme 63

α-Silylated silacyclopentanes **49** can be considered as synthetic equivalents of 1-lithiobutane-1,4-diol. This is illustrated in Scheme 64: **49b** can be alkylated in the 2-position, subsequent oxidative cleavage of the endocyclic Si–C bonds followed by removal of the TMS-group with tetrabutylammonium fluoride gives the diols **198e**,**f**.[65]

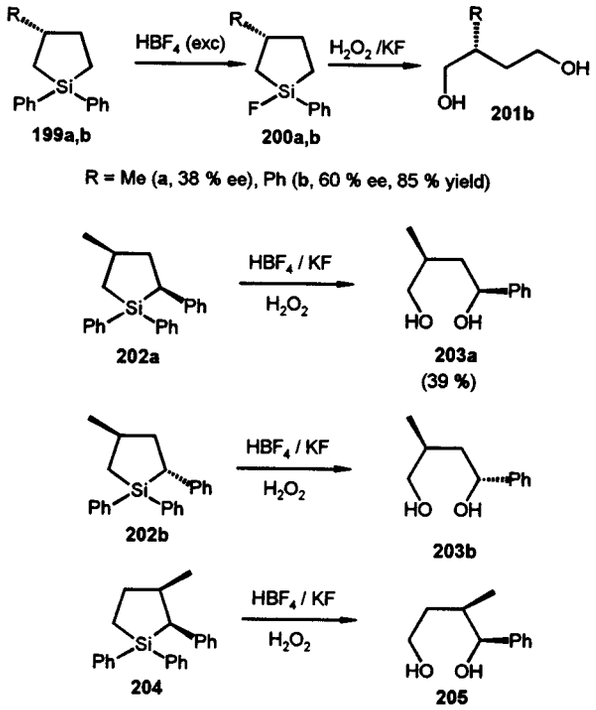


Scheme 64

1,1-Diphenylsilacyclopentanes may also serve as precursors for 1,4-diols. In these cases, however, protodesilylation with HBF_4 is always necessary. Protodesilylation and oxidative cleavage are normally conducted in a one-pot procedure without isolation of the 1-fluoro intermediates (*e.g.* **200a**,**b**). Scheme 65 summarizes transformations leading to enantiomerically enriched diols (**201a**,**b**)[55] and to diastereoisomerically pure diols **203a**,**b** and **205**.[136]

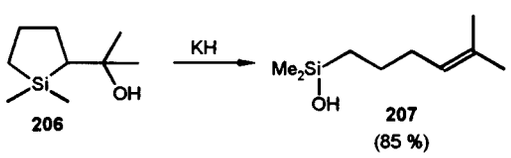
4.2.2 Alkenols

Silacyclopentanes with a hydroxyalkyl side chain are substrates for an intramolecular Peterson olefination. Thus, silacyclo-



Scheme 65

pentane **206** undergoes rearrangement to the silanol **207** upon treatment with potassium hydride (Scheme 66).[137] The silanols resulting from the Peterson elimination are prone to oxidation of the silicon–carbon bond.[138]



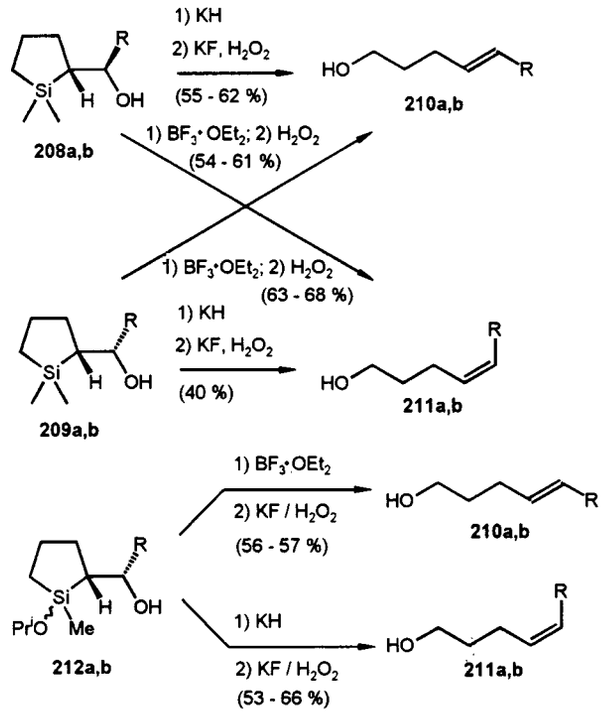
Scheme 66

If molecules with two adjacent stereogenic centers are employed in the reaction, the configuration of the double bond is determined by the relative stereochemistry of the precursor and by the reagent used to induce the Peterson olefination. This has been elegantly demonstrated for the diastereoisomers of silacyclopentanes **208a**,**b** and **209a**,**b**: from **208a**,**b** result the *E*-alkenols **210a**,**b** upon treatment with KH, whereas the same diastereoisomers give *Z*-alkenols **211a**,**b** with boron trifluoride–diethyl ether. The diastereoisomeric compounds **209a**,**b** give complementary stereochemistries under the same conditions.[136] Hetero substituents at the silicon do not seem to have a significant influence on the overall yield. This has been illustrated for silacyclopentanes **212a**,**b** with an alkoxy substituent at the silicon (Scheme 67).[135]

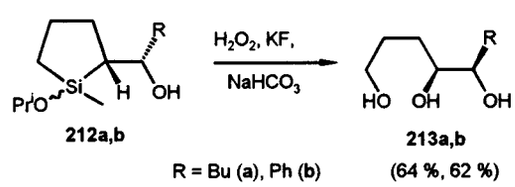
4.2.3 1,2,5-Triols

Starting from silacyclopentanes **212a**,**b**, triols **213a**,**b** have been prepared stereoselectively by oxidative cleavage of both Si–C bonds. Phenyl derivative **212b** is obviously very labile towards Peterson elimination under the conditions of the oxidation, resulting in the formation of **210b** as a by-product in 10% yield (Scheme 68).[135,138]

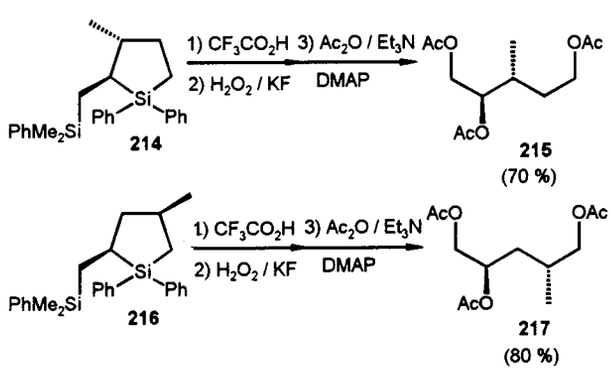
Alternatively, 1,2,5-triols can be generated stereoselectively starting from silacyclopentanes with an additional exocyclic silyl group. Protodesilylation using trifluoroacetic acid, oxidation and protection of the hydroxy functions as acetates lead to the protected triols **215** and **217** starting from **214** and **216**, respectively, in good yield (Scheme 69).[139]



Scheme 67



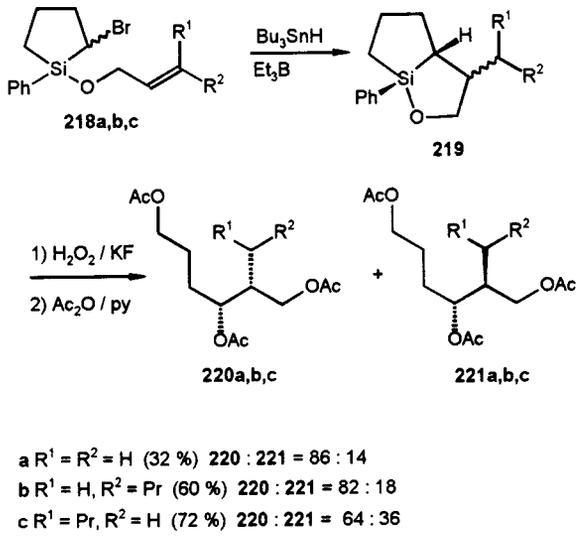
Scheme 68



Scheme 69

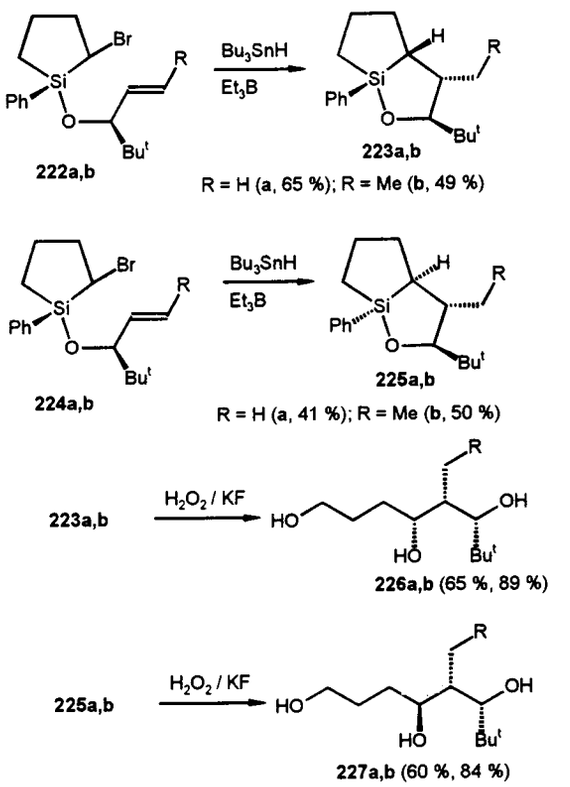
4.2.4 1,3,6-Triols

Free radical cyclization and oxidative cleavage of two silicon–carbon and one silicon–oxygen bonds represent a sequence for the stereoselective preparation of 1,3,6-triols.[140,141] Precursors suited for free radical cyclization are α-brominated or iodinated silacyclopentanes bearing an allyl alcohol substituent at the silicon. For example, compounds **218** undergo cyclization to the bicyclic systems **219** in the presence of tributyltin hydride and triethylborane. After protection of the alcohol functions, oxidative removal of the silicon liberates the triacetates **220** and **221**. Diastereomeric ratios vary between 2:1 and 6:1. The configuration of the double bond in the starting material has a significant influence on the stereochemical outcome: in the case of the *Z*-allyl alcohol derivative **218c**, stereoselectivity is significantly lower compared to **218a**,**b** (Scheme 70).



Scheme 70

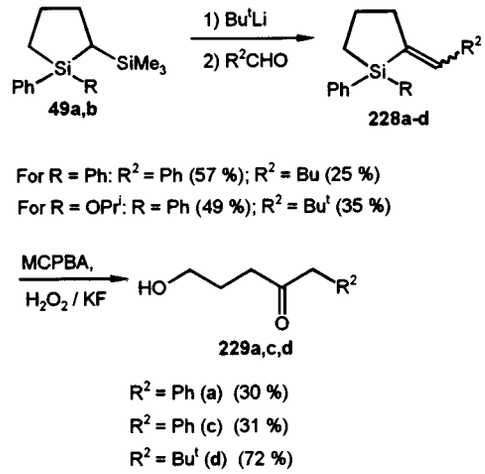
Exclusive formation of one diastereoisomer is normally observed if an additional substituent is attached to the allylic position of the starting material. Thus, free radical cyclization of the diastereoisomers **222** and **224** is highly stereospecific, leading to single diastereoisomers of the bicyclic systems **223** and **225**. However, regioisomeric by-products (resulting from 6-*endo*-cyclization) and the dehalogenation products are isolated from these reactions in yields up to 20%. The bicyclic systems **223** and **225** have been separated from the byproducts and oxidized under the standard conditions to yield the triols **226** and **227** (Scheme 71).



Scheme 71

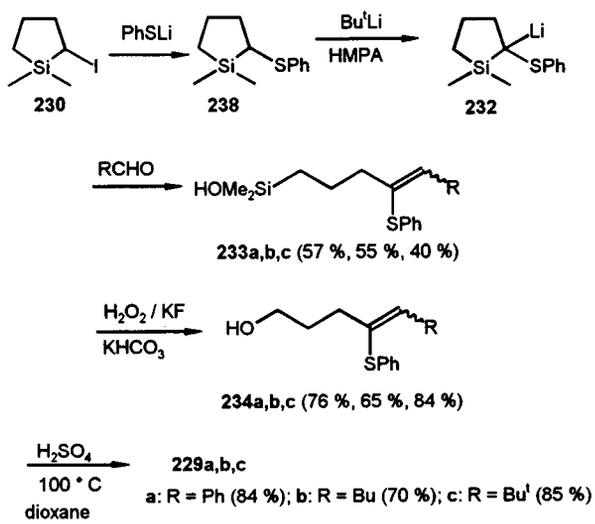
4.2.5 γ-Hydroxy ketones

Silylated silacyclopentanes **49a**,**b** not only represent synthetic equivalents for 1-lithiobutane-1,4-diol, but they can also be converted to γ-hydroxy ketones in two steps. Starting from **49a**,**b**, deprotonation with Bu^{t}Li and subsequent treatment with aldehydes yield *exo*-methylene silacyclopentanes **228a**–**d**. Epoxidation of the double bond and rearrangement of the resulting silylated epoxides leads to the carbonyl functionality whereupon oxidative cleavage of the remaining silicon–carbon bond generates hydroxy ketones **229a**,**c**,**d** (Scheme 72).[142]



Scheme 72

Alternatively, compounds **229** can be prepared starting from the α-iodosilacyclopentane **230**. Substitution of the iodide by thiophenol, α-lithiation and addition of the α-lithio intermediate **232** to aldehydes results in the formation of silanols **233a**,**b**,**c**. Oxidative cleavage gives thioenol ethers **234a**,**b**,**c**, which are hydrolyzed in the presence of sulfuric acid to the hydroxy ketones **229a**,**b**,**c** (Scheme 73).[142]



Scheme 73

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