Journal of Organometallic Chemistry, 267(1984)1-71
Elsevier Sequoia S.A., Lausanne - Printed in the Netherlands

Review

Organo-1,3,2-dioxasilaheterocycles

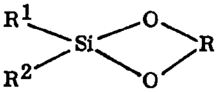
R. Harry Cragg and Rob D. Lane

The Chemical Laboratory, University of Kent at Canterbury (Great Britain)

0022-328X/84/$21.30

1. Introduction

The scope of this review has been limited primarily to organosilicon heterocycles derived from organo, difunctional, silanes and organic dihydroxy compounds.



(R^1 = alkyl or aryl; R^2 = alkyl, aryl or any other univalent atom or group; R = divalent organic group)

Excluded therefore are spirosilicates, cyclic siloxanes and the silatranes (for which a comprehensive review has recently been published [1]).

The beginning of interest in these compounds was undoubtedly heralded by the much-quoted work of Krieble and Burkhard in 1947 [2]. Since then reports on their preparation and properties have appeared sporadically up until the present time, though there has been no comprehensive study of a wide range of compounds, particularly with regard to modern spectroscopic techniques. The literature over this period is here comprehensively reviewed.

2. Methods of Preparation

The two most widely used methods, involving reaction of dichloro- or dialkoxy-silanes with diols, were established in 1947 [2]. These, together with others reported prior to 1966 were reviewed and discussed in a comprehensive paper by Voronkov and Romadan [3]. They are listed below, together with all other methods of synthesis reported up to the present time, according to the type of silicon bond undergoing fission. Methods of preparation for individual compounds are given in Tables 1-6.

A. Dichlorosilane + diol

The ready availability of certain diorganodichlorosilanes has meant that their direct reaction with diols has been the most frequently used method for preparing these heterocycles.

The reaction is facile, usually proceeding rapidly and relatively independently of conditions, although these may be important in determining the yields of monomeric products. Poor yields are normally attributable to polymerization which is usually all-too-obvious from the viscous and intractable nature of the crude products.

Whilst neat reactants have been used [2], it is more common to employ a large volume of some suitable solvent (e.g. benzene or diethyl ether)[4,5,6], adding one reactant slowly to the other with stirring. The hydrogen chloride produced may be allowed to escape during reflux [2,7] or be taken up by activated charcoal [4] but is most commonly removed as it is formed, as the hydrochloride of a suitable tertiary base such as triethylamine or pyridine [3,8,9]. The precipitate is filtered off when cold. We have found it preferable to use the calculated amount of base (usually pyridine in benzene solvent, giving a less flocculent precipitate than triethylamine) rather than an excess which sometimes appeared to lead to greater retention of hydrochloride in solution, making subsequent purification of the product more difficult.

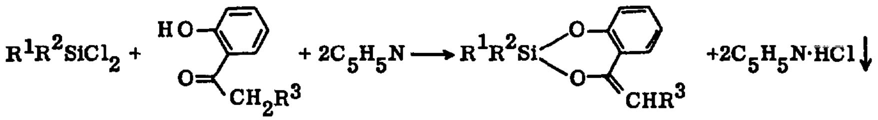
After removal of solvent by distillation, the product is obtained by distillation, at or below atmospheric pressure, or by recrystallization.

The lead salt of catechol has been used successfully as an alternative to catechol itself in this method [10].

Although one hydroxy group may be derived from the acid group of a hydroxycarboxylic acid, monomeric products are difficult to prepare by this method, except for those of the salicylic acids [11].

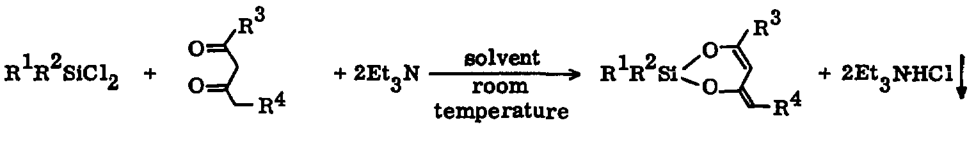
B. Dichlorosilane + 2-hydroxyketone, β-diketone or ketone

Each method has only been singly reported. (2-hydroxyphenyl)ketones react with diorganodichlorosilanes, according to a procedure essentially similar to that described for method A, to give (styryl-α, 2-dioxy)silanes in excellent yield [12].



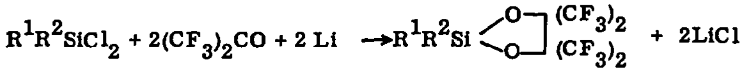
(R^1,R^2 = alkyl, alkenyl or aryl; R^3 = H or alkyl)

A similar reaction takes place, under mild conditions, with β-diketones [12a].



(R^1R^2 = Me_2 or Ph_2; R^3 = Me; R^4 = alkyl or aryl)

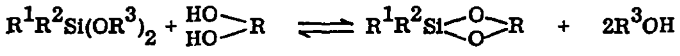
When diorganodichlorosilanes are added slowly to a solution of hexafluoropropanone in tetrahydrofuran, containing lithium, at a temperature of -10 to +15°C, the mixture finally affords 4,4,5,5-tetrakis(trifluoromethyl)-1,3,2-dioxasilacyclopentanes in varying yield (17-80%) [13].



(R^1R^2 = Me, $CH_2=CH$; Me_2; MePh; $(CH_2)_5$)

C. Dialkoxysilane + diol

Krieble and Burkhard [2] observed that the diol alcoholysis of dialkoxysilanes was less likely to produce side reactions than the corresponding reaction with dichlorosilanes (method A) and the method has been widely used [3,14,15,16,17].



(R^3 is commonly Me or Et)

The reactants are boiled together under reflux in equimolar amounts, with or without solvent, the displaced alcohol then being removed by distillation. It has been suggested that loss of dimethyldiethoxysilane in azeotropic admixture with ethanol means that a higher homologue, such as dimethyldi-n-butoxysilane, is preferable for the preparation of 2,2-dimethyl compounds [3].

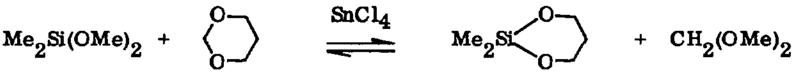
Whilst acid catalysts such as p-toluenesulphonic acid [2,18] and acid-form cation-exchange resins [14] have been successfully employed it is claimed that the use of basic catalysts, such as sodium methoxide or the sodium salt of the diol, are superior since polymer formation is less likely [3].

In variations of this method, acetylated [19] and trimethylsilylated [20] diols have been used.

D. Dialkoxysilane + 1,3-dioxane

This novel synthesis was briefly reported for the first time in 1980 [21]. The reaction between dimethyldimethoxysilane and 1,3-dioxanes apparently takes place with tin(IV)chloride as catalyst, affording yields between 29 and 62% for three compounds.

e.g.

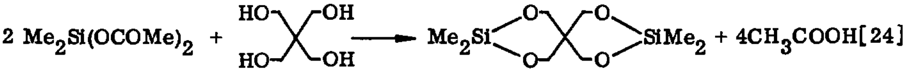


Although it is claimed that the formation of secondary products were not observed, the reported proton NMR shifts given for 2,2-dimethyl-1,3,2-dioxasilacyclohexane are not consistent either with other literature values or with our own results for the monomer and seem more likely to apply to dimer [73].

E. Diacetoxysilane + diol

This method has been little used but appears to be a viable alternative to the use of dichloro- or dialkoxy-silanes. Hence derivatives of diols [22] and pentaerythritol [23,24] were obtained in good yield by direct reaction at room temperature or above, products being separated by distillation.

e.g.



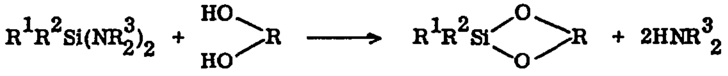
F. Polydialkylsiloxane + diol

Good yields of 2,2-dialkyl-1,3,2-dioxasilacycloalkanes have been obtained by the reaction of linear or cyclic polydialkylsiloxanes with diols in the presence of alkali as catalyst, water being distilled off continuously in azeotropic admixture with the benzene solvent [3].

e.g.

G. Mono- or bis(dialkylamino)silane + diol

Reaction with bis(dialkylamino)silane takes place readily on heating the mixture without solvent, dialkylamine vapour being allowed to escape continuously to leave crude product as the only residue.

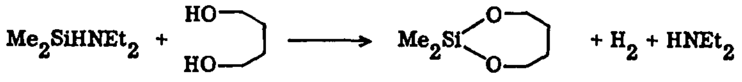


(R^3 = Me or Et)

This method was first reported in 1967 [25] but does not appear to have been used subsequently, possibly because of the need to first prepare the extremely hydrolytic bis(dialkylamino)silanes. We have used it to obtain three 1,3,2-dioxasilacycloalkanes (Tables 2 and 3), from either the bis-(dimethylamino)- or bis(diethylamino) silane, and have found the procedure to be simple and convenient once a stock of the starting material is available.

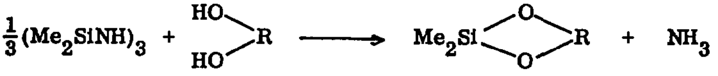
A similar reaction takes place between dialkyl (diethylamino) silanes and diols, with the evolution of hydrogen and diethylamine [26].

e.g.



H. Hexamethylcyclotrisilazane + diol

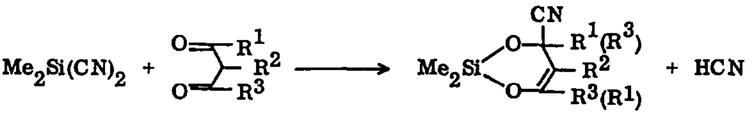
Birkofer and Stuhl have used this reaction to prepare a variety of 1,3,2-dioxasilaheterocycles [27,28,29]. Reactants were heated under reflux in benzene or toluene for 8 hours.



Use of the method has also been reported several times in the patent literature [18,30,31,32].

I. Dicyanosilane + β-diketone or 2-hydroxyketone

In the course of their investigation of cyanosilylated derivatives of monosilylated β-diketones Ryu et al. (1978) [33] found that reaction between dimethyldicyanosilane and β-diketones led to the formation of a number of 6-cyano-1,3,2-dioxasilacyclohex-4-enes

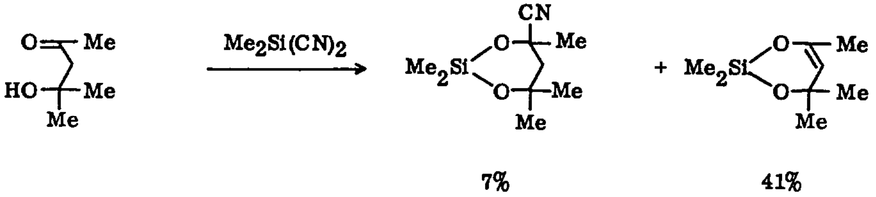


(R^1, R^2 and R^3 indicate various possible substituents)

In a typical procedure, diketone (10 mmol) was added slowly to a solution of the dicyanosilane (12 mmol) in dichloromethane at -40°C. Removal of hydrogen cyanide and solvent, followed by distillation or recrystallization, afforded the required product in high yield.

In cases where the diketone was unsymmetrically substituted, the product was either an isomeric mixture or, if the orientation of enolization is determined by conjugation, a single isomer (see Table 2 for individual products).

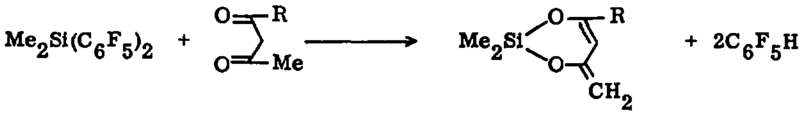
Whilst this novel synthesis may have important synthetic applications [33] it has only limited scope as a general method of preparing 1,3,2-dioxasila heterocycles since the products contain a cyano substituent. However, it is noteworthy that similar derivatives were also obtained using β-hydroxyketones in place of β-diketones and that the major product from diacetone alcohol lacked a cyano substituent.



In the present context this may therefore be of more interest than the reaction of β-diketones themselves, providing a possible route to 1,3,2-dioxasilacycloalkenes.

J. Bis(pentafluorophenyl)silane + β-diketone

In a general study of reactions of (pentafluorophenyl)silanes with carbonyl compounds, Gostevskii et al. [34] prepared 6-methylene-1,3,2-dioxasilacyclohex-4-enes by reacting dimethylbis(pentafluorophenyl)silane with either acetylacetone or benzoylacetone in ethereal solution and with a potassium cyanide, 18-crown-6 catalyst.



(R = Me or Ph)

The method may be compared to that already described using dicyanosilanes (method I) but differs in that dehydrogenative silylation is more effective [34].

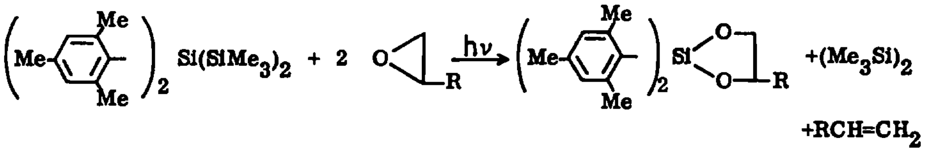
K. From polysilanes via silylenes

Ando and Ikeno first reported the formation of 4,5-dialkyl-1,3,2-dioxasilacyclopent-4-enes in 1979 [35]. Synthesis involved the photolysis of an ethereal solution of dodecamethylcyclohexasilane (1 mmol) in the presence of α-diketones (1 mmol) using a low-pressure mercury lamp. Products were isolated in over 50% yield by preparative g.l.c. and were found to be extremely moisture sensitive.

$$(Me_2Si)_6 \xrightarrow{h\nu} Me_2Si:$$

(R^1R^2 = Me_2, MeEt, nPr_2, iPr_2)

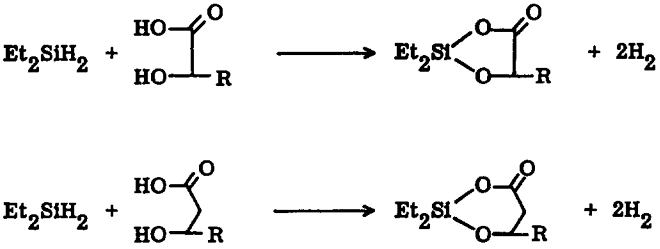
The same authors subsequently prepared dimesitylsilanone-epoxide adducts, in fairly low yield (9-24%), by photolysis of an ethereal solution of 2,2-dimesitylhexamethyltrisilane in the presence of epoxides [36].



(R = H, Me, Et or Ph)

L. Silane + hydroxy- or keto-acid

In the presence of colloidal nickel or palladium, aliphatic α- and β-hydroxy acids react with diethylsilane to give 1,3,2-dioxasilacyclopentan-4-ones [37] and 1,3,2-dioxasilacyclohexan-4-ones [38] respectively, in high yield.



(R is alkyl or aryl)

α-Keto acids react similarly [39] provided that R is not an aryl group.

These would appear to be useful routes to such hydroxy-acid derivatives as they are otherwise difficult to prepare.

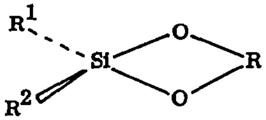
3. Structure and Physical Properties

Formulae, methods of preparation and physical constants for all compounds, up to April 1983, are compiled in Tables 1-5. The availability of other data from each quoted reference is also indicated.

A representative number of spirosilicates are given for comparison in Table 6 and some compounds which are not strictly organosilicon, but which are of some relevance, are included in the main Tables.

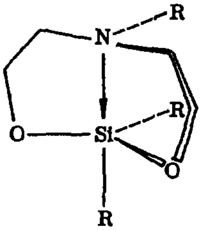
A. Structure

i) Monomeric 1,3,2-dioxasilaheterocycles are silicon analogues of cyclic acetals and ketals [2].



(R^1, R^2 = H, alkyl or aryl; R = divalent organic group)

The only structural data available come from x-ray diffraction studies on 1,3,2-dioxasila-6-azacyclooctanes [17,40,41] and are therefore not only limited in number but are also unrepresentative of the majority of 1,3,2-dioxasilaheterocycles. However, whilst the interest in these particular compounds lay in the possibility of N→Si co-ordination, bond angle data which may be extracted from the results could have wider application. The compounds were shown to have distorted trigonal-bipyramidal structures involving weak N→Si interactions and with both oxygen atoms in the equatorial plane.

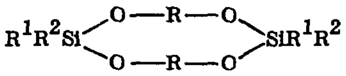


OSiO bond angles are all close to the trigonal angle of 120° (111-122°), as would be expected from this structure, and cannot be translated to heterocycles containing a strictly 4-co-ordinate silicon atom.

SiOC bond angles are surprisingly large however (124-133°) and significantly exceed even the trigonal angle. Since there does not appear to be any purely steric requirement for this (OCC and CCN angles for the same compounds are in the ranges 110-128° and 107-118° respectively), it is arguable that large SiOC bond angles might be expected in all 1,3,2-dioxasilaheterocycles. This is supported by an x-ray diffraction study of α-naphthylphenylfluoromenthoxysilane which found a value of 128° for the open-chain SiOC bond angle [42]. The tentative connection between silicon-29 NMR shifts and ring strain [73] is also compatible with a requirement for large SiOC bond angles in these structures, as is the important chemical evidence that the 5-membered, monomeric 1,3,2-dioxasilacyclopentanes are often unobtainable [2,8].

ii) The general assumption has been made in literature reports that dimeric products, as indicated by molecular mass determinations, have a macrocyclic structure [2,3,8].

i.e.



$$R^1R^2Si\begin{array}{c}O-R-O\\O-R-O\end{array}SiR^1R^2$$

The isolation of individually characterized monomeric and dimeric 2,2-diphenyl-1,3,2-dioxasilacycloheptanes from the same reaction mixture is in strong support of this presupposition, as are their NMR and mass spectra [43]. The term 'dimer' is therefore used throughout the review with this particular connotation.

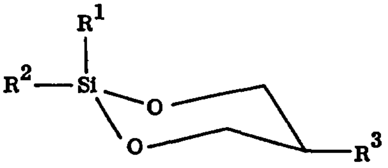
(Products of higher mass than dimer are referred to generally as polymers.)

B. Conformation

The earliest reported conformational study involving 1,3,2-dioxasilacycloheterocycles appears to have been by Urbanski et al. (1963) [44]. Dipole moment measurements on five 5-alkyl-2,2-dimethyl-5-nitro-1,3,2-dioxasilacyclohexanes were inconclusive, suggesting either a chair-chair equilibrium, with the nitro group axial or equatorial, or a boat form with the same group axial.

In a brief communication by Hellier (1970) [45] on six 2,5-substituted 1,3,2-dioxasilacyclohexanes, proton NMR shift data were said to indicate conformationally mobile systems including contributions from flexible forms. Similar conclusions were reached by Voronkov et al. (1969) [46] except that 5-nitro-2,2,5-trimethyl-1,3,2-dioxasilacyclohexane was said to exist in a boat conformation due to interaction between the nitro group and silicon, although a later study of the same compound appears to suggest a chair form with the nitro group in an axial position [47]. (There is therefore a need for the conflicting evidence on this particular compound to be resolved.)

Albriktsen and Heggelund (1974) [48] undertook a full proton NMR analysis of six different 1,3,2-dioxasilacyclohexanes of the type:

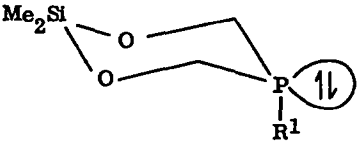


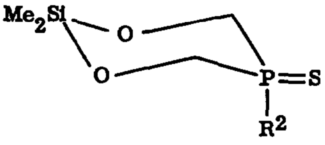
(R^1, R^2 = Me or tBu; R^3 = H, Me or tBu)

They concluded that the barrier to ring inversion is less in these heterocycles than in analogous 1,3-dioxanes. The compounds exist predominantly in either the chair form or a rapid chair-chair equilibrium, though twist and boat contributions to the equilibria also have to be considered. There was no evidence for any axial substituent at carbon 5, the free energy difference between axial and equatorial substituents in this position apparently being larger than for 1,3-dioxanes.

In a series of investigations (1978-9) into the stereochemistry of 1,3,2-dioxasila-5-phosphorinanes [16,49] by proton NMR and the corresponding 5-sulphides [50] by dipole moment measurements the chair form was found to predominate, the phosphorus lone-pair or sulphur atom lying in a preferred equatorial position. (An earlier report that these compounds exist in a boat conformation [51] was here refuted [16].)

i.e.





(R^1 = Me, Et or iPr; R^2 = Me, Pr or iPr)

If R^1 is phenyl, a chair-chair equilibrium exists, with the phenyl group axial or equatorial [52].

C. Vibrational Spectra

The only systematic infra-red study of relevant heterocycles appears to have been that by Marchand and Valade (1968) [53] in which they investigated a total of seven 2,2-dialkyl-1,3,2-dioxasilacycloalkanes (together with a number of dialkoxydialkysilanes), covering ring sizes of 5,6,7 and 10 (dimer) atoms, in the region 4000-2600 and 1700-350 cm^{-1}. They were able to identify some characteristic vibrations associated with the cyclic structures and also of methyl and butyl groups bonded to silicon.

Andrianov et al. [54] identified changes in the infra-red spectrum of dimethyl(1,2-phenylenedioxy)silane which are associated with its reversible dimerization. In particular, a band at 1020 cm^{-1} was attributed solely to the monomer and one at 1375 cm^{-1} to the dimer.

Specific IR bands have been assigned for some 5-[28], 6-[16], 7-[27,29], 8- and 9-[29] membered rings. Raw IR data are given in several papers, the chief examples being indicated in the Tables.

D. NMR Spectra

The number of NMR studies connected with organo-1,3,2-dioxasilaheterocycles has been extremely limited and this has prompted our recent investigation of the carbon-13 and silicon-29 NMR spectra of these compounds.

i) Proton

Conformational studies based on proton NMR data have already been referred to [16,45-49,52].

The technique has found application in investigations of the reversible dimerization of dimethyl-[55,56] and methylphenyl-[57] (1,2-phenylenedioxy)-silanes, since SiMe resonances differ for monomers and dimers.

References to proton NMR data for individual compounds are given in the Tables.

ii) Carbon-13

Shift assignments have been reported for dimeric dimethyl(1,2-phenylenedioxy)silane [56], a series of nine derivatives of salicylic (and related) acids [11], a comprehensive range of the title compounds [73] and five 2,2-dimethyl-1,3,2-dioxasila-5-phosphorinanes [49]. The last reference also contains phosphorus-31 NMR shifts together with ^{1}H-^{1}H, ^{31}P-^{1}H and ^{31}P-^{13}C coupling constants.

iii) Silicon-29

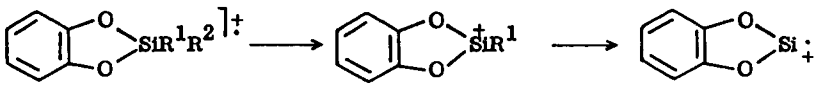
We have previously reported silicon-29 NMR shifts for nine derivatives of salicylic, and related, acids [11] and for monomeric and dimeric forms of three 2,2-diphenyl-1,3,2-dioxasilacycloheptanes [43]. We have recently recorded the silicon-29 NMR shifts for over fifty compounds covering ring sizes from 5-14 atoms as indicated in the Tables.

As far as it is known, the only other reported shift is one assigned to a proposed 1,3,2-dioxasilacyclopentane [58].

E. Mass Spectra

Reports of mass spectral studies for these systems have also been scanty.

Monomeric (1,2-phenylenedioxy)silanes have been the subject of two investigations [59,60]. Geminal cleavage of silicon substituents from the parent ion was remarked on in both of these and was attributed to low Si-C and Si-H bond energies [59].

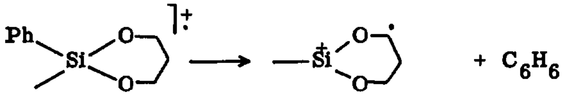


(R^1R^2 = HMe, Me_2 [59]; MePh, Ph_2 [60])

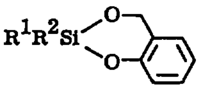
The preferred sequence of cleavage was H $>$ Me $>$ Ph [60]. Other silicon-containing, and hydrocarbon, rearrangement ions were identified for the phenyl-substituted compounds.

Lageot and Guillemonat [61] recorded spectra for five 4,4,5,5-tetramethyl-1,3,2-dioxasilacyclopentanes and concluded that the presence of two oxygen atoms simplified noticeably the number of fragmentations, as compared to those of silacyclopentanes themselves. Various fragmentations were proposed.

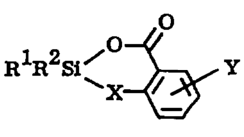
Based on the spectra of sixteen 2-phenyl-1,3,2-dioxasilacyclohexanes, loss of a benzene molecule from the parent ion ($^m/e$, M-78) has been established as an important common fragmentation process for these heterocycles [62]. The elimination is believed to involve hydride migration from the ring.



Principal ions and proposed fragmentation patterns for derivatives of 2-hydroxybenzyl alcohol [63] and salicylic acids [11] have been reported.

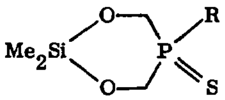


(R^1R^2 = Me_2, Ph_2)



(R^1R^2 = Me or Ph; X = O,S or NMe; Y = H,Me,OMe or Cl)

Also, principal ions in the mass spectra of some 2,2,5-triorgano-1,3,2-dioxasila-5-phosphorinane-5-sulphides [64].



(R = Me, Et, iPr or Ph)

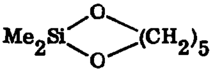
4. Chemical Properties

A. Nature of Products

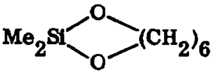
i) The majority of monomeric products which have been reported are 6- and 7-membered (Tables 2 and 3). Stable 5-membered rings cannot be obtained from many 1,2-diols [2,3,8,14,15,65] and those consisting of 8-10 atoms are decreasingly few in number. The claim of Krieble and Burkhard [2] that ring sizes of up to 11 atoms are easy to prepare must be qualified by emphasizing that their heterocycles of 8 or more ring atoms contained more than two oxygens and an attempted synthesis of 2,2-dimethyl-1,3,2-dioxasilacyclononane yielded linear polymer only.

Nearly all the large rings, of 8 or more atoms, reported since then have contained other heteroatoms or large ring-substituents (Tables 4 and 5). It is noteworthy that only two, simple, 1,3,2-dioxasilacycloalkanes of more than 7 ring atoms have appeared in the literature;

i.e.



and



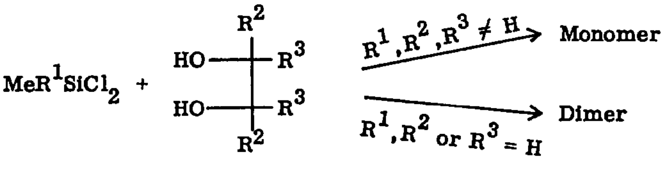
[3,22]

Voronkov and Romadan [3] stated that ring sizes of 8 or more atoms could only successfully be obtained by the base-catalysed thermal depolymerization of initially formed, polymeric product. Our own, very limited, attempts to prepare these larger rings have failed and it must be concluded at this time that the stability of 1,3,2-dioxasilacycloalkanes decreases markedly above a ring size of 7 atoms. Stability appears to be conferred by the introduction of oxygen [2] or nitrogen as heteroatoms and by the incorporation of aromatic substituents into the ring itself (Tables 4 and 5).

ii) Five-membered rings have received by far the most attention with respect to both the nature of the products and factors determining their formation. Krieble and Burkhard [2] first noted that ethylene glycol could not be made to form monomeric 2,2-dimethyl-1,3,2-dioxasilacyclopentane. Instead the dimer was obtained which polymerized further on standing, although depolymerization was easily effected at 130-150°C to yield the dimer once more.

Calas and Nicou (1959) [8] reacted methyl- and dimethyl-dichlorosilanes with a number of substituted 1,2-diols in order to investigate the effect of steric interactions on the nature of products. Their results indicated that dimer formation was to be expected unless both the silicon and functional-carbon atoms were fully substituted, as in the reaction between dimethyldichlorosilane and different pinacols, when monomers were obtained.

i.e.



These findings were rationalized on the assumption that dimer would be the preferred product, owing to ring strain in the monomer, and that monomeric products could only be expected when steric interactions between substituents prevented dimer formation (shown to be likely by space-filling, molecular models). This view was later reiterated by Voronkov and Romadan [3] who also pointed out that geminal substitution should, according to the Thorpe-Ingold hypothesis, cause ring compression thus stabilizing the monomer.

Other work, in addition to our own,has broadly supported these conclusions though it is clear that no hard-and-fast rule can be applied when the diol is only partially substituted. Hence Sprung [14] and Voronkov and Romadan [3] both obtained monomeric 2,2,4,4-tetramethyl-1,3,2-dioxasilacyclopentane when freshly distilled, the former noting that the product polymerized on standing. When dialkyl- and diphenyl- dichlorosilanes were reacted with butan-2,3-diol [3] monomeric products, which dimerized rapidly after distillation, were obtained in each case. These examples illustrate an important aspect of the nature of 1,3,2-dioxasilacyclopentanes and it should be realized that physical constants given in the literature for an ostensibly monomeric product cannot necessarily be taken to imply that the monomer is stable, particularly when the diol fragment is only mono- or disubstituted.

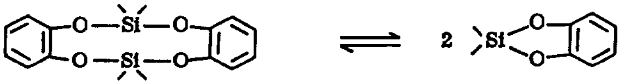
Frye [15] has shown that similar considerations apply to spirosilicates derived from 1,2-diols. Hence ethan-1,2-diol and 2-methylpropan-1,2-diol gave undistillable polymeric products whilst the pinacol derivative was obtained as monomer, by recrystallization. He also makes the important general point that these reaction mixtures can involve an equilibrium (in the presence of catalysts at least) and that the position of equilibrium will be shifted as monomer is removed by distillation. Applied to the discussion above this explains the isolation of unstable, monomeric products by distillation. It is also worth stating that, for the same reason, 1,3,2-dioxasilacyclopentanes in general cannot be unambiguously characterized by mass spectrometry.

Recent reports of monomeric 1,3,2-dioxasilacyclopentanes containing one [28] or no [58] ring-carbon substituents must therefore be viewed with some scepticism, though it may be that the relatively large, single, substituents at ring-carbon or silicon atoms stabilized the monomer in these cases.

1,3,2-Dioxasilacyclopentan-4-ones, prepared by the reaction of α-hydroxy acids with diethylsilane in the presence of a nickel catalyst, appear to be exceptionally stable as monomers [37].

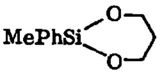
In a different approach to the problem of predicting the nature of products formed in reactions between dichlorosilanes and diols, Pommier, Calas and Valade (1968) [65] related the degree of polymerization of product to the intra-molecular bonding between hydroxyl groups in the parent diol, as assessed by an infra-red absorption technique. If the bonding was strong a monomeric, and if weak a dimeric (or polymeric), product was indicated. Whilst the findings were generally consistent with this rule, the method does not appear to offer any particular advantage over considerations already discussed above.

iii) A special case of 5-membered heterocycles are the (1,2-phenylenedioxy)-silanes and these have received considerable attention. Products have sometimes been reported as being either monomeric [3,4,10,66] or dimeric [7,66, 67] but it has been realized by several workers that a reversible dissociation of dimer into monomer takes place at elevated temperatures [8,54-57].

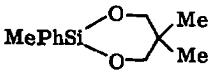


Freshly distilled samples are therefore likely to be characterized as monomers whereas recrystallization affords dimers. Our own results are fully consistent with such an equilibrium and indicate that dimer stability is also affected by substitution at silicon. The dimers show no signs of polymerizing further.

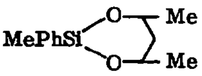
iv) The possibility of dimeric products being formed in the case of 6- and 7-membered rings seems to have been largely ignored. Presumably it has been assumed that since these should be relatively strain-free systems products should, as a matter of course, be monomeric (as is usually the case). However we have recently reported the preparation and properties of some dimeric 2,2-diphenyl-1,3,2-dioxasilacycloheptanes [43]. We have also observed that dimerization occurs in certain 1,3,2-dioxasilacyclohexanes, e.g. methylphenyl-1,3,2-dioxasilacyclohexane [73]. For the latter, stability is conferred on the monomer by substituents on ring-carbons, those at the 4- and 6- positions being more effective than at the 5- position. Hence, of the following compounds I was difficult to prepare in good yield and gradually polymerized on standing, II was readily prepared but dimerized on standing and III was readily prepared as a stable monomer.



I



II



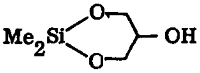
III

A corresponding stabilizing effect of alkyl substituents in spirosilicates derived from diols has been investigated [15] and it was similarly shown that substituents on the functional carbons of the diol produced the greatest effect.

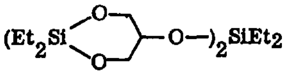
v) Some cyclic derivatives of polyols have been reported. The spiro compound IV has been made from pentaerythritol [3,19,24].

IV

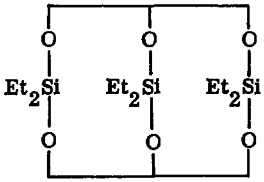
Glycerol can be made to form the cyclic monomer V which readily polymerizes [3,68] and a compound which could either have the structure VIa or VIb [24].



V

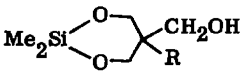


VIa



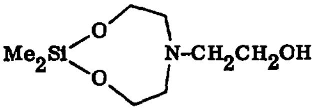
VIb

The (hydroxyalkyl)-substituted compounds VII [18] and VIII [32] have been prepared from their respective triols.



(R = Me, Et or pentyl)

VII



VIII

B. Thermal and Hydrolytic Stability

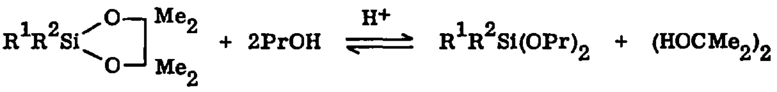
Monomers have generally high thermal stabilities, as evidenced by boiling points of up to 300°C (see Tables).

It is well known that these compounds hydrolyse, even on exposure to moist air, though the apparent rate can vary considerably and, for example, 2,2'-dihydroxybiphenyl derivatives required refluxing with alcoholic potassium hydroxide [66]. No quantitative studies appear to have been undertaken. We have found that, typically, a residual liquid product left in a pipette will hydrolyse completely in a matter of hours to leave a white, solid residue.

Hydrolysis regenerates the parent diol [65,66], hydroxyketone [12] or hydroxy acid [37,38]. The configuration of a diol fragment should be retained during hydrolysis [2] and Pommier et al. [65] were able to separate cis- and trans-isomers of cyclohexan-1,3-diol in this way by first preparing the respective monomeric and polymeric products from the mixed diol.

C. Kinetic Studies

i) Bøe (1972) [5] carried out a detailed investigation into the mechanism of the acid-catalysed propanolysis of 4,4,5,5-tetramethyl-1,3,2-dioxasilacyclopentanes, propanol being in large excess.

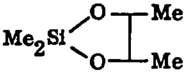


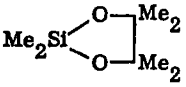
$(R^1R^2 = Me_2, Et_2, Pr_2, MePh)$

The reactions were found to obey a first-order rate law, the rate also being proportional to concentration of acid catalyst.

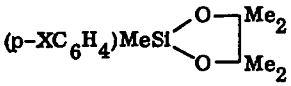
Ring opening is fast, followed by a rate-determining step for which a bimolecular mechanism was proposed.

Rate constants decreased with the size of alkyl groups in the order Me > Et > Pr.

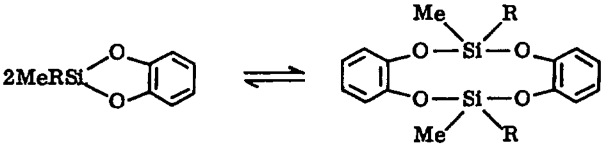
Semi-quantitative data for the propanolysis of  showed it to be considerably more reactive than

 demonstrating that tertiary carbons β to silicon greatly reduce the rate of alcoholysis.

Rate constants for the acid-catalysed propanolysis of

 (X = F, Cl, Br, H, Me, MeO) followed the Hammett equation (log $^{k}/k_{o}$ = $-0.41\ \sigma^{o}$), showing the rate to be slightly increased by electron-donating para-substituents.

ii) The reversible dimerization of (1,2-phenylenedioxy)silanes has been the subject of three studies:



(R = Me [55,56]; R = Ph [57])

The kinetics for the dimethyl compound could be described by a bimolecular dimerization and monomolecular backreaction [56]. A low activation energy for the dimer formation was remarked on; ΔG^{o}_{298} (-9.6 kJ mol^{-1}) and ΔH^{o}(-43 kJ mol^{-1}) and other kinetic parameters were given.

Possible transition states and 10-membered heterocyclic structures were proposed.

For the methylphenyl compound it was established that monomer and dimer (2 isomers) were in equilibrium in solution, the extent of dimerization being dependent both on concentration and temperature. ΔH^o for the dimerization appears to be given as $-31.4\ \mathrm{kJ\,mol^{-1}}$.

5. Application

The following examples of possible uses of 1,3,2-dioxasilaheterocycles have appeared in the literature: as heat transfer media [13,69], hydraulic fluids [13,15,69,70], lubricants [13,70], insect repellants [70], anticholesteremics and antihypercholesteremics [30, 32], release agents [18,68], for dispersibility improvement of titanium dioxide pigments [71] and as intermediates in organic synthesis [33].

6. Tables of Compounds

Notes

i) Within each Table, compounds are ordered according to the following priorities:

- a) Increasing size of the smallest substituent at silicon involving a Si-C bond. Examples of compounds with no Si-C bonds are placed at the end.
- b) Increasing size of second substituent at silicon.
- c) Increasing number and size of ring-carbon substituents.
- d) Increasing number of unsaturated bonds in the ring.
- e) Increasing number of ring heteroatoms.

ii) Dimers are entered in the Table of the corresponding monomers and are signified by 'D' after the formulae.

iii) Symbols and Abbreviations

Me	methyl
Et	ethyl
Pr	propyl
Bu	butyl
Ph	phenyl
n	normal
i	iso
t	tertiary
p	para
d	density (d_4^{20} unless stated)
n	refractive index (n_D^{20} unless stated)
IR	Infra-red spectroscopy
UV	Ultra-violet spectroscopy
DM	Dipole moment
NMR	Nuclear magnetic resonance spectroscopy
MS	Mass spectroscopy

Table 1 5-membered monomers, 8- and 10-membered dimers.

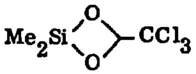
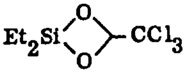
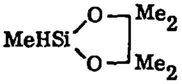
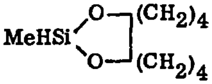
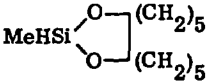
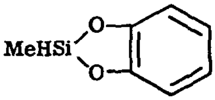
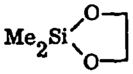
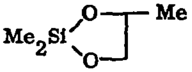
Compound		Method	b.p. (^{o}C/mm) (m.p., ^{o}C)	Other data	Ref.
	D	A	(124-40)	-	72
	D	A	122-8/0.001	-	72
	D	A	103/15	-	8
	D	A	175/0.5 (approx 50)	-	8
	D	A	(104)	-	8
		A	-	MS	59
	D	A,C	178 (55)	d, 1.0585 n, 1.4388	2
"	D	C	(53-4)	-	14
"	D	E	78-80/10 (56)	-	22
"	D	C	181/770 84-6/10	n, 1.4379	3
"	D	G	177-8 (54)	-	26
"	D	A	-	IR	53
	D	E	160-2.5/761.5	d, 1.0067 n, 1.4300	22
"	D	A	160/765	n, 1.4323	3
"	D	G	162-3	n, 1.4310	25,26
"		A	150-60/atm	^{13}C, $^{29}SiNMR$; MS	73

Table 1 (cont'd)

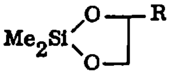
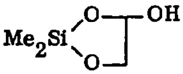
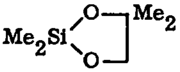
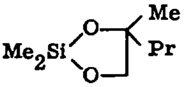
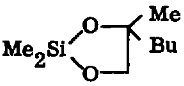
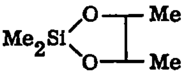
Compound	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
	H		IR, ^{1}HNMR	28
R = CH_2Cl		96-8/11 (25)	n, 1.4674	
CH_2Br		106-8/14	1.4858	
CH_2I		117/13	1.5270	
CH_2OMe		93-4/13	1.4440	
CH_2OEt		105/16	1.4412	
CH_2OnPr		110-1/13	1.4425	
CH_2OnBu		118-20/14	1.4445	
CH_2OiBu		117-8/14	1.4415	
CH_2OCH_2Ph		104/0.04	1.5113	
CH_2OPh		164-7/12 (98)	1.5190	
 D	-	-	-	74
	A	125.5-7.0/755	n, 1.4285	14
	A	127/762	n, 1.4285	3
	-	200	-	78
	-	92-3/10	-	78
	C	61.5-2.5/63	n, 1.4272	3
"	A	120-6/atm	^{13}C, ^{29}SiNMR;MS	73
"	C	140	-	78

Table 1 (cont'd)

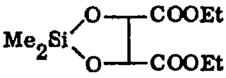
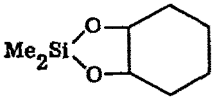
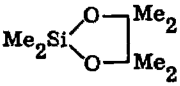
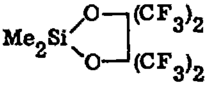
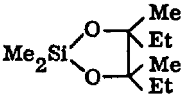
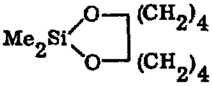
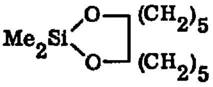
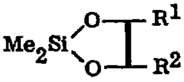
Compound	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
	H	54-6/0.005	-	28
 trans D	A	(110)	-	8
cis	A	46-7/1.3	d, 1.0298 n, 1.4560	65
	A,C	152/760	n, 1.4220	3
"	A	148-52/atm	^{13}C, ^{29}SiNMR;MS	73
"	A	152-3	-	75
"	G	157-9	n_D^{25}, 1.4207	76
"	-	151/762	n_D^{25}, 1.4219	77
"	A	-	IR	53
"	-	-	MS	61
	B	148-9	n_D^{25}, 1.3342	13
	-	74/20	n_D^{21}, 1.4341	78
	-	74/20; 194-5	-	79
	A	(53)	-	8
	A	(61)	-	8
	K	-	IR, ^1HNMR	35
R^1,R^2=Me,Et,nPr or iPr				

Table 1 (cont'd)

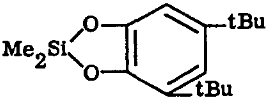
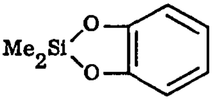
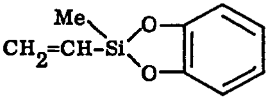
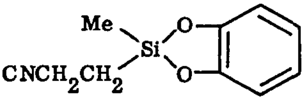
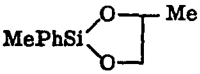
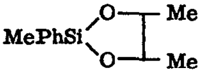
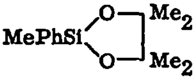
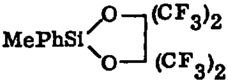
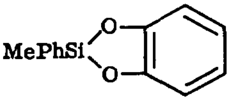
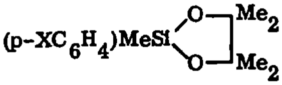
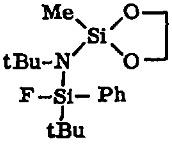
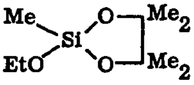
Compound	Method	b.p. ($^oC/mm$) (m.p., ^oC)	Other data	Ref.
	K	-	-	35
	A	108-10/17	-	10
"	A	108/15	-	4
"	A,C	71/3; 211/754	n, 1.5325	3
"	A	–	MS	59
" D	A	(96)	-	8
" D	A	120/12 (93)	^{1}HNMR, dimerization kinetics	55,56
" D	A	97-100/5-7 (71-2)	-	67
" D	A	82/0.5 (84-8)	$^{13}C, ^{29}SiNMR$;MS	73
" D	A	-	IR	54
 D	A	113.5-15/5-6 (74)	-	67
 D	A	196-7/5-6 (90)	-	67
 D	A	104-48/atm	$^{13}C, ^{29}SiNMR$;MS	73
	C	80-90/0.2	"	73
	A	84/0.2	"	73
"	-	122-4/13	-	78

Table 1 (cont'd)

Compound	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
"	A	-	Mechanism of propanolysis	5
"	-	-	MS	61
	B	207	n_D^{25}, 1.4007	13
	A	(103.5)	MS	60
" D	A	152/1	-	7
" D	A	123-5/1-2 (109)	-	67
" D	A	cis (105) trans (121) mixed (100-10)	IR, ^{1}HNMR, Dimerization kinetics	57
" D	A	110-20/0.1 (109-15)	^{13}C, ^{29}SiNMR;MS	73
				
X = F, Cl, Br	-	-	MS	61
X = F, Cl, Br, Me, MeO	A	-	Mechanism of propanolysis	5
	*	92/0.01	^{1}H, ^{19}F, ^{29}SiNMR	58
	-	180-4	n, 1.4165	78

*Fluorosilyl-substituted disilazane + $(CH_2ONa)_2$

Table 1 (cont'd)

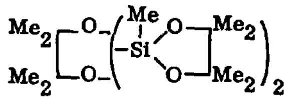
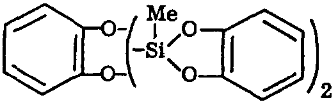
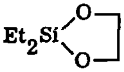
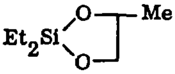
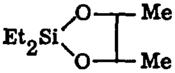
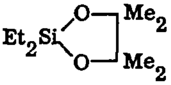
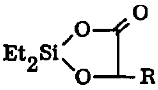
Compound	Method	b.p. (^oC/mm) (m.p., ^oC)	Other data	Ref.
	-	140/0.4 (38-40)	-	78
	A	240/17	-	10
 D	A,C	204.5/762	n, 1.4481	3
 D	A	178-9	n, 1.4430	3
	A	172-3/758	n, 1.4412	3
	A	194-6/760	n, 1.4350	3
"	A	-	Mechanism of propanolysis	5
	L		-	37
R = pentyl		133-4/6		
hexyl		134-5/2		
heptyl		139-42/2		
octyl		144-5/2		
nonyl		149-50/2		
t-pentyl		121-3/4		
1-methylpentyl		134-5/8		
phenyl		152-5/7		
p-tolyl		170-2/10		

Table 1 (cont'd)

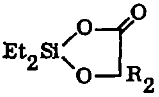
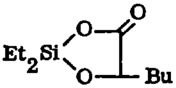
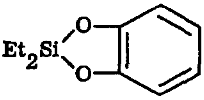
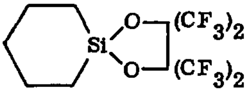
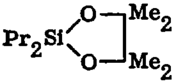
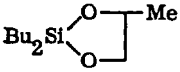
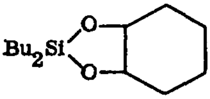
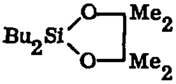
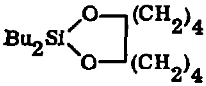
Compound	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
o-tolyl		160-2/8		
2,5-xylyl		175-7/5		
mesityl		180-3/5		
				
R = o-tolyl		218-20/5		37
	L	128-30/6		39
 D	A	99-102/5-6	d, 1.1223 n, 1.5286	67
	B	55-6/0.18	n_D^{25}, 1.3706	13
	A	-	Mechanism of propanolysis	5
 D	A	77-80/0.7	d, 0.9315 n, 1.4490	65
 cis D	A	113/0.5	d, 0.9692 n, 1.4670	65
	A	135-7/30	d, 0.9006 n, 1.4395	65
	A	113/0.4	d, 0.9656 n, 1.4732	65

Table 1 (cont'd)

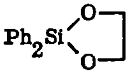
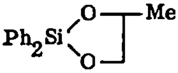
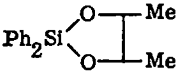
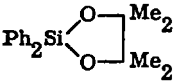
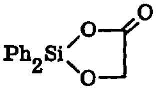
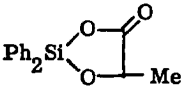
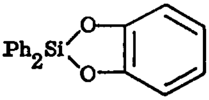
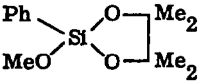
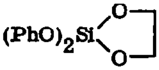
Compound	Method	b.p. (^{o}C/mm) (m.p., ^{o}C)	Other data	Ref.
 D	A	210-5/10	-	3
 D	A	186-8/6	-	3
" D	A	(130-44)	^{13}C, ^{29}Si NMR;MS	73
	A	171-4/6.5	-	3
"	-	-	^{13}C, ^{29}Si NMR;MS	73
	A	160/0.2 (172-85)	"	73
	A	150-6/0.3	^{29}Si NMR;MS	73
	A	150/0.3	"	73
	A	(162.2-3.5)	-	66
"	A	(170.7)	MS	60
" D	A	203-8/1-2	-	67
" D	A	(126-30)	^{13}C, ^{29}Si NMR;MS	73
	C	85/0.15	n_D^{25}, 1.4890; ^{1}H NMR	15
 D	A	235-40/0.1	-	80

Table 1 (cont'd)

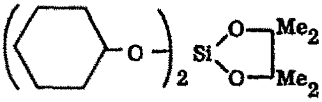
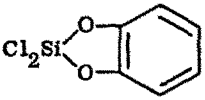
Compound	Method	b.p. (^{o}C/mm) (m.p., ^{o}C)	Other data	Ref.
	A	128/0.2		80
	A	-	-	81

Table 2 6-membered monomers

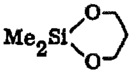
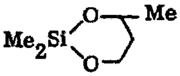
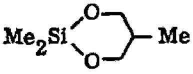
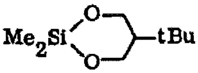
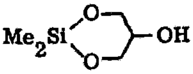
Compound	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
	C	121.7	d, 0.9703 n, 1.4120	2
"	A,C,F	122/763	n, 1.4130	3
"	D	123/752	d, 0.9701 n, 1.4118 ^{1}H NMR	21
"	A,C	122/760; 35/22	n, 1.4132; ^{1}H NMR	48
"	C	114/atm	^{13}C,^{29}Si NMR;MS	73
"	-	-	^{1}H NMR	45,46
"	-	-	^{1}H NMR;DM	47
"	A	-	IR	53
	C,F	39/7;119-21/758	n, 1.4107	3
"	G	122-3/atm	^{13}C,^{29}Si NMR;MS	73
"	-	150/783	n, 1.4172	77
	A,C	29/8	n, 1.458; ^{1}H NMR	48
	A	69-71/9.5	n, 1.4373, ^{1}H NMR	48
	C	67-8/7	n, 1.434	48
	C	147/18	n, 1.4554	3
	H	112-29/4	d_4^{25}, 1.117-1.113 n_D^{25},1.4387-1.4452	68
	A	-	-	71

Table 2 (cont'd)

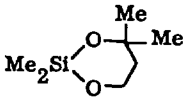
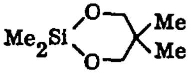
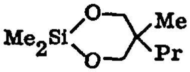
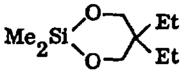
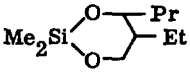
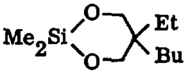
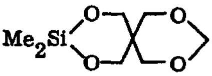
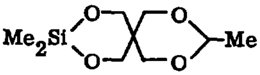
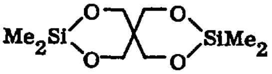
Compound	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
	D	139/754	d, 0.9421 n, 1.4213	21
	C	144-5/762	n, 1.4272	3
"	A	24-5/5	n, 1.417	9
"	A	142-5/atm	^{13}C, ^{29}Si NMR;MS	73
"	C	140	-	78
"	A	-	^{1}H NMR	45
"	-	-	^{1}H NMR	46
"	A	-	IR	53
	A	37-9/2	n, 1.429	9
	A	45/3	n, 1.434	9
	C	203	n, 1.4325	78
	A	72-3.5/4	n, 1.438	9
	C	126-36/10	-	78
	E	(64)	-	23
	C	244-5/751	-	3
	C	230-40/atm (135)		19

Table 2 (cont'd)

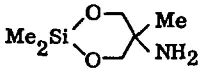
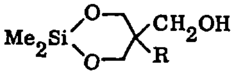
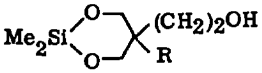
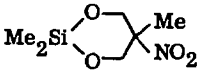
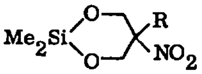
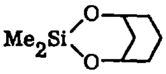
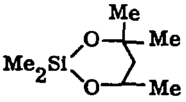
Compound	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
	E	243-5/749 (136)		24
	C	67-9/9	-	3
"	-	-	^{1}H NMR	46
"	-	-	^{1}H NMR;DM	47
 (R=Me,Et,pentyl)	A	-	-	18
 (R=Me,Et)	A	-	-	71
	C	109-10/12	-	3
"	-	-	^{1}H NMR	46
 (R=Me,Et,nPr,nBu,n-pentyl)	E	-	DM, stereochemistry	44
 (cis)	A	46-7/1.3	d, 1.0298 n, 1.4560	65
	D	146/749	d, 0.9363 n, 1.4263	21
	A	136-40/atm	^{13}C,^{29}Si NMR;MS	73
	-	142-4	n, 1.4110	78

Table 2 (cont'd)

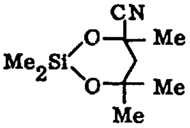
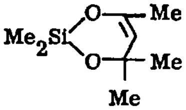
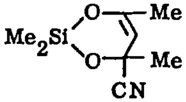
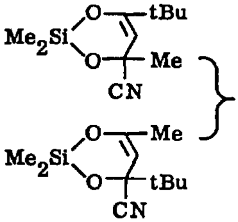
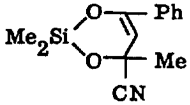
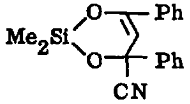
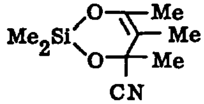
Compound	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
	I	63-4/8	IR; ^{1}H NMR	33
	I	56-8/38	"	"
	I	87-90/20	"	"
 mixture	I	108-10/23	"	"
	I	101-4/0.3	"	"
	I	(68.5-70.0)	"	"
	I	101-3/26	"	"

Table 2 (cont'd)

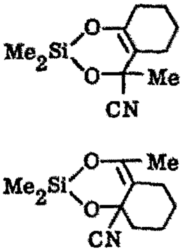
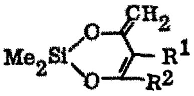
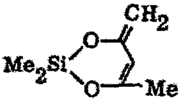
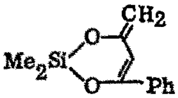
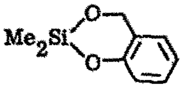
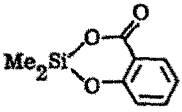
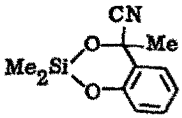
Compound	Method	b.p. (^oC/mm) (m.p., ^oC)	Other data	Ref.
 mixture	I	109-11/7	"	"
	B	–	six compounds	12a
	J	74-6/50	n, 1.4671; IR; ^{1}H NMR	34
	J	74-6/1	n, 1.5601; ^{1}H NMR	34
	A	52-4/0.05	n_D^{25}, 1.5119; MS	63
"	A	89/10	IR; ^{1}H NMR	82
	A	119/14 (62)	IR; ^{1}H NMR	6
	A	85-115/0.1	^{13}C, ^{29}Si NMR; MS	11,73
	I	77-8/0.35	IR; ^{1}H NMR	33

Table 2 (cont'd)

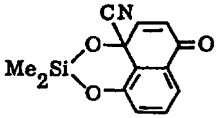
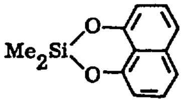
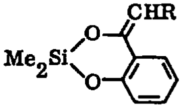
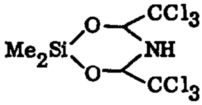
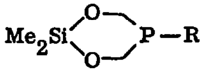
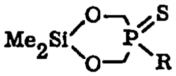
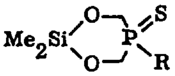
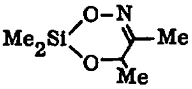
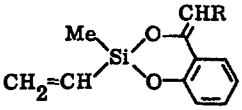
Compound	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
	I	(132-4)	"	"
	A	(53.5-5)	-	7
	B			12
R = H		80/0.2	n, 1.5371	
Me		80/0.2	n, 1.5358	
Et		81/0.5	n, 1.5296	
	-	108-13/1	-	84
	-	-	^{1}H, ^{13}C, ^{31}P NMR	49
R = Me	A	52/10	d, 1.0544 n, 1.4802	16
	C	58-9/11	d, 1.0540 n, 1.4800	16
Et	A	29.5-30/1.5	d, 1.0262 n, 1.4733	16
	C	57-9/6	d, 1.0260 n, 1.4732	16

Table 2 (cont'd)

Compound	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
Pr	C	71/6	d, 1.0354 n, 1.4789	16
iPr	A	28.5-29/1	d, 1.0018 n, 1.4714	16
Ph	C	93-6/1.5	-	16
"	-	-	^{1}H NMR;DM	52
"	-	-	UV	83
	*		^{31}P NMR;MS	64
R = Me		(93-5)		
Et		(85-7)		
iPr		(111-2)		
Ph		(80-1)		
 (R=Me,Pr,iPr)	-	-	DM	50
	G	120/0.1	IR, ^{1}H NMR	84a
	B			12
R = H		79/0.4	n, 1.5461	
Me		88/0.9	n, 1.5454	
Et		87/0.5	n, 1.5362	

* Elementary sulphur + parent heterocycle

Table 2 (cont'd)

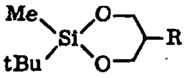
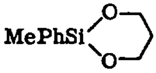
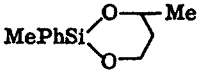
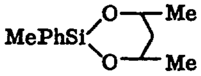
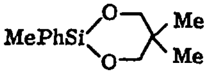
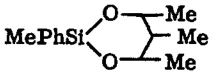
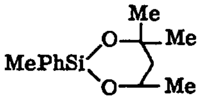
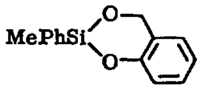
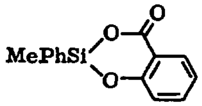
Compound	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
	A or C		^{1}H NMR	48
R = H		38/30		
Me		60-1/16		
	A/C	70-5/0.25	^{13}C, ^{29}Si NMR;MS	73
"	A	-	^{1}H NMR	45
	A	76-8/0.1	^{13}C, ^{29}Si NMR;MS	73
	A	90/1.2	"	"
	A	82-4/0.2	"	"
"	A	-	^{1}H NMR	45
	A	86-93/1.0	^{13}C, ^{29}Si NMR;MS	73
	A	80-4/0.2	"	"
	A	120-4/0.2	"	"
	A	150-60/0.1	^{13}C, ^{29}Si NMR;MS	11,73

Table 2 (cont'd)

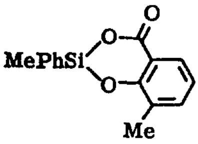
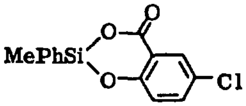
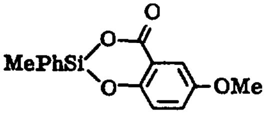
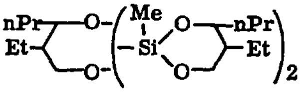
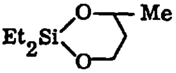
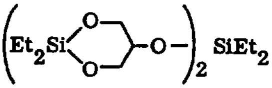
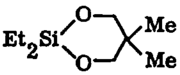
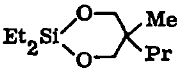
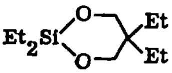
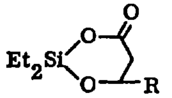
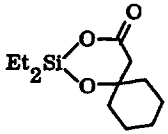
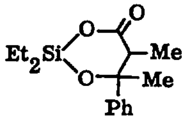
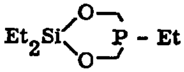
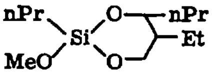
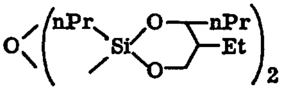
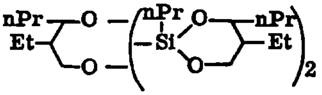
Compound	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
	A	169/0.25	"	11,73
	A	160-5/0.1	"	11,73
	A	160-70/0.1	"	11,73
	C	170/0.5 (-50)	-	15,70
	E	53-53.7/7	d, 0.9350 n, 1.4262	22
 (1 of 2 possible structures)	E	230-3/14	d, 1.0521 n, 1.4605	24
	A	46/5	n, 1.4333	3
	A	42-3/3	n, 1.433	9
	A	64-6/4	n, 1.440	9
	A	72-4/4	n, 1.444	9

Table 2 (cont'd)

Compound	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
	L			38
R = iPr		130-1/5	d, 0.9992 n, 1.4430	
iBu		134-5/5	d, 0.9867 n, 1.4440	
heptyl		163-5/10	d, 0.9601 n, 1.4475	
Ph		176-8/8	-	
	L	142-5/5	-	38
	L	188-91/8	-	38
	C	84-6/7	d, 1.0146 n, 1.4778	16
	C	114/10	$n_D^{25.8}$, 1.4339	15
	*	155/0.5	$n_D^{25.8}$, 1.4475	15
	C	185/0.3 (-63)	n_D^{25}, 1.4525	15,70

* hydrolysis of compound immediately above

Table 2 (cont'd)

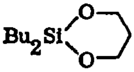
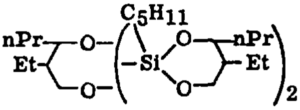
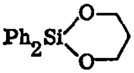
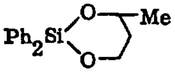
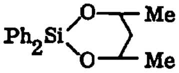
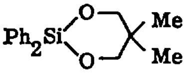
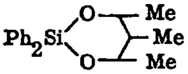
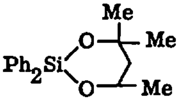
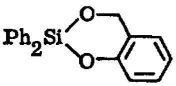
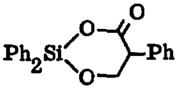
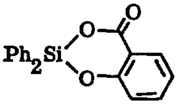
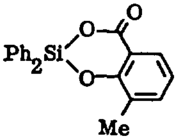
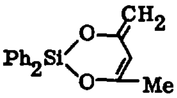
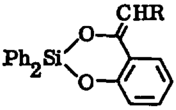
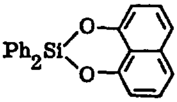
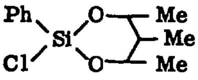
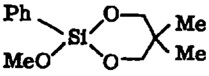
Compound	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
	A	87/2	d, 0.9132 n, 1.4451	65
"	A	"	IR	53
	C	180/0.05 (-62)	$n_D^{25.4}$, 1.4550	15,70
	A	125/0.01	^{13}C, ^{29}Si NMR;MS	73
	A	-	^{1}H NMR	45
	-	-	^{13}C, ^{29}Si NMR;MS	73
	A	(42-50)	"	73
	A	149-50.5/2.5 (63-4)	-	9
"	-	-	^{13}C, ^{29}Si NMR;MS	73
"	A	-	^{1}H NMR	45
	-	-	^{13}C, ^{29}Si NMR;MS	73
	-	-	"	73
	A	166-8/0.05	n_D^{25}, 1.6043;MS	63
"	A	163-72/0.3	^{13}C, ^{29}Si NMR;MS	73

Table 2 (cont'd)

Compound	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
	A	(145-54)	^{29}Si NMR;MS	73
	A	188-95/0.4	^{13}C,^{29}Si NMR;MS	11,73
	A	198/0.2	"	11,73
	B	-	-	12a
	B			12
R = H		-	n, 1.6118	
Me		-	n, 1.6026	
Et		-	n, 1.5747	
	A	(110-11)	-	7
	A	118-22/0.2	^{13}C,^{29}Si NMR	73
	*	95/0.05	"	73

*from compound of type immediately above + MeOH

Table 2 (cont'd)

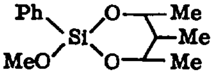
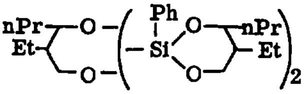
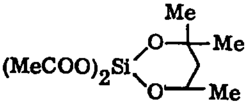
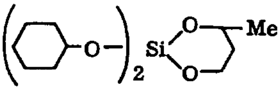
Compound	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
	as above	108/0.1	^{13}C, ^{29}Si NMR	73
	C	250/0.01 (-33)	n_D^{24}, 1.5022	15,70
	E	88-92/0.4-0.6	-	85
	A	188-90/10	-	80

Table 3 7-membered monomers, 14-membered dimers.

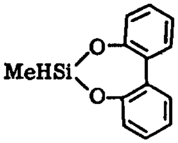
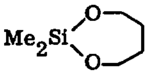
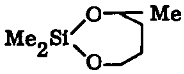
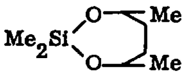
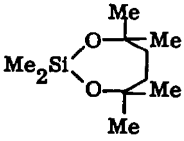
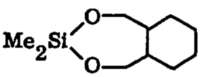
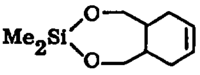
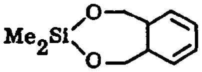
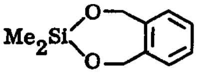
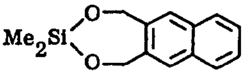
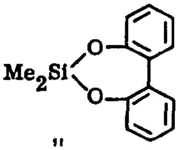
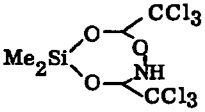
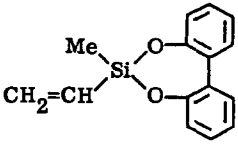
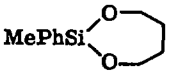
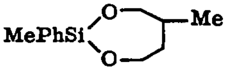
Compound	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
	-	120-5/1	-	78
	C	142	n, 1.4218	2
"	C	142-4/758	n, 1.4220	3
"	E	145-7/751	d, 0.9622 n, 1.4222	22
"	G	142-3	n, 1.4220	25
"	G	142-3	n, 1.4219	26
"	G	104-24/atm	^{13}C,^{29}Si NMR;MS	73
"	C	143/734	d_{17}, 1.0059	86
"	A	-	IR	53
	C	145/746	n, 1.4258	3
"	A	26/1.0	^{13}C,^{29}Si NMR;MS	73
	G	23/0.1	"	73
	C	178	-	78
 cis	H	48/0.1	n, 1.4627;IR; ^{1}H NMR;MS	29
trans	H	51/0.1	n, 1.4586; IR; ^{1}H NMR;MS	29
	H	50/0.1	n, 1.4335;IR; ^{1}H NMR;MS	29

Table 3 (cont'd)

Compound	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
	H	77-80/0.1	n, 1.4837; IR;^{1}H NMR;MS	29
	H	113/12	n_D^{24}, 1.5120 IR;^{1}H NMR	27
	H	155/0.1 (117)	IR;^{1}H NMR;MS	29
	A	172.5-3.5/14.5 (35.0-35.5)	n^{22}, 1.5843	66
"	A	136/2.5 (40)*	-	69
"	C	168/12; 180/25 (50)	-	88
"	-	178/24	-	78
	-	(109-10)	-	84
	A	140-1/1.4	-	87
	A	82/6.0	^{13}C,^{29}Si NMR;MS	73
	A	80-8/0.1	"	73

* m.p. values for this and the 2,2-diphenyl compound have been interchanged from original paper since they appeared inconsistent.

Table 3 (cont'd)

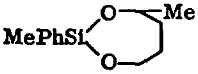
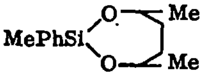
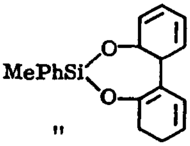
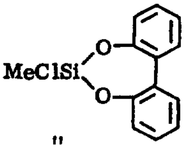
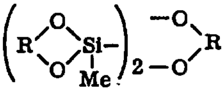
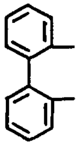
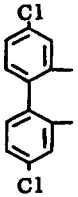
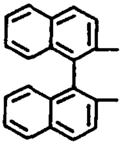
Compound	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
	A	75-80/0.05	"	73
	A	75-8/0.02	"	73
	A	(101.0-101.2)	-	66
"	A	168-76/0.1 (103.5)	^{13}C,^{29}Si NMR;MS	73
	-	230/1.25 (58)		78
"	-	108/0.05		88
	C			88
R = 		300/0.35 (70)		
		(80)		
		(190-220)		

Table 3 (cont'd)

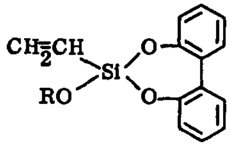
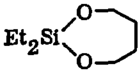
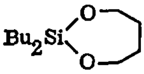
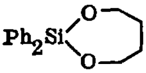
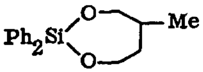
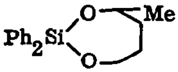
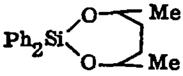
Compound	Method	b.p. (^{o}C/mm) (m.p., ^{o}C)	Other data	Ref.
	A			87
R = octyl		203-4/1.8		
decyl		197-200/1.2		
dodecyl		225-30/0.7		
hexadecyl		265-8/1.0		
Ph		172-4/1.0		
p-tolyl		192-5/1.9		
p-chlorophenyl		185-7/0.7		
	A,C	189/758	n, 1.4371	3
	A	78/1	n, 1.4451	65
"	A	-	IR	53
	A	115-34/0.1	^{13}C, ^{29}Si NMR;MS	73
" D	A	(176-84)	"	73
	A	148-70/0.15	"	73
" D		(154-75)	"	73
	A	125-37/0.05	"	73
	A	130-40/0.1 (55-75)	"	73
" D	A	(155-70)	"	73

Table 3 (cont'd)

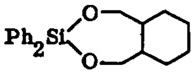
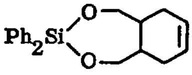
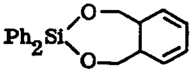
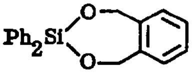
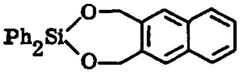
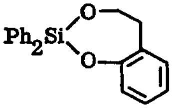
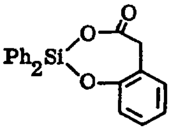
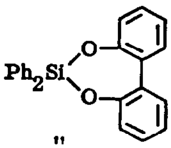
Compound	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
 cis	A	174-82/0.2	"	73
" cis	A	167/0.05 (48)	n, 1.5624; IR; ^{1}H NMR;MS	29
" trans	A	152/0.04 (54)	n, 1.5667; IR; ^{1}H NMR;MS	29
	A	168/0.07 (84)	IR; ^{1}H NMR;MS	29
	A	186/0.1	n, 1.5872; IR; ^{1}H NMR;MS	29
	A	(130.6)	IR; ^{1}H NMR	27
"	A	(129-31)	^{13}C,^{29}Si NMR;MS	73
" D	A	(245-50)	"	73
	A	(207)	"	29
	A	164-74/0.5	^{13}C,^{29}Si NMR;MS	73
	A	188-90/0.1	^{29}Si NMR;MS	73
	A	(120.5-121.5)	-	66
"	A	235-6/0.5 (124)	-	69
"	A	(125-6)	^{13}C,^{29}Si NMR;MS	73

Table 3 (cont'd)

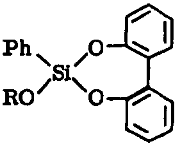
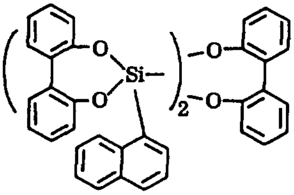
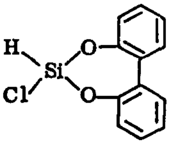
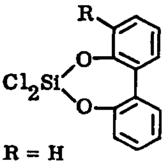
Compound	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
	A		n =	69
R = octyl		230-5/0.8	1.5662	
decyl		241-5/0.8	1.5556	
2-methyl-4-t-hexylphenyl		275-80/1.5	n_D^{70}, 1.5728	
phenyl		228-30/1.5	1.5451	
cyclododecyl		297-302/2.5	n_D^{70}, 1.5615	
1-methyl-4-ethylhexyl		210-6/0.2	1.5488	
1,4-diethylhexyl		220-4/0.3	1.5484	
1-methyl-4-ethyloctyl		226-8/0.3	1.5418	
1,4-diethyloctyl		235-6/0.6	1.5400	
	-	(90)		88
	-	154/6	-	88
				
R = H	A	174/16; 136/1 (48)	-	89
H	A	176-7/16	-	92

Table 3 (cont'd)

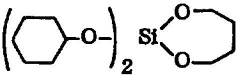
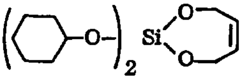
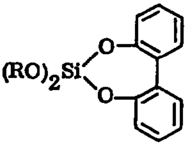
Compound	Method	b.p. ($^{\circ}C$/mm) (m.p., $^{\circ}C$)	Other data	Ref.
Pr	-	155/2	-	93
$CH_2=CH-CH_2-$	-	155/2	-	93
	A	148/1		80
	A	188-9/10		80
	A,C			89,90 91,92
10 compounds R=alkyl or aryl				
e.g. Et	A	153-4/2.5	d_4^{21}, 1.170	89
cyclohexyl	A	226/3.5	-	89
2-diphenyl	A	309-11/4	-	89

Table 4 8-membered monomers.

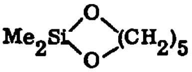
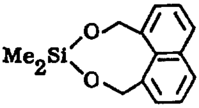
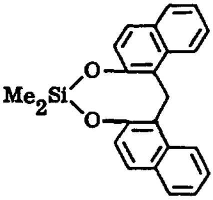
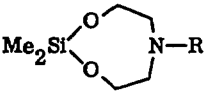
Compound	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
	C	163.5/764	n, 1.4330	3
"	E	46-7/8	d, 0.96664 n, 1.4308	22
	H	148/0.1 (93)	IR; ^{1}H NMR;MS	29
	-	(154-5)	-	88
				
R = H	C	93-4/30	n, 1.4547	3
Me D	C	74-8/10	n, 1.4450	78
Et	C	200/755; 77-8/10	n, 1.4496	3
CH_2CH_2OH	H	-	-	32
Ph	C	(102.5)	x-ray analysis	17
$CH_2CH_2O_2CCHPh_2$	H	-	-	31
$CH_2CH_2O_2CCMe_2O$-  -Cl	H	-	-	30
CHO	C	102-3/3	n, 1.4700	20
$COOSiMe_3$	C	182-4/4	n, 1.4450; ^{1}H NMR	20

Table 4 (cont'd)

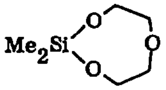
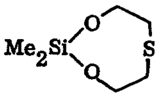
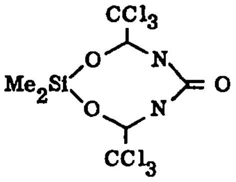
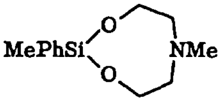
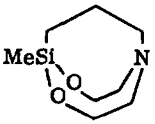
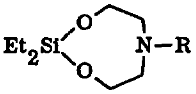
Compound	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
	A,C	90/50	d, 1.0452 n, 1.4331	2
"	C	166.5/761; 89-90/54	n, 1.4338	3
"	D	168	n, 1.4335	25
	G	168	n, 1.4335	26
	C	204.5/756; 102-3/26	n, 1.4858	3
 D	-	(127)	-	84
	C	137-41/10	n, 1.5156	78
	-	-	x-ray diffraction	94
				
R = H D	C	100-3/0.1	n, 1.4611	78
Me	-	-	-	78

Table 4 (cont'd)

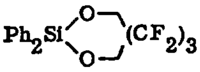
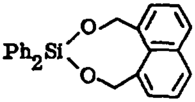
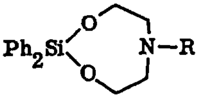
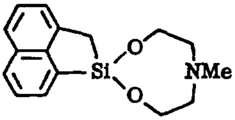
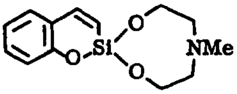
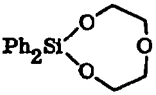
Compound	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
	A	178-80/7 (69-70)		95
	A	(186)	IR, ^{1}H NMR;MS	29
				
R = H	C	(120-3)	-	78
H	-	-	x-ray analysis	41
Me	C	(73)	x-ray analysis	17
Me	C	(65-8)	-	78
tBu	C	(92)	x-ray analysis	17
Ph	C	(86)	x-ray analysis	17
	-	-	x-ray analysis	96
	-	-	x-ray analysis	40
	A	218-28/0.1	^{29}Si NMR	73

Table 4 (cont'd)

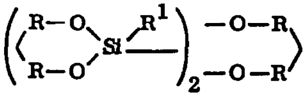
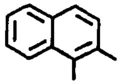
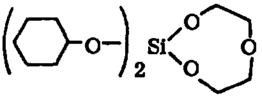
Compound	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
				
R =  R^1 = Me	-	(136-60)	-	88
Ph	-	(100)		88
	A	138-40/0.2		80

Table 5 9- to 11-membered monomers.

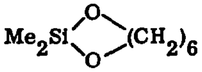
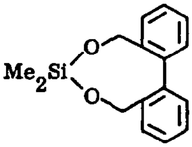
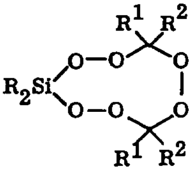
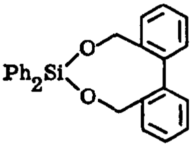
Compound	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
9-				
	C	183.5/764; 52/4	n, 1.4398	3
	E	65-6/6	d, 0.9660 n, 1.4402	22
	H	128/0.1	n, 1.5650 IR; ^{1}H NMR;MS	29
	-	-	-	97
R=Me, R^1=Me, R^2=Et R=Me, R^{1}R^2=(CH$_2$)$_5$ R=Et, R^{1}R^2=(CH$_2$)$_5$				
	A	183/0.07 (101)	IR; ^{1}H NMR;MS	29

Table 5 (cont'd)

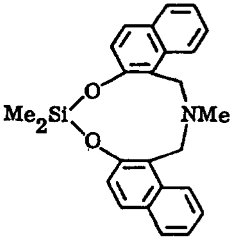
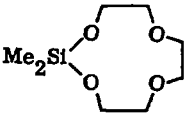
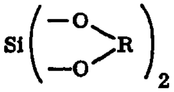
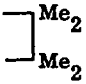
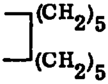
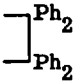
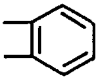
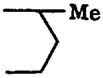
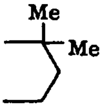
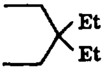
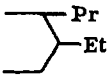
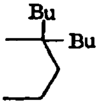
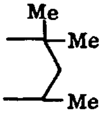
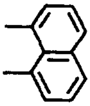
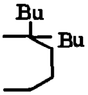
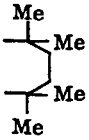
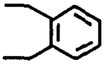
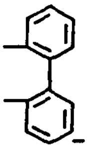
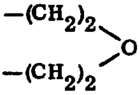
Compound	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
10- 	-	(137-8)	-	78
11- 	A	96/9	d, 1.0704 n, 1.4487	2

Table 6 Representative Spirosilicates.

Compounds	Method	b.p. (°C/mm) (m.p., °C)	Other data	Ref.
				
R = 	A	115-8/15; 238/758 (112)	-	98
"	C	(112)	-	15
"	E	110-15/1.5	-	66
	A	(282)	-	98
	*	(240-5)	-	99
	A	(116)	-	100
	A	-	-	81
	E	118.5/15	n, 1.4412 d, 1.1163	22
	A	115/11.5	-	98
	C	67/2.4	^{1}H NMR	15
	C	130-3/0.8 (61-3)	n_D^{26}, 1.4633	15
	C	134-7/0.8	n_D^{25}, 1.4536	15

*$SiCl_4$ + benzophenone/magnesium

Table 6 (cont'd)

Compound	Method	b.p. (^oC/mm) (m.p., ^oC)	Other data	Ref.
	C	150-5/0.5	n_D^{25}, 1.4631	15
	C	-	^{1}H NMR	15
	C	(73-7)	-	15
	E	66-7/0.3	-	66
	A	(329-31)	-	7
	A	(46)		98
	C	110/4.5	$n_D^{26.5}$, 1.4430	15
	C	153/0.6	-	15
	C	(81-3)	-	15
	C	(159.5)	IR; ^{1}H NMR	27
	A	(313)	-	89
	A	-	-	81
$-(CH_2)_5$	-	108/3 (84-5)	-	101
	A	108/3 (84-5)		98

References

1. M.G. Voronkov, V.M. Dyakov and S.V. Kirpichenko, J. Organometal. Chem., 1982, 233, 1.

2. R.H. Krieble and C.A. Burkhard, J. Amer. Chem. Soc., 1947, 69, 2689.

3. M.G. Voronkov and Yu. P. Romadan, Khim. Geterotsikl. Soedin, 1966, 879.

4. M. Jacovic, Z. anorg. allgem. Chem., 1956, 288, 324.

5. B. Bøe, J. Organometal. Chem., 1972, 43, 275.

6. M. Wieber and M. Schmidt, Chem. Ber., 1963, 96, 1561.

7. C.M. Silcox and J.J. Zuckerman, J. Organometal. Chem., 1966, 5, 483.

8. R. Calas and P. Nicou, Compt. Rend., 1959, 249, 1011.

9. N. Spassky, Compt. Rend., 1960, 251, 2371.

10. S.D. Radosavljevic, M.S. Jacovic and M.D. Dragojevic, Ber. chem. Ges. Beograd., 1955, 20, 273.

11. R.H. Cragg and R.D. Lane, J. Organometal. Chem., 1981, 212, 301.

12. R.M. Ismail, J. Organometal. Chem., 1968, 11, 49.

12a. J.A. Cella and T.D. Mitchell, J. Organometal. Chem., 1983, 244, C5.

13. R.A. Braun, U.S.P. 3,433, 819/1969.

14. M.M. Sprung, J. Org. Chem., 1958, 23, 58.

15. C.L. Frye, J. Org. Chem., 1969, 34, 2496.

16. M.G. Voronkov, N.M. Kudyakov, V.M. D'yakov, V.I. Glukhikh and R.K. Valetdinov, Dokl. Akad. Nauk S.S.S.R., 1979, 247, 609.

17. A. Kemme, J. Bleidelis, I. Urtane, G. Zelchan and E. Lukevics, J. Organometal. Chem., 1980, 202, 115.

18. A. Boeckmann, G. Trenezek, H. Rudolph, W. Wiegreffe and W. Ritter, Ger. Offen. 2, 113, 296/1972.

19. L.W. Breed, W.J. Haggerty, Jr., and J. Harvey, J. Org. Chem., 1960, 25, 1804.

20. V.D. Sheludyakov, N.I. Kirilina, E.L. Kotrikadze, L.M. Khananashvili and A.D. Kirilin, Zh. Obshch. Khim., 1981, 51, 489.

21. V.I. Larionov, R.S. Musavirov, E.A. Kantor, S.S. Zlotskii, D.L. Rakhmankulov and R.A. Karakhanov, Proc. Acad. Sci. (U.S.S.R.), 1980, 255, 532.

22. M.G. Voronkov, V.P. Davydova and B.N. Dolgov, Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk, 1958, 698.

23. M.F. Shostakovskii, A.S. Atavin, E.P. Vyalykh and B.A. Trofimov, U.S.S.R.P., 165, 452/1964.

24. V.P. Davydova and M.G. Voronkov, J. Gen. Chem. (U.S.S.R.), 1958, 28, 1922.

25. K.A. Andrianov, T.K. Dzhashiashvili, V.V. Astakhin and G.N. Shumakova, Zh. Obshch. Khim., 1967, 37, 928.

26. K.A. Andrianov, T.K. Dzhashiashvili, V.V. Astakhin and G.N. Shumakova, Izv. Akad. Nauk S.S.S.R., Ser. Khim., 1966, 2229.

27. L.Birkofer and O. Stuhl, J. Organometal. Chem., 1979, 164, C1.

28. L. Birkofer and O. Stuhl, J. Organometal. Chem., 1980, 187, 21.

29. L. Birkofer, W. Gruner and O. Stuhl, J. Organometal. Chem., 1980, 194, 159.

30. J.B. Fourtillan, J.P. Pometan and R.J.R. Dang, Fr. Demande 2,251, 311/1975.

31. J.B. Fourtillan, J.P. Pometan and R.J.R. Dang, Fr. Demande 2,251, 313/1975.

32. J.B. Fourtillan, J.P. Pometan and R.J.R. Dang, Fr. Demande 2,273, 548/1976.

33. I. Ryu, S. Murai, A. Shinonaga, T. Horiike and N. Sonoda, J. Org. Chem., 1978, 43, 780.

34. B.A. Gostevskii, O.A. Kruglaya, A.I. Albanov and N.S. Vyazankin, J. Organometal. Chem., 1980, 187, 157.

35. W. Ando and M. Ikeno, J.C.S. Chem. Comm., 1979, 655.

36. W. Ando, M. Ikeno and Y. Hamada, J.C.S. Chem. Comm., 1981, 621.

37. I.I. Lapkin, T.N. Povarnitsyna and T. Yu. Subocheva, Zh. Obshch. Khim., 1972, 42, 399.

38. I.I. Lapkin, T.N. Povarnitsyna and T. Yu. Denisova, Zh. Obshch. Khim., 1972, 42, 2032.

39. I.I. Lapkin, T.N. Povarnitsyna and V.V. Dvinskikh, Zh. Obshch. Khim., 1978, 48, 607.

40. O.A. D'yachenko, L.O. Atovmyan, S.M. Aldoshin, T.L. Krasnova, V.V. Stepanov, E.A. Chernyshev, A.G. Popov and V.V. Antipova, Bull. Acad. Sci. U.S.S.R., 1974, 2561.

41. J.J. Daly and F. Sanz, J.C.S. Dalton, 1974, 2051.

42. F. Dahan and Y. Jeannin, J. Organometal. Chem., 1979, 171, 283.

43. R.H. Cragg and R.D. Lane, Inorganica Chimica Acta, 1981, 54, L115.

44. T. Urbanski, D. Gurne, R. Kolinski, H. Piotrowska, A. Jonczyk, B. Serafin, M. Szretter-Szmid and M. Witanowski, Nitro Compds., Proc. Intern. Symp., Warsaw 1963, 195 (Publ. 1964).

45. D.G. Hellier, Chem. and Ind., 1970, 1323.

46. M.G. Voronkov, V.A. Pestunovich and Yu.P. Romadan, Khim. Geterotsikl. Soedin., 1969, 178.

47. L.K. Yuldasheva, R.P. Arshinova, Yu. Yu. Samitov, J. Romadans and M.G. Voronkov, Izvest. Akad. Nauk S.S.S.R., Ser. Khim., 1974, 323.

48. P. Albriktsen and S. Heggelund, Acta Chem. Scand., (B), 1974, 28, 573.

49. V.I. Glukhikh, N.M. Kudyakov, V.M. D'yakov and M.G. Vornokov, Dokl. Akad. Nauk S.S.S.R., 1979, 247, 1179.

50. I.I. Patsanovskii, E.A. Ishmaeva, N.M. Kudyakov, V.M. D'yakov, O.A. Varnavskaya, M.G. Voronkov and A.N. Pudovik, J. Gen. Chem. (U.S.S.R.), 1979, 49, 2117.

51. O.A. Varnavskaya, E.A. Ishmaeva, V.M. D'yakov and N.M. Kudyakov, Izvest. Akad. Nauk S.S.S.R., Ser. Khim., 1978, 2129.

52. E.A. Ishmaeva, I.I. Patsanovskii, T.A. Zyablikova, E.N. Strelkova and I.P. Romanova, Zh. Obshch. Khim., 1982, 52, 2249.

53. A. Marchand and J. Valade, J. Organometal. Chem., 1968, 12, 305.

54. K.A. Andrianov, A.V. Varlamov, L.M. Khananashvili and N.P. Gashnikova, Bull. Acad. Sci., U.S.S.R., 1968, 622.

55. H. Meyer, G. Nagorsen and A. Weiss, Z. Naturforsch., 1975, 30b, 488.

56. H. Meyer, J. Klein and A. Weiss, J. Organometal. Chem., 1979, 177,323.

57. A. Nagata and J. Iyoda, Nippon Kagaku Kaishi, 1975, 1545.

58. J. Neemann and U. Klingebiel, J. Organometal. Chem., 1981, 208, 293.

59. J.G. Liehr and W.J. Richter, Org. Mass Spectrom., 1973, 7, 53.

60. B.Y.K. Ho, L. Spialter and L.D. Smithson, Org. Mass Spectrom., 1975, 10, 361.

61. C. Lageot and A. Guillemonat, Org. Mass Spectrom., 1977, 12, 515.

62. R.H. Cragg and R.D. Lane, J. Organometal. Chem., 1978, 154, C6.

63. R.H. Cragg and M. Nazery, J. Organometal. Chem., 1974, 71, 225.

64. M.G. Voronkov, V.Yu. Vitkovskii, N.M. Kudyakov and R.K. Valetdinov, J. Gen. Chem. (U.S.S.R.), 1981, 51, 1872.

65. J-C. Pommier, R. Calas and J. Valade, Bull. Soc. chim. France, 1968, No.4, 1475.

66. H.J. Emeleus and J.J. Zuckerman, J. Organometal. Chem., 1964, 1, 328.

67. K.A. Andrianov, A.V. Varlamov and L.M. Khananashvili, Khim. Geterotsikl. Soedin., 1967, 160.

68. Midland Silicones Ltd., B.P. 749, 958/1956.

J.L. Speier, Jr. and L.M. Shorr, U.S.P. 2,811, 542/1957.

69. R.M. Ismail, Z. Naturforsch., 1964, 19b, 873.

70. C.L. Frye, U.S.P. 3,465,020/1969.

71. A. Boeckmann, H. Rudolph, G. Trenczek, W. Wiegreffe and W. Ritter, Ger. Offen. 2,113,297/1972.

72. F.A. Henglein and H. Niebergall, Chem.-Ztg., 1956, 80, 611.

73. R.D. Lane, Ph.D. Thesis, University of Kent at Canterbury, 1983.

74. V.P. Davydova, Dissertation, Leningrad, 1958.

75. R.A. Hall, B.P. 791,169/1958.

76. P.L. De Benneville and M.J. Hurwitz, U.S.P. 2,876,209/1959.

77. V.P. Davydova, M.G. Voronkov and B.N. Dolgov, Trudy konferencii, Khimiya i prakticheskoe primenenie kremneorganicheskikh soedinenii, Leningrad, 1958, 1, 204.

78. Unpublished results from V. Bazant, V. Chvalovsky and J. Rathovsky, "Organosilicon Compounds", Academic Press, New York, 1965.

79. B.P. 800,554.

80. H. Staudinger and W. Hahn, Makromol. Chem., 1953, 11, 24.

81. H.R. Allcock, T.A. Nugent and L.A. Smeltz, Syn. Inorg. Metal-Org. Chem. 1972, 2, 97.

82. M. Wieber and M. Schmidt, J. Organometal. Chem., 1963, 1, 93.

83. A.M. Panov, G.V. Ratovskii, N.M. Kudyakov and M.G. Vornokov, Zh. Obshch. Khim., 1981, 51, 2631.

84. F.A. Henglein and H. Graser, Makromol. Chem., 1958, 26, 236.

84a. J. Kaufmann and F. Kober, J. Organometal. Chem., 1974, 82, 333.

85. R.C. Mehrotra and B.C. Pant, J. Indian Chem. Soc., 1964, 41, 563.

86. H.W. Kohlschutter and G. Jaekel, Z. anorg. allg. Chem., 1953, 271, 185.

87. R.M. Ismail, Z. Naturforsch, 1963, 18b, 1122.

88. B.P. 857,153.

89. R. Schwarz and W. Kuchen, Z. anorg. allg. Chem., 1955, 279, 84.

90. R. Schwarz and W. Kuchen, G.P. 1,053,518/1959.

91. R. Schwarz and W. Kuchen, G.P. 1,057,129/1959.

92. B.P. 798,163/1958.

93. G.P. 1,032,747.

94. F.P. Boer and J.W. Turley, J. Amer. Chem. Soc., 1969, 91, 4134.

95. Ye.L. Zaitseva, A.Ya. Yakubovich, T.V. Rozantseva, Yu.A. Aleksandrova and A.N. Pravednikov, Polymer Science, U.S.S.R., 1968, 10, 2408.

96. O.A. D'yachenko, L.O. Atovmyan, S.M. Aldoshin, N.G. Komalenkova, A.G. Popov, V.V. Antipova and E.A. Chernyshev, Bull. Acad. Sci. U.S.S.R., 1975, 990.

97. B.P. 824,315.

98. W. Hahn, Makromol. Chem., 1953, 11, 51.

99. F.S. Kipping and J.T. Abrams, J. Chem. Soc., 1944, 81.

100. H. Meyer and G. Nagorsen, Angew. Chem. Int. Ed. Engl., 1979, 18, 551.

101. G.P. 929,189.