Journal of Organometallic Chemistry, 289 (1985) 23–44
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

CONTRIBUTIONS TO GROUP IV ORGANOMETALLIC CHEMISTRY

VIII *. PREPARATION AND PROPERTIES OF SOME ORGANO-1,3,2-DIOXASILACYCLOHEPTANES AND THEIR CYCLIC DIMERS

R. HARRY CRAGG and ROB D. LANE

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

(Received January 7th, 1985)

Summary

The preparation and properties of some organo-1,3,2-dioxasilacycloheptanes are reported and their mass spectra, ^{13}C and ^{29}Si NMR spectra are fully discussed.

Introduction

In the course of the wider study of 1,3,2-dioxasilaheterocycles, the reaction of dichlorodiphenylsilane with different butane-1,4-diols led to the unexpected isolation of separate monomeric and dimeric cyclic products [1]. Since reactions of difunctional silanes with diols normally yield either monomeric or dimeric products but not both, and only monomeric 7-membered rings had previously been reported [2–7], these constituted an interesting set of compounds. Accordingly, further reactions were carried out using a greater range of 1,4-dihydroxy starting materials with other dichlorosilanes and a comprehensive number of physical and spectroscopic data were obtained for twenty products. Four dimers were isolated, these being 2,2,9,9-tetraphenyl-substituted in each case, though ^{13}C and ^{29}Si NMR spectra indicated the presence also of dimeric species in some nominally monomeric 2,2-dimethyl- and 2-methyl-2-phenyl-substituted products.

The isolation of 2,2-diphenyl monomers and 2,2,9,9-tetraphenyl dimers from the same reaction mixture is facilitated by the low solubility of the dimers in a petroleum ether/benzene solvent. The more soluble monomers can be recovered, after recrystallization of dimer and removal of solvent, by vacuum distillation. The two forms appear to be stable and to have no tendency to equilibrate on standing.

---

* For part VII see ref. 15.

This is most clearly seen where the monomer is a liquid, in contrast to its crystalline dimer.

Evidence from the mass spectra, NMR spectra and ebullioscopic molecular weight determinations of these fully phenyl-substituted compounds points to the existence of stable 7- and 14-membered rings. Hence the mass spectra of dimers contain molecular ion peaks (*m/e*, 540 to 636) and are different in essence from the spectra of monomers. A simple association dimer could reasonably be expected to dissociate in the mass spectrometer and to yield a significant monomer molecular-ion peak. The fact that this is not found indicates that a true macrocyclic structure is more probable. Equally, the respective melting points of monomers and dimers vary widely (a difference of approximately 100°C) and molecular weights measured in boiling benzene appear constant and are close to theoretical values. ^{29}Si NMR shifts for dimers are consistent with four-coordinate, dioxadiphenyl-substituted, silicon atoms in virtually strain-free molecules.

Preparation

All compounds except one could be satisfactorily prepared by interaction of the appropriate dichlorosilane and dihydroxy compound, with pyridine as base, in a large volume of benzene.

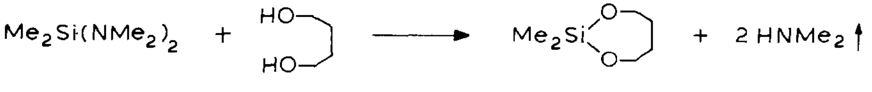
(R^1 , R^2 = Me or Ph ; R = as below)

Reaction mixtures were refluxed for, typically, half an hour and then allowed to cool before removal of hydrochloride by filtration. After removal of solvent under reduced pressure, any solid products were purified by recrystallization from a benzene/petroleum ether mixture and liquids were distilled under vacuum.

In the case of three 2,2-diphenyl derivatives, removal of solvent from solutions left after recrystallization of the dimer afforded mobile residues which distilled to yield monomeric products.

The reaction between diphenyldichlorosilane and benzene-1,2-dimethanol produced both monomer and dimer as solids (IIIf and IVf). However, the dimer proved to be so insoluble, even in benzene alone, that separation was readily achieved by fractional crystallization.

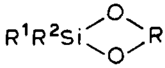
Use of the above method for 2,2-dimethyl-1,3,2-dioxasilacycloheptane (Ia) resulted in a very poor yield. Instead, the compound was prepared by heating bis(dimethylamino)dimethylsilane with butane-1,4-diol, under reflux, until the calculated mass of dimethylamine had been lost.



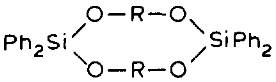
The residue was distilled at atmospheric pressure over an oil bath, the product coming over slowly and with difficulty at a temperature well below the literature values. The liquid product was shown to be predominantly dimeric after a short time.

Results and discussion

Products are denoted by the main class of compound to which they belong (I–IV) and by the identity of the diol fragment (R = a–h).



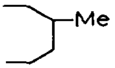
(I, $R^1 = R^2 = Me$;
II, $R^1 = Me$; $R^2 = Ph$;
III, $R^1 = R^2 = Ph$)



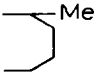
(IV).

R =

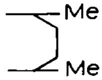
(a)



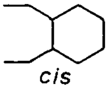
(b)



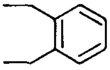
(c)



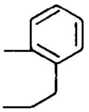
(d)



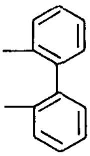
(e)



(f)



(g)



(h)

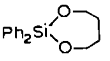
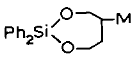
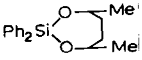
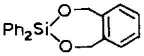
The following twenty compounds were prepared and their mass spectra, ^{13}C and ^{29}Si NMR spectra are fully discussed: Ia, b, d; IIa, b, c, d, h; IIIa–h; IVa, b, d, f.

A comparison of physical constants for monomers and dimers

The isolation of monomeric and dimeric 2,2-diphenyl-substituted products ap-

TABLE 1

PHYSICAL CONSTANTS FOR MONOMERIC (M) AND DIMERIC (D) 2,2-DIPHENYL-1,3,2-DIOXASILACYCLOHEPTANES

Compound		M.p. (°C)		B.p. (°C/mmHg)		Mass spectrum *m/e*, Molecular ion		Ebullioscopic relative molecular mass	
		M	D	M	D	M	D	M	D
	IIIa	liquid at room temp.		115–134/0.1		270		260	
	IVa		176–184		–		540		519
	IIIb	liquid at room temp.		148–170/0.15		284		283	
	IVb		154–175		–		568		567
	IIId	55–75		130–140/0.1		298		306	
	IVd		155–170		–		596		587
	IIIf	129–131		–		318		317	
	IVf		245–250		–		636		681

pears to have been largely fortuitous in that the dimers were readily crystallized from organic solvent. Once obtained, the two forms remained apparently unchanged on standing either as clear, mobile, liquid monomer and crystalline dimer or both as crystalline solids. It seems likely therefore that the formation of monomer and dimer is kinetically controlled during the initial reaction between dichlorosilane and diol and that subsequent equilibration does not occur.

Physical constants for monomer/dimer pairs are given in Table 1. Other compounds of class III, which could only be prepared as monomers, gave no indication of dimerization on standing.

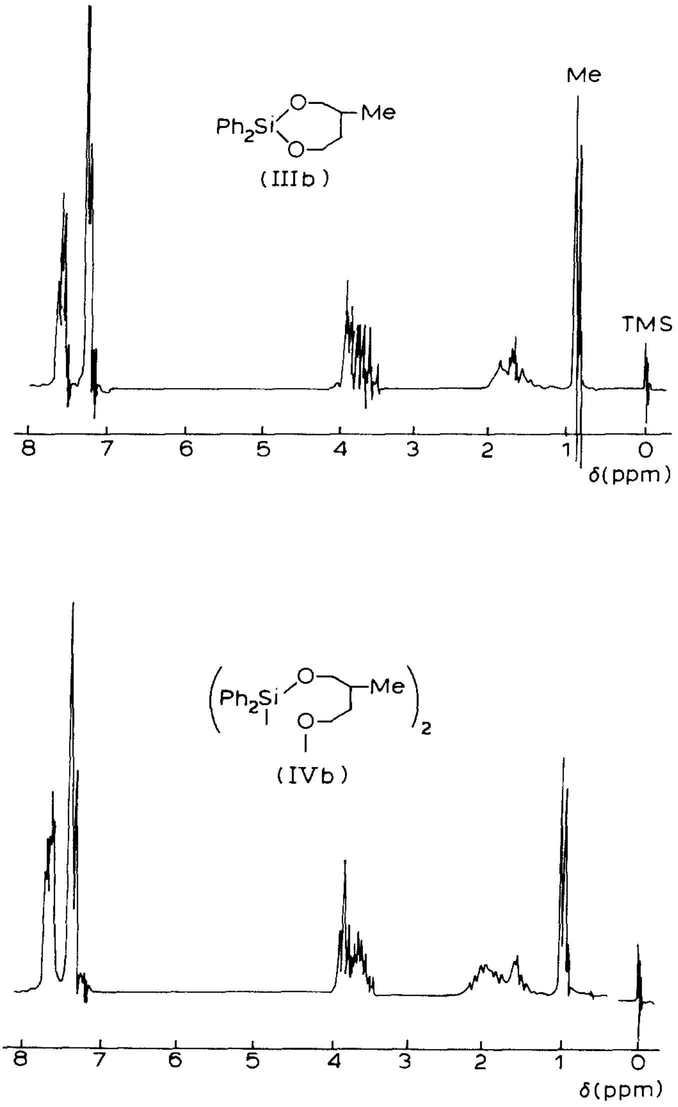


Fig. 1. ^{1}H NMR spectra of IIIb and IVb.

^{1}H NMR spectra

Spectra were obtained, in all cases, as an initial check on the identity and purity of freshly prepared compounds. However their complexity, resulting from the large size of molecules and presence of isomers in many cases, meant that they yielded structural information less readily than either the ^{13}C or ^{29}Si NMR spectra.

Detectable shift difference do occur for some nuclei in the case of monomeric and dimeric products. The example of 5-methyl-2,2-diphenyl-1,3,2-dioxasilacycloheptane is shown in Fig. 1 where it can be seen, for instance, that the methyl doublet is approximately 0.1 ppm to lower field in the dimer.

^{13}C NMR spectra

^{13}C NMR shifts for all compounds are given in Table 2. Assignments (for all except the exocyclic aromatic carbons) were made as follows:

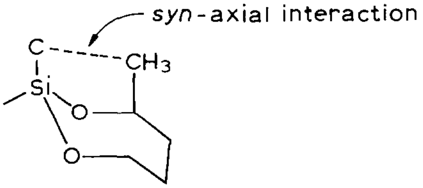
(a) Silicon-phenyl on the basis of published data [8] and relative peak intensities.

(b) Ring carbons by comparison with values for the acyclic compounds and from relative peak intensities. Where difficulties arose with unsymmetrical rings, comparison was made with the corresponding symmetrical compounds.

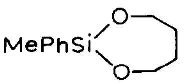
(c) Monomer/dimer values on the basis of trends known from unambiguous data obtained on compounds of classes III and IV.

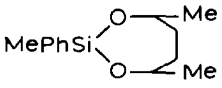
(i) Substituent effects. In keeping with the ^{13}C NMR results for analogous 5- and 6-membered rings [16] stepwise phenyl substitution at the silicon atom has little effect on shifts of other carbon atoms except for a small but progressive downfield shift of the functional ring carbon resonances (C(4) and C(7)).

Similarly, the effect of ring-methyl substituents at C(4) and C(7) is much as might be expected, with the *syn–axial* interaction (δ-effect) [9] apparently operative in producing small downfield shifts for both silicon-methyl and phenyl-C$_1$ atoms.



The marked variation of silicon-methyl shifts for different isomers is also explainable, assuming this effect, with groups in pseudo-axial positions producing the greatest change in shift. This may be contrasted with the upfield ^{29}Si NMR shifts produced by γ-effect of the same substituents, e.g.:





(3 isomers)

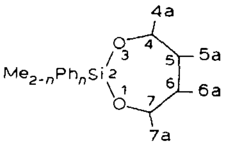
$\delta(^{13}C)$	−3.40	−3.27, −2.54, −0.84 ppm
$\delta(^{29}Si)$	−10.81	−14.89, −15.81, −16.89 ppm

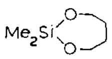
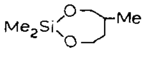
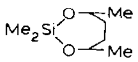
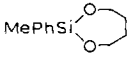
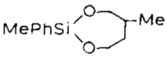
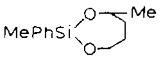
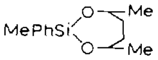
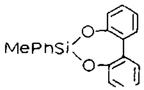
(ii) Ring size. Like those of ^{29}Si, ^{13}C NMR shifts move to higher field by a remarkably constant amount for the transition from a monomeric to a dimeric ring,

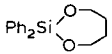
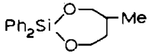
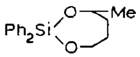
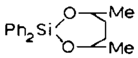
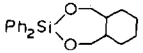
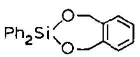
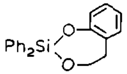
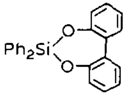
(Continued on p. 30)

TABLE 2

NMR SHIFT ASSIGNMENTS [a,d] (δ in ppm)



Compound	Ring size [c]	δ(4)	δ(4a/7a)	δ(5)	δ(5a/6a)	δ(6)	δ(7)	δ(Si-Me)	δ(Phenyl)			
									C_1	*o*-	*m*-	*p*-
	M	64.07(s)	–	32.52(s)	–	32.52(s)	64.07	−1.09 or −2.79 [e]	–	–	–	–
	D	(62.24)		(29.00)		(29.00)	(62.24)	(−3.28)				
	M	69.40	–	40.77	17.47	36.88	62.12	−2.91	–	–	–	–
	D	(67.58)		(36.28)	(16.86)	(32.51)	(60.54)	(−3.15)				
	M	70.13	25.23	38.82	–	38.82	70.13	+0.24	–	–	–	–
		69.77	23.54	35.31		35.31	69.77	−1.94				
								−2.66				
 [b]	M	64.80(s)	–	32.64(s)	–	32.64(s)	64.80	−3.40	Only one set of peaks discernable			
	D	(62.73)(l)		(29.12)(l)		(29.12)(l)	(62.73)(l)	(−4.13)(l)	(134.93)	(134.08)	(127.89)	(130.08)
	M	69.77(l)	–	40.52(l)	17.35(l)	36.76(l)	62.61	−3.76	134.81	133.84	127.77	130.07
	D	(67.83)(s)		(36.03)(s)	(16.74)(s)	(32.27(s)	(60.91)(s)	(−4.36)(s)				
	M	70.74	24.99	39.07(l)	–	31.66	64.55	−3.15	135.17	133.84	127.77	129.83
		70.49(l)	24.63(l)			31.30(l)		−3.51				
	D	(68.67)(s)	(23.54)(s)	(35.67)(s)		(28.63)(s)	(62.85)(s)					
	M	70.62	23.66	34.94	–	34.94	70.62	−0.84	–	133.84	127.77	129.83
			24.99	35.18		35.18		−2.54				129.59
			25.23	38.70		38.70		−3.27				
 [b]	M	152.4	–	–	–	–	152.4	−3.86	–	134.7	128.8	130.8

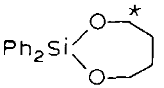
	M	65.16	–	32.51	–	32.51	65.16	–	133.35	134.68	127.89	130.32
	D	63.09		28.75		28.75	63.09		132.86	134.81	127.77	130.20
	M	70.13	–	40.40	17.35	36.76	62.97	–	133.23	134.68	127.77	130.20
	D	67.95		36.28	17.35	32.39	61.52		132.9 (est.)	134.93	127.89	130.20
	M	70.98	24.75	39.07	–	31.42	64.91	–	133.71	134.56	127.77	130.07
	M	70.98	25.11 23.54	38.82 35.06	–	38.82 35.06	70.98	–	134.08	134.68	127.77	130.07
	D	70.48 69.89 69.16	23.78 23.29 22.81	35.91 34.46		35.91 34.46	70.48 69.89 69.16	–	134.08	135.05	127.53	129.83
 (*cis*)	M	66.37	–	41.86	27.54	41.86	66.37	–	132.86	134.68	127.77	130.32
	M	66.37		139.17		139.17	66.37	–	132.26	134.81	128.01	130.56
	D	No results due to insolubility of product							(most likely peaks in aromatic region)			
	M	153.98	–	–	–	36.52	65.64	–	132.62	134.56	128.01	130.56
	M	151.43	–	–	–	–	–	–	134.23	134.87	127.93	131.14

---

[a] All shifts are referenced to internal TMS except where indicated. [b] Shifts calculated using known TMS frequency. [c] M = monomer, D = dimer. [d] Values in parentheses attributed to the presence of dimer in nominally monomeric samples. For these spectra relative peak intensities for monomer/dimer pairs are denoted by large (l) or small (s) where they differ significantly. [e] Small signals appear for each, one being spurious. By comparison with other compounds −2.79 ppm is likely to be the required shift.

differences being relatively independent of the extent of phenyl substitution at silicon or of methyl substitution at ring carbons. Approximate ranges for the shift changes of different carbon atoms are: Si-Ph 0, Si-Me < 1, C(4/7) 2, C(5/6) 3–4.5, C-Me < 1.5.

The greatest changes therefore occur for the ring carbons and, as discussed for ^{29}Si shifts, this would suggest alleviation of ring strain as the main factor. Corresponding acyclic structures should then give rise to the highest field shifts of all and this is seen to be so. e.g.:

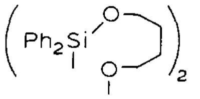
		$\delta(^{13}C)$(ppm)
	Monomer	65.16
	Dimer	63.09
$Ph_2Si(O\overset{*}{C}H_2CH_3)_2$		58.85

An elegant example of both the effect of dimerization on ^{13}C NMR shifts and of the slow dimerization of a 1,3,2-dioxasilacycloheptane is furnished by two spectra of 2,2,5-trimethyl-1,3,2-dioxasilacycloheptane recorded at different times after distillation of the product (Fig. 2). After 3 weeks, the spectrum is essentially that of the monomer but also contains a set of very small peaks such that each one is slightly to highfield of a monomer peak. After 5 months the pairs of peaks are of almost equal intensity. The differences in shift values match closely those of known monomer and dimer 2,2-diphenyl- compounds and the higher field peaks of Fig. 2 can therefore be assigned to the presence of dimer. Similar duplicate peaks were evident in other spectra and shift values were assigned to dimers on the same basis (Table 2).

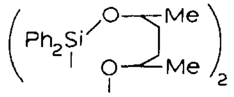
^{29}Si NMR spectra

^{29}Si shifts for all compounds are given in Table 3 and are discussed in the general context of ^{29}Si NMR. However, certain features merit comment inasmuch as they relate specifically to the monomer/dimer characteristics of these heterocycles.

Dimers are clearly distinguished from their monomers by the remarkably constant upfield shift difference of about 7 ppm. It is found that their shifts correspond closely to those of comparable acyclic compounds and the conclusion may be drawn that cyclization does not significantly affect ^{29}Si shifts per se but only as a result of strain in the smaller ring structures. The closeness of shift values for dimeric and acyclic compounds is therefore consistent with the formulation of dimers as true macrocyclic structures. e.g.:



−32.25 ; $Ph_2Si(OEt)_2$ −32.36 ppm



−35.17
−37.78 ; $Ph_2Si(O\text{-}i\text{-}Pr)_2$ −35.78 ppm

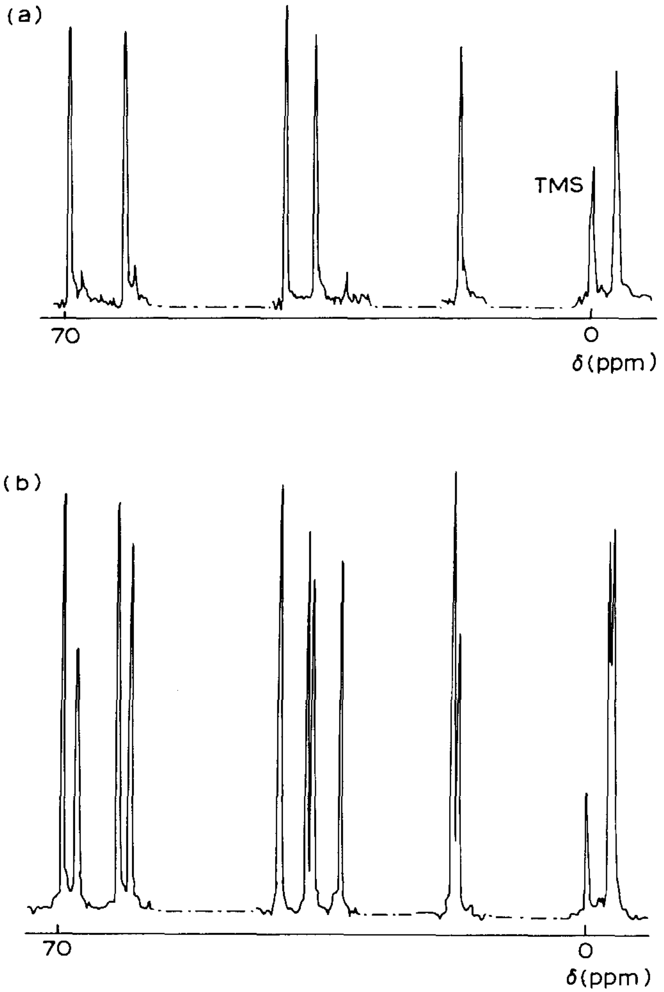


Fig. 2. ^{13}C NMR spectra of 2,2,5-trimethyl-1,3,2-dioxasilacycloheptane (Ib). (a) 3 weeks after distillation; (b) 5 months after distillation showing growth of dimer signals.

Coordination dimers would require a change in hybridization of the silicon atom and higher-field shifts might be expected as is the case for the silatranes [10] and five- and six-coordinate organosilicon complexes [11].

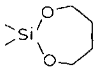
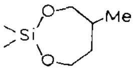
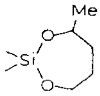
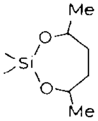
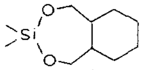
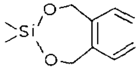
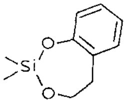
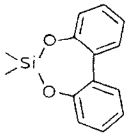
Having established a dimerization shift for the 2,2-diphenyl compounds, and the similarity of shifts for dimers and acyclic compounds, spectra for some nominally monomeric 2,2-dimethyl and 2-methyl-2-phenyl analogues could be interpreted.

The spectra of four compounds are shown in Fig. 3, all consisting of negative peaks except for the positive TMS signals. Whilst peak intensities are not strictly quantitative, due to the Nuclear Overhauser Effect, it is evident that some dimerization has occurred in all cases and the signal intensities are deemed to be sufficiently different to give some measure of the relative abundances of monomer and dimer.

Dimerization is most marked when the diol fragment is unsubstituted and there is no phenyl substituent at silicon. Conversely, the only product featured in Fig. 3 to

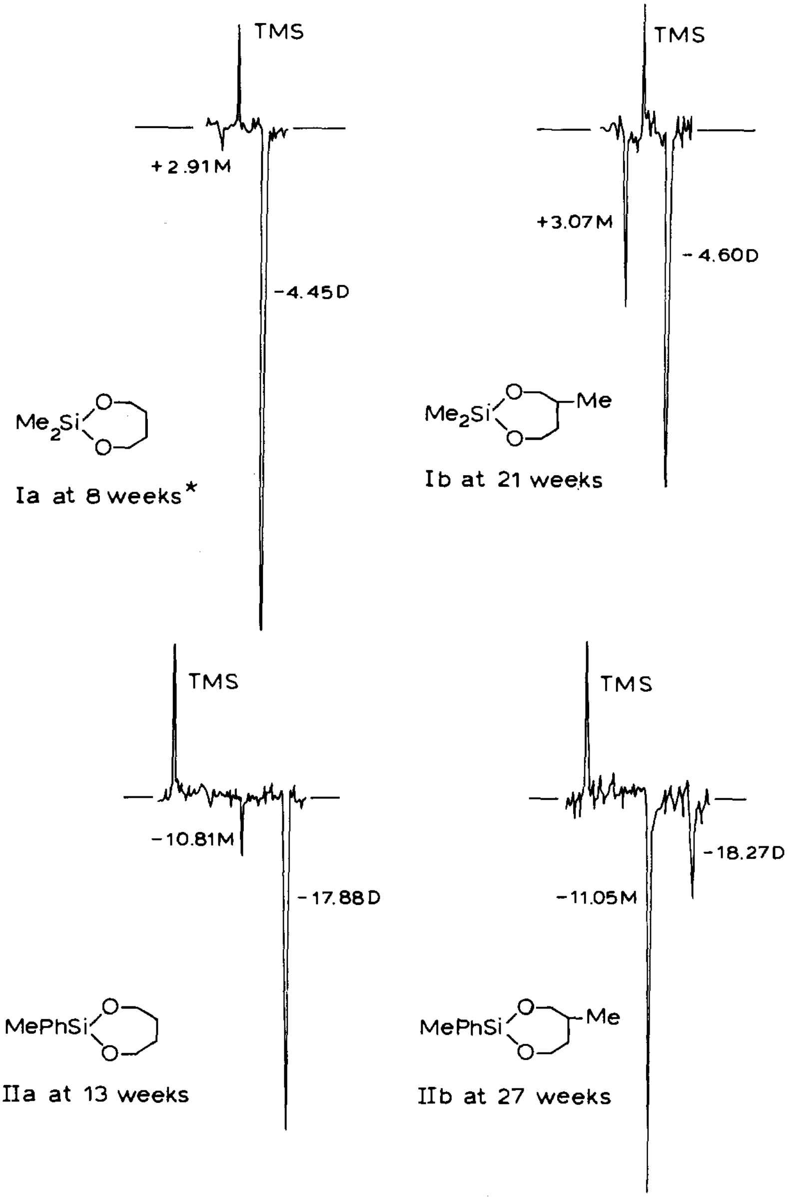
TABLE 3

^{29}Si NMR SHIFTS FOR 1,3,2-DIOXASILACYCLOHEPTANES AND THEIR CYCLIC DIMERS (δ in ppm)

Compound	Ring size [a]	Silicon atom substituents		
		$\delta(Me_2)$	δ(MePh)	$\delta(Ph_2)$
	M D	+2.91 -4.45	-10.81 -17.88	-25.49 -32.25
	M D	+3.07 -4.60	-11.05 -18.27	-25.49 -32.09 -32.40 -32.71
	M	-	-12.44 -12.90	-27.33
	M	-0.92 -2.45	-14.89 -15.81 -16.89	-29.02 -30.25
	D	-	-	-35.17 -37.78
 (*cis*)	M	-	-	-24.88
	M	-	-	-23.65
	M	-	-	-33.17
	M	-	-3.63	-19.50

---

[a] M = monomer, D = dimer.



Ia at 8 weeks*

Ib at 21 weeks

IIa at 13 weeks

IIb at 27 weeks

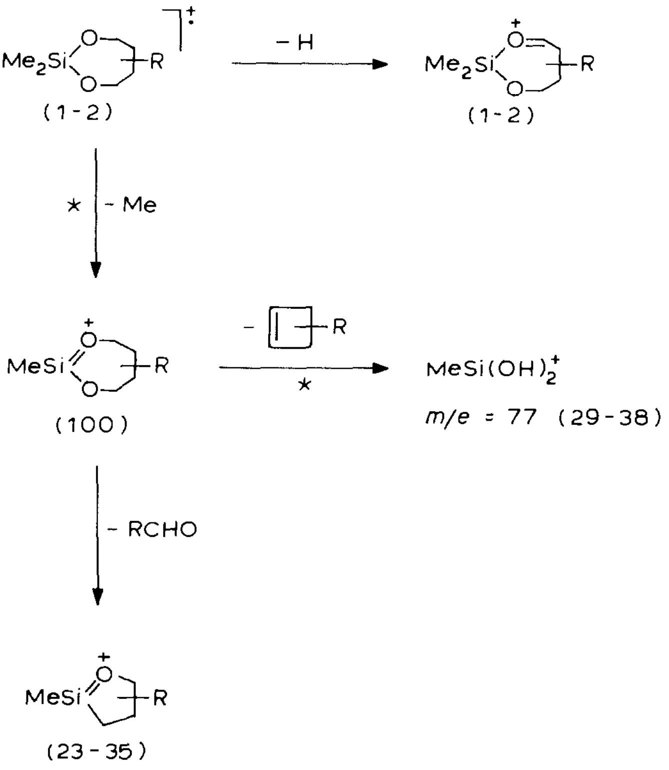
Fig. 3. Monomer (M) and dimer (D) peak intensities in the ^{29}Si NMR spectra of some 2,2-dimethyl and 2-methyl-2-phenyl compounds. Shifts given in ppm rel. to TMS. ★ Length of time after distillation.

remain predominantly monomeric is that containing both ring-methyl and silicon-phenyl substituents (IIb). Spectra of the corresponding 4,7-dimethyl compounds gave no indication of the presence of dimer, even, in one case, 6 months after distillation. It seems likely that all freshly distilled products are monomeric but that they may then dimerize slowly on standing, with the rate determined by the type and extent of substitution.

It is paradoxical that the most stable monomers should be those of the 2,2-diphenyl compounds when it was for these, only, that dimers were isolated. The most reasonable conclusion would seem to be that two phenyl groups on the silicon atom confer stability on both monomeric and dimeric compounds, and that the nature of the product must therefore be determined kinetically at the time of formation. The enhanced stability itself could be attributed either to relatively less labile silicon–oxygen bonds or to a lack of reactivity resulting from greater steric crowding around the silicon atom.

In summary it may be concluded that 2,2-dimethyl-1,3,2-dioxasilacycloheptanes show a marked tendency to dimerize but that this is progressively diminished by phenyl substitution at silicon or by methyl substitution at ring carbons. 2,2-Di-

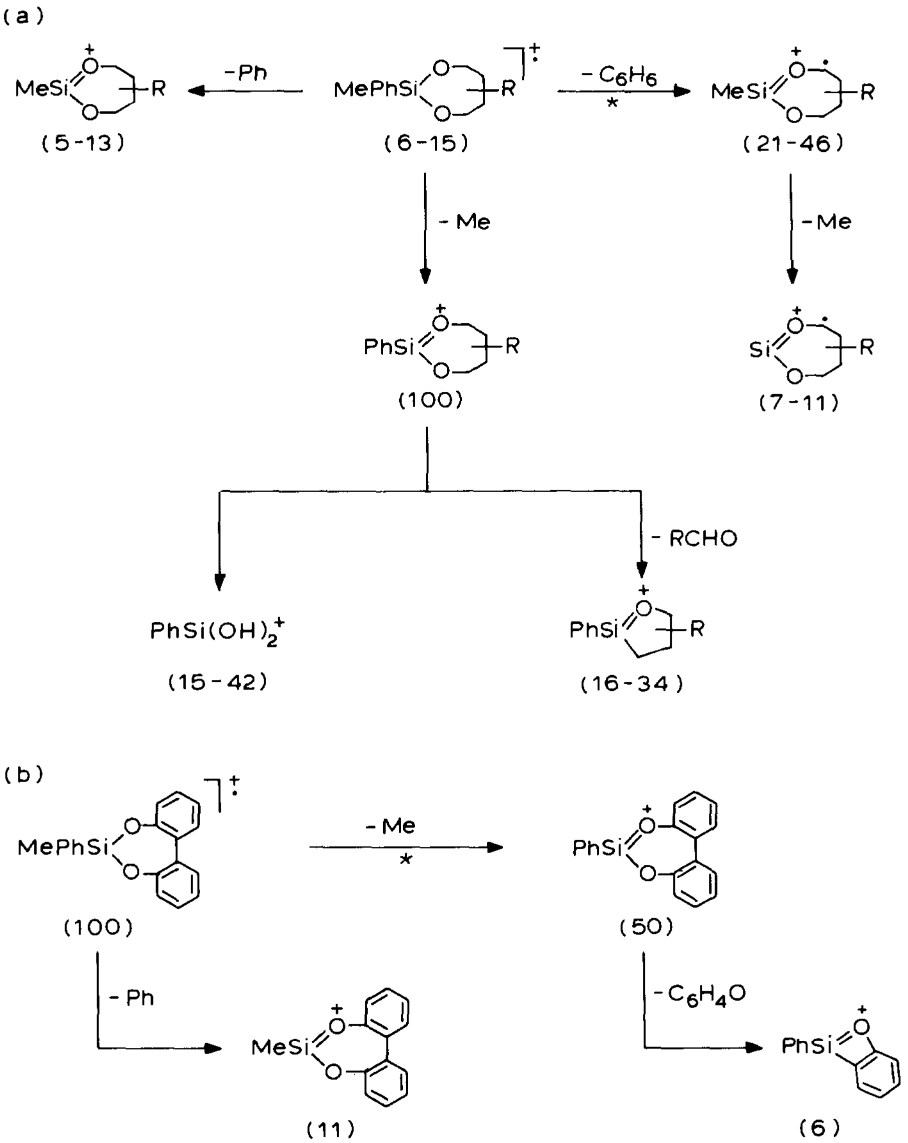
(Continued on p. 37)



SCHEME 1. Proposed fragmentation patterns for compounds Ia, b and d. Relative intensities (%) are given in brackets. Asterisks indicate that metastable-supported fragmentations were present in all spectra, though many others were found for individual compounds. R signifies substitution corresponding to any of the diol fragments. Where fragmentation involves the loss of heterocyclic ring atoms, the new ion is formulated with a cyclic structure retained, wherever this seems reasonable.

Other common ions and suggested formulae:

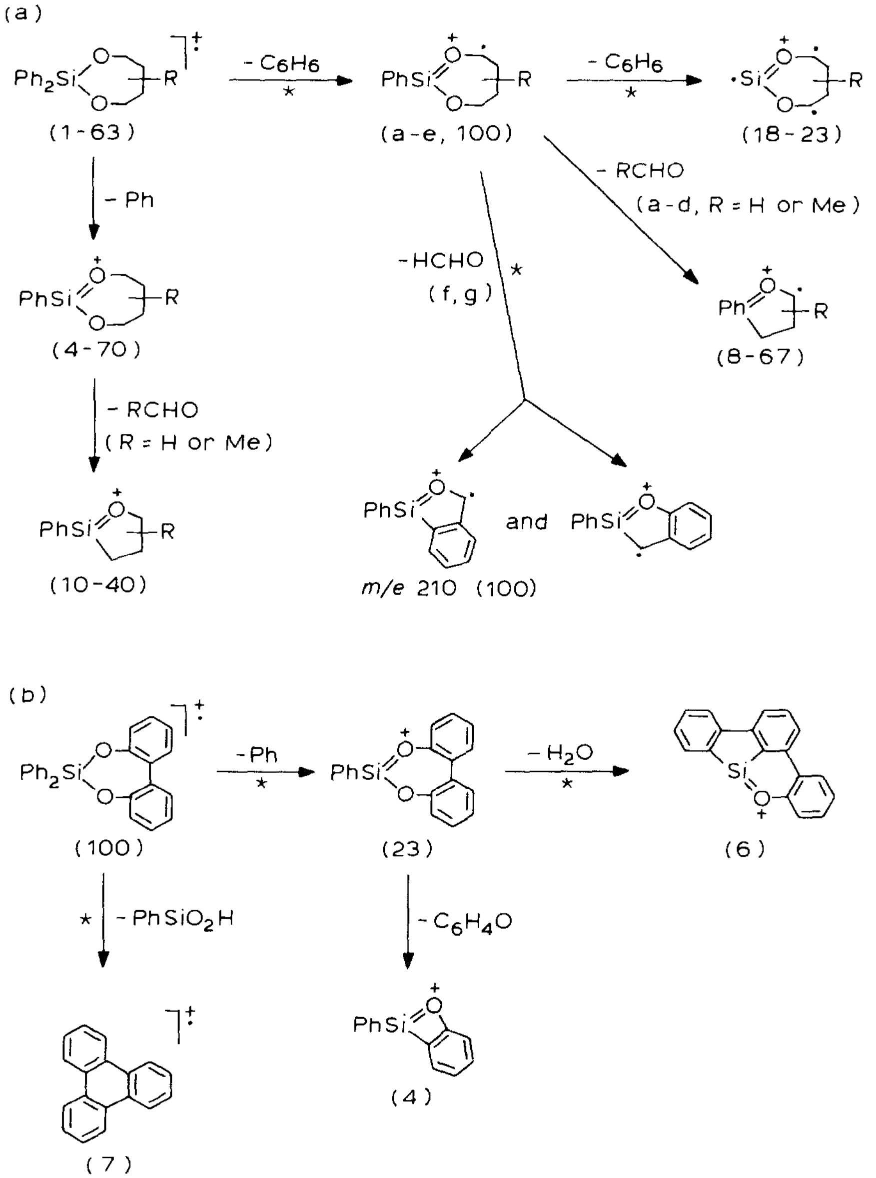
m/e		$I_{\text{rel.}}$ (%)
75	Me_2SiOH^+	10–48
61	$HMeSiOH^+$	6–13
59	Me_2SiH^+	4–11
45	$SiOH^+$	8–15



SCHEME 2. Proposed fragmentation patterns for compounds IIa–d (a) and IIh (b). Relative intensities (%) are given in brackets. Asterisks indicate that metastable-supported fragmentations were present in all spectra, though many others were found for individual compounds. R signifies substitution corresponding to any of the diol fragments. Where fragmentation involves the loss of heterocyclic ring atoms, the new ion is formulated with a cyclic structure retained, wherever this seems reasonable.

Other common ions and suggested formulae:

m/e		$I_{\text{rel.}}$ (%)	*m/e*		$I_{\text{rel.}}$ (%)
137	MePhSiOH$^+$	6–38	77	$C_6H_5^+$	5–15
123	HPhSiOH$^+$	9–13	61	HMeSiOH$^+$	<8
121	MePhSiH$^+$	<13	51	C_4H_3	<8
105	PhSi$^+$	7–19	45	SiOH$^+$	6–29
91	$C_7H_7^+$	11–16			



SCHEME 3. Proposed fragmentation patterns for compounds IIIa–g (a) and IIIh (b). Relative intensities (%) are given in brackets. Asterisks indicate that metastable-supported fragmentations were present in all spectra, though many others were found for individual compounds. R signifies substitution corresponding to any of the diol fragments. Where fragmentation involves the loss of heterocyclic ring atoms, the new ion is formulated with a cyclic structure retained, wherever this seems reasonable. Individual spectra for compounds of class III varied widely in detail, as might be expected from the range of diols used, and this scheme shows only the major initial fragmentation pathways.

Other common ions and suggested formulae for a–e only:

m/e		$I_{rel.}$ (%)	m/e		$I_{rel.}$ (%)
211	$Ph_2Si\overset{O^+}{<\|}$	9–26	139	$PhSi(OH)_2{}^+$	13–51
199	Ph_2SiOH^+	7–37	105	$PhSi^+$	7–31
181 – 3	Ph_2Si^+ and related ions	< 39	Lower ions as in Scheme 2		
152 – 4	$Ph_2{}^+$ and related ions	< 25			

phenyl-substituted dimers are therefore unlikely to have been formed by dimerization of their monomers and are most likely to have been produced in the initial reaction between dichlorosilane and diol.

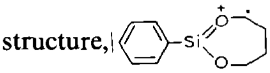
Whilst it has not been possible, as part of the present work, to attempt any kinetic studies on these compounds, there is clearly scope for further research and clarification in this area. In particular, the possibility of monomer/dimer equilibria, as found for 1,2-dihydroxybenzene derivatives [17] might usefully be investigated.

Mass spectra

Mass spectra were obtained for all compounds in order to determine molecular masses and to establish common fragmentation patterns. Each class of compound gave distinctive fragmentation pattern and possible schemes are proposed (Schemes 1–4).

In each case the main feature is retention of the silicon atom or atoms though hydrocarbon rearrangement ions are also important for phenyl-substituted compounds. The major fragmentation for compounds of class I and II, which all contain a silicon–methyl bond, involves loss of a methyl radical from the molecular ion.

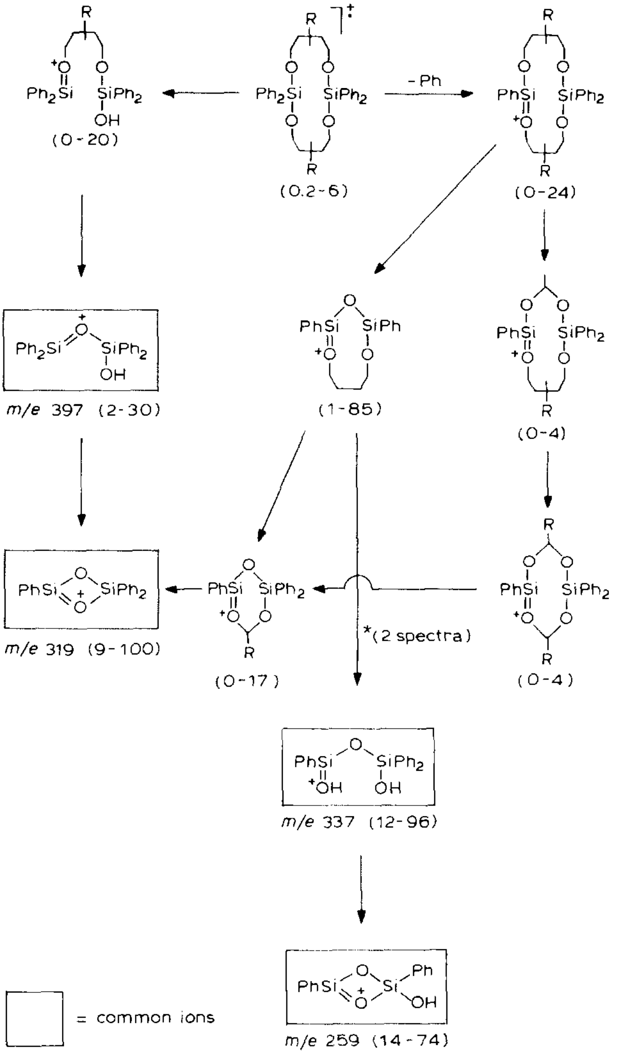
We have previously reported the loss of a benzene molecule, involving hydrogen atom migration across the heterocyclic ring, in the fragmentation of some 2-phenyl-1,3,2-dioxasilacycloalkanes [12]. This feature is found to be important here in the spectra of compounds of class II and III and gives rise to the base peak ion in the majority of compounds of the latter.

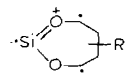
In marked contrast the same fragmentation does not occur to any significant extent in any of the compounds of class IV even though the only obvious difference is one of ring size. It seems reasonable to rationalize these findings in terms of the possible alleviation of ring strain and stability of the ion produced when both a phenyl group and a hydrogen atom are lost from the seven-membered rings. In the proposed structure,  (see Scheme 3), the ion could be virtually planar about the silicon atom allowing for considerable delocalization of charge. In contrast, ring strain in the parent fourteen-membered dimer is likely to be negligible and similar advantage would not be served by the loss of an annular hydrogen atom.

In the same connection it is noteworthy that for class I compounds, where loss of a benzene molecule is impossible, $[M-1]^+$ ions are formed in each case. Whilst only accounting for a very small proportion of the total ion current, the abundance of the ions is of the same order as that of the molecular ions ($I_{\mathrm{rel.}}$ 1–2%) and initial loss of a hydrogen atom may have some significance therefore.

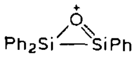
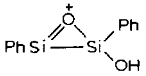
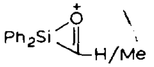
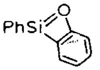
Loss of a hydrogen atom from the molecular ion does not occur to any significant extent for the other monomers and is completely overshadowed by the loss of either a phenyl radical or, more importantly, of a benzene molecule. Compounds IIh and IIIh are exceptional, having no annular hydrogens, and the molecular ion gives rise to the base peak in each case.

One consequence of the elimination of a neutral benzene molecule from the molecular ion of the compounds containing a silicon–phenyl bond is that odd-electron (even mass) ions are a feature of these spectra. The odd electron is often retained in subsequent fragmentations and in compounds of class III the sequential loss of two benzene molecules is observed. Although the sequential loss of groups

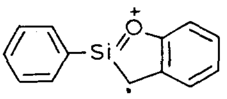


bonded to silicon has previously received some attention [13,14], this particular fragmentation pathway appears to be unique to these heterocycles. It is difficult to give any obvious representation of the ion formed in each case though it is tempting to postulate the cyclic structure,  shown in Scheme 3 where the presence of unbonded electrons on five of the seven ring atoms could produce an extensively delocalized π-electron system.

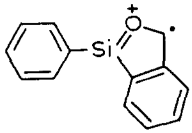
Delocalization is clearly important in determing pathways for the fragmentation of compounds having a phenyl substituent at the silicon atom. Hence the base peak ions, for compounds IIIf and IIIg have a potentially planar and completely delocalized structure since all the atoms are likely to be sp^2-hybridized.

m/e		$I_{rel.}$ (%)
303		< 8
243		<15
225 211		< 7
197		6 - 20
167	PhSi(OH)–SiOH$^+$	7 - 15
123	PhHSiOH$^+$	< 9
118	$C_9H_{10}^+$	3 - 60
104	$C_8H_8^+$	10-100

SCHEME 4. Proposed fragmentation patterns for compounds IVa, b, d and f. Relative intensities (%) are given in brackets. Asterisks indicate that metastable-supported fragmentations were present in all spectra, though many others were found for individual compounds. Where fragmentation involves the loss of heterocyclic ring atoms, the new ion is formulated with a cyclic structure retained, wherever this seems reasonable. This scheme is largely speculative due to the absence in the spectra of clear metastable ion peaks and contains several ions which are independent of the identity of the diol fragment. These are outlined and their masses given. R signifies substitution corresponding to any of the diol fragments.

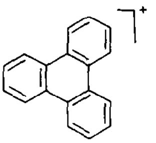


and



(*m/e* 210),

The ion of mass 228 in the spectrum of compound IIIh can only reasonably be the result of a hydrocarbon rearrangement. It would seem likely to have the triphenylene structure and, if so, would appear to be a novel rearrangement for such organosilicon compounds.



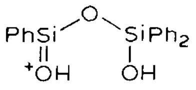
A number of interesting observations may be made with regard to the tetraphenylsubstituted dimers of class IV:

(i) Apart from the occurrence of common ions of low mass, the spectra are distinctive and bear little resemblance to those of the corresponding monomers. All the spectra contain an observable, though small ($I_{rel.}$ 0.2–6.0%), molecular ion peak.

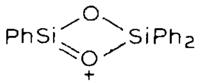
Since the masses are relatively high (*m/e* 540–636) this can be taken as an indication of stably-bonded molecules and is suggestive of true macrocyclic structures rather than of coordination dimers, which might well be expected to dissociate completely in the mass spectrometer.

(ii) Monomer molecular ions are absent in all but one of the spectra (IVd, $I_{\text{rel.}}$ 8%) showing that there is no dissociation or fragmentation of the dimers into monomers and strongly supporting the inference in (i) above.

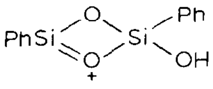
(iii) Both silicon atoms are retained in the most important fragmentations except for those producing low mass hydrocarbon ions. The retention of silicon atoms in positive ions is a characteristic feature of organosilicon mass spectra and is a consequence of the greater capacity of a silicon atom, compared with a carbon atom, to accommodate a positive charge [4]. Ions of mass 337, 319 and 259 are of particular interest since they are of high relative intensity (9–100%) and occur independently of the organic part of the heterocycle. They appear to be formed by initial loss of a phenyl group, followed by fragmentation of the ring to give siloxane-like ions which may be formulated as follows (see Scheme 4):



m/e 337



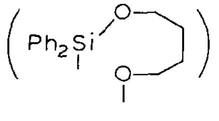
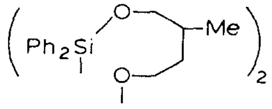
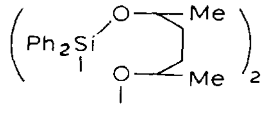
m/e 319



m/e 259

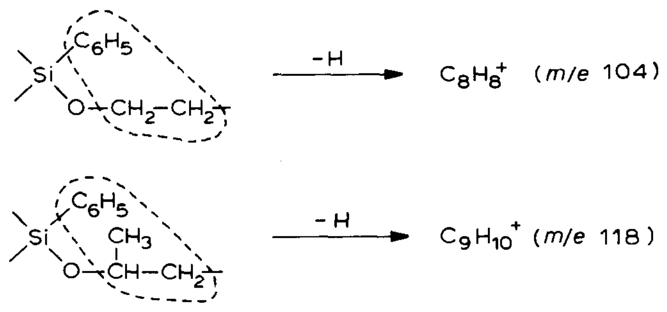
They are potentially useful identifiers of this class of compound, especially where it may not be possible to observe the molecular ion. However, it must be added that the same ions could also conceivably occur in the spectra of more highly polymerized products.

(iv) Ions of mass 104 and 118 are more significant for dimers than for monomers. A precise mass determination on the ion of mass 104 indicated the formula to be $C_8H_8^+$ and excluded $SiC_6H_4^+$ as a possibility. The two fragments are therefore assumed to be $C_8H_8^+$ and $C_9H_{10}^+$ and must arise from rearrangements involving a phenyl group and two or three ring carbon atoms. In the absence of metastable ions fragmentation pathways are not clear but the relative intensities of the two peaks (given below) suggest that carbons α- and β- to oxygen are likely to be involved

	m/e 104	*m/e* 118
	100	3
	46	21
	10	60

since the proportion of the higher-mass ion increases with increasing methyl substitution at these positions.

The following rearrangements would be consistent with these trends:



The more common tropylium ion, $C_7H_7^+$ (*m/e* 91), is also more abundant in the spectra of these dimers, again indicating that hydrocarbon rearrangements are more important than for the monomers.

Experimental

Molecular weights were determined using a Gallenkamp semimicro ebulliometer with sodium dried benzene as the solvent and naphthalene as the reference standard and an accuracy of the order of $\pm 5\%$ was estimated.

The mass spectra were recorded using an AEI MS902 mass spectrometer at 70 eV. The source was maintained at 170°C and the compounds were introduced using a variable-temperature, direct-insertion probe. In general only those peaks of relative intensity greater than 5% were considered.

NMR spectra were recorded on a JEOL-PS-100 NMR spectrometer with the instrument in the continuous-wave mode for ^{13}C and FT mode for ^{29}Si spectra. Samples used were as solutions in either or CCl_4 with internal TMS as standard. For some ^{29}Si spectra it was found necessary to add a trace of chromium acetylacetonate as a relaxation agent.

The necessary precautions were taken as is usual for air-sensitive starting materials and products and solvents were dried over sodium wire and distilled before use. Two methods were used for the synthesis of the organo-1,3,2-dioxasilacycloheptanes and examples of both methods are reported in detail. The physical constants and analytical data for all compounds are given in Table 4.

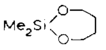
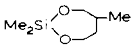
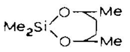
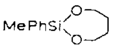
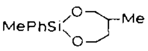
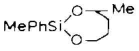
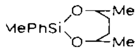
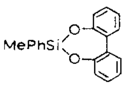
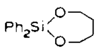
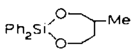
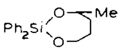
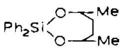
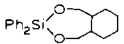
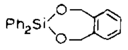
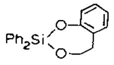
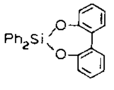
Method 1. Dichlorosilane + diol

Preparation of 2,5-dimethyl-2-phenyl-1,3,2-dioxasilacycloheptane

A solution of 2-methylbutane-1,4-diol (3.84 g, 0.037 mol) and pyridine (5.38 g, 0.074 mol) in benzene (75 cm^3) was added dropwise, and with stirring, to a solution of dichloromethylphenylsilane (7.05 g, 0.037 mol) in benzene (200 cm^3). The resulting solution was refluxed for 30 min and then allowed to cool to room temperature. Pyridine hydrochloride was filtered off and after removal of solvent, under reduced pressure, the residue on distillation afforded 2,5-dimethyl-2-phenyl-

TABLE 4

SEVEN-MEMBERED HETEROCYCLIC DIOL DERIVATIVES

Compound	Method	Yield (%)	B.p.(°C/mmHg) (M.p.) [a]	Analysis (Found (calcd.(%)) C	Analysis (Found (calcd.(%)) H
	2	40	104–24/atm [142 [2]]	49.1 (49.3)	9.8 (9.7)
	1	23	26/1.0 [145/746 [3]]	52.9 (52.5)	9.9 (10.1)
	2	40	23/0.1	55.2 (55.1)	9.3 (10.4)
	1	10	82/6.0	64.4 (63.4)	8.9 (7.7)
	1	49	80–88/0.1	65.0 (64.8)	7.8 (8.2)
	1	33	75–80/0.05	64.8 (64.8)	8.3 (8.3)
	1	24	75–78/0.02	65.8 (66.1)	8.8 (8.5)
	1	25	168–176/0.1 (103.5) [(101.0–101.2) [4]]	75.5 (75.1)	5.5 (5.3)
	1	10	115–134/0.1	71.2 (71.1)	6.9 (6.7)
" dimer	1	11	(176–184)	71.4 (71.1)	6.8 (6.7)
	1	18	148–170/0.15	71.9 (71.8)	7.2 (7.1)
" dimer	1	7	(154–175)	72.2 (71.8)	7.0 (7.1)
	1	68	125–137/0.05	71.7 (71.8)	6.9 (6.7)
	1	21	130–140/0.1 (55–75)	72.1 (72.5)	7.5 (7.4)
" dimer	1	17	(155–170)	72.9 (72.5)	7.5 (7.4)
 (cis)	1	50	174–182/0.2 [167/0.05 [5]]	74.4 (74.0)	7.5 (7.5)
	1	22	(129–131) [(130.6) [6]]	75.5 (75.4)	5.7 (5.7)
" dimer	1	35	(245–250)	75.3 (75.4)	5.6 (5.7)
	1	26	164–174/0.5	75.5 (75.4)	5.8 (5.7)
	1	70	(125–126) [(124) [7]]	78.7 (78.7)	4.8 (5.0)

---

[a] Values in brackets indicated the Ref. b.p. (m.p.).

1,3,2-dioxasilacycloheptane as a colourless liquid (4.0 g, 49%), b.p. 80–88°C/0.1 mmHg (Found: C, 65.0; H, 7.8. $C_{12}H_{18}O_2Si$ calcd.: C, 64.8; H, 8.2%).

Preparation of 4,7-dimethyl-2,2-diphenyl-1,3,2-dioxasilacycloheptane (monomer) and 4,7,11,14-tetramethyl-2,2,9,9-tetraphenyl-1,3,8,10-tetraoxa-2,9-disilacyclotetradecane (dimer)

A solution of hexane-2,5-diol (4.66 g, 0.0395 mol) in benzene (50 cm^3), containing a slight excess of pyridine, was added dropwise, and with stirring, to a solution of dichlorodiphenylsilane (10.0 g, 0.0395 mol) in benzene (150 cm^3). The resulting solution was refluxed for 30 min and then allowed to cool to room temperature. Pyridine hydrochloride was filtered off and after removal of solvent, under reduced pressure, the colourless residue crystallized on cooling until almost solid. Recrystallization from petroleum ether (b.p. 60–80°C) afforded the dimer 4,7,11,14-tetramethyl-2,2,9,9-tetraphenyl-1,3,8,10-tetraoxa-2,9-disilacyclotetradecane (2.0 g, 17%), m.p. 155–170°C (Found: C, 72.8; H, 7.5. $C_{36}H_{44}O_4Si_2$ calcd.: C, 72.5; H, 7.4%).

The mother liquor from the recrystallization gave, after removal of solvent, a mobile residue which on distillation afforded 4,7-dimethyl-2,2-diphenyl-1,3,2-dioxasilacycloheptane as colourless crystals in the condenser (2.5 g, 21%), b.p. 130–140°C/0.1 mmHg, m.p. 55–75°C (Found: C, 72.1; H, 7.5. $C_{18}H_{22}O_2Si$ calcd.: C, 72.5; H, 7.4%).

Preparation of 5,6-benzo-2,2-diphenyl-1,3,2-dioxasilacycloheptane (monomer) and 5,6,12,13-dibenzo-2,2,9,9-tetraphenyl-1,3,8,10-tetraoxa-2,9-disilacyclotetradecadiene (dimer)

A solution of benzene-1,2-dimethanol (5.00 g, 0.036 mol) in benzene (30 cm^3), containing a slight excess of pyridine, was added dropwise, and with stirring, to a solution of dichlorodiphenylsilane (9.16 g, 0.036 mol) in benzene (150 cm^3). The resulting solution was refluxed for 1 h and then allowed to cool to room temperature. Pyridine hydrochloride was filtered off and after removal of solvent, under reduced pressure, a white powdery residue was obtained which afforded both monomer and dimer by fractional crystallization as follows. The residue was dissolved in a minimum of boiling benzene and on cooling the solution deposited fine white crystals of the dimer 5,6,12,13-dibenzo-2,2,9,9-tetraphenyl-1,3,8,10-tetraoxa-2,9-disilacyclotetradecadiene (4.0 g, 35%), m.p. 245–250°C (Found: C, 75,3; H, 5.6. $C_{40}H_{36}O_4Si_2$ calcd.: C, 75.4; H, 5.7%).

Crystallization from the residual solution afforded 5,6-benzo-2,2-diphenyl-1,3,2-dioxasilacycloheptene (2.5 g, 22%). m.p. 129–131°C (Found: C, 75.5; H, 5.7. $C_{20}H_{18}O_2Si$ calcd.: C, 75.4; H, 5.7%).

Method 2. Bis(dialkylamino)silane + diol

Preparation of 2,2-dimethyl-1,3,2-dioxasilacycloheptane

Dimethylbis(dimethylamino)silane (7.50 g, 0.051 mol) and butane-1,4-diol (4.62 g, 0.051 mol) were heated together, under reflux, up to a final temperature of 100°C. Dimethylamine was allowed to escape through a drying tube and the theoretical mass was soon lost. Distillation of the residue at atmospheric pressure afforded 2,2-dimethyl-1,3,2-dioxasilacycloheptane, with some difficulty, as a colourless liquid (3.0 g, 40%), b.p. 104–124°C/atm., (Found: C, 49.1; H, 9.8. $C_6H_{14}O_2Si$ calcd.: C, 49.3; H, 9.7%).

Acknowledgement

We thank Dr. Smith for recording the NMR spectra and Mr. S. Smith for recording the mass spectra.

References

1 R.H. Cragg and R.D. Lane, Inorg. Chim. Acta, 54 (1981) L115.
2 R.H. Krieble and C.A. Burkhard, J. Amer. Chem. Soc., 69 (1947) 2689.
3 M.G. Voronkov and Yu.P. Romadan, Khim. Geterotsikl. Soedin., (1966) 879.
4 H.J. Emeléus and J.J. Zuckermann, J. Organomet. Chem., 1 (1964) 328.
5 L. Birkoffer, W. Gruner and O. Stuhl, J. Organomet. Chem., 194 (1980) 159.
6 L. Birkoffer and O. Stuhl, J. Organomet. Chem., 164 (1979) C1.
7 R.M. Ismail, Z. Naturforsch. B, 19 (1964) 873.
8 P.E. Rakita and L.S. Worsham, J. Organomet. Chem., 137 (1977) 145.
9 P.E. Rakita and L.S. Worsham, Inorg. Nucl. Chem. Letters, 13 (1977) 547.
10 R.K. Harris, J. Jones and S. Ng, J. Magn. Reson., 30 (1978) 521.
11 J.A. Cella, J.D. Cargioli and E.A. Williams, J. Organomet. Chem., 186 (1980) 13.
12 R.H. Cragg and R.D. Lane, J. Organomet. Chem., 154 (1978) C6.
13 J.G. Liehr and W.J. Richter, Org. Mass Spectrom., 7 (1973) 53.
14 B.Y.K. Ho, L. Spialter and L.D. Smithson, Org. Mass Spectrom., 10 (1975) 361.
15 R.H. Cragg and R.D. Lane, J. Organomet. Chem., 277 (1984) 199.
16 R.D. Lane, Ph.D Thesis U.K.C. 1983.
17 R.H. Cragg and R.D. Lane, J. Organomet. Chem., 270 (1984) 25.