Journal of Organometallic Chemistry, 270 (1984) 25–37
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

CONTRIBUTIONS TO GROUP IV ORGANOMETALLIC CHEMISTRY

VI *. PREPARATION AND PROPERTIES OF SOME ORGANOSILICON DERIVATIVES OF CATECHOL

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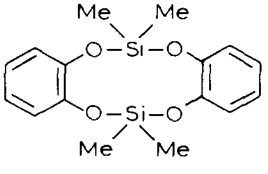
(Received March 1st, 1984)

Summary

The preparation and properties of some organosilicon derivatives of catechol are reported and their mass spectra and ^{1}H, ^{13}C and ^{29}Si NMR spectra discussed in detail.

Over a number of years there have been a number of conflicting reports concerning the nature and properties of organosilicon derivatives of catechol (Table 1). As part of a wider study concerning 1,3,2-dioxasila heterocycles we have recently investigated the properties of I, II and III.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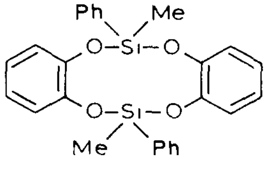
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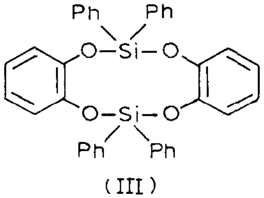
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* For part V see ref. 18.

0022-328X/84/$03.00

The synthesis of these heterocycles was via the interaction of the appropriate dichlorosilane with 1,2-dihydroxybenzene in the presence of pyridine. After removal of pyridine hydrochloride and solvent, recrystallisation of the residue afforded products which were dimeric at room temperature. Spectroscopic results are consistent with their formulation as 10-membered rings.

At higher temperatures reversible dissociation occurs and the ease with which dimeric and monomeric forms are interconvertible provides an elegant example of the importance of both types in 1,2,3-dioxasilaheterocycles.

Since the nature of the products can depend on both temperature and length of time elapsed after distillation it is hardly surprising that, where the importance of a monomer/dimer equilibrium has not been appreciated (or stated), some literature reports may appear contradictory on this point.

Results and discussion

(A) Physical constants

Melting points and boiling points with literature values for comparison are given in Table 1. The range of values presumably reflects different degrees of dissociation although greater agreement might well be expected. The melting point of compound III was checked on a freshly recrystallised sample and the difference between this and known literature values is unaccounted for. However, the higher values do seem to be greater than might be predicted from a consideration of the melting points of compounds I and II.

It may be noted that whereas dissociation takes place rapidly in solution at 80 °C (see later) any dissociation of solid dimer, below its melting point, must be very much slower.

(B) Proton and Carbon-13 NMR spectra

Proton NMR shifts are given in Table 2 and are in accord with published data [6,10] for compounds I and II. Phenylene and silicon-methyl protons give rise to

TABLE 1

MELTING AND BOILING POINTS OF COMPOUNDS I, II AND III

Compound	M.p. (°C)		B.p. (°C/mmHg)	
	Found	Literature	Found	Literature
I	84–88	71–12 [1] 93 [2] 96 [3]	82/0.5	71/3; 211/754 [4] 97–100/5–7 [1] 108/15 [5] 120/12 [2]
II	90–100 (distilled) 109–115 (crystallized and higher in *trans* isomer)	100–110 ([6] mixed isomers) 105 ([6] *cis*-) 121 ([6] *trans*-) 103.5 [7] 109 [1]	110–120/0.1	123–125/1–2 [1] 152/1 [8]
II	126–130	157–158 [1] 162.2–163.5 [9] 170.7 [7]	160–180/0.1 (impure product)	203–208/1–2 [1]

TABLE 2

PROTON NMR SHIFTS (ppm)

Compound	Phenylene	Methyl	Phenyl
I	6.83 (s)	0.35 (s)	–
II *trans* [6]	6.78 (s)	0.53 (s)	
cis	6.70 (s)	0.68 (s)	7.38 (m), 7.75 (m)
III	6.78 (s)	–	7.38 (m), 7.70 (m)

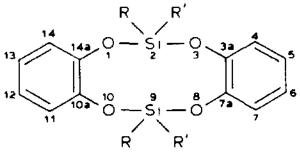
singlets on the spectra, that of compound II containing two large peaks due to *cis*- and *trans*-dimer and a small one due to a trace of monomer (0.68, 0.53 and 0.78 ppm, respectively) [6].

Carbon-13 NMR shifts for compounds I, II and III are given in Table 3. The phenylene carbons 4–7/11–14 gave rise to two peaks of equally large intensity and in close proximity to each other (separation approximately 1 ppm) in all three spectra and separate assignments were not attempted. The shift values for these carbons in compound I are at variance with those quoted by Meyer, Klein and Weiss [10] (120.99 and 113.33 ppm). The discrepancy of about 8 ppm is large and difficult to explain. It may be that the sample used was freshly distilled, therefore being mainly monomeric and possibly giving a different spectrum, or that the peak at 113.33 ppm was due to an impurity. A small signal, not much above 'noise' level, does appear on our own spectrum at exactly this value (Fig. 1).

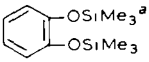
Although carbon-13 NMR spectra were initially only recorded using solutions of dimer crystals at room temperature, additional ones were later obtained using solutions which had been freshly refluxed ($CDCl_3$ solvent, b.p. approx. 60 °C) for 30–45 minutes. Results from these were of limited value and open to interpretation but were clearly more complex than before, as was to be expected if dissociation had occurred. The spectra for I were very similar and there was no significant increase in

TABLE 3

CARBON-13 NMR SHIFTS (ppm)



(I R = R' = Me,
II R = Me, R = Ph,
III R = R' = Ph)

Compound	3a,7a,10a,14a	4–7/11–14	Methyl	Phenyl			
				C(1)	*o*	*m*	*p*
I	145.00	122.67, 121.58	−2.06	–	–	–	–
II	144.88	122.79, 121.46	−3.76	133.23	133.96	128.01	130.56
III	144.63	122.67, 121.34	–	–	134.93	127.65	130.56
 OSiMe$_3$ [a] OSiMe$_3$	146.34	121.65, 120.86	0 [b]	–	–	–	–

[a] Included for comparison. [b] Peak could not be resolved from the TMS signal.

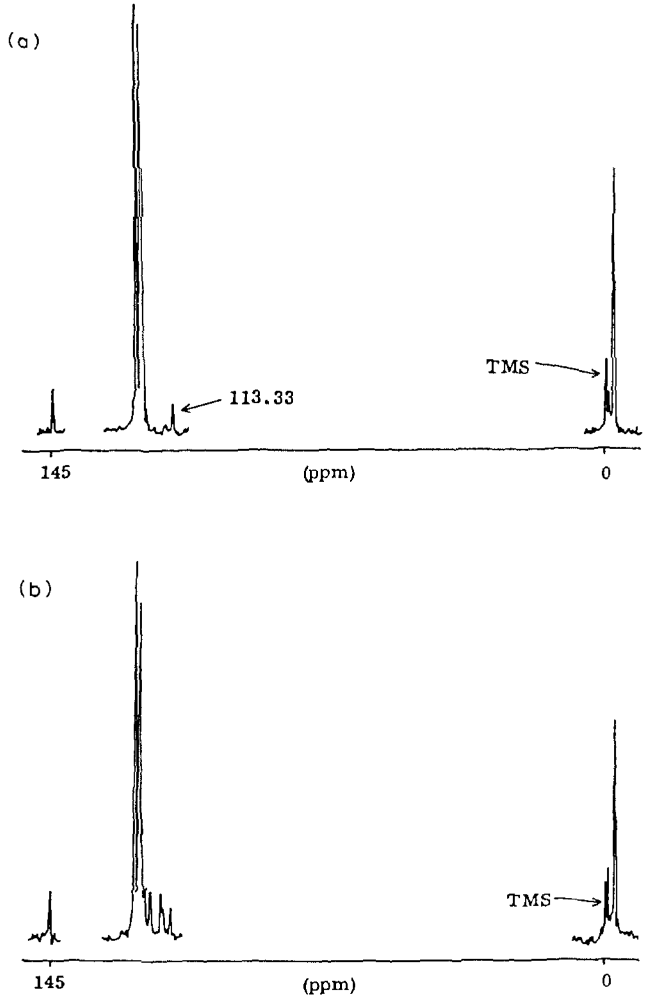


Fig. 1. Carbon-13 NMR spectra of I. (a) Solution of dimer crystals at room temperature, (b) solution of dimer crystals refluxed for 30 min, spectrum at room temperature.

the intensity of the peak at 113.33 ppm (Fig. 1). The most significant feature appears to be an increase in the intensity of a small peak at -0.6 ppm, relative to that at -2.06 ppm, and this could be tentatively assigned to the silicon-methyl of the monomer. A more striking change was seen in the spectrum of compound III (Fig. 2), as might be expected in view of its greater tendency to dissociate at elevated temperatures. The phenyl peaks are clearly split and a new peak is seen at 113.69 ppm though, again, it is difficult to know what significance to attach to this. Some properly conducted variable temperature carbon-13 NMR experiments on these compounds would undoubtedly be worthwhile and should resolve the question of phenylene-carbon assignments.

(C) Silicon-29 NMR spectra

The extreme simplicity of silicon-29 NMR spectra for molecules containing one

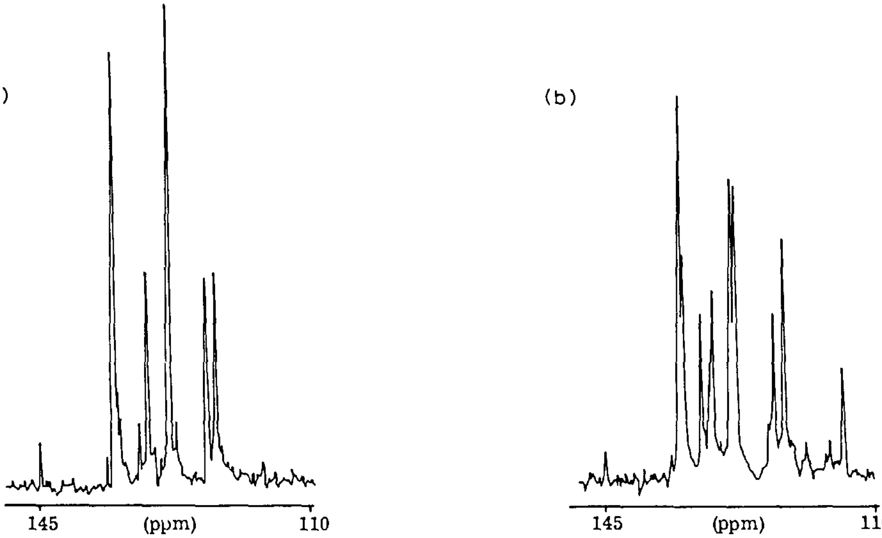


Fig. 2. Carbon-13 NMR spectra of III. (a) Solution of dimer crystals at room temperature, (b) solution of dimer crystals refluxed for 45 min, spectrum at room temperature.

or two silicon atoms provided an ideal method for demonstrating the monomer/dimer equilibria of these compounds. In addition, the large difference in shifts expected for 5- and 10-membered rings was borne out by the results and is strong evidence for the cyclic nature of both monomeric and dimeric forms.

The spectra and shifts for compounds I, II and III, at room temperature and 59 °C, are shown in Fig. 3 and Table 4. The low intensities of some of the peaks was undesirable but resulted from the low solubilities of the compounds coupled with the existence of both monomer and dimer in equilibrium. However, the peaks were sufficiently above noise level, and broad, to be taken as "real". The validity of the signals is also endorsed by the fact that shift values for all three compounds demonstrate a clear and predictable trend (Table 4).

The characteristic (methyl → phenyl) substituent shift of about −15 ppm for the dioxasilicon atom [19] is clearly seen in these results. Of more particular interest for these compounds are the following observations.

(i) Dimer peaks are all singlets (2 isomers for compound II). This suggests either a single conformer for each compound, with both silicon atoms equivalent, or a time-averaged structure with each silicon equivalent. Proton and carbon-13 NMR results also point to symmetrical structures with all equivalent atoms producing singlets (section B).

(ii) Dimer peaks for compounds II and III disappear completely at 59 °C, whereas compound I appears to be predominantly dimeric at this temperature. The relatively greater stability of this compound as a dimer is also indicated by ebullioscopic molecular weight determination (195 at equilibrium in boiling benzene) and its mass spectrum (*m/e* 332, 5% base). Molecular weights and mass spectra of compounds II and III, obtained under the same conditions, indicated almost complete dissociation to monomers. Any explanation of these, and the foregoing, observations must therefore take into account the following facts:

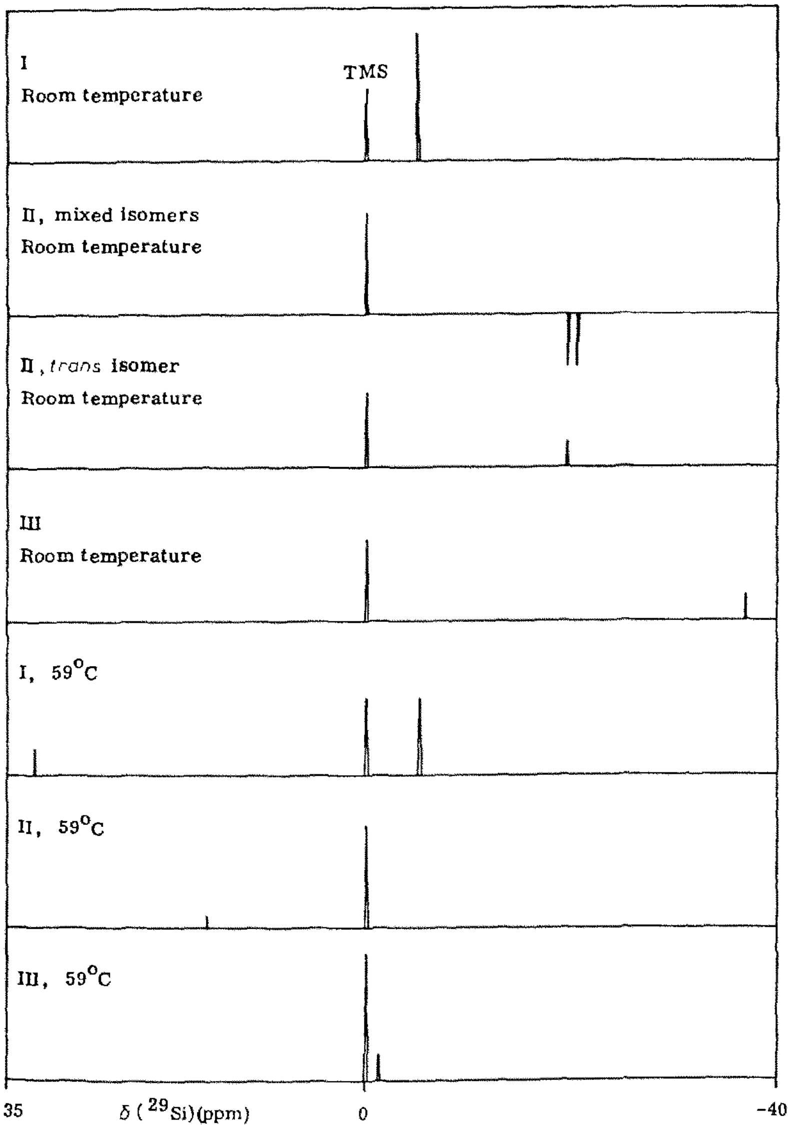


Fig. 3. The effect of elevated temperature on silicon-29 NMR spectra (spectrum II with negative NOE was from solution without $Cr(acac)_3$).

TABLE 4

SILICON-29 NMR SHIFTS (ppm)

	I	II	III
Room temperature	−4.96	−19.81 −20.73	−37.00
59 °C	−5.30 +32.19	+15.48	−1.37
$\Delta\delta(^{29}Si)$ (r.t. −59 °C)	+37.15	+35.29 +36.21	+35.63

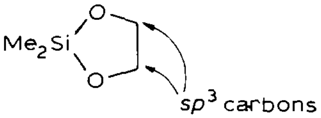
(a) The equilibria appear to involve only monomeric and dimeric species without apparent tendency to further polymerization.

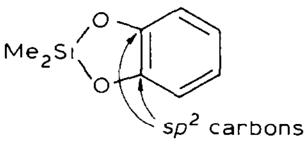
(b) Interconversion of monomer and dimer is rapid at only moderately elevated temperatures.

(c) Substitution of methyl by phenyl groups at the silicon atom renders the dimer less stable to dissociation.

(d) Similar atoms and groups within the dimer molecule appear to be equivalent.

The problem may be approached by a consideration either of factors which affect the stability of monomers or of those which affect the stability of dimers. If monomer is considered to be the initially expected product then the formation of dimer can be attributed to ring strain [2,12] in the monomer. This is reasonable for any 1,3,2-dioxasila-five-membered ring since the requirement for average bond angles $\leqslant 108°$ cannot be met unless at least some of the angles are compressed below the tetrahedral value of 109.5°. "Formation of an unstrained 5-membered ring >C–O–Si–O–C< requires decrease in the usual tetrahedral valence angles of C–C–O, C–O–Si or O–Si–O, i.e. ring compression" [4]. However, this argument should be even more relevant in the case of 1,2-dihydroxybenzene derivatives since the annular carbon atoms are aromatic and therefore sp^2 hybridized, with expected bond angles of 120°. It is therefore instructive to compare the relative stabilities of these monomers with those derived from aliphatic diols. For example, 2,2-dimethyl-1,3,2-dioxasilolane can only be obtained as a dimer or higher polymer [13] and yet a consideration of bond angles indicates that the monomer ring should be less strained than in the case of (1,2-phenylenedioxy)dimethylsilane since two of the angles will be tetrahedral rather than trigonal:





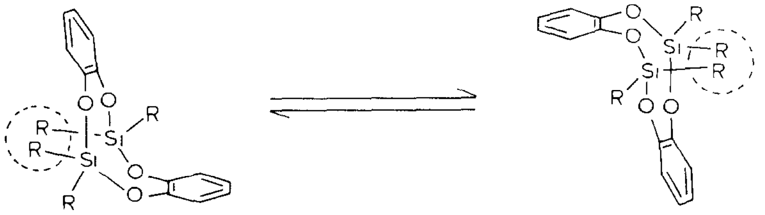
At the same time, pinacol derivatives are normally monomeric [3]. 2,2,4,4,5,5-Hexamethyl-1,3,2-dioxasilacyclopentane was obtained only as a monomer by us and appeared to be stable. Although *gem*-dimethyl substituents on the ring carbons might, on the Thorpe–Ingold hypothesis, be expected to reduce the tetrahedral angle [4], it is difficult to imagine that this factor alone would have such a significant effect on the stability of the monomer. Hence, whilst ring strain must certainly be a factor it appears that substitution per se may also be important in determining the nature of the products. We favour the theory put forward by Calas and Nicou [3], who investigated various α-dihydroxy derivatives of dimethyldichlorosilane, that dimeric products are to be expected unless substitution is such that dimer formation is unlikely on steric grounds. (If the argument is extended, higher degrees of polymerization might presumably be excluded for the same reason.) It is thus the presence of dimethyl groups on both silicon and carbon atoms that prevents dimer formation in the example of the pinacol derivative given above. When either the silicon atom, or each carbon atom, is only monosubstituted then the product is again dimeric [3,4].

Returning to the (1,2-phenylenedioxy)silanes and applying the same reasoning, a rationalization for the existence of an equilibrium situation becomes apparent. The monomeric ring is likely to be severely strained, due to excessively diminished bond angles, whilst at the same time the dimer may be unstable due to steric hindrance.

The difference in this case, as opposed to that of the dioxasilacyclopentanes, is that any steric hindrance will be between silicon atom substituents since the planar aromatic rings are unlikely to come into close proximity either with each other or with the silicon substituents. On this model steric interactions ought to be greatest, and the dimer least stable, when both silicon atoms are substituted by two phenyl groups; a prediction which is in full agreement with the experimental results. An investigation of the monomer/dimer equilibrium for (1,2-phenylenedioxy)methylsilane would be of interest in this context as the presence of only one silicon atom substituent ought to lead to enhanced dimer stability.

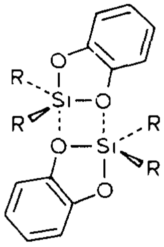
To propose possible structures for, or to make models of, the compounds is difficult since values for bond angles cannot be assumed. In particular, Si–O–C angles generally would seem to be different from, and substantially greater than, the tetrahedral angle. Examples are those of 121° in $MeOSiH_3$ [14] and 125° in $Ph_2Si(OCH_2CH_2)_2NH$ [15]. The most relevant X-ray diffraction studies appear to be those for penta- [16] and hexa-coordinate [17] silicates containing 1,2-phenylenedioxy groups which indicate O–Si–O bond angles of approximately 88° (90° could be expected for sp^3d and sp^3d^2 hybridized silicon atoms) and virtually equivalent Si–O–C and O–C–C bond angles in the range 111–115°, O–Si–O and 1,2-phenylene moieties being coplanar. This suggests that the oxygen atoms also have distorted sp^2 hybridization since there seems little reason to suppose that essentially tetrahedral (sp^3) angles would be increased due to 5-membered ring formation. If a parallel situation exists for the monomeric (1,2-phenylenedioxy)silanes under consideration then the presence of a tetrahedral, rather than a penta- or hexa-coordinate, silicon atom would be expected to give rise to greater O–Si–O bond angles; thereby leading to increased ring strain.

Assuming all angles to be trigonal, except for those of silicon which were taken to be essentially tetrahedral, framework models of the dimer were made. Several conformers were possible, including two which were similar to those suggested by Meyer et al. [10]. One of these fulfils the requirement that both silicon atoms be equivalent, and its apparent ease of inversion means that the silicon atom substituents and 1,2-phenylene groups are also equivalent on average. For the latter, only three carbon-13 NMR signals would be expected and this is found to be the case (section B).



In these extreme forms, which from the models appear to correspond to energy minima, considerable steric hindrance is likely and particularly so if R = phenyl. Although these structures are purely speculative it is therefore possible to imagine how steric interactions can arise in the dimer molecules and that these occur between silicon atom substituents.

The two isomers of compound II are easily envisaged as essentially *cis*- and *trans*-forms, whatever the actual conformations. The apparent ease of interconversion of monomeric and dimeric heterocycles can thus be explained as resulting from a balance between two essentially unstable structures, the monomer due to ring strain and the dimer due to steric hindrance. The low activation energy of dimerization has been noted [10] and a possible mechanism and transition state have been suggested [2]. A transition state containing penta-coordinate silicon atoms is attractive since, apart from any other considerations, this would require a decrease of the silicon bond angles and would therefore reduce the strain in the monomeric ring. For this to be true the qualification must be added that, in the transition state, the two phenylene oxygens would need to occupy one axial and one equatorial position (as was found in the X-ray studies of pentacoordinate silicates containing *o*-phenylenedioxy groups) [17], i.e.:



Co-planar except for R

Comment can be made, in passing, that the alternative formulation of these compounds as coordination dimers would require a similar type of structure and therefore non-equivalent oxygen atoms. The fact that only one peak for the carbons bonded to oxygen is found in the carbon-13 NMR spectra (section B) strongly suggests that this is not the case.

(iii) Silicon-29 NMR dimerization shifts are virtually constant for each compound and are within the range −35.29 to −37.15 ppm (Table 4). They are therefore somewhat greater than the corresponding values of about −30 ppm for aliphatic α-diol derivatives [20]. Since the dimer shifts are roughly comparable (e.g. III, −37.00; $(\mathrm{Ph_2\overline{SiOCMe_2CMe_2O}})_2$, −38.24 ppm) the difference can be attributed to the more downfield monomer values (e.g. III monomer, −1.37; $\mathrm{Ph_2\overline{SiOCMe_2CMe_2O}}$, −10.88) which are themselves explainable in terms of the greater strain in a partially unsaturated ring.

(iv) When crystals of compound III (obtained by recrystallization were distilled, the product gave a clear, single peak on the silicon-29 NMR spectrum. The shift of −32.58 ppm is very different from that of the dimer crystals themselves (−37.00 ppm). Though the identity of the compound responsible has not been confirmed, other results give some indication that it could have the structure:

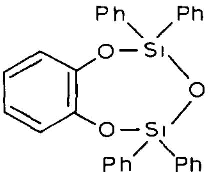


TABLE 5

MASS SPECTRA

Compound	Monomer mass	m/e (% base peak) for ions > 5%
I	166	332 (5), 317 (5), 225 (3), 166 (100), 151 (81), 136 (27), 133 (6)
II	228	228 (100), 213 (87), 151 (6), 136 (19), 114 (5)[a], 91 (5), 77 (19), 51 (7)
III	290	290 (100), 213 (33), 145 (5)[a], 136 (8), 77 (14)

[a] Doubly charged ions.

D. Mass spectra

The mass spectra and fragmentation patterns of the dissociated, monomeric compounds are given in Table 5 and Fig. 4. The principal features are their simplicity and the sequential loss of both silicon-atom substituents from the molecular ion and are in agreement with previous work [11,7].

In addition, it can be seen that the dimer molecular ion, together with other dimer fragments, is significant for compound I and a fragmentation scheme is suggested (Fig. 5). Here, sequential loss of silicon substituents is not observed and initial loss of one methyl radical is followed by ring contraction.

Although the spectra of compounds II and III were obtained using dimer crystals, the highest peaks were of the monomer molecular ion in each case (base peaks). That such macrocyclic structures can survive in the mass spectrometer is demonstrated by

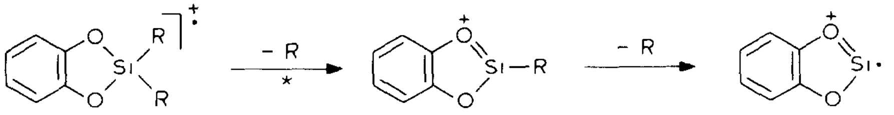


Fig. 4. Monomer fragmentation scheme (R = Me, Ph), * metastable-supported in each case.

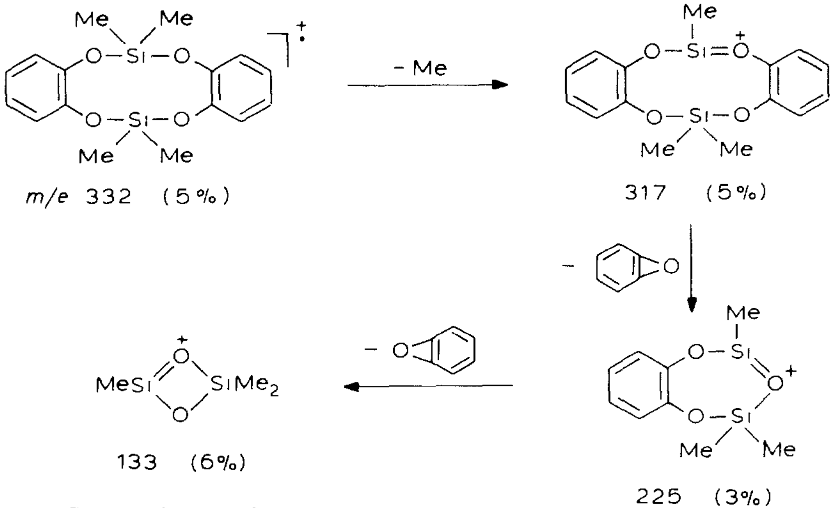
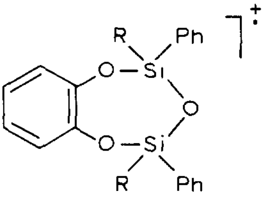


Fig. 5. Compound I dimer fragmentation.

the 14-membered dimers of some 1,3,2-dioxasilacycloheptanes which produce spectra quite distinct from those of their monomers [21]. In comparison, therefore, these 10-membered heterocycles appear to be unstable and to dissociate readily into monomers under the operating conditions of the mass spectrometer. The fact that compound I is the only one to give rise to dimer-related peaks is in keeping with molecular weight and silicon-29 NMR results which both indicate it to be the most stable of the three dimers.

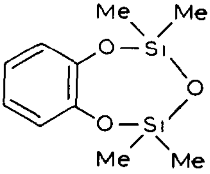
Spectra of distilled samples of compounds II and III contained several peaks above those of the monomer molecular ion. Although it may be fortuitous, the incidence of the highest-mass ion as [dimer $-92]^+$ in each case (*m/e* 364 and 488 respectively; both > 5% Rel. Int.) suggests the most likely structure to be:



(R = Me or Ph)

The point has not been pursued and further work would be needed in order to clarify the effect of distillation on these compounds. However, the results are indicative that these derivatives should always be purified by recrystallization rather than by distillation.

It is of interest that the compound:



has been prepared and has been shown to be monomeric [12].

E. Molecular weights

Given satisfactory analyses, and molecular ions from mass spectra, approximate molecular weight determinations were carried out with a view to establishing the monomer/dimer nature of the products. Ebullioscopic determinations with benzene as solvent were carried out for all three compounds. The calculated molecular weights decreased rapidly to an almost constant value after a few minutes, indicating that dissociation into monomer was occurring readily at the boiling point of benzene (80 °C). (The alternative of slow dissolution of the crystals was discounted as they were known to be readily soluble in hot benzene.) Values obtained after 10 to 20 minutes were as follows: I: found, 195 (calcd. for monomer 166); II, found 220 (calcd. for monomer 228; III, found 291 (calcd. for monomer 290).

Hence at 80 °C the dissociation of compounds II and III into monomer is virtually complete.

An experiment to follow the decrease in molecular weight of compound III with time gave results consistent with a first order rate expression and indicated a half-life time of under 2 minutes. A similar experiment with compound I showed dissociation to be approximately 20% after 2 and 50% after 7 minutes. In this case a half-life time is not valid since the rate of the back reaction appears to be significant, with the establishment of an equilibrium. However, the conclusion can reasonably be drawn that dissociation is more rapid in the case of the diphenyl-substituted compound III.

A cryoscopic molecular weight determination on compound III, in benzene, indicated it to be almost purely dimeric (found 544; calcd. for dimer 580).

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 ±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 proton spectra and in the Fourier transform mode for carbon-13 and silicon-29 spectra. Samples used were as solutions in either $CDCl_3$ or CCl_4 with internal TMS as standard. For some silicon-29 spectra it was found necessary to add a trace of chromium acetylacetonate as a relaxation agent.

Preparation of 3a,7a,10a,14a-dibenzo-2,9-dimethyl-2,9-diphenyyl-1,3,8,10-tetraoxa-2,9-disilacyclodecadiene

A solution of 1,2-dihydroxybenzene (5.76 g, 0.052 mol) and pyridine (8.40 g, 0.106 mol) in benzene (100 ml) was added dropwise, and with stirring, to a solution of dichloromethylphenylsilane (10.0 g, 0.052 mol) in benzene (300 ml). The resulting solution was refluxed for $2\frac{1}{2}$ h and then allowed to cool to room temperature. Pyridine hydrochloride was filtered off and after removal of the solvent, under reduced pressure, the residue crystallised on cooling. Recrystallisation from petroleum ether (b.p. 60–80 °C), containing a minimum of benzene, afforded 3a,7a,10a,14a-dibenzo-2,9-dimethyl-2,9-diphenyl-1,3,8,10-tetraoxa-2,9-disilacyclodecadiene as colourless crystals (7.0 g, 59%), m.p. 109–115 °C. (Found: C, 68.9; H, 5.3. $C_{26}H_{24}O_4Si_2$ calcd.: C, 68.4; H, 5.3%).

The 2,9-tetramethyl compound m.p. 84–88 °C (Found: C, 58.1; H, 6.0. $C_{16}H_{20}O_4Si_2$ calcd.: C, 57.8; H, 6.1%) and the 2,9-tetraphenyl compound m.p. 126–130 °C. (Found: C, 74.7; H. 4.7. $C_{36}H_{28}O_4Si_2$ calcd.: C, 74.5; H, 4.9%) derivatives in yields of 46 and 60% were prepared from the interaction of 1,2-dihydroxybenzene and the corresponding dichlorosilane in the presence of pyridine.

Acknowledgements

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

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