Journal of Organometallic Chemistry, 212 (1981) 301—310
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

CONTRIBUTIONS TO GROUP IV ORGANOMETALLIC CHEMISTRY

IV *. PREPARATION AND PROPERTIES OF SOME ORGANOSILICON DERIVATIVES OF SALICYLIC AND RELATED ACIDS

R. HARRY CRAGG and ROB D. LANE

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

(Received December 22nd, 1980)

Summary

The preparation and properties of some 2-methylphenyl-4-oxobenzo-1,3,2-dioxasilanes and related compounds are reported and their general mass spectral features and ^{13}C and ^{29}Si NMR spectra are fully discussed.

The synthesis of 1,3-dioxa-2-silacycloalkanes of the type $R^1R^2\overline{SiO(CH_2)_nO}$, via the interaction of a dihalo- or a dialkoxy-silane and a diol, is well established [2,3]. By contrast, reference to heterocyclic dioxasilanes not derived from diols is rather limited and we have therefore embarked upon an extensive study of the preparation and properties of such systems. In this paper we report the results of our investigations concerned with the synthesis and properties of 1,3-dioxa-2-silacyclo-derivatives of some salicyclic and related acids. Mehrotra and Narain [4] have published their results of a study of the reactions between tri- and tetra-alkoxy silanes and various hydroxy acids, including salicyclic acid. However, it is doubtful in some cases whether the compounds were carefully purified and there was also a lack of information concerning their properties. Lapkin and workers reported the reaction of dialkylsilanes with hydroxy- and keto-acids, in the presence of a colloidal nickel catalyst, leading to the formation of cyclic 1,3-dioxa-2-sila-ones [5,6,7]. Our own investigations so far indicate that cyclic products are obtained only with great difficulty, and usually not at all, in the reaction of dichlorosilane with aliphatic hydroxy acids. Properties of those compounds prepared will be described in a future paper.

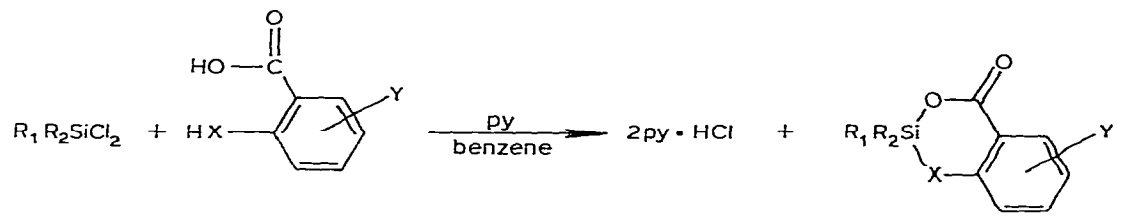
We have synthesised a series of monomeric 1,3-dioxa-2-silacyclo derivatives of some salicyclic acids and related compounds via the interactions of a dichloro-

---

* For part III see ref. 1.

0 022-328X/81/0000—0000/$02.50

silane and the corresponding organic acid in benzene in the presence of pyridine (for designation of R_1, R_2, X and Y see Table 1).



It is noteworthy that these compounds, in contrast to the similar derivatives of aliphatic hydroxy acids, were isolated with comparative ease. The physical constants, yields and analytical data of the compounds synthesised are given in Table 1. All compounds were purified by vacuum distillation. The compounds are high boiling viscous liquids, three of them (III, VII and IX) solidified on standing. The yields reported in the Table are minimum values obtained after at least two distillations.

^{13}C NMR

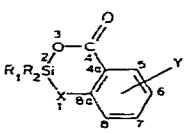
The ^{13}C NMR spectra of the compounds synthesised were recorded and the assignments of the lines in each spectrum are given in Table 2. The assignments proposed were based on the following assumptions.

(1) The silicon—phenyl assignments were made on the basis of published data and relative peak intensities [8].

(2) Assignments for the carbon atoms of the acid nucleus were made by initially obtaining approximate values using 128.5 for benzene and accepted substituent effects for $—CO_2H$ and —OH. The values obtained were then compared with the observed values for compound I which does not contain any phenyl—silicon carbon atoms. Using relative intensities, assignments were

TABLE 1

ANALYSIS, YIELDS AND B.P.'s FOR COMPOUNDS OF THE TYPE



Compound	R^1	R^2	X	Y	Yield (%)	B.p. (°C/ mmHg)	Analyses found (calcd.) (%)		
							C	H	N
I	Me	Me	O	H	50	85—115/0.1	54.65 (55.66)	5.96 (5.19)	
II	Me	Ph	O	H	45	150—160/0.1	65.90 (65.59)	4.92 (4.72)	
III	Me	Ph	S	H	21	190—192/1.2	61.46 (61.73)	4.21 (4.44)	
IV	Me	Ph	NMe	H	35	182—192/0.5	67.36 (66.88)	6.29 (5.61)	4.88 (5.20)
V	Me	Ph	O	8-Me	35	169/0.25	66.41 (66.63)	5.68 (5.22)	
VI	Me	Ph	O	6-Cl	25	160—165/0.1	57.77 (57.80)	4.02 (4.81)	
VII	Me	Ph	O	6-OMe	21	160—170/0.1	62.10 (62.90)	4.96 (4.93)	
VIII	Ph	Ph	O	H	36	188—195/0.4	72.08 (71.60)	4.55 (4.43)	
IX	Ph	Ph	O	8-Me	50	198/0.2	72.33 (72.26)	5.19 (4.85)	

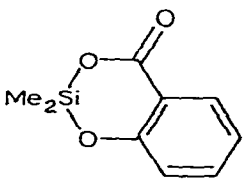
then made with what we believe to be acceptable accuracy.

(3) The assignments proposed for compound I were then used as a basis for the predicted assignments of the ^{13}C spectra of the rest of the derivatives in conjunction with accepted substituent effects for benzene and relative peak intensities. Where there is any doubt as to the assignment of a peak, for any reason, indication is made in the Table.

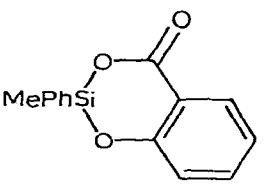
The proposed assignments of the peaks in the spectra are generally in good agreement with the predicted values and it is observed that long range substituent effects across the oxygen—silicon bonds are very small. As a result the values for the methyl—silicon peaks were virtually unaffected by substituents in the acid nucleus and the values for phenyl—silicon remained remarkably constant even when an annular oxygen atom was substituted by either nitrogen or sulphur. However, by contrast the substitution of an oxygen atom by sulphur resulted in a downfield shift of the methyl—silicon value whilst substitution of an oxygen atom by NMe resulted in an upfield shift. This result would not be expected from a consideration of the relative electronegativities of N, O and S and it is attractive to suggest that $p\pi$—$d\pi$ bonding from oxygen or nitrogen to the silicon atom is an important feature in these compounds. These observations are consistent with those of Rakita and Worsham [9] who reported similar up-field shifts of the methyl—silicon ^{13}C resonances when methylsilyl compounds are substituted by first row donor atoms (C, N and O). Substitution by SMe produced a slight up-field shift for the first substitution and small down-field shifts for second and third substitutions.

^{29}Si NMR

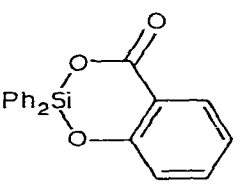
The ^{29}Si NMR spectra were recorded on all of the compounds and their shifts with respect to internal TMS are given in Table 3. All compounds showed negative Overhauser effects. The results compared favourably with those obtained via ^{13}C. It was observed that the acid nucleus had very little effect on the δ values as is demonstrated by the values obtained for compounds 2, 5, 6, 7, 8 and 9. In contrast, a successive substitution of methyl by phenyl on the silicon atom had a marked and noticeable additive effect, i.e.



δ (ppm) 12.48



−4.42



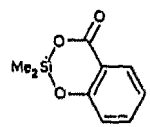
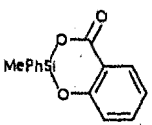
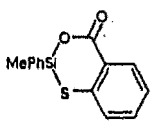
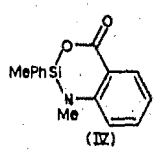
−21.32

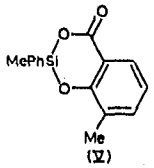
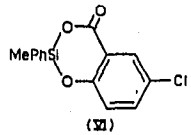
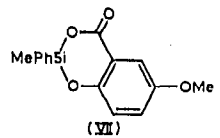
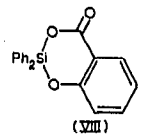
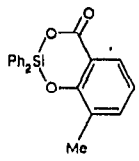
The difference in δ of 16.90 ppm in each case is very much larger than shifts of around 4 ppm for successive phenyl substitutions in tetramethylsilane [10,11]. With the increasing number of ^{29}Si NMR data available [12] it is clear that substituent effects are extremely dependent on other atoms attached to the silicon. Hence, the values given above and also our unpublished data on other 1,3,2-dioxasilane compounds indicate that $Me_2 \rightarrow MePh$ and $MePh \rightarrow Ph_2$ substitutions produce an up-field shift of 13—17 ppm, provided that two oxygen atoms are directly bonded to the silicon atom. Our findings are in agreement

(Continued on p. 306)

TABLE 2

^{13}C NMR ASSIGNMENTS (ppm)

Compound	Si—Me*	Si-Phenyl				4a	8a	8	7	6	5	4	Other
		i	*o*	*m*	*p*								
 (I)	−0.84	—	—	—	—	117.45 116.73 (117.9)	155.92 (156.9)	120.00 (115.8)	136.02 (135.0)	122.06 (121.2)	131.89 (131.4)	160.65	—
 (II)	−2.18	— (133.85)	133.84 (133.68)	128.74 (127.64)	132.38 [a] (129.75)	117.34 (117.9)	156.53 (156.9)	120.37 (115.8)	136.51 (135.0)	122.68 (121.2)	132.38* (131.4)	160.90	—
 (III)	−0.31	— (133.85)	133.53 [a] (133.68)	128.31 (127.64)	131.71 (129.75)	129.16 (129.74)	134.50 (135.03)	132.68 [c] (132.77)	133.53 [a] (135.61)	126.61 (126.68)	131.34 [c] (131.48)	161.80	—
 (IV)	−3.39	— (133.85)	133.71 (133.68)	128.37 (127.64)	132.38 [b] (129.75)	114.30 (113.84)	149.97 (150.83)	113.21 (116.87)	135.53 (135.81)	118.42 (118.81)	131.65 [b] (131.68)	161.99	N—Me* 30.57

 (V)	−2.30	— (133.85)	133.73 (133.68)	128.63 (127.64)	132.15 (129.75)	116.86 (117.24)	154.60 (157.23)	129.12 (129.27)	137.25 (137.21)	121.96 (122.58)	129.84 (129.48)	161.15	C—$\overset{*}{\text{M}}$e 16.15
 (VI)	−2.54	— (135.85)	133.61 (133.68)	128.63 (127.64)	132.27 (129.75)	118.07 (118.64)	154.72 (154.63)	121.84 (121.67)	136.03 (136.91)	127.54 (128.88)	131.30 (132.78)	159.45	
 (VII)	−2.54	— (133.85)	133.73 (133.68)	128.63 (127.64)	132.15 (129.75)	117.10 (118.34)	150.47 (148.83)	121.35 (121.37)	124.63 (122.11)	154.60 (154.08)	113.58 117.98	160.91	O—$\overset{*}{\text{M}}$e 55.95
 (VIII)	—	— (133.85)	134.68 (134.70)	128.37 (127.69)	132.14 (130.00)	117.09 (117.9)	156.28 (156.9)	120.12 (115.8)	136.14 (135.0)	122.43 (121.2)	128.56 (131.4)	160.41	—
 (IX)	—	— (133.85)	134.81 (134.70)	128.38 (127.69)	132.26 (130.00)	116.97 (117.24)	154.69 (157.23)	128.86 127.89 (129.27)	137.12 (137.21)	121.95 (122.58)	129.96 (129.48)	—	C—$\overset{*}{\text{M}}$e 16.02

Values are given with respect to TMS. Those for compounds II, V, VI and VII were based on the central $CDCl_3$ peak taken as 77.42 ppm. ( ) predicted values.
[a] Intensities indicate peaks likely to be overlapping. [b] Possibly interchangeable. [c] Intensities less than expected. Where two values are given, either is possible.

TABLE 3

^{29}Si NMR SHIFTS W.R.T. TMS [a]

Compound	I	II	III	IV	V	VI	VII	VIII	IX
δ (ppm)	12.48	—4.42	8.94	—5.01	—4.66	—3.88	—4.76	—21.32	—21.50

[a] Negative values up-field of TMS.

with conclusions made by Lipmaa et al. [13] and by Schraml and Bellama [12], in their review of ^{29}Si NMR that the usefulness of additive substituent effects is questionable and likely to lead to erroneous assignments. This would seem to be particularly true for compounds of the type being considered here, where *p*-electron involvement is possible from all atoms directly bonded to silicon and a single substitution could lead to significant changes in all of these bonds. The question of the relative importance of $(p\rightarrow d)\pi$ bonding in silicon compounds is still the subject of considerable discussion [14—16]. Whatever the theoretical considerations, however, it would seem that when $(p\rightarrow d)\pi$ back donation might reasonably be expected (i.e. in Si—O, Si—N, Si—Cl) as a result of substitution, up-field shifts are observed provided that there is already one (or though not necessarily the same) of such bonds present. Hence in the compounds under discussion here, the substitution of an annular oxygen by sulphur leads to a marked down-field shift. When the oxygen is replaced by NMe a slight up-field shift is observed. This follows the same pattern as seen in the ^{13}C spectra.

It must be noted that only single resonances were recorded for Si—$^{13}CH_3$, N—$^{13}CH_3$ and ^{29}Si in compound IV. However, it is not possible at this time to say whether this is due to rapid nitrogen inversion or to sp^2 hybridization;

More of our ^{29}Si data and further discussion will be published shortly.

Mass spectra

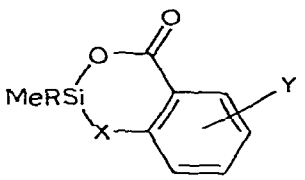
A study of the mass spectra showed that they had a number of common features and two general fragmentation patterns emerged with those of the diphenyl compounds differing in one important aspect from the rest.

A common feature of the spectra of compounds I—VII was the loss of a methyl radical from the parent ion followed by the loss of CO_2. These fragmentations gave rise to the most prominent peaks in many of the spectra which in the majority of cases were supported by metastable ions. The major ions of interest are given in Table 4. A fragmentation scheme which includes the major ions common to the spectra of these seven compounds is proposed (Scheme 1). A precise mass determination of the ion *m/e* 120 in compound VIII confirmed it to be $C_7H_4O_2$ and not the possible alternative C_6H_4SiO and this assignment is assumed to be the case of the corresponding ion observed in other compounds.

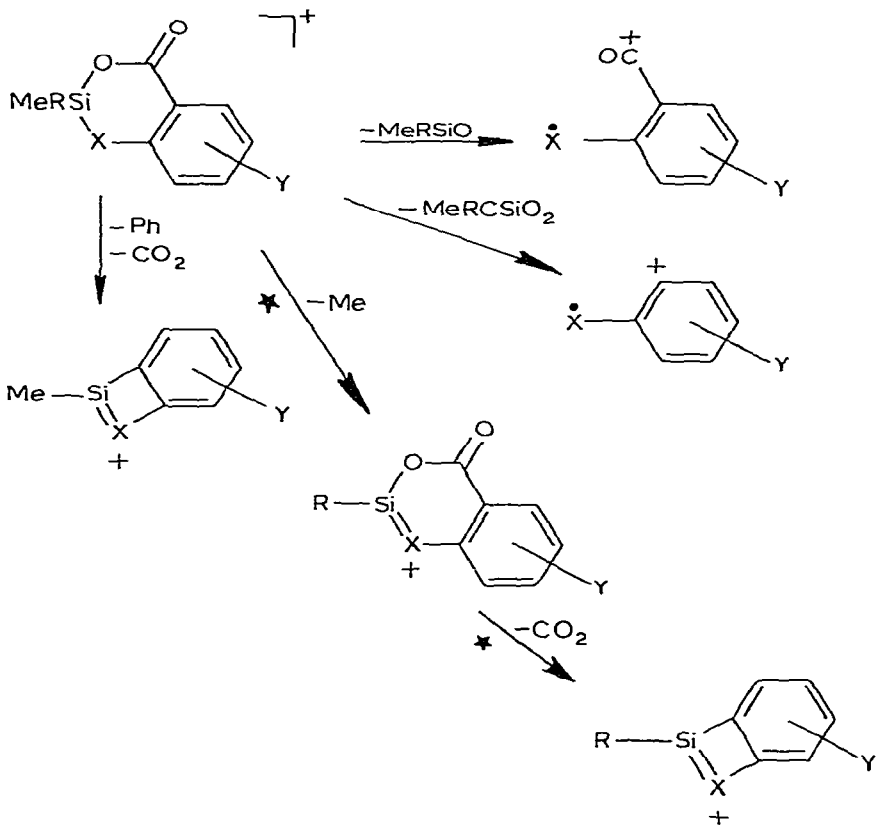
A similar picture was true for compounds VIII and IX i.e. loss of a phenyl radical from the parent ion followed by loss of CO_2 (Table 5).

In addition, however, an important peak appears at *m/e P* — 45 (also found in the other spectra but to a much lesser extent). This could arise by the loss of HCO_2 from the parent ion or, as seems more likely, by the loss of a proton from the parent ion followed by loss of CO_2. Small metastable peaks were apparent

SCHEME 1

PROPOSED FRAGMENTATION PATTERN FOR 

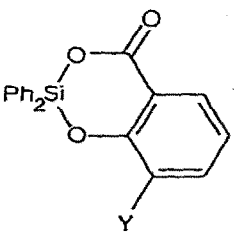
(for X and Y see Table 2)

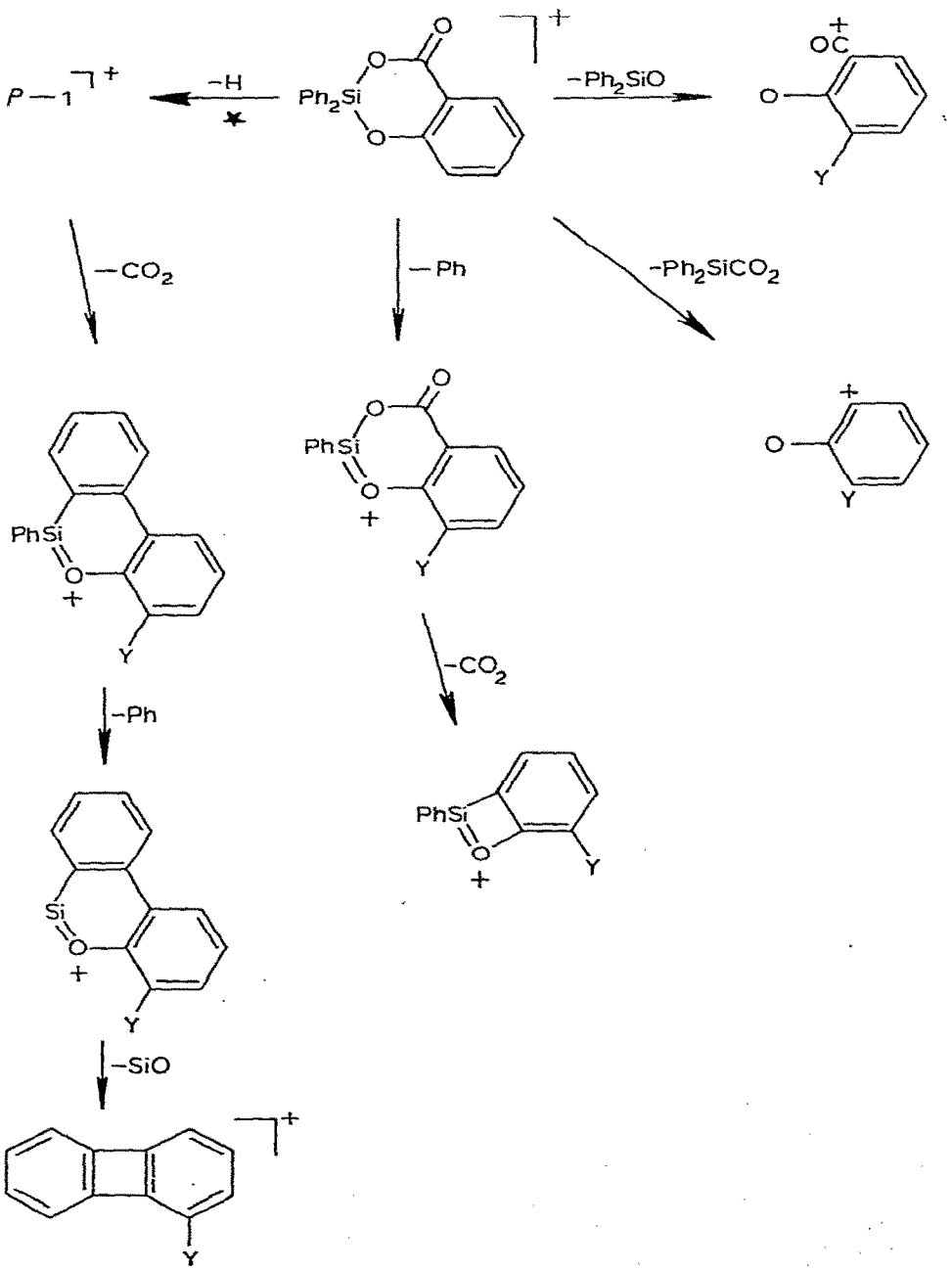


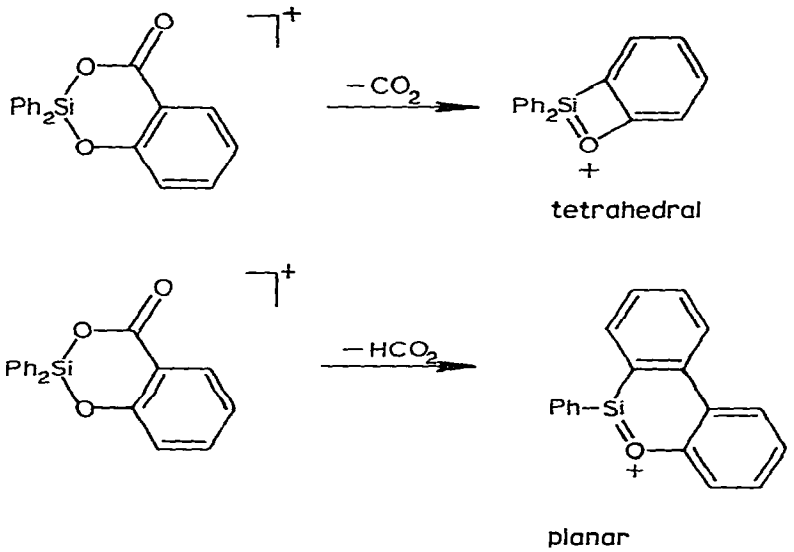
on both spectra for $m/e\ P-1$ but unfortunately clear metastables were not found to support either of the other suggested fragmentations. A posible fragmentation scheme, including the important ions common to both spectra, is suggested in Scheme 2.

It is possibly surprising that none of the compounds give rise to a major ion of $m/e\ P-44$. In the case of the dimethyl and methylphenyl compounds, this is explainable in terms of the apparently facile loss of a methyl radical from the parent ion. In the case of the diphenyl compounds however, it is likely to be due to the relative stability of the planar ion that could be formed by the net loss of HCO_2 from the parent ion.

SCHEME 2

PROPOSED FRAGMENTATION PATTERN FOR  (Y = H or M





Experimental

The mass spectra were recorded using an AEI MS 902 spectrometer at 70 eV. The source was maintained at 170°C and the compounds were introduced using a cooled direct-insertion probe. In general only those peaks of relative intensity greater than 5% were considered. ^{13}C and ^{29}Si NMR spectra were recorded on a JEOL PS100FT spectrometer and line positons are relative to internal TMS. As the experimental procedure was the same in all cases only two examples are discussed in detail and all analytical and physical data are given in Table 1.

Preparation of 2-methylphenyl-4-oxobenzo-1,3,2-dioxasilane

Dichloromethylphenylsilane (10.0 g, 0.052 mol), excess pyridine and salicyclic acid (7.23 g, 0.052 mol) were refluxed in benzene (150 cm^3) for one hour. On cooling the pyridine hydrochloride was filtered off and after removal

TABLE 4

MASS SPECTRA OF COMPOUNDS I–VII

Compound	*m/e* [a]		
	P	*P* − 15	(*P* − 15) − 44
I	53	33	100
II	77	44	100
III	73	15	100
IV	100	2.5	77
V	100	30	90
VI	100	41	82
VII	100	17	29

[a] Values are given as % base in each case.

TABLE 5

MASS SPECTRA OF COMPOUNDS VIII AND IX

Compound	*m/e* [a]					
	P	*P* − 1	*P* − 45	*P* − 77	*P* − 121 (77 + 44)	*P* − 122 (77 + 45)
VIII	97	11	26	15	100	9
IX	100	6	14	7	51	14

[a] Values are given as % base in each case.

of the solvent, under reduced pressure, the residue on distillation afforded 2-methylphenyl-4-oxobenzo-1,3,2-dioxasilane (6.0 g, 45%) b.p. 150—160°C/0.1 mmHg (Found: C, 65.90; H, 4.92; *M* = 256. $C_{14}H_{12}O_3Si$ calcd.: C, 65.59; H, 4.72%; *M* = 256).

Preparation of 2-methylphenyl-4-oxobenzo-3,1,2-oxathiasilane

Dichloromethylphenylsilane (10.0 g; 0.052 mol), excess pyridine and thiosalicylic acid (8.06 g; 0.052 mol) were refluxed in benzene (150 cm^3) for 1 hour. On cooling, the pyridine hydrochloride was filtered off and after removal of the solvent, under reduced pressure, the residue on distillation afforded 2-methylphenyl-4-oxobenzo-1,3,2-oxathiasilane (3.0 g, 21%), b.p. 190—192°C/1.2 mmHg, (Found: C, 61.46; H, 4.21; *M* = 272. $C_{14}H_{12}O_2SSi$ calcd.: C, 61.73; H, 4.44%; *M* = 272).

Acknowledgements

We thank Mr. T. Hillyar for recording the mass spectra, Dr. D. Smith for recording the NMR spectra and Dr. C. Brown for helpful discussion.

References

1 M.J. Buchanan, R.H. Cragg and A. Steltner, J. Organometal. Chem., 120 (1976) 189.
2 R.H. Krieble and C.A. Burkhard, J. Amer. Chem. Soc., 69 (1947) 2690.
3 M.G. Voronkov and Yu.P. Romadan, Khim. Greterotsikl Snedin, (1966) 879.
4 R.C. Mehrotra and R.P. Narain, Indian J. Chem., 6 (1968) 110.
5 I.I. Lapkin, T.N. Povarnitsyna and T.Yu. Subocheva, Zh. Obshch. Khim., 42 (1972) 399.
6 I.I. Lapkin, T.N. Povarnitsyna and T.Yu. Denisova, Zh. Obshch. Khim., 42 (1972) 2032.
7 I.I. Lapkin, T.N. Povarnitsyna and V.V. Dvinskikh, Zh. Obshch. Khim., 48 (1978) 607.
8 P.E. Rakita and L.S. Worsham, J. Organometal. Chem., 137 (1977) 145.
9 P.E. Rakita and L.S. Worsham, Inorg. Nucl. Chem. Lett., 13 (1977) 547.
10 G. Engelhardt, R. Radeglia, H. Jancke, E. Lippmaa and M. Magi, Org. Magn. Reson., 5 (1973) 561.
11 B.K. Hunter and L.W. Reeves, Can. J. Chem., 46 (1968) 1399.
12 J. Schraml and J.M. Bellama, Determination of Organic Structures by Physical Methods, Vol. 6, Academic Press, 1976, Chap. 4.
13 E. Lippmaa, M. Magi, G. Engelhardt, H. Jancke, V. Chvalovsky and J. Schraml, Collect. Czechsolov. Chem. Commun., 39 (1974),1041.
14 J. Schraml, J. Vcelak and V. Chvalovsky, Collect. Czechoslov. Chem. Commun., 39 (1974) 267.
15 J. Schraml, Nguyen-Duc-Chuy, V. Chvalovsky, M. Magi and E. Lippmann, Org. Magn. Reson., 7 (1975) 379.
16 M.L. Filleux-Blanchard and Nguyen Dinh An, Org. Magn. Reson., 12 (1979) 12.