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GROUP IV ORGANOMETALLIC COMPOUNDS

I. SYNTHESIS AND PROPERTIES OF HETEROCYCLIC SILICON AND GERMANIUM COMPOUNDS OF *o*-HYDROXYBENZYL ALCOHOL

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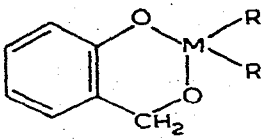
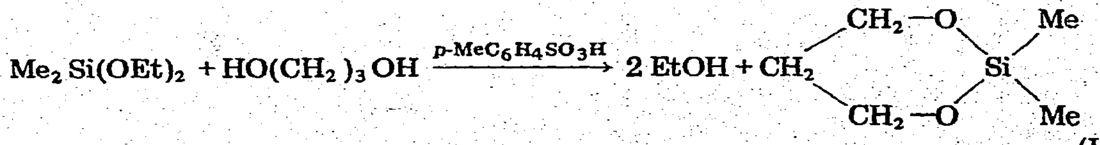
Summary

The synthesis and properties of compounds of the general formula:



(where R = alkyl or phenyl and M = Si or Ge) are described and the mass spectra of these compounds are discussed.

There is considerable interest in utilizing the interaction of dihydric alcohols and organosilicon compounds to form cyclic organosilanes. Unlike the analogous synthesis of cyclic organoboranes, by the interaction of a dichloroborane with a dihydric alcohol, the reactions of dichlorosilanes are not so predictable. For example, the reaction of dichlorodimethylsilane and 1,3-propanediol results in the formation of a polymer and no cyclic compound I. However, the existence of compound I has been demonstrated. The reaction between diethoxydimethylsilane and 1,3-propanediol, in the presence of an acid catalyst, resulted in the formation of 2,2-dimethyl-1,3,2-dioxasilinan (I) [1].

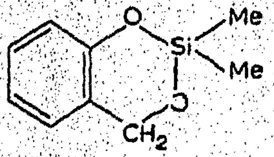
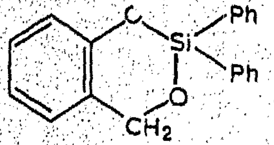
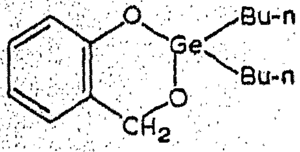
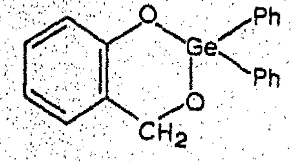
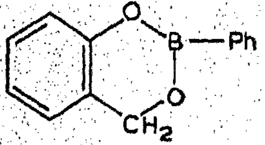


(I)

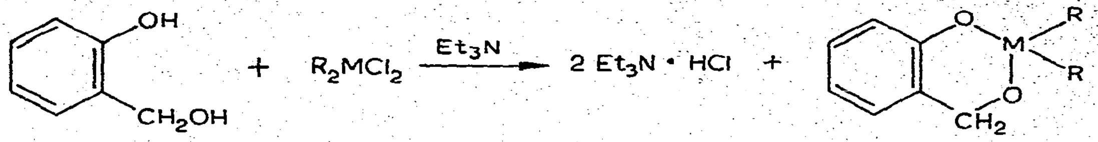
$$Me_2Si(OEt)_2 + HO(CH_2)_3OH \xrightarrow{p\text{-}MeC_6H_4SO_3H} 2\,EtOH + CH_2\begin{matrix} CH_2{-}O \\ \\ CH_2{-}O \end{matrix}\,Si\begin{matrix} Me \\ \\ Me \end{matrix}$$

We have recently been engaged on a study of organoboron derivatives of *o*-hydroxybenzyl alcohol [2] and have now extended these studies to heterocyclic derivatives of silicon and germanium.

TABLE 1

Compound	*P*		*P—H*		*m/e*		*P—exo*		*m/e*		*P—H*$^{2+}$	
	m/e	(%)	*m/e*	(%)	106 (%)	100 (%)	*m/e*	(%)	91	78	*m/e*	(%)
	180	72.2	179	100	0.75	3.3	150	1.2	5.3	4.4	89.5	>1
	304	100	303	47.3	2.8	14.4	150	4.5	6.6	25.7	151.5	>1
	310	86.1	309	100	3.6	7.8	196	7.5	7.5	13.8		
	350	85.7	349	100	13.9	26.7	196	3.2	3.6	28.2	174.5	>1
	210	70.5	209	100	12.8	10.9	133	1.1	0.93	25.0	104.5	14.0

The general method of synthesis of the silicon and germanium derivatives was by the reaction of o-hydroxybenzyl alcohol with the corresponding dichlorosilane or dichlorogermane in the presence of a tertiary base (In the absence of a tertiary base only a polymeric material was obtained.).



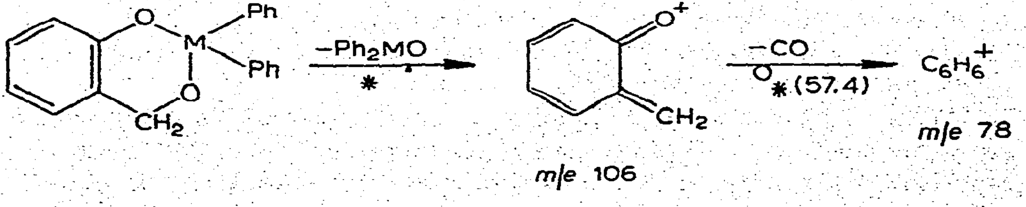
R = Ph, Me; M = Si
R = Ph, Bu; M = Ge

All four compounds were mobile liquids, the diphenylgermane derivative solidified on standing at room temperature, and found by mass spectrometry to be monomeric in the gaseous phase.

Mass spectra

We have been interested in mass spectral fragmentations of organoboranes for some time especially in the electron-impact-induced rearrangement processes of phenyl organoboranes, containing $PhBOCH_2$ groupings, which yield hydrocarbon (mainly tropylium) ions [3]. We were therefore surprised to find that the yield of tropylium ions from 2-phenyl-1,3,2-dioxabenzo[*d*]borinan was less than 1% (compared to the base peak) and this was the first example of a compound which contains a $PhBOCH_2$ grouping where this process is not significant [2]. It seemed therefore of interest to study the corresponding silicon and germanium compounds. Table 1 lists the ions of interest in the mass spectra of the o-hydroxybenzyl alcohol derivatives of silicon and germanium. Also included for comparison are details for the corresponding boron compound. To give some idea of the fragmentation processes these are given in full (Figs. 1 and 2) for the diphenyl- and dimethyl-silane compounds. Those for the germane derivatives were very similar. Only peaks of greater than 5% (compared to the base peak) are included.

In the phenyl compounds a loss of Ph_2MO to give an ion *m/e* 106, which then fragmented in an analogous way to that for the corresponding ion in o-hydroxybenzyl alcohol, was observed. The tropylium ion, checked by precise mass measurement, obtained by an electron-impact-induced rearrangement process, was observed in each case and this process appears to be of more significance than in the corresponding organoborane.



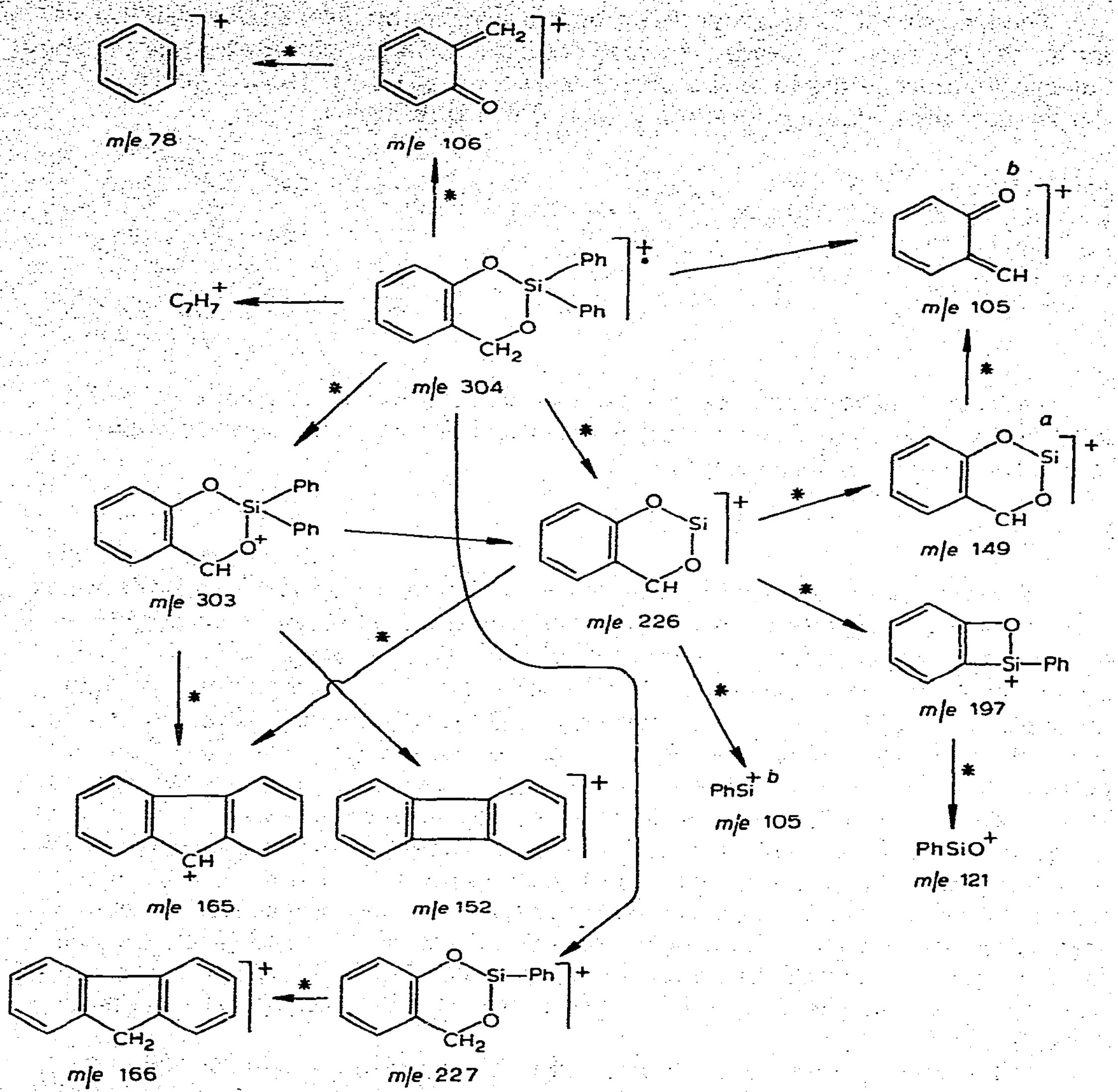


Fig. 1. Proposed fragmentation pattern for 2,2-diphenyl-1,3,2-dioxabenzo[*d*]silinan. [a] Confirmed by precise mass measurement. [b] *m/e* 105 peak was confirmed by precise mass measurement to be a mixture of both PhSi and C_7C_5O.

The major ion of importance is that due to *m/e P*—1. With the exception of the diphenylsilyl compound, this ion was found to be the base peak, and with the exception of the di-n-butylgermyl compound a doubly charged ion associated with the *P*—1 ion was observed, although of less than 1% intensity compared to 15% for the organoborane compound.

This strongly suggests that the *P*—H ions (A) have considerable stability which could possibly be due to p_π—d_π bonding via partial delocalisation of the lone pair on the oxygen into the *d* orbital on silicon or germanium thus giving (A) pseudo-aromatic character.

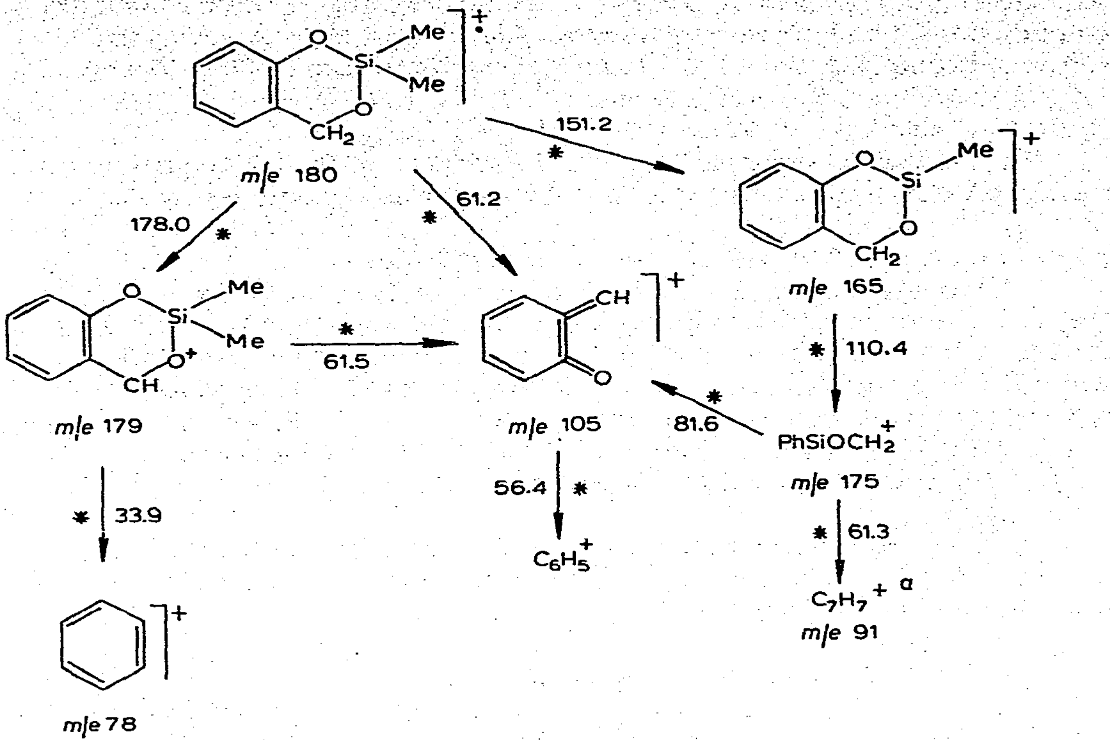
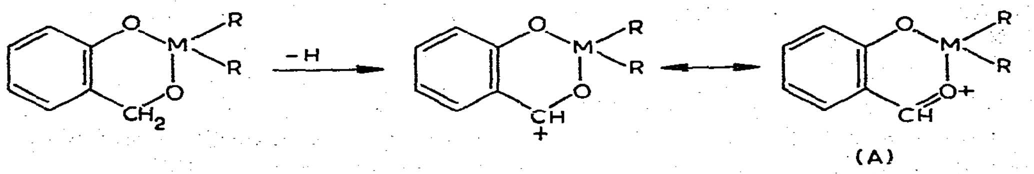


Fig. 2. Proposed fragmentation pattern for 2,2-dimethyl-1,3,2-dioxabenzo[d]silinan. [a] Confirmed by precise mass determination.



Experimental

General procedures

All solvents were dried over sodium wire and distilled before use. Mass spectra were recorded, using an A.E.I. MS 902 mass spectrometer, at 70 eV. The source was maintained at 170° and the compounds were introduced as neat liquids using an unheated direct-insertion probe. The usual precautions were taken as is usual for air-sensitive starting materials and products. All analyses were determined by Weiler and Strauss of Oxford.

Preparation of 2,2-dimethyl-1,3,2-dioxabenzo[d]silinan

o-Hydroxybenzyl alcohol (3.01 g, 0.02 *M*) in benzene (25 ml) was slowly added to dichlorodimethylsilane (3.18 g, 0.021 *M*) in benzene (25 ml) at room temperature. Excess triethylamine was then added. After allowing the mixture to stand at room temperature for two hours the insoluble triethylamine hydrochloride was filtered off and the residue, after removal of the benzene under vacuum afforded 2,2-dimethyl-1,3,2-dioxabenzo[*d*] silinan (3.35 g, 77%) b.p. 52—54°/0.05 mm, n_D^{25} 1.5119. (Found: C, 59.54; H, 6.94. Mol. wt. 180. $C_9H_{12}O_2Si$ calcd.: C, 60.01; H, 6.66%. Mol. wt. 180.)

The reaction was repeated without the addition of the triethylamine. After refluxing for 24 h the solvent was removed leaving an intractible polymer

Preparation of 2,2-diphenyl-1,3,2-dioxabenzo[d] silinan

A benzene solution, 25 ml, of *o*-hydroxybenzyl alcohol (3.0 g, 0.01 *M*) and excess triethylamine was slowly added to dichlorodiphenylsilane (1.47 g, 0.01 *M*) in benzene (20 ml). The mixture was refluxed for two hours after which the insoluble amine hydrochloride was filtered off. After removal of the solvent, the residue on distillation afforded 2,2-diphenyl-1,3,2-dioxabenzo[*d*]-silinan (2.57 g, 71.3%), b.p., 166—168°/0.05 mm, n_D^{25} 1.6043. (Found: C, 74.94; H, 5.39. Mol. wt. 304. $C_{19}H_{16}O_2Si$ calcd.: C, 75.00; H, 5.26%. Mol. wt. 304.)

The reaction between silicon tetrachloride and *o*-hydroxybenzyl alcohol under the above conditions resulted in the formation of an intractible polymer which did not melt below 250°.

Preparation of 2,2-di-n-butyl-1,3,2-dioxabenzo[d] germinan

A benzene solution of *o*-hydroxybenzyl alcohol (2.4 g, 0.01 *M*) and excess triethylamine was slowly added to dibutyldichlorogermane (5 g, 0.01 *M*) in benzene (25 ml) at room temperature. The mixture was refluxed for 30 min after which the insoluble triethylamine hydrochloride was filtered off. After removal of the solvent the residue on distillation afforded 2,2-di-*n*-butyl-1,3,2-dioxabenzo[*d*] germinan (5.40 g, 90.1%), b.p., 122—126°/0.1 mm, n_D^{21} 1.5193. (Found: C, 58.60; H, 7.80. Mol. wt. 308. $C_{15}H_{24}O_2Ge$ calcd.: C, 58.34; H, 7.77%, Mol. wt. 308.)

Preparation of 2,2-diphenyl-1,3,2-dioxabenzo[d] germinan

A benzene solution of *o*-hydroxybenzyl alcohol (1.25 g, 0.01 *M*) and excess triethylamine was slowly added to dichlorodiphenylgermane (3.0 g, 0.01 *M*) in benzene (25 ml) at room temperature. The mixture was refluxed for 30 min after which the insoluble aminohydrochloride was filtered off. On removal of the solvent, under reduced pressure, the residue on distillation afforded 2,2-diphenyl-1,3,2-diozabenzo[*d*] germinan (2.51 g, 71.5%), b.p., 182—186°/0.1 mm, n_D^{23} 1.6200 (Found: C, 65.18; H, 4.61. Mol. wt., 348. $C_{19}H_{16}O_2Ge$ calcd.: C, 65.51; H, 4.59%. Mol. wt. 348.)

Acknowledgement

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References

1 R.H. Krieble and C.A. Burkhard, J. Amer. Chem. Soc., 69 (1947) 2689.
2 R.H. Cragg and M. Nazery, J. Chem. Soc. Dalton Trans., (1973) in press.
3 R.H. Cragg, G. Lawson and J.F.J. Todd, J. Chem. Soc., Dalton Trans., (1972) 878.