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Macrocyclic Condensation Products from the Reactions between Dichlorodiphenylsilane and 1,4-Diols

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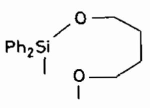
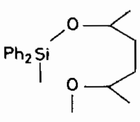
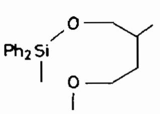
The interaction between dichlorosilanes and diols and the products resulting from these reactions are well documented [1, 2, 3]. However, at the present time there appears to be no way of predictig the nature of the products from such reactions. Early reports on the reaction of dichlorodimethylsilane with diols [1] indicated that the reaction usually produced monomeric heterocycles of six atoms or more. In the case of the reaction with ethane-1,2-diol, distillation of the product yielded a 10-membered dimer which reverted to a greatly more polymeric form on standing. That a 5-membered ring is often not formed has been demonstrated by Calas and Nicou [3] who investigated the reaction between dichlorosilanes and α-dihydroxy compounds. Their results indicated that the amount of substitution on the silicon and functional carbon atoms appeared to determine whether the 5- or 10-membered ring is formed. However it is generally the case that either a monomeric cyclic product is formed or merely a higher polymer which is presumably linear and not identifiable as any simple product.

We have recently embarked on a ^{29}Si study of heterocyclic organosilanes and have reinvestigated the nature of the products from the interactions between diols and dichlorosilanes. Our results of the interaction of 1,4-diols and dichlorodiphenylsilane indicate that the products from such reactions contain appreciable amounts of both the monomeric and dimeric heterocycles. The heterocycles are obtained from the interaction of the diol and pyridine with dichlorophenylsilane in sodium dried benzene. After refluxing for 30 minutes pyridine hydrochloride was filtered off and the filtrate afforded both monomer and dimer with the latter being considerably less soluble. Satisfactory elemental analyses were obtained for the compounds referred to in Table I. Ebullioscopic molecular weights, physical properties (*i.e.* melting points and boiling points) and ^{29}Si NMR values all point to the existence of two different and stable forms. In addition the molecular ion was obtained in each case for both monomer and dimer with the fragmentation pattern of the latter showing none of the major ions observed in the spectra of the monomer. In addition the base peak in the mass spectrum of each monomer was due to M-78.

Meyer, Klein and Weiss [4] have recently reported the reversible dimerisation of 2,2-dimethyl-1,3,2-

TABLE I. Physical, Analytical and Spectroscopic Data for the Compounds.

		M. Pt. °C	B. Pt. °C/mm	m/e		M.W. (ebullioscopic)	δ ^{29}Si^{a}
				Molecular ion	Base peak		
	Monomer	–	115–134/0.1	270	192	260	25.49
	Dimer	176–184	–	540	104 (319)^{b}	519	32.25
	Monomer	–	148–170/0.15	284	206	283	25.49
	Dimer	154–175	–	568	319	567	32.09 32.40 (isomers) 32.71
	Monomer	55–75	130–140/0.1	298	220	306	29.02 30.25 (isomers)
	Dimer	155–170	–	596	337	587	35.17 37.78 (isomers)

^{a} ^{29}Si shifts are given w.r.t. TMS. All are upfield. ^{b}Second-largest peak.

benzodioxasilole. The energy of activation was found to be remarkably low and ready interconversion between the two forms was observed, the dimer being produced from the initial reaction. Why some of our reactions resulted in the formation of monomeric and dimeric forms, which do not appear to equilibrate, is open to speculation. We are presently widening the scope of our investigations in an attempt to rationalise these findings.

References

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2 N. Spassky, *Compt. Rend., 251,* 2371 (1960).
3 R. Calas and P. Nicou, *Compt. Rend., 249,* 1011 (1959).
4 H. Meyer, J. Klein and A. Weiss, *J. Organometal. Chem., 177,* 323 (1979).