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CONTRIBUTIONS TO GROUP IV ORGANOMETALLIC COMPOUNDS

V*. ORGANO-1,3,2-DIOXASILACYCLOHEXANES

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Summary

The ^1H NMR spectra of 2,2-dimethyl-1,3,2-dioxasilacyclohexane and 2-methyl-2-phenyl-5,5-dimethyl-1,3,2-dioxasilacyclohexane are reported and demonstrate the effect of polymerisation on the spectra of this class of organosilane.

We have for some time been interested in the synthesis and properties of organo-1,3,2-dioxasilacycloalkanes [2,3]. A recent report of the synthesis of monomeric dimethyl-1,3,2-dioxasilacyclohexanes [4] prompts us to suggest caution in the interpretation of ^1H NMR spectra of such compounds.

Organo-1,2,3-dioxasilacyclohexanes are readily obtained from the interaction of dichlorosilanes and diols in the presence of pyridine. We have observed in many cases that products of such reactions are monomeric but polymerise after a relatively short time. In the ^1H NMR spectra we observe that the effect of polymerisation is relatively small, being most distinct for the O–CH shifts, which are approximately 0.2 ppm to lower field for the monomer. To illustrate these observations the spectra of 2,2-dimethyl-1,3,2-dioxasilacyclohexane and 2-methyl-2-phenyl-5,5-dimethyl-1,3,2-dioxasilacyclohexane are discussed in detail. The spectrum of 2,2-dimethyl-1,3,2-dioxasilacyclohexane (Fig. 1) was recorded immediately after isolation and then again after three days, during which the product visibly polymerised from a watery (b.p. 114°C) to a much more viscous liquid. Although the two spectra are very similar, inspection shows that the OCH_2 triplet has moved to a higher field (from δ 3.92 to 3.72 ppm). The δ value for the monomer is in close agreement with reported shifts (3.97 [5], 3.98 [6] and 3.93 [7] ppm) except for one of 3.75 [4] ppm which, by comparison, would appear to have been obtained using a polymerised

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* For part IV see ref. 1.

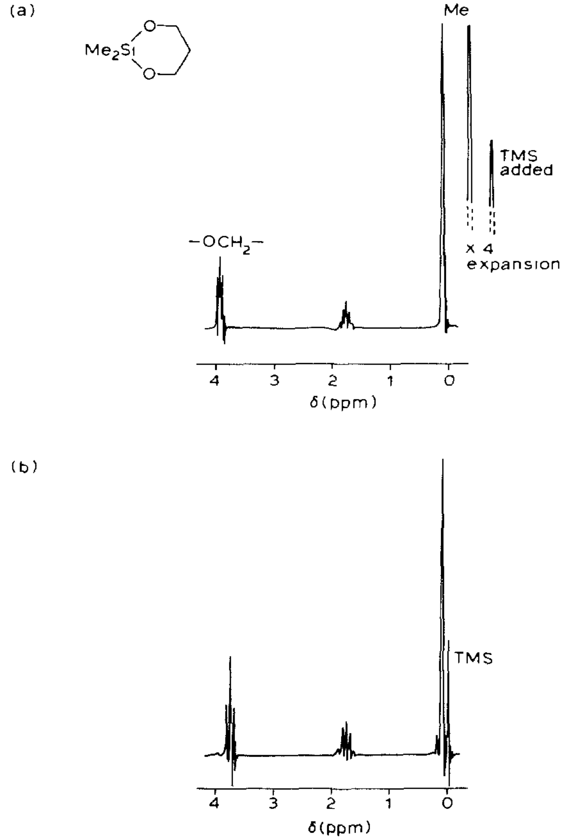

Fig. 1. Proton NMR spectra of 2,2′-dimethyl-1,3,2-dioxasilacyclosilane: (a) from a solution prepared immediately after distillation, (b) from a solution prepared three days later.

product. This observation may be significant since the authors claim that their method of preparation, based on the reaction of dimethyldimethoxysilane with 1,3-dioxanes in the presence of stannic chloride, does not lead to the formation of secondary products. Our observations indicate that unsubstituted and partially substituted monomers have a distinct tendency to polymerise and it is not apparent why this should be prevented as a result of any particular method of preparation.

A more impressive demonstration of the change in ^1H NMR spectra with time is given in Fig. 2 which shows spectra of 2-methyl-2-phenyl-5,5-dimethyl-1,3,2-dioxasilacyclohexane recorded at times twenty four days apart, and reveal the presence of the polymer along with the monomer after this period.

Experimental

2,2′-Dimethyl-1,3,2-dioxasilacyclohexane [8] and 2-methyl-2-phenyl-5,5′-dimethyl-1,3,2-dioxasilacyclohexane [6] were prepared by established methods. The ^1H NMR spectra were recorded on a JEOL-PS-100 NMR spectrometer as solutions in either $CDCl_3$ or CCl_4 with internal TMS as a reference.

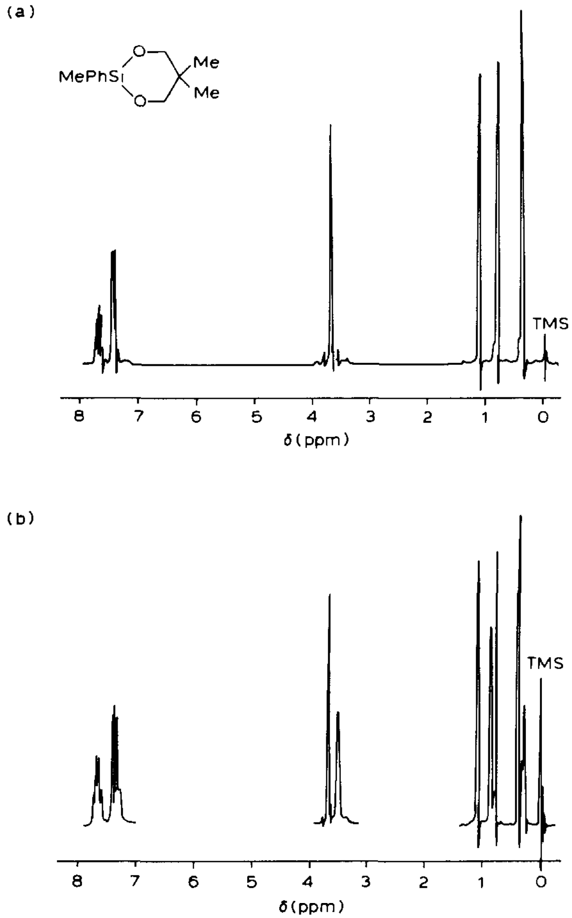

Fig. 2. Proton NMR spectra of 2-methyl-2-phenyl-5,5-dimethyl-1,3,2-dioxasilacyclosilane: (a) 1 day after distillation, (b) 25 days after distillation showing growth of new peaks attributed to the dimer.

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