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PRELIMINARY COMMUNICATION

STEREOISOMERS OF ORGANOCYCLOSILTHIANES

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Since the preparation of organocyclosilthianes in 1952[1], little has been reported concerning their structure and properties[2-4]. Stereoisomers are possible for unsymmetrically substituted cyclosilthianes and we have initiated a study of these systems. Stereoisomers of the analogous siloxane systems have been reported[5].

When a solution of methylphenyldichlorosilane in hexane was treated with hydrogen sulfide in the presence of pyridine, a crystalline solid was isolated after removal of pyridinehydrochloride by filtration. This substance, melting at 112.5–114° after recrystallization from n-hexane, was characterized as 2,4,6-trimethyl-2,4,6-triphenylcyclotrisilthiane by its elemental analysis and molecular weight in benzene (found 454, calc. 457). This trimer reacts rapidly with water and alcohol and is soluble in common organic solvents.

If one assumes a chair conformation for this cyclic trimer, then four geometrical isomers are possible[6,7]. Nuclear magnetic resonance is of considerable aid in differentiating among these possibilities.

The NMR spectrum of the isomer melting at 114° in CCl_4 exhibits a complex phenyl resonance centered at τ 2.5 ppm and two singlets in the methyl region at τ 9.17 and 9.44 ppm with an intensity ratio of 2 to 1 respectively. These singlets do not coalesce up to 177° The structure shown in Fig. 1 is consistant with these data.

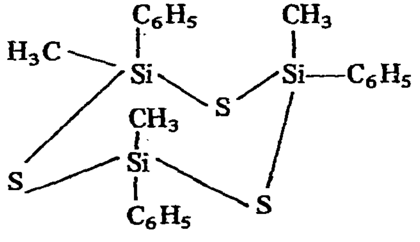

Fig.1

We believe that the isomer with two phenyl groups in the axial position is unlikely on steric grounds.

When this isomer is distilled through a four foot column at reduced pressure, a white solid melting at 137–139° is obtained after one recrystallization from n-hexane.

This substance was characterized as dimethyldiphenylcyclodisilthiane by its molecular weight (found 304, calc. 305) and elemental analysis.

This dimer reacts with moisture more rapidly than the trimer. The NMR spectrum of the dimer consists of phenyl resonances and a single proton resonance in the methyl region at τ 8.95 ppm. This does not differentiate between the *cis* and *trans* structures possible for this dimer.

When the trimer is heated at 200° for 24 h, the NMR spectrum contains several resonances in the methyl region in addition to those characteristic of the trimer and dimer reported above.

Work is in progress on the isolation of these substances and the preparation of other unsymmetrically substituted organocyclosilthianes. More details on the chemistry of these systems will be published later.

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