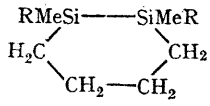
cis- and *trans*-1,2-Dimethyl-1,2-diphenyl-1,2-disilacyclohexane: Preparation and Stereospecific Oxidation with Perbenzoic Acid

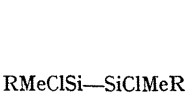
By K. TAMAO, M. ISHIKAWA, and M. KUMADA*

(*Department of Synthetic Chemistry, Kyoto University, Kyoto, Japan*)

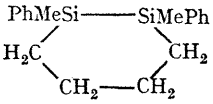
SINCE the discovery of optically active α-naphthylphenylmethylsilanes,[1] much research has centred on the stereochemistry of acyclic organosilicon compounds,[2] but little is known of the stereochemistry of silicon-containing heterocyclic compounds.[3] We have synthesised the *cis*- and *trans*-isomers of 1,1,2,2-tetrasubstituted 1,2-disilacyclohexanes (I) and carried out the stereospecific oxidation of the phenyl derivative (Ia) with perbenzoic acid.



(Ia) R=Ph
(Ib) R=*p*-ClC_6H_4



(IIa) R=Ph
(IIb) R=*p*-ClC_6H_4



(III)

A mixture of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane (Ia) was prepared (75%) by the reaction of the di-Grignard reagent from 1,4-dibromobutane with 1,2-dichloro-1,2-dimethyldiphenyl-1,2-disilane (IIa) in tetrahydrofuran. The disilane (IIa) was obtained (50%) by the action of phenylmagnesium chloride on *s*-tetrachlorodimethyldisilane.[4] Similarly, a mixture of *cis*- and *trans*-1,2-bis-(*p*-chlorophenyl)-1,2-dimethyl-1,2-disilacyclohexane (Ib) was prepared (70%) from the corresponding dichlorodisilane (IIb). The isomers of both cyclic systems (I) could be separated by fractional distillation or preparative v.p.c.

The geometrical configuration of the *p*-chlorophenyl compound (Ib) was determined from dipole moment data. Thus, the isomer with a shorter retention time on v.p.c. had a larger value ($2{\cdot}9_2$ D) than the other ($2{\cdot}1_2$ D), and the results indicated that the former is *cis* and the latter is *trans*. The isomers of the phenyl derivative (Ia) were assigned to *cis*- and *trans*-forms by correlation with the *p*-chlorophenyl derivative (Ib) by the techniques of Summerbell *et al.*[5] Thus the action of ethyl bromide and magnesium on both the *cis*- and the *trans*-isomer of the *p*-chlorophenyl derivative (Ib) in tetrahydrofuran, followed by hydrolysis, converted them, with the asymmetric silicon centres intact, into the *cis*- and the *trans*-isomer, respectively, of the phenyl derivative in excellent yield.

For both cyclic systems (I), the *cis*-isomers have smaller physical constants and shorter retention times on v.p.c. than the *trans*-isomers. ^{1}H N.m.r. spectroscopy showed that the methyl protons in *cis*-isomers of both the phenyl and *p*-chlorophenyl derivatives absorb *ca.* 0·07 p.p.m. to lower field than those in the *trans*-isomers. This is consistent with the above assignments in view of the larger effect of magnetic anisotropy of the benzene ring expected for the *trans*-isomers.

Both the *cis*- and the *trans*-isomer of the phenyl derivative (Ia) reacted with perbenzoic acid in dichloromethane at room temperature to afford quantitatively the *cis*- or the *trans*-2,7-dimethyl-2,7-diphenyl-1-oxa-2,7-disilacycloheptane (III), respectively. This very high stereospecificity of reaction supports the molecular mechanism previously suggested for the perbenzoic acid oxidation of the silicon–silicon bond.[6]

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