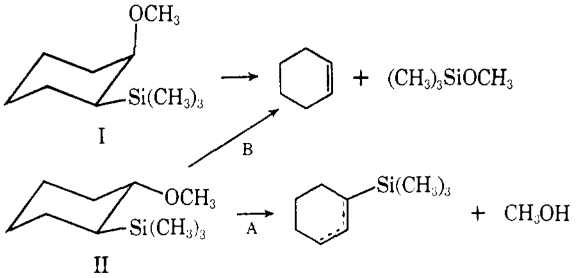
# The Stereochemistry of β-Elimination Reactions in Organosilanes

*Sir:*

The facile decomposition of β-substituted organosilanes to give an olefin and a substituted silane is a well-known reaction.[1-3] However, the stereochemistry of the reaction has not been studied. Since the inductive effect of silicon in *cis* and *trans* β-substituted organosilylcyclohexanes is constant, the stereoelectronic factors which control these elimination reactions can be assessed by comparing the reactivity of these two isomers. We wish to report that an investigation of the thermal and acid-catalyzed decomposition of the *cis*- and *trans*-2-trimethylsilylcyclohexyl methyl ethers[4] has shown that these isomers decompose at different rates to give different products.

The thermal decomposition of *cis*-2-trimethylsilylcyclohexyl methyl ether (I) from 233 to 276° proceeds by a first-order process to give a quantitative yield of cyclohexene and trimethylsilyl methyl ether. *trans*-2-Trimethylsilylcyclohexyl methyl ether (II) decomposes slower than the *cis* isomer by two competing processes. The predominant path (A) is the elimination of *methanol* to give a mixture of 2- and 3-trimethylsilylcyclohexenes. The alternative path (B) leads to cyclohexene and trimethylsilyl methyl ether.



To compare the reactions in the cyclohexane series with an acyclic compound, the decomposition of 2-trimethylsilylethylmethyl ether (III) was examined. This reaction is first order and gives a quantitative yield of trimethylsilyl methyl ether and ethylene.

$$(CH_3)_3SiCH_2CH_2OCH_3 \longrightarrow (CH_3)_3SiOCH_3 + CH_2{=}CH_2$$

III

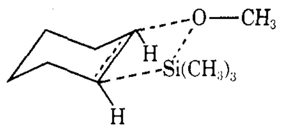
The decomposition reactions were carried out at three different temperatures in sealed nmr tubes suspended in the vapors of a refluxing solvent. The rates of reaction were determined by removing the nmr tubes from the refluxing solvents at various times, cooling, and integrating the requisite regions of the spectra. For example, the rate for the decomposition of I was followed by relating the amount of cyclohexene (vinyl C-*H*) formed to the amount of starting ether ($COCH_3$) remaining.

The first-order rate constant for the decomposition of the *cis* isomer I is $9.5 \times 10^{-5}$ sec$^{-1}$ at 276° ($\Delta H^{\ddagger} = 34 \pm 1$ kcal/mol, $\Delta S^{\ddagger} = -12 \pm 1$ eu). For the acyclic ether III, the first-order rate constant is $1.6 \times 10^{-5}$ sec$^{-1}$ at 276° ($\Delta H^{\ddagger} = 25 \pm 1$ kcal/mol, $\Delta S^{\ddagger} = -19 \pm 1$ eu).

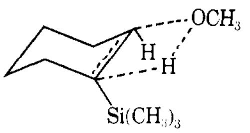
Kinetic parameters for the decomposition of the *trans* isomer could not be obtained due to the catalytic effect of the glass tubes used in the reaction. The results obtained for this compound are not reproducible and vary with the treatment of the tube prior to reaction.[5]

However, the decomposition of the *trans* isomer is always slower than that of the *cis* isomer, and the amount of methanol formed (path A) is about three times greater than the amount of silyl ether (path B). The rate of methanol formation in this reaction is somewhat faster than the rate of methanol formation in the thermal decomposition of cyclohexyl methyl ether.

The thermal decomposition of the *cis* isomer I and the acyclic ether III undoubtedly proceeds through a four-centered activated complex (IV). In order for the *trans* isomer II to yield cyclohexene and trimethylsilyl methyl ether in a concerted elimination, a strained activated complex would be required. The activation energy necessary to achieve the four-centered activated complex having a significant amount of Si–O bond formation would be extremely high. Therefore, the small amount of cyclohexene and trimethylsilyl methyl ether which is observed may result from a catalyzed reaction induced by the glass tube and not from an intramolecular process. However, methanol may be eliminated in an intramolecular process through a four-centered activated complex (V) to give the trimethylsilylcyclohexenes.



IV



V

The rate of the acid-catalyzed (*p*-toluenesulfonic acid in benzene at room temperature) decomposition is opposite to that observed in the thermal decompositions. The *trans* isomer II reacts extremely rapidly whereas the *cis* isomer I does not react at all under these conditions. In these acid-catalyzed reactions the *trans*-coplanar orientation of leaving groups in the activated complex is easily achieved in the *trans* isomer but impossible in the *cis* isomer. It is worth noting that the acyclic compound III does not react with acid under these conditions. Further work on the decomposition of β-substituted organometallic compounds is in progress.

**Acknowledgment.** We wish to thank the National Science Foundation (GP-5716) for support of this research.

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(1) C. Eaborn, "Organosilicon Compounds," Academic Press Inc., London, 1960, p 133.

(2) L. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

(3) I. M. T. Davidson, M. R. Jones, and C. Pelt, *J. Chem. Soc., B*, 937 (1967).

(4) W. K. Musker and G. L. Larson, *Tetrahedron Letters*, 3481 (1968).

(5) The nmr tubes were treated with either nitric acid or sodium hydroxide, rinsed with water, and dried at 150° for about 8 hr. Although the decomposition occurred more rapidly in the acid-treated tubes than in the untreated or base-treated tubes, duplicate runs were not reproducible.

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*Received October 26, 1968*