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SYNTHESIS OF THE CIS- AND TRANS-ISOMERS OF 2-TRIMETHYLSILYLCYCLOHEXANOL

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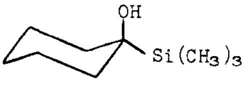
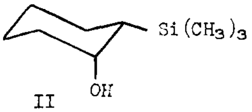
In continuing our study[1] of intramolecular interactions in Group IV compounds it was necessary to prepare organosilicon compounds having a nucleophilic substituent in a unique stereochemical relationship to silicon. The ideal set of isomers having different stereochemical environments but identical inductive parameters would be the cis- and trans-β-substituted trimethylsilylcyclohexane derivatives. However, no example of cis- or trans-isomers of β-substituted Group IV organometallic cyclohexanes had been reported. Only the related cis- and trans-isomers of 3- and 4-trimethylsilylcyclohexanols had been reported by Fessenden and coworkers.[2]

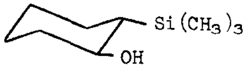
We now wish to describe the synthesis and characterization of the three remaining isomeric trimethylsilylcyclohexanols; 1-trimethylsilylcyclohexanol (I), cis-2-trimethylsilylcyclohexanol (II) and trans-2-trimethylsilylcyclohexanol (III).



I

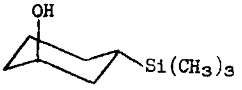


II

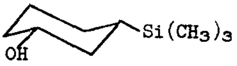


III

Hydroboration of 1-trimethylsilylcyclohexene with borane in tetrahydrofuran at room temperature followed by alkaline hydrogen peroxide oxidation gave a 65% yield of alcohol products consisting of 90% I (bp 69-70°C/3 torr; 3,5-DNB mp 111.5-112.5°C) and 10% III (mp 47-48°C; 3,5-DNB mp 98-99°C). The strong directive effect of silicon in this hydroboration reaction to give predominantly the less favored alcohol (I) is attributed to $d\pi$-$p\pi$ overlap between silicon and the double bond. This directive effect has been noted before in the hydroboration of trimethylvinylsilane[3] and 1,1-diphenyl-1-sila-2-cyclohexene.[4] In order to overcome this directive effect, the more hindered thexylborane[5] was used as the hydroborating agent. The reaction of 1-trimethylsilylcyclohexene with thexylborane was very slow requiring 72 hours for completion at room temperature and resulting, after oxidation, in the formation of a 70% yield of four isomeric trimethylsilylsubstituted cyclohexanols: I, III, *trans*-3-trimethylsilylcyclohexanol (IV)[2] and *cis*-3-trimethylsilylcyclohexanol (V)[2] in a ratio of 30:9:22:39 respectively. No evidence for the presence of II was found in the hydroboration reactions.



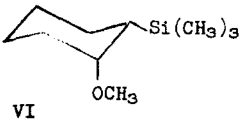
IV



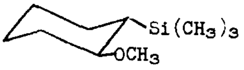
V

The formation of IV and V can be rationalized in terms of an elimination of thexylborane from the initial hydroboration product to give 3-trimethylsilylcyclohexene which is subsequently rehydroborated. Thus, a better yield of III is obtained when the hydroboration is carried out at 0°C for 138 hours to give I, III, IV, V in a ratio of 10:57:22:11. However the reaction was only 65% complete as shown by the amount of residual hydride determined by hydrolysis with water.

Oxymercuration of 1-trimethylsilylcyclohexene with mercuric acetate in a water-tetrahydrofuran mixture as described by Brown and Geoghagen[6] gives a 15% yield of alcohols consisting of II (mp 59-60°C; 3,5-DNB, mp 105-106°C) and III in a ratio of 70:30. No evidence for the formation of I is found in this reaction, indicating that the mercury attaches itself exclusively to the same carbon as the silicon. This is analogous to the results of the oxymercuration of trimethylvinylsilane.[7] A major side product is cyclohexanol, which increased in amount with increasing time of reaction with a corresponding decrease in II and III. If the reaction is carried out in anhydrous methanol as the nucleophile a 20% yield of the isomeric 2-(trimethylsilyl)cyclohexylmethyl ethers (bp 95-97°C/31 torr) is obtained with a *cis* (VI) to *trans* (VII) ratio of 65:35.



VI



VII

The structures of IV and V were established by a comparison of their retention times on a DEGA column and their nmr and infrared spectra with authentic samples. The structure of the tertiary alcohol (I) was established by the lack of a peak in the nmr spectrum in the 3-5 ppm region where a proton *alpha* to a hydroxyl group would be expected.

The nmr spectra of II and III served to establish their structures. In *cis*-2-trimethylsilylcyclohexanol (II) the resonance of the proton alpha to the hydroxyl group was centered at 247 cps downfield from TMS or at 4.15 ppm, with a spread of 11 cps which is consistent with a proton in the equatorial position.[8] The structures of the cis- and trans-2-(trimethylsilyl)cyclohexylmethyl ethers were also assigned by nmr spectroscopy, again using the position of the proton alpha to the methoxy group as a criterion. All of the structural assignments are based on the assumption that the trimethylsilyl group occupies an equatorial position (an assumption which does not appear unreasonable).[2] Further studies on the characteristics and reactivities of these compounds are now underway.

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