

## NOTE

### STEREOCHEMICAL CROSSOVER IN HYDROGEN-HYDROGEN EXCHANGE AT SILICON

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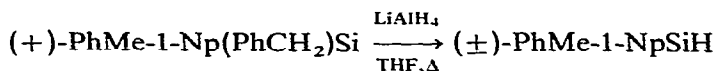
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The recent report by Sommer and Fujimoto<sup>1</sup> of a solvent dependent stereochemical crossover during alkoxy-alkoxy exchange reactions at silicon prompts us to report a similar solvent dependent change in stereochemistry during hydrogen-hydrogen and hydrogen-deuterium exchange at silicon.

An early attempt to obtain hydrogen-deuterium exchange at silicon failed<sup>2</sup>, presumably because in the reagents used the deuterium was positively polarized while the hydrogen to be displaced was negatively polarized<sup>3</sup>. Sommer and Frye<sup>4,5</sup> found that exchange could be effected by using lithium aluminium hydride or deuteride as a source of negatively polarized hydrogen or deuterium. Thus when optically active methyl-1-naphthylphenylsilane ( $R_3Si^*H$ ) was treated with lithium aluminium deuteride in such relatively non-polar ethers as ethyl ether and n-butyl ether very slow hydrogen-deuterium exchange with retention of configuration was observed. Similarly when  $R_3Si^*D$  was refluxed with lithium aluminium hydride in non-polar ethers deuterium-hydrogen exchange with retention of configuration was observed. Since,  $R_3Si^*H$  can be refluxed in non-polar ethers in the presence of lithium aluminium hydride without racemization it seems reasonable to assume that hydrogen-hydrogen exchange under these conditions also occurs primarily with retention of configuration. Hydrogen-deuterium exchange at silicon in the presence of transition metals<sup>6,7,8</sup> has also been found to proceed with retention of configuration<sup>8</sup>.

Our investigation of hydrogen-deuterium exchange at silicon arose from the observation, that when the benzyl group was cleaved from (+)-benzylmethyl-1-naphthylphenylsilane by lithium aluminium hydride in refluxing THF, the silane,  $R_3SiH$ , isolated was racemic<sup>9</sup>.



When (+)- $R_3Si^*H$  was stirred with an excess of lithium aluminium deuteride for 2 h in THF at room temperature hydrogen-deuterium exchange and racemization to give ( $\pm$ )- $R_3SiD$  took place. Similarly, (+)- $R_3Si^*H$  was completely racemized by stirring with lithium aluminium hydride for  $\frac{1}{2}$  h at room temperature.

Thus the change in solvent from ethyl ether-n-butyl ether to THF resulted in a change in stereochemistry of hydrogen-deuterium and of hydrogen-hydrogen

exchange at silicon from retention of configuration to inversion of configuration. It also led to a large increase in the rate of exchange.

These results are in agreement with the observations of Sommer and Fujimoto<sup>1</sup> that more polar solvents favor exchange with inversion. Presumably the THF assists in the removal of hydride making the hydrogen on silicon a better leaving group and thus favoring a  $S_N2-Si$  type mechanism<sup>10</sup>. The marked increase in rate is presumably also due to a variation in the nature of the nucleophile and stabilization of the leaving group. However, a detailed consideration of what is occurring is complicated by a lack of understanding of the structure of lithium aluminium hydride in solution<sup>11</sup>.

In an extension of these studies (–)-methyl-1-naphthylphenylgermane<sup>12</sup>, ( $R_3Ge^*H$ ) was stirred for 2 h at room temperature in THF with an excess of lithium aluminium deuteride. No racemization or hydrogen–deuterium exchange occurred. When the mixture was refluxed for 2 h less than 5% racemization or hydrogen–deuterium exchange occurred.

The slower rate of hydrogen–deuterium exchange at germanium compared to silicon under these conditions is probably due to germanium's resistance to nucleophilic attack<sup>9,13</sup> and the reversal of polarization in going from a silicon–hydrogen ( $Si^+-H^-$ ) to a germanium–hydrogen ( $Ge^- - H^+$ ) bond.

In conclusion, when lithium aluminium hydride in THF is used as a reagent with organosilicon compounds the possibility of silicon–carbon bond cleavage<sup>9</sup> and of rapid hydrogen–hydrogen exchange with inversion of configuration should be considered.

#### EXPERIMENTAL

The THF used was freshly distilled from lithium aluminium hydride before use. The lithium aluminium hydride was supplied by Research Organic/Inorganic Chemical Co., and lithium aluminium deuteride by Carl Roth OHG. All reactions were carried out under a dry nitrogen atmosphere.

##### (+)-Methyl-1-naphthylphenylsilane

(a) A solution of 0.25 g (0.001 mole) of (+)-methyl-1-naphthylphenylsilane,  $[\alpha]_D^{33}$  (c 4.6, cyclohexane) in 4 ml of THF was stirred for 2 h with 0.045 g (0.0011 mole) of lithium aluminium deuteride. Wet ethyl ether was then added to destroy the deuteride, the ether was washed with dilute hydrochloric acid followed by water and then dried over sodium sulfate. The ether was removed under reduced pressure to obtain 0.2 g of a racemic mixture of ( $\pm$ )-methyl-1-naphthylphenylsilane (20%)\*, ( $R_3SiH$ ) and ( $\pm$ )-methyl-1-naphthylphenylsilane-*d* (80%)\*, ( $R_3SiD$ ).

(b) A solution of 0.25 g (0.001 mole) of (+)- $R_3SiH$ ,  $[\alpha]_D^{33}$  (c 4.6, cyclohexane) in 4 ml of THF was stirred for 0.5 h at room temperature with 0.057 g (0.0015 mole) of lithium aluminium hydride in THF. Following work-up as above the recovered silane was found to be racemic.

\* The relative amounts of deuterated and undeuterated compound was estimated by an analysis of the NMR spectrum of the mixture.

(-)-Methyl-1-naphthylphenylgermane

(a) A solution of 0.29 g (0.001 mole) of (-)-methyl-1-naphthylphenylgermane  $[\alpha]_D - 14^\circ$  (c 4.0, cyclohexane) in 4 ml of THF was stirred for 2 h at room temperature with 0.06 (0.0014 mole) of lithium aluminium deuteride. Following work-up as above the recovered germane,  $[\alpha]_D - 14^\circ$  (c 4.5, cyclohexane), was identical in all respects to the starting material.

(b) When a similar reaction mixture was refluxed for 2 h the recovered germane was slightly racemized  $[\alpha]_D 12.7^\circ$  (c 5.6, cyclohexane), and approximately 5% of  $R_3GeD$  could be detected by NMR and IR spectroscopy.

## ACKNOWLEDGEMENT

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