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## H–D Exchange, Configurational Isomerization, and Hydrogenolysis of 1,2-Dimethylsilacycloalkanes on Copper

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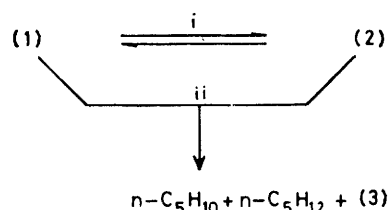
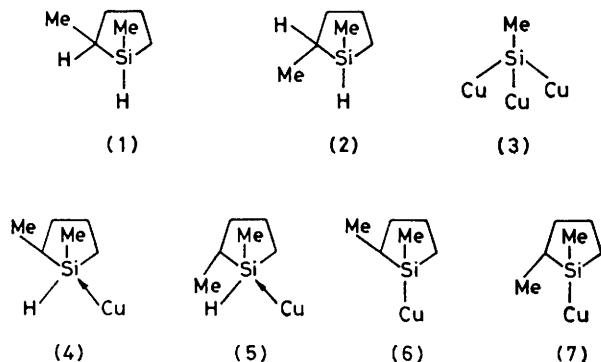
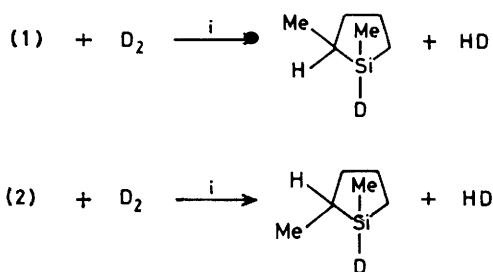
The hitherto unreported H–D exchange, configurational isomerization, and hydrogenolysis of *Z*- and *E*-1,2-dimethylsilacycloalkanes on copper have been studied, and evidence has been obtained for the first time that copper is able to catalyse configurational isomerization.

The complex study of H–D exchange in alkanes<sup>1</sup> and the configurational isomerization and hydrogenolysis of multi-substituted cycloalkanes<sup>2</sup> is now an important method for investigating metal catalysis. Although important results have been reported concerning the reactions of organosilicon compounds on metals, including the Si–H + D<sub>2</sub> reaction,<sup>3–7</sup> very little information is available as yet on the metal-catalysed transformations of compounds containing Si–C and Si–H bonds. We have not been able to find any experimental observations in the literature on the configurational isomerization and hydrogenolysis of silacycloalkanes or on the transformations of organosilicon compounds on Cu. Therefore we have studied the reactions of the stereoisomeric organosilanes (1) and (2) on Cu.

Three techniques were used involving a pulse microreactor, a static microreactor, and a flow microreactor, in the temperature range 100–250 °C.

The 5% Cu on Cab-O-Sil catalyst was prepared and characterized as described earlier.<sup>8</sup> The irreversible chemisorption of the silanes leads to a decrease in the activity of the catalyst, indicating the participation of the more highly dissociated species (3). As a consequence of this poisoning, fresh catalyst was used for every measurement.

The results clearly show the following. (i) The Si–H + D<sub>2</sub> → Si–D + HD exchange proceeds with 100% selectivity (see Scheme 1). Since the isomerization (1) ⇌ (2) did not occur in the course of the exchange, the reaction Si–H → Si–D was accompanied by retention of configuration at the silicon atom (see Scheme 1). (ii) Cu is capable of catalysing not only the hydrogen-exchange of silanes by the action of D<sub>2</sub>, but also their configurational isomerization (selectivity 0–100%) and hydrogenolysis (selectivity 0–80%) (see Scheme 2). The selectivities of the two competitive reactions vary with the temperature and the surface state of the catalyst. (iii) The rates of the three reaction types depend mainly on the temperature and the nature of the active centres of the Cu. Since exchange occurs on a poisoned Cu catalyst on which no configurational isomerization and hydrogenolysis is observed,



Scheme 2. i, Cu, 150–200 °C; ii, Cu, >200 °C, H<sub>2</sub>.

it is our view that exchange is 'structure-insensitive',<sup>9</sup> whereas the other two reactions are 'structure-sensitive'. (iv) The experimental data further reveal that the rate of the configurational isomerization depends on hydrogen in accordance with a first-order reaction, which indicates that hydrogen plays a role in the rate-determining step.

The experimental results show that, as a consequence of the interaction between the occupied d orbitals of the Cu and the empty d orbitals of the Si, the silanes are adsorbed on Cu *via* the Si atom. Thus, the reactions may take place *via* associative surface species of types (4) and (5), and dissociative surface species of types (6) and (7), as for other metals.<sup>5-7</sup>

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