Thermolysis of Hexamethyldisilane

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THERMOLYSIS of hexamethyldisilane (I) in a quartz tube heated at 600° was first reported by Shiina and Kumada.[1] Products detected were trimethylsilane and trimethyl(dimethylsilylmethyl)-silane (II).[1,2] However, Band, Davidson, Lambert, and Stephenson[3] have suggested an approximate stoicheiometry for the pyrolysis of (I) between 523 and 550° at 0·2–0·8 mm.Hg:

$$11\,Me_6Si_2 \rightarrow 5\,Me_3SiH + Me_4Si + 4\,Me_5Si_2CH_2SiMe_3 + (Me_5Si_2)_2CH_2$$

At the same time, it has been claimed that there is no evidence for the thermal rearrangement of (I) to (II).[4] Prompted by these observations, we have re-investigated the thermolysis of (I) and found that it can rearrange thermally to give the isomer (II) in high yield under certain conditions.

When 0·54 g. of (I) was thermolysed at 400° for 3 hr. in a 5·0 c.c. sealed tube, (II) was obtained as the sole product in 74% yield together with unchanged (I). At 450° for 1 hr., (II) was obtained almost quantitatively. In all cases, a trace amount of trimethylsilane was detected by v.p.c. That the product of the reaction, (II), was stable up to 500° in these reaction conditions was shown by an independent experiment.

Therefore, it is clear that (II) is the primary product of the thermolysis of (I) at least under the present conditions. The course of thermolysis was almost unaffected by whether the sealed tube was degassed or not prior to the reaction, and the presence of toluene did not change the product.

$$Me_3SiSiMe_3\ (I) \rightarrow Me_3SiCH_2{\cdot}SiMe_2H\ (II)$$

Since the reaction in a small sealed tube at high temperature may proceed at considerably high pressure and may have a different mechanism at low pressure, the thermolysis of (I), together with other related compounds, needs further investigation.

(*Received, April 22nd*, 1968; *Com.* 489.)

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